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Transferhydrogenation with Amino-Olefin Complexes

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Für meine Eltern und meinen Bruder

Auch aus Steinen, die dir in den Weg gelegt werden, kannst du etwas Schönes bauen.
Erich Kästner

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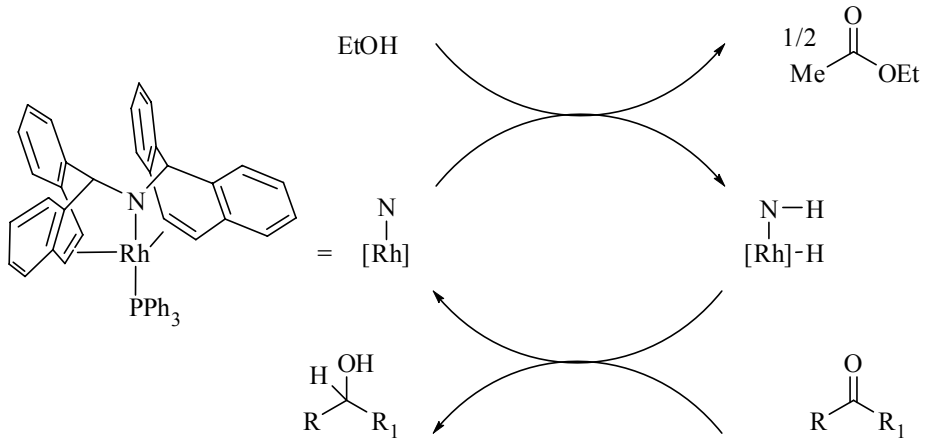
Last but not least, my family and my friends, especially Andreas, for their patience and optimism, and for believing in me.

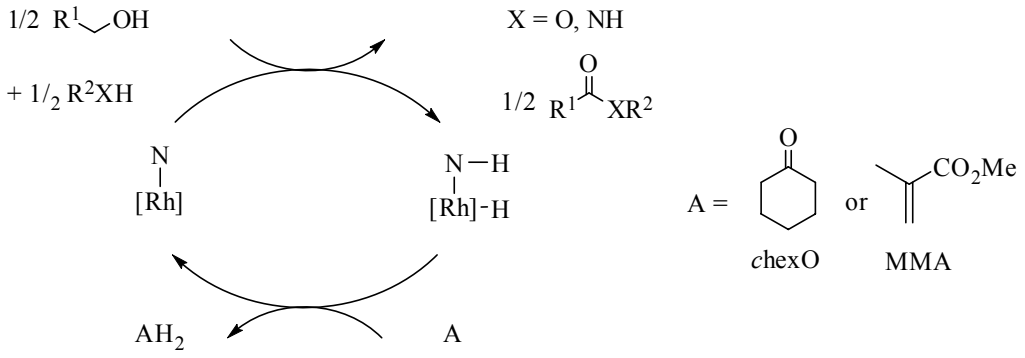
Abstract

This thesis describes the application of rhodium and iridium complexes of the tridentate amine-diolefin ligand bis(5H-dibenzo[a,d]cyclohepten-5-yl)amine ($trop_2NH$) in transfer hydrogenation and in dehydrogenative oxidation reactions.

Homogenously catalyzed transfer hydrogenation is an important and valuable tool in synthetic organic chemistry for the reduction of C=O double bonds. Rhodium (I) amides with a saw horse structure of the type $[Rh(trop_2N)(PPh_3)]$ reduce ketones and activated olefins using ethanol as hydrogen donor. Under mild reaction conditions the corresponding alcohols and ethyl acetate are formed with very high efficiency and turnover frequencies above 500'000 h^{-1} at a substrate to catalyst ratio (S/C) of 100'000.



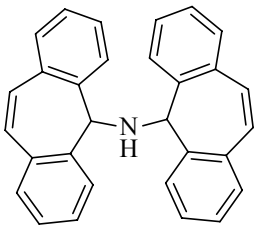
Oxidation of primary alcohols to acids and acid derivatives is of key importance in organic chemistry. Because many methods are available for this reaction, practicality is important. This includes mild reaction temperatures, low catalyst loading, functional group tolerance, simple protocols, easy workup and the ability to chemoselectively oxidize an alcohol. $[Rh(trop_2N)(PPh_3)]$ is a highly efficient catalyst for the dehydrogenative coupling of primary alcohols with water, methanol, or primary amines to give carboxylic acids, methyl carboxylates, or carboxylic amides, respectively. Importantly the amido ligand plays a crucial role in the catalytic process and behaves as a cooperating ligand.



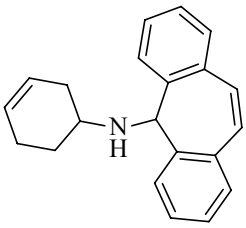
The catalyst system was studied in detail and the ancillary ligand PPh_3 varied. Alkyl phosphines, aryl phosphines, phosphites, phospholes, carbenes and N-donors have been tried. Best results were obtained with aryl phosphines, other phosphines and phosphites. An iridium complex [Ir($trop_2N$)(PPh_3)] analogous to the rhodium complex was prepared and tested in transfer hydrogenation.

The conditions of the transfer hydrogenation in ethanol have been optimized thoroughly.

A chiral ligand analogous to $trop_2NH$ was prepared by replacing one trop- with a cyclohexenyl moiety. The enantiomers of the resulting ligand (N-cyclohex-3'-en-1'-yl-5*H*-dibenzo[*a,d*]cycloheptene-5-amine (cyhtropNH) were separated, and rhodium complexes of this ligand applied in transfer hydrogenation. 40% ee was obtained at a substrate to catalyst ratio (S/C) of 10'000 in ethanol.



$trop_2NH$



cyhtropNH

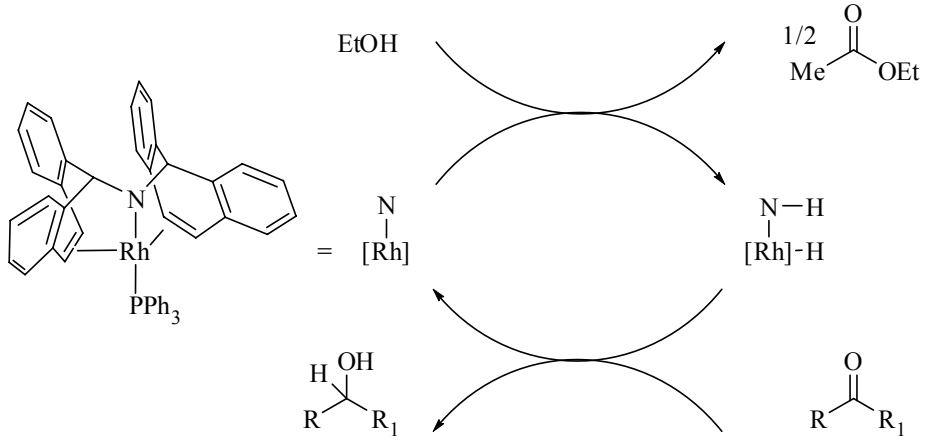
Taking bis(trop)amine as prototype, tridentate amine ligands with only one trop moiety and other donor functionalities, namely a nitrogen, a sulfur and a phosphine group were synthesized and tested in transfer hydrogenation.

Furthermore various cooper, a silver and a gold complex of $trop_2NH$ have been prepared. A new oxazoline olefine ligand was synthesized as well as the reduction potentials of its rhodium complex determined.

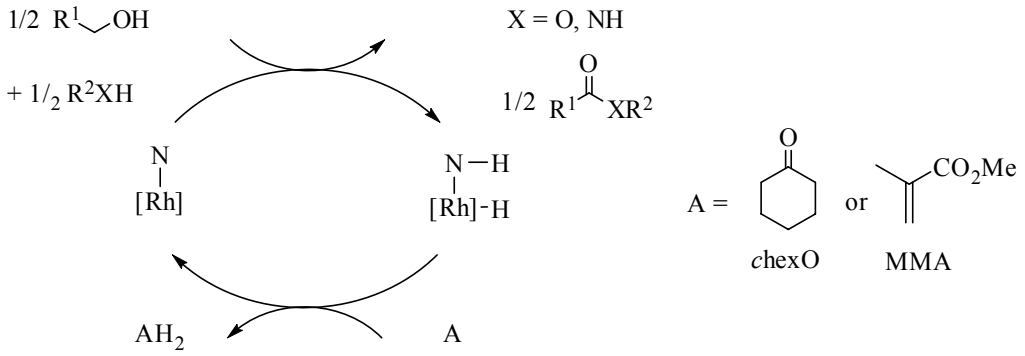
Zusammenfassung

In dieser Arbeit wird die Anwendung von Rhodium und Iridium Komplexen des tridentaten Amino-Diolefin Liganden bis(5H-dibenzo[a,d]cyclohepten-5-yl)amine ($trop_2NH$) in der Transferhydrierung und dehydrogenativen Oxidationsreaktionen beschrieben.

Homogen katalysierte Transferhydrierung ist ein wichtiges und wertvolles Werkzeug in der synthetischen organischen Chemie zur Reduktion von C=O Doppelbindungen. Rhodium(I) Amide mit einer Sägebock Struktur des Typs [$Rh(trop_2N)(PPh_3)$] reduzieren Ketone und aktivierte Olefine mit Ethanol als Wasserstoffdonor. Unter milden Reaktionsbedingungen und mit sehr hoher Effizienz werden die entsprechenden Alkohole und Ethylacetat gebildet. Turnover-Frequenzen über 500'000 h^{-1} wurden gemessen bei einem Substrat zu Kaltalysator Verhältniss von 100’000.



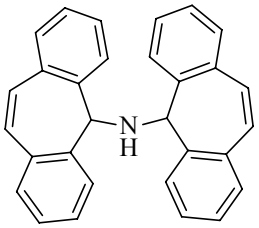
Oxidation primärer Alkohole zu Carbonsäuren und Säurederrivaten ist eine Schlüsselreaktion der organischen Chemie. Weil es schon viele Methoden für diese Reaktion gibt, ist die verbesserte Anwendbarkeit wichtig. Dazu gehören die Verwendung geringer Katalysatormengen, einfache Durchführung und Aufarbeitung, Toleranz vieler funktioneller Gruppen und die Möglichkeit chemoselektiv Polyalkohole zu oxidieren. [$Rh(trop_2N)(PPh_3)$] ist ein hoch effizenter Katalysator zur dehydrogenativen Kopplung primärer Alkohole mit Wasser, Methanol oder primären Aminen zu Carbonsäuren, Methylestern und Säureamiden. Der Amid Ligand des Komplexes hat eine wichtige Rolle im Mechanismus des Prozesses und ist ein kooperativer Ligand.



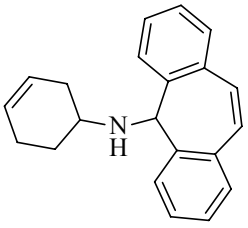
Das Katalysatorsystem wurde detailliert studiert und der zusätzliche Ligand PPh_3 variiert. Es wurden Alkylphosphine, Arylphosphine, Phosphite, Phosphole, Carbene sowie N-Donoren getestet. Die besten Katalysatoren waren Komplexe mit Arylphosphinen, anderen Phoshinen sowie Phosphiten als zusätzlichem Ligand. Ein Iridium Komplex [Ir($trop_2N$)(PPh_3)] analog zum Rhodium Komplex wurde synthetisiert und in der Transferhydrierung getestet.

Die Bedingungen der Transferhydrierung in Ethanol wurden gründlich untersucht und optimiert.

Es wurde an $trop_2NH$ ein Trop-Rest durch ein Cyclohexenyl-Rest ersetzt und der chirale Ligand (N-cyclohex-3'-en-1'-yl-5*H*-dibenzo[*a,d*]cycloheptene-5-amine (cyhtropNH) erhalten. Die Enanitiomeren dieses Liganden konnten mittels präperativer HPLC getrennt werden. Rhodium Komplexe dieses Liganden wurden in der Transferhydrierung ausprobiert und 40% ee bei einem Substrat Kaltalysator Verhältniss von 10'000 in Ethanol erreicht.



$trop_2NH$



cyhtropNH

Ausgehend von Bis(trop)amine als Prototyp wurden tridentate Amino Liganden mit nur einem Trop-Rest und anderen Donor-Funktionen, wie etwa ein Pyridin-, ein Thiophen- sowie ein Phosphin-Rest synthetisiert und in der Transferhydrierung angewendet.

Des weiteren wurden Komplexe von $trop_2NH$ mit Kupfer, Silber sowie Gold hergestellt. Ein neuer Oxazolin-Olefin Ligand wurde dargestellt und sein Rhodium Komplex mittels cyclischer Voltametrie untersucht.

Publications

Grützmacher H., Büttner T., Maire P., Ramseier M., Scheschkewitz D., Zweifel T., Lanxess Deutschland Gmbh, New tropylideneamine compounds useful in transition metal complexes, which are useful to prepare catalysts; Patent EP1614674-A2; DE102004027771-A1; JP2006008682-A; US2006036109-A1; CN1706805-A; IN200501433-I1; **2006-01-11**.

Theo Zweifel, Jean-Valère Naubron, Dr., Torsten Büttner, Dr., Timo Ott, Hansjörg Grützmacher, Prof. Dr.: Ethanol as Hydrogen Donor: Highly Efficient Transfer Hydrogenation with Rhodium(I) Amides, *Angewandte Chemie* **2008**, *120*, 3289-3293; *Angewandte Chemie-International Edition* **2008**, *47*, 3245-3249.

Theo Zweifel, Jean-Valère Naubron, Dr., Hansjörg Grützmacher, Prof. Dr.: Catalyzed dehydrogenative coupling of primary alcohols with water, methanol, or amines to acids, methylesters, or amides, *Angewandte Chemie* **2009**, 121, 567-571; *Angewandte Chemie-International Edition* **2009**, 48, 559-563;

Public Presentations

PhD students Symposium of the Laboratorium für Anorganische Chemie 2006, ETH Zürich, Oral Presentation “Transferhydrogenation with Rhodium Diolefin Amide Complexes”.

1st European Chemistry Congress 2006, Budapest, Hungary, Poster Presentation “Rhodium Diolefin Amide Complexes As Highly Efficient Transfer Hydrogenation Catalysts In Ethanol”.

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I. Introduction

1 Transferhydrogenation

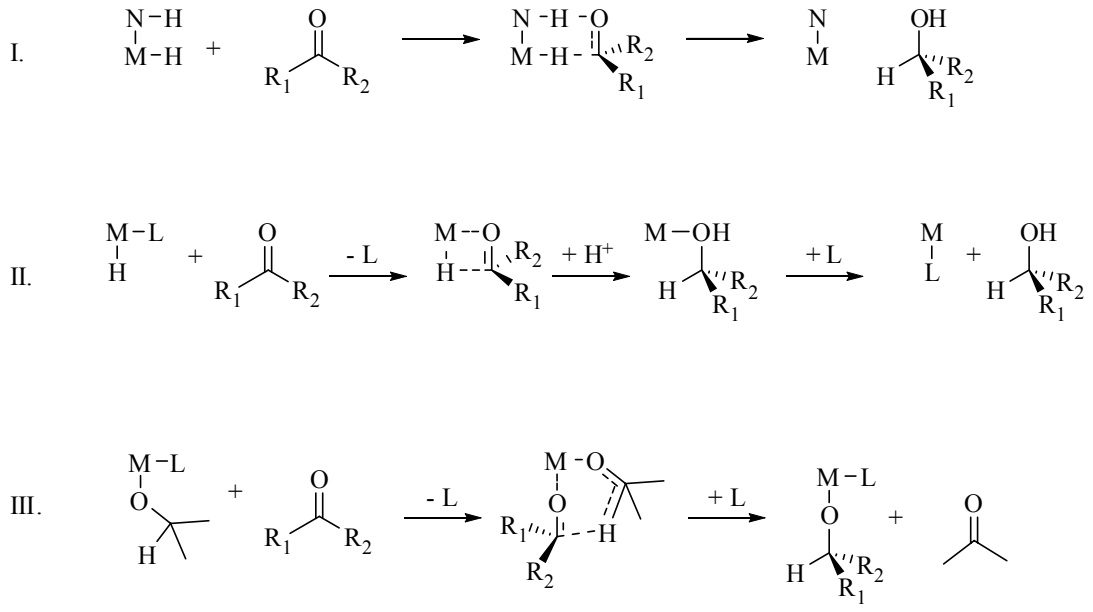
Homogeneously catalyzed transfer hydrogenation became a powerful tool in synthetic chemistry and a wide range of unsaturated substrates can be employed in this reaction. In asymmetric versions very high enantioselectivities are routinely achieved.[1-4] Early transition metals and lanthanoids[5, 6] as well as late transition metals, mostly ruthenium,[7-12] iridium[13, 14] and rhodium,[15-17] have been used. Ruthenium(II) arene complexes and rhodium(III)(cyclopentadienyl) complexes in combination with isopropanol or formic acid/triethylamine mixtures are among the most popular catalytic systems employed.[17] Impressive activities ($> 1 \times 10^6\ h^{-1}$) and selectivities have been reached. Le Floch et al. reported a TOF of $1.33 \times 10^6\ h^{-1}$ for cyclohexanone and $1.2 \times 10^6\ h^{-1}$ for acetophenone at 90 °C and substrate to catalyst ratio (S/C) of 20×10^6 with a cationic 1-(2-methylpyridine)-phosphole cymene ruthenium complex in isopropanol.[7] Baratta et al. reported a TOF = $1.5 \times 10^6\ h^{-1}$ (cyclohexanone or acetophenone) at S/C of 100'000 with a ruthenium complex in isopropanol.[11]

Classical methods for the reduction of double bonds use molecular hydrogen as reductant and heterogeneous[18] or homogeneous[19, 20] catalysts. While hydrogen is one of the cleanest reductants it is also highly flammable. Transfer hydrogenation avoids the dangers associated with hydrogen and the use of high pressures requiring special equipment. Because transfer hydrogenation can be conveniently applied on a laboratory scale it helps to circumvent the application of stoichiometric hydrides as reducing agents such as $LiAlH_4$[21] or $NaBH_4$[22] producing large amounts of waste.

Most known systems for transfer hydrogenation require elevated temperatures and the reaction is often carried out in refluxing isopropanol (80° C).[23] Only few catalysts having sufficient reactivity at room temperature are currently known.[17]

Mechanism of the transfer hydrogenation

For transfer hydrogenation three mechanisms were broadly experimentally and computationally studied,[3, 24-26] They can be classified how the hydrogen is transferred on the ketone (Scheme 1).



Scheme 1: Common transfer hydrogenation mechanisms.

I. Concerted transfer of a proton from the amine ligand and hydride from the metal to the ketone. This is often termed metal-ligand bifunctional or Noyori mechanism and is very important for late transition metals with amine ligands. The ketone does not coordinate to the metal, the reaction happens in the outer sphere of the catalyst. The metal and the amine ligand cooperate in a synergistic manner facilitating hydrogen transfer.[27]

II. Insertion of the ketone in the M-H bond of the hydride. This hydridic mechanism is observed in transition metal catalysts lacking suitable amine functions.

III. Direct transfer of the α-hydrogen of the metal alcoholate to the ketone. This is known as Meerwein-Pondorf-Verley mechanism and is most often found in main group elements, early transition metals and lanthanoids.

In mechanisms I. and II. formation of the hydride occurs by a reversal of the hydrogenation of the ketone as required by the principle of microscopic reversibility.

The transition states and their energies involved in a catalytic reaction are dependent on the reaction mechanism. As in any catalytic reaction the mechanism determines the activation barriers involved and therefore the efficiency of the catalyst.

2 Dehydrogenation

A flaw of transfer hydrogenation in isopropanol is the intrinsic reversibility of the reaction. However, this can be used for the dehydrogenative oxidation of secondary alcohols. The classic example is the Oppenauer oxidation catalyzed by aluminium isopropoxide.[28, 29] One of the main benefits of the Oppenauer oxidation is that it uses relatively non-toxic and cheap chemicals. With catalysts bearing chiral ligands the same principle has been applied to the kinetic resolution of secondary alcohols.[30, 31] The reaction has been modified by the use of other acceptors, e.g. chloral[32] and nitrobenzaldehyde.[33] These have higher oxidation potentials[34] shifting the reaction equilibrium to the product side but are more expensive and more difficult to remove than acetone and isopropanol.

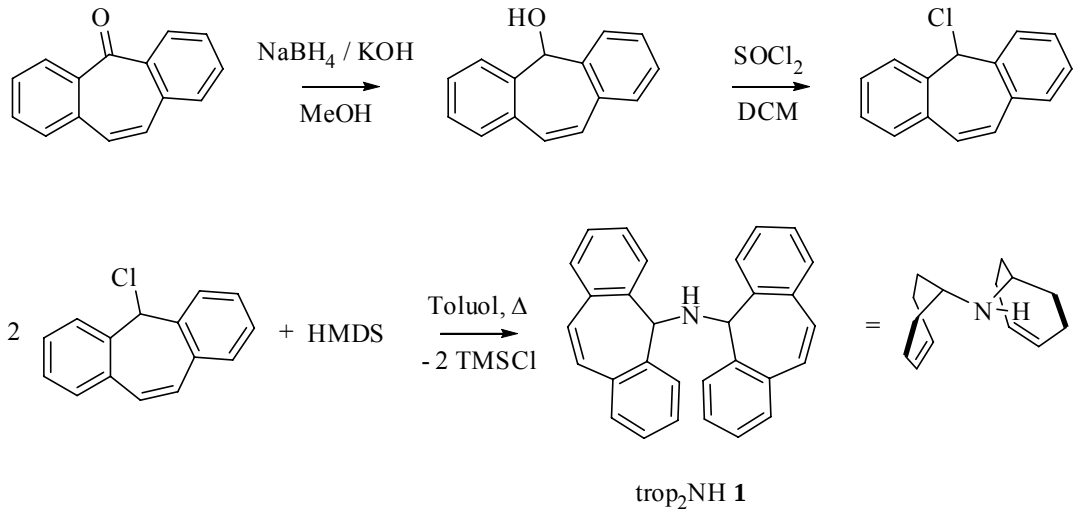
Acceptorless dehydrogenation of substrates under evolution of H_2 is a field of ongoing research. However, for most organic substrates the thermodynamics of this reaction is unfavourable. Therefore the equilibrium of the reaction has to be shifted by applying elevated temperatures and continuous removal of the generated hydrogen. One problem is that dehydrogenation of volatile materials is not possible. In homogenous versions relatively stable transition metal complexes have to be used due to the high temperatures.

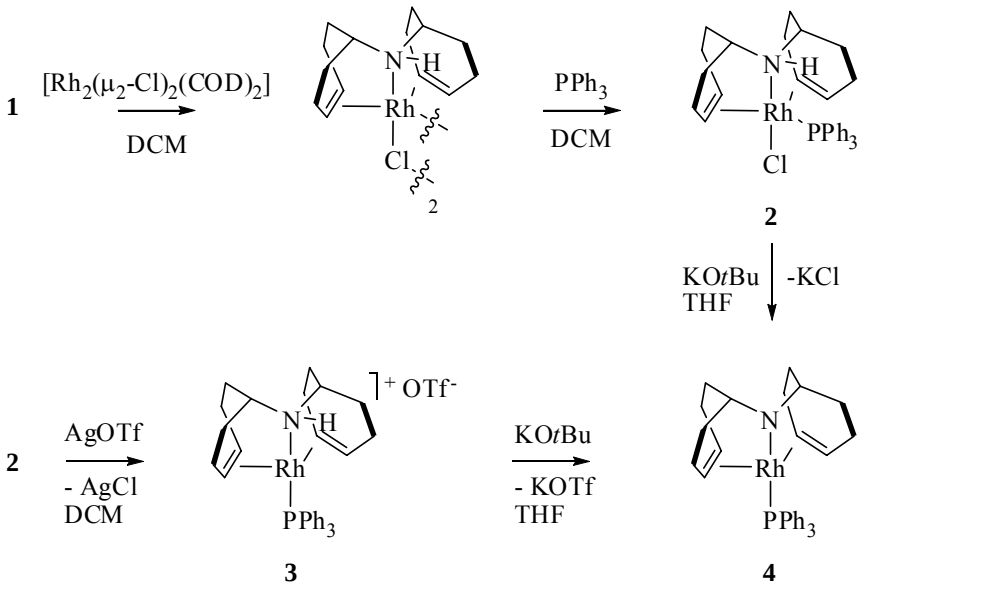
Another possibility is the use of light as energy source to produce hydrogen from organic substrates but also, as ultimate goal, from water.[35]

The catalyzed dehydrogenation of primary alcohols to give symmetrical esters, RCO(OR), with pincer type ruthenium complexes has been reported recently.[36, 37] This was further developed into the acceptorless dehydrogenation of primary alcohols and amines to amides by Milstein, a new reaction.[38]

3 Synthesis of the trop$_2$NH ligand and complexes

The ligand used in large parts this work, bis(5-H-dibenzo[a,d]cyclohepten-5-yl)amine (trop$_2$NH) can be conveniently prepared in high yield by reacting readily available 5-chloro-5-H-dibenzo[a,d]cyclohepten (tropCl) with hexamethyldisilazane (HMDS).[39, 40]





Scheme 2: Simple and straight forward synthesis of trop$_2$NH and of its triphenyl rhodium amide complex.

Reaction of trop$_2$NH in DCM with $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$ gives in a very clean reaction the dimer $[Rh_2(\mu_2\text{-}Cl)_2(trop_2NH)_2]$. This dimer is split with triphenylphosphine and complex [Rh(Cl)(trop$_2$NH)(PPh$_3$)] **2** is obtained. From this complex chloride can be

abstracted with silver triflate to give the complex [Rh(trop$_2$NH)(PPh$_3$)]OTf **3**. Both **2** and **3** can be deprotonated to the neutral amide [Rh(trop$_2$N)(PPh$_3$)] **4**. A crystal structure of an analogous complex with diphenyl tolyl phosphine [Rh(trop$_2$N)(PPh$_2$Tol)] **4*** was obtained by our group. [41]

4 The Catalyst

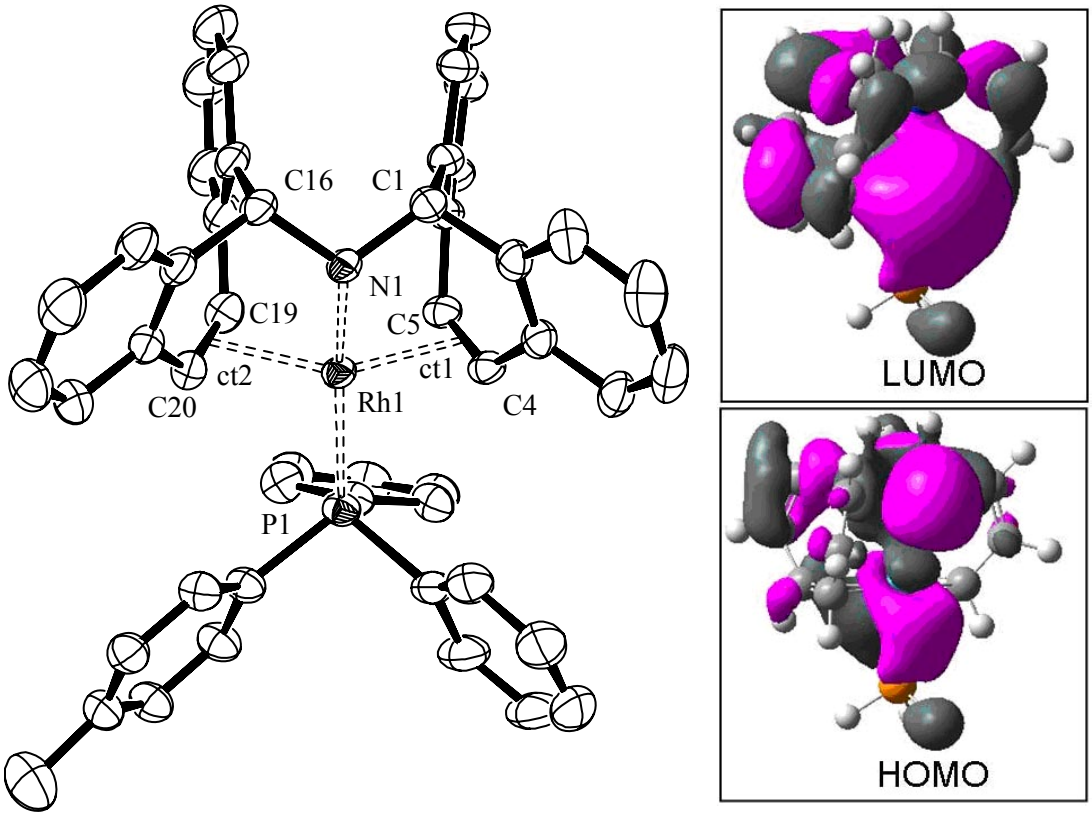


Figure 1: Ortep plot (at 50% ellipsoid probability) of [Rh(trop$_2$N)(PPh$_2$Tol)] **4***[41] (left) and calculated HOMO and LUMO of the model molecule [Rh(cht$_2$N)(PH$_3$)] **4'**(right, see section II). In the Ortep plot hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°](ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh-N1 2.007(1), Rh1-P1 2.316(1), Rh1-C5 2.165(2), Rh1-C4 2.190(2), Rh1-C19 2.174(2), Rh1-C20 2.199(2), Rh1-ct1 2.058(2), Rh1-ct2 2.070(2), C4=C5 1.423(3), C19=C20 1.407(3); N1-Rh-P1 166.18(5), ct1-Rh-ct2 135.81(7), C16-N1-C1 109.5(1), C16-N1-Rh 118.5(1), C1-N1-Rh 119.0(1).

The structure of compound **4** strongly deviates from the expected planar form of a tetra-coordinated ML$_4$ complex (M = d^8 metal center, L = 2 electron donor ligand) with a 16 valence electron configuration. Instead a "saw-horse" type structure is created by the combination of two π-acceptor olefinic binding sites and an amido and phosphane σ-donor function each in trans-position. As a result, the amido function is Lewis-basic (the highest occupied orbital (HOMO) is localized on the N center) and

the adjacent rhodium center is Lewis-acidic (the lowest unoccupied orbital (LUMO) is localized on the metal center). Due to this **4** easily cleaves H_2 heterolytically across the Rh-N bond and is a catalyst for the hydrogenation of unsaturated compounds R_2=X (X = O, NR').[41] Much of the observed chemistry discussed in this work can be explained by the special electronic situation in the Rh(I) diolefin amido complex **4** and related complexes.

II. Transfer hydrogenation in ethanol

1 Introduction

Ethanol is a renewable resource and has spurred considerable interest as an alternative to fossil fuels[42] and as feed-stock for the chemical industry.[43, 44] Production from potential food sources is highly controversial due to ethical problems and may not reduce greenhouse gas emissions as much as expected. However, second generation cellulosic ethanol from waste products may help to alleviate these problems.[45-47]

Nevertheless, ethanol is a common solvent in the chemical industry, especially for products intended for human contact or consumption, including scents, flavorings, colorings, and medicines.

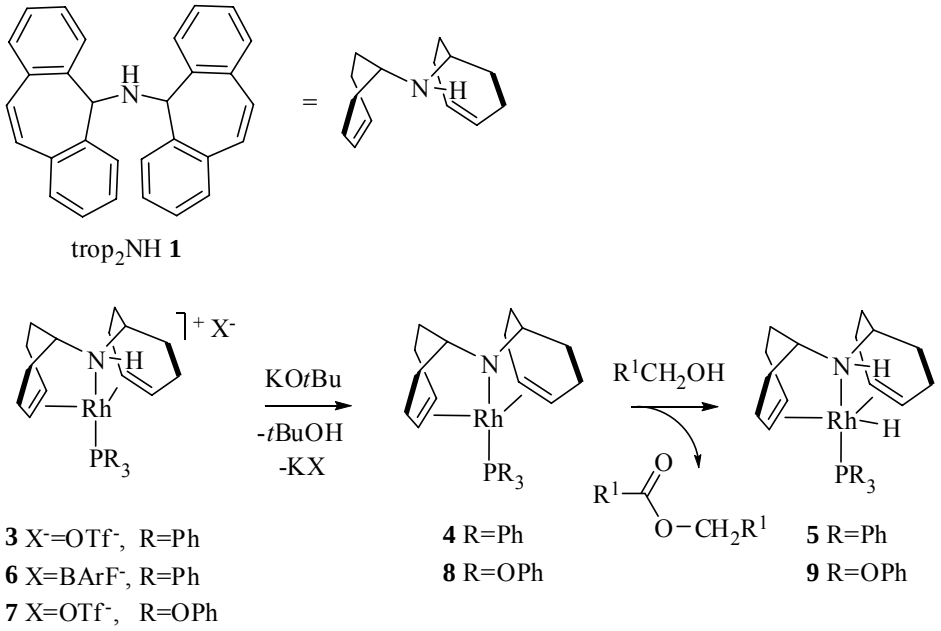
Although reduced organometallic complexes are often prepared by reacting a complex with the metal in a higher oxidation state with ethanol [i.e. Rh(III) $\rightarrow$ Rh(I) or Ru(III) $\rightarrow$ Ru(II)], ethanol has not been investigated systematically as hydrogen source in transfer hydrogenation.[48, 49] This may be due to the fact that ethanol frequently poisons the catalyst by forming stable and inactive carbonyl complexes[50-55] and that under basic conditions aldol condensation products are easily formed with acetaldehyde.

Maire et al. previously reported that the d^8-Rh(I) diolefin amide [Rh($trop_2N$)(PPh_3)] **4** is an active catalyst for ketone and imine hydrogenation with hydrogen $trop_2N$ = bis(5-H-dibenzo[a,d]cyclohepten-5-yl)-amide).[41] We found that these Rh(I) amide complexes are very efficient catalysts for the reaction

$$2\ R_2C{=}O + 2\ EtOH \rightarrow 2\ R_2HC\text{-}OH + MeCOOEt,$$

in which ethanol serves as hydrogen donor and is converted to ethyl acetate. This reaction is irreversible and for many substrates exothermic by about 10 kcal mol^{-1}. Consequently, it should be possible to perform the transfer hydrogenation (TH) in neat ethanol at high substrate concentrations. Ethyl acetate is a valuable byproduct because it is often used as solvent.

2 Synthesis of the complexes and application in catalysis



Scheme 3: Synthesis of amino olefine complexes **3**, **6**, **7** the corresponding amido complexes **4, 8** and their reaction with methanol or ethanol to give the amino hydride complexes **5**, **9**.

The complexes [Rh(trop$_2$NH)(PPh$_3$)]OTf **3**, [Rh(trop$_2$NH)(PPh$_3$)]BArF **6** and [Rh(trop$_2$NH)(P(OPh)$_3$)]OTf **7** used as precatalysts were prepared in high yield following an established synthesis protocol.[40, 41] The structures of **6** and **7** were determined by X-ray diffraction (see Figure 2 and Figure 3). The cations in both complex salts adopt a saw-horse type structure with a N-Rh-P angle of 172° and a ct-Rh-ct angle of 145°. There are no close contacts between the cation and the anion. The NH function in the [Rh(trop$_2$NH)(PR$_3$)]$^+$ cations **3**, **6** and **7** are sufficiently acidic to be quantitatively deprotonated by KO*t*Bu or Li[N(SiMe$_3$)$_2$] to give the neutral amides [Rh(trop$_2$N)(PR$_3$)] **4** and **8** (Scheme 1; **4**: R = Ph; **8**: R = OPh). For related complexes pK_a values below 19 were determined in DMSO.[39, 56] The amides react with two equivalents of methanol or ethanol to give quantitatively the hydrides [RhH(trop$_2$NH)(PR$_3$)] **5**, **9** and formic acid methyl ester, HCOOMe, or ethyl acetate, MeCOOEt. The structures of a related amide **4*** and amino hydride **5*** with PR$_3$ = PPh$_2$tol are known from our previous investigations.[41] A comparison between **6**, **4***, and **5*** shows that the bond lengths and angles are similar (see Table 2).

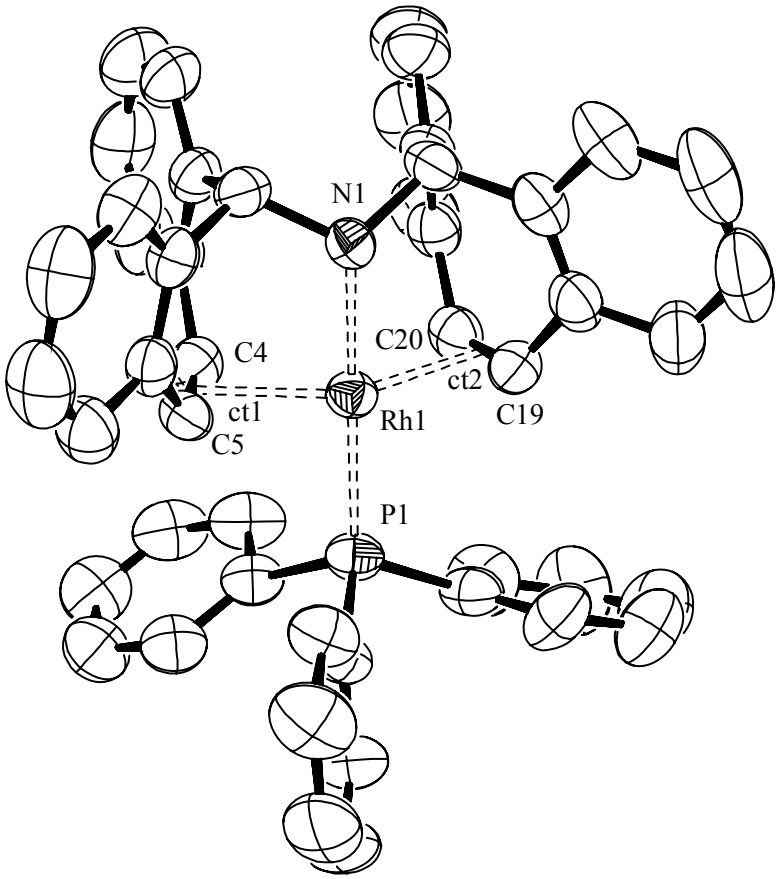


Figure 2: Ortep plot (at 50% ellipsoid probability) of the structure of **6**. The BArF anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°](ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.155(2), Rh1-P1 2.279(1), Rh1-ct1 2.075(8), Rh1-ct2 2.079(8), Rh1-C5 2.193(3), Rh1-C4 2.191(2), Rh1-C19 2.195(4), Rh1-C20 2.189(4), C4=C5 1.406(4), C19=C20 1.389(4); N1-Rh1-P1 173.1(2), ct1-Rh1-ct2 144.7(4).

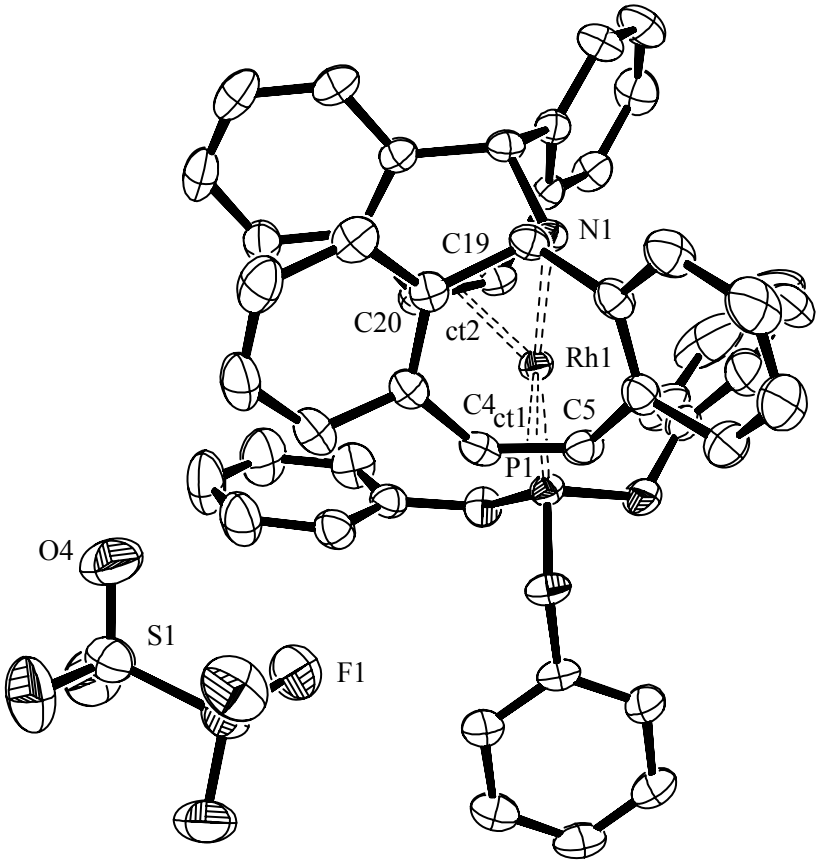
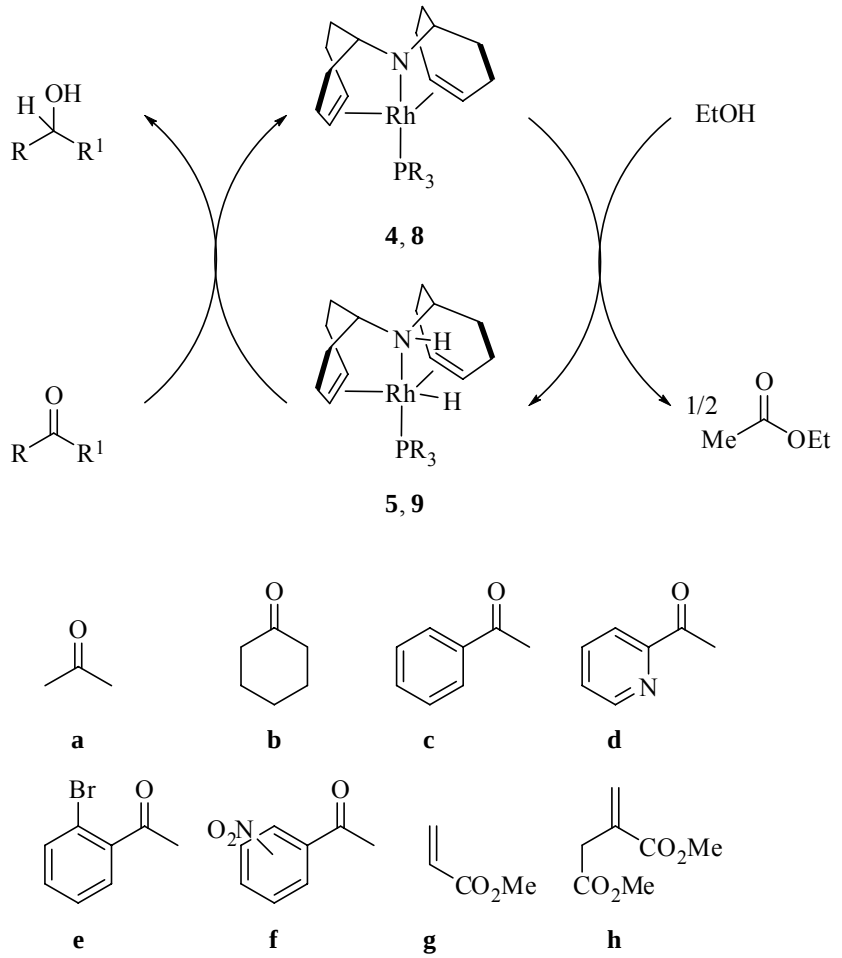


Figure 3: Ortep plot (at 50% ellipsoid probability) of the structure of [Rh(trop$_2$NH)(P(OPh)$_3$]OTf **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles[°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.147(1), Rh1-P1 2.203(1), Rh1-ct1 2.074(4), Rh1-ct2 2.133(5), Rh1-C4 2.180(2), Rh1-C5 2.201(2), Rh1-C19 2.241(1), Rh1-C20 2.247(2), C4=C5 1.412(2), C19=C20 1.396(2); N1-Rh1-P1 170.1(4), ct1-Rh1-ct2 145.5(5).

The rhodium amide complexes **4** and **8** are direct catalysts in the reactions described below. Because of their sensitivity, it is more convenient to use the easily storable amino complexes **3**, **6** and **7** as catalyst precursors in combination with a small amount of base. Potassium tert-butoxide (KO*t*Bu) or potassium carbonate as heterogeneous base, $[K_2CO_3]_{het}$, were applied. No catalytic turnover was observed with **3**, **6** and **7** in absence of base. The anion (OTf^-, $BARF^-$) of the precatalyst has no influence on the catalyst activity. Methanol is not an efficient hydrogen donor in catalytic TH and only a few catalytic cycles were observed. However, the efficiency with ethanol is excellent (Table 1, entry 1-3).[1-4, 7, 17] Isopropanol can be used as hydrogen donor but is less efficient and requires more dilute conditions in order to obtain comparable conversions (Table 1, last entries 11, 12).



Scheme 4: Simplified catalytic transfer hydrogenation cycle by which substrates ***a-h*** are quantitatively converted to the corresponding alcohols with catalysts **4** and **8**.

The performance of **4** and **8** is impressively demonstrated when acetone – the by-product in the classical transfer hydrogenations with isopropanol as hydrogen donor – is quantitatively converted to isopropanol in the reaction,

$Me_2C{=}O + 2\ EtOH \rightarrow Me_2CH\text{-}OH + MeCO(OEt)$ (see Table 1, entry 1).

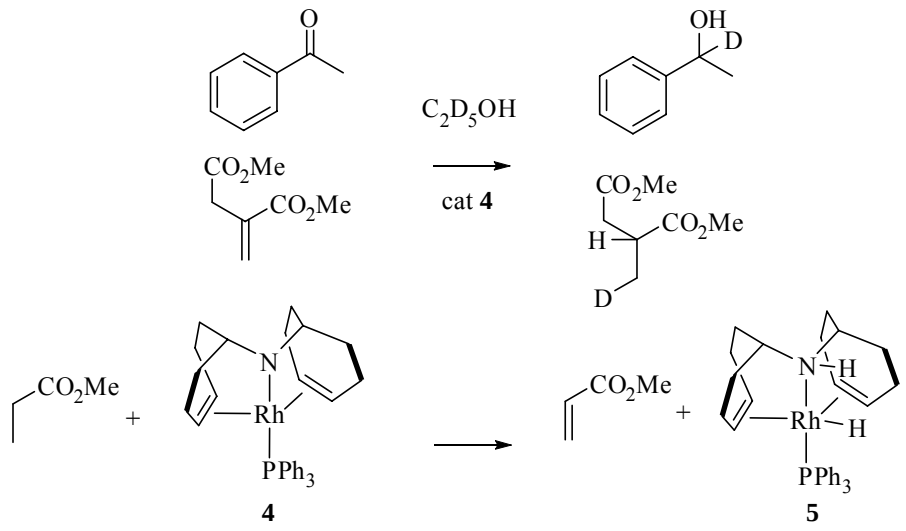
The computed reaction enthalpy for this reaction is $\Delta H_r = -14$ kcal mol^{-1}. Under the given conditions, this reaction proceeds with a $TOF_{50} = 500'000\ h^{-1}$ at room temperature. The results listed in Table 1 show that the catalysts **4** and **8** tolerate a variety of functional groups and are not deactivated by nitrogen donors (entry 2, substrate ***d***). Notably, with the triphenyl phosphite complex **7** as catalyst precursor, ortho-bromoacetophenone **e** (entry 3) or the nitro-acetophenones o/m/p-***f*** (entries 4 -6) are converted with high activity under mild conditions (40 °C and 1 mol% of $[K_2CO_3]_{het}$). Transferhydrogenations of the substrates ***e, f*** listed in Table 1 were reported but never above S/C ratios of 1000.[57, 58] No reduction of the nitro moiety

was observed and no aldol type condensations were detected despite the high CH-acidity. Remarkable is the high efficiency with which electron poor olefins like acrylic acid methylester ***g*** or itaconic acid dimethylester ***h*** are cleanly converted at S/C 10'000 under base free conditions. Both non-activated and electron rich olefins such as styrene or 3,4-dihydro-2H-pyrane are not hydrogenated.

Table 1: Transfer hydrogenations with complexes **3**, **6** and **7** as catalyst precursors or amide **4** as catalyst. In all cases >98% conversion was achieved.[a] **3** or **6**, 1 mol% KO*t*Bu, substrate 2 M in ethanol, RT; [b]: **7**, 1mol% $[K_2CO_3]_{het}$, Substrate 2 M in ethanol, 40 °C; [c]: **4**, Substrate 2 M in ethanol, RT, [d] **3**, 1mol% KOtBu, substrate 0.5 M in *i*PrOH

Entry	Substrate	S/C	TOF_{50} [h^{-1}]
1	Acetone ***a*** [a]	100'000	500'000
2	Cyclohexanone ***b*** [a]	100'000	750'000
3	Acetophenone ***c*** [a]	100'000	600'000
4	2-Acetylpyridin ***d*** [b]	100'000	300'000
5	2-Bromoacetophenon ***e*** [b]	5'000	5'000
6	2-Nitroacetophenon o-***f*** [b]	5'000	5'000
7	3-Nitroacetophenon m-***f*** [b]	10'000	5'000
8	4-Nitroacetophenon p-***f*** [b]	20'000	25'000
9	Acrylic acid methyl ester ***g*** [c]	10'000	300'000
10	Itaconic acid dimethyl ester ***h*** [c]	10'000	90'000
11	Cyclohexanone ***b*** [d]	100'000	150'000
12	Acetophenone ***c*** [d]	10'000	100'000

Addition of a large excess of triphenylphosphine (100 eq.) with respect to **4** has no influence on the catalyst's activity. This supports the assumption that **4** is involved in the catalytic cycle and not a species formed by PPh_3 dissociation. TH of acetophenone in [D_5] ethanol resulted in complete deuteration of the 1 position of 1-phenylethanol (Scheme 3). When itaconic acid dimethylester ***h*** was transfer hydrogenated with [D_5] ethanol, deuterium was exclusively incorporated in the β position of methylsuccinic acid dimethyl ester. Furthermore, the amide **4** cleanly dehydrogenates propionic acid methylester to give acrylic acid methylester ***g*** and the hydride **5**.



Scheme 5: Selective deuterium incorporation into acetophenone and itaconic acid dimethylester and dehydrogenation of propionic methylester promoted by **4**.

The computed ΔH_r for the reaction of the model complex [Rh(cht$_2$N)(PH$_3$)] **4'** + H$_2$ → [Rh(cht$_2$NH)(H)(PH$_3$)] **F** is −32.6 kcal mol^{-1} (0 K, gas phase, DFT at B3PW91/BS211B3PW91/BS1 level); the reported hydrogenation enthalpy for acrylic acid is less exothermic (−30.3 kcal mol^{-1}) in agreement with the experimental finding that propionic acid ethyl ester is dehydrogenated. These findings suggest a Noyori-type mechanism (see I.1) also for the transfer hydrogenation of activated C=C bonds. Based on computations, such a mechanism was suggested in the literature, but until now not closely investigated.[59]

3 Computational study of the mechanism

The observation that the formation of ethyl acetate is efficiently promoted by the isolated amide **4** in the absence of any additional external base, prompted us to investigate this process by DFT calculations (B3PW91/BS211B3PW91/BS1; for computational details see the experimental part). [Rh(cht$_2$N)(PH$_3$)] **4'** was used as model complex for **4**. The impact of several combinations of basis sets on the geometry of **4'** was evaluated. The use of basis set **BS1** showed a good agreement between the structure of **4'** and the X-Ray data of **4*** (see Table 2).

Table 2: Comparison of selected structural data between [Rh(trop$_2$N)(PPh$_2$tol)] **4***[41], [RhH(trop$_2$NH)(PPh$_2$tol)] **5***[41], [Rh(trop$_2$NH)(PPh$_3$)]BArF **6**, and the model complexes [Rh(cht$_2$N)(PH$_3$)] **4'**, [Rh(H)(cht$_2$NH)(PH$_3$)] **F** and [Rh(cht$_2$NH)(PH$_3$)]$^+$ **6'**. Selected bond lengths [Å] and angles [°] are given from X-ray diffraction studies and DFT calculations (B3PW91/BS2//B3PW91/BS1).

	Rh-N	Rh-P	N-Rh-P	ct-Rh-ct
4*[41]	2.007(1)	2.316(1)	166.18(5)	135.81(7)
4'	2.014	2.304	171.2	144.2
5*[41]	2.178(1)	2.230(1)	169.95(3)	132.54(5)
F	2.170	2.227	170.0	136.4
6	2.155(2)	2.279(1)	173.1(2)	144.7(4)
6'	2.143	2.274	173.7	150.0

The mechanism is divided into two parts which are graphically displayed in Figure 4 to Figure 6. Step 1 is the reaction of the model complex [Rh(cht$_2$N)(PH$_3$)] **4'** (see Figure 4) with ethanol leading to adducts **A**, **B** or **C** (cht = cycloheptatrienyl). Adduct **A,** in which ethanol is merely H-bonded to the Rh amide nitrogen, is slightly more stable than **B** and **C** in which also the oxygen center interacts with the Rh atom.

Adducts **A** and **B** are interconverted via inversion at the oxygen center and are in rapid equilibrium. Adduct **C**, best described as an ethoxide complex, is almost isoenergetic to **B** and the activation barrier E_a(**B**,**C**) via **TS1** is very low (2.9 kcal mol^{-1}). Adduct **A** lies on the reaction coordinate which leads to the formation of the primary oxidation product acetaldehyde. We find that the OH bond of the coordinated ethanol molecule is cleaved first via **TS2a** leading to the intermediate **D** and subsequently the α-CH bond is broken via **TS2b**. However, **TS2a** is lower in energy than **D** and at this point we simply note that the potential surface is very flat in this region of the reaction. The calculated maximal barrier on the way from **A** to the acetaldehyde adduct **E** is given by E^{ZPE}(**TS2b**) – E^{ZPE}(**A**) = 7.5 kcal mol^{-1}.

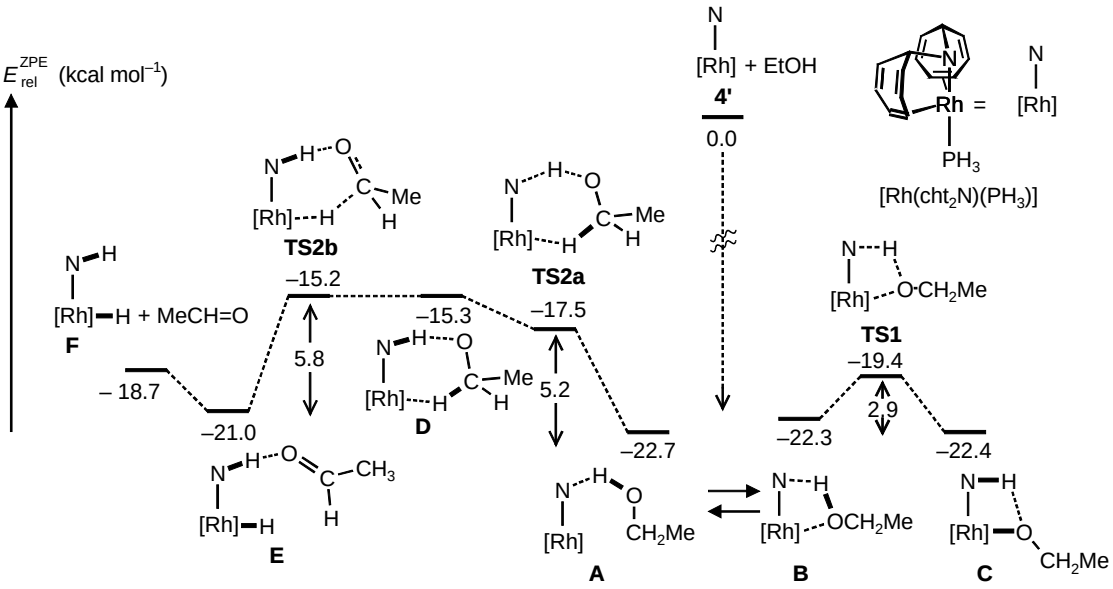


Figure 4: Rhodium amide, [Rh(cht$_2$N)(PH$_3$)] **4'**, catalyzed formation of acetaldehyde (step 1) according to DFT calculations

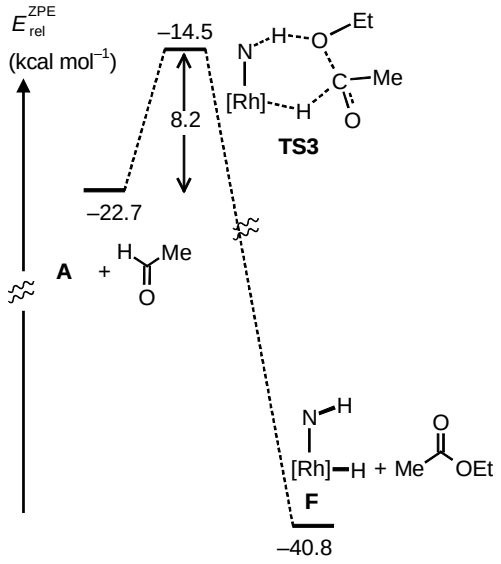


Figure 5: [Rh(cht$_2$N)(PH$_3$)] **4'**, catalyzed *concerted* formation of ethyl acetate (step 2a) according to DFT calculations.

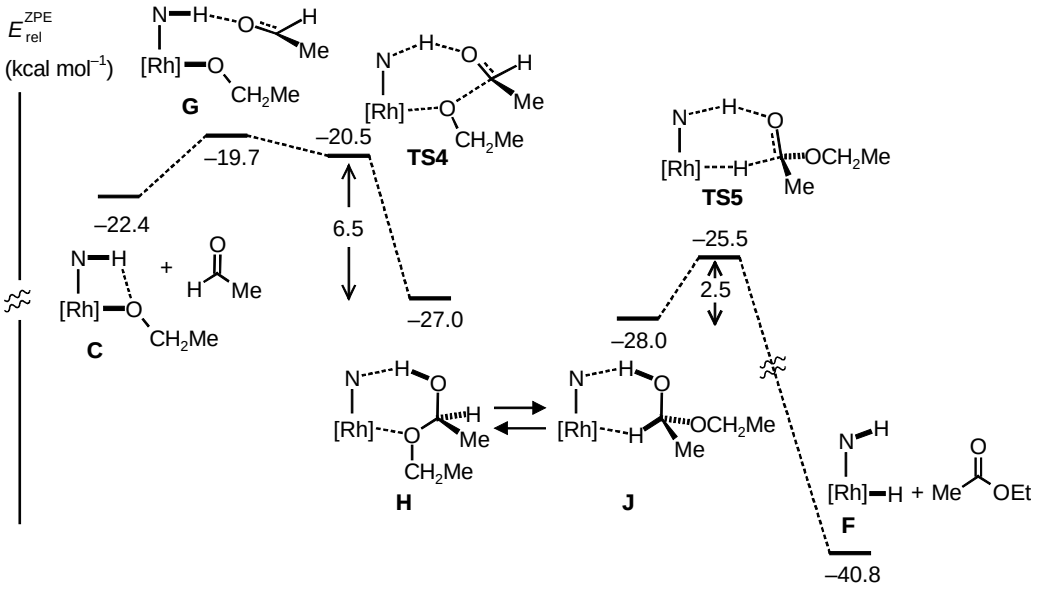


Figure 6: Rhodium amide, [Rh(cht$_2$N)(PH$_3$)] **4**', catalyzed *stepwise* formation of ethyl acetate (step 2b) according to DFT calculations.

Dissociation of acetaldehyde from **E** to give the amino hydride **F** is slightly endothermic. Overall the dehydrogenation of ethanol by the rhodium amide follows the meanwhile well-established mechanism of metal-ligand bifunctional catalysis[12, 24-26, 48, 59, 60]. Possible ways for the formation of ethyl acetate are shown in Figure 5 (step 2a) and Figure 6 (step 2b). In Figure 5 (step 2a) a concerted reaction is shown which starts with the ethanol adduct **A** to which acetaldehyde is added. In a single step via the transition state **TS3**, a simultaneous nucleophilic attack of the acetaldehyde carbonyl group by the oxygen atom of the coordinated ethanol molecule accompanied by a concerted transfer of the OH and CH hydrogen occurs to give the rhodium amino hydride **F** and ethyl acetate. The calculated activation barrier for this process is low (8.2 kcal mol^{-1}). A second way is shown in Figure 6 (step 2b). The ethoxide complex **C** reacts with acetaldehyde to give the adduct **G** which immediately rearranges via **TS4** to give the hemiacetal complex **H**. This may easily rearrange into the reactive conformation **J**. A concerted hydrogen transfer from the OH and σ-CH group concludes via the very low lying transition state **TS5** the exothermic formation of ethyl acetate and the rhodium amino hydride complex **F**. The latter transfers the hydrogen to the substrate to give the hydrogenated product under regeneration of catalyst **4**'. In Figure 7 the reaction profile for the reduction of acetone by catalyst [Rh(cht$_2$N)(PH$_3$)] **4**' is given.

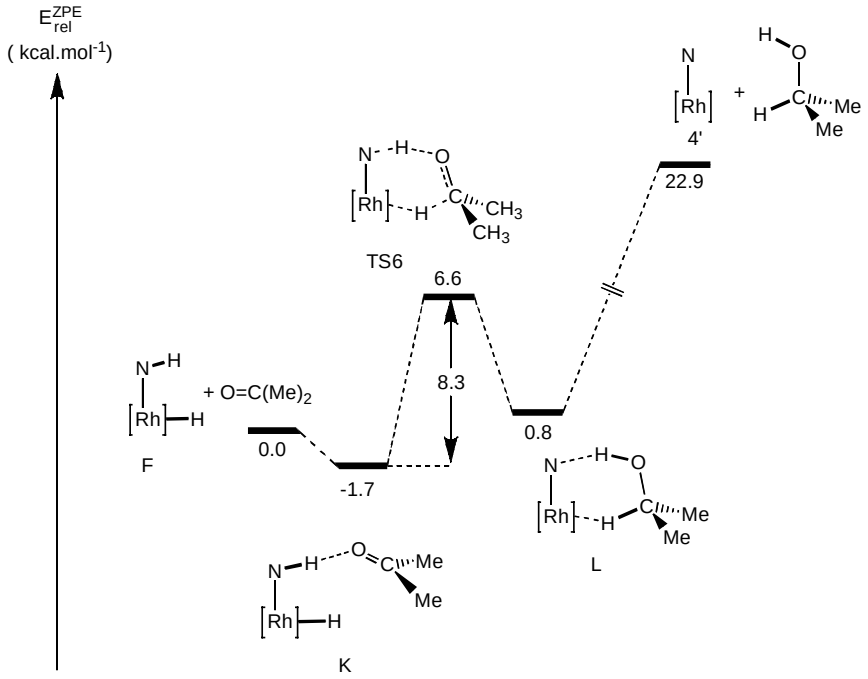


Figure 7: Reaction profile for the reduction of acetone by catalyst [Rh(cht$_2$N)(PH$_3$)] **4**'

The computation of species **K** did not converge properly because of the flatness of the energy hypersurface in this region. In order to achieve a better convergence criterion, we could have reduced the integration grid, which however significantly enhances the computational costs. It was not our objective to re-calculate the well-established Noyori-mechanism (see [12, 24-26, 48, 59, 60]) but the elucidation of the mechanism of ethyl acetate formation. Thus, we estimate the energy of **K** to be accurate within the applied grid in our computations (< 0.1 kcal mol^{-1}). The dissociation energy for the reaction **K** $\rightarrow$ **F** + Me$_2$C=O is in the same range as the dissociation of **E** to **F** and formaldehyde ($\Delta E_{diss} \approx$ 1.7 - 1.8 kcal mol^{-1}, see Figure 4). The computed reaction enthalpy (B3PW91/BS211B3PW91/BS1, at T = 0 K in the gas phase) for the reaction

$$Me_2C{=}O + 2\ EtOH \rightarrow Me_2CH\text{-}OH + MeCO(OEt)$$

is ΔH_r = -14 kcal mol^{-1}, which is in good agreement with the experimental value.

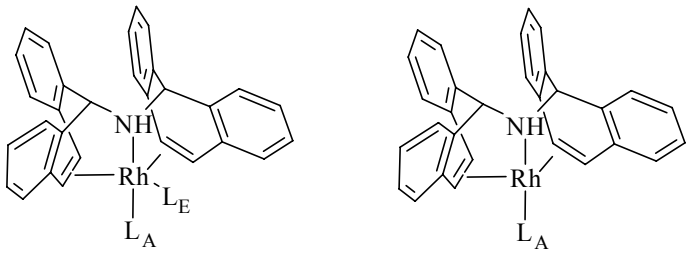
In summary, the rhodium amides **4** and **8** with a saw-horse type structure are highly efficient catalysts for the transfer hydrogenation of ketones and activated olefins using ethanol as hydrogen donor which is irreversibly converted to ethyl acetate. The reactions can be performed at high substrate concentrations in neat ethanol at room temperature. Although we do not exclude that the hemiacetal, MeHC(OH)(OEt), is formed classically in a non-metal assisted reaction (and enters via **H** or **J** see catalytic cycle, see step 2b in Figure 6), results from DFT calculations show that its formation

may be also a metal catalyzed reaction. According to the calculations only very low activation barriers (< 10 kcal mol^{-1}) are encountered along the reaction path which explains the high catalytic activity.

III. Detailed Investigation of the Catalyst System

1 Introduction

Since the results obtained with ethanol were very encouraging the catalyst system was further studied. The modular design of the precatalyst [Rh(trop$_2$NH)(PPh$_3$)]OTf **3** permits the simple modification of the catalyst by established synthesis protocols.[39, 41]



A **B**

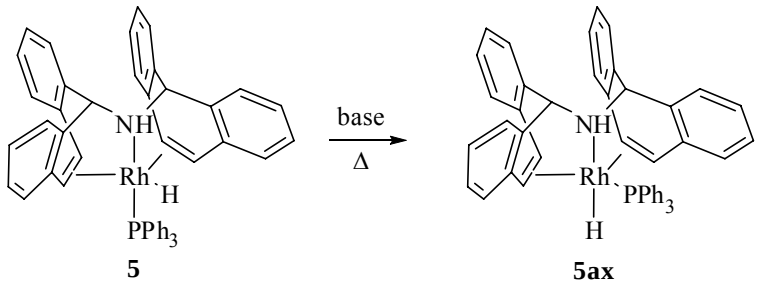
Scheme 6: The [Rh(trop$_2$NH)(L_E)(L_A)] cation adopting trigonal bipyramidal (**A**) or saw-horse structures (**B**) in metal complexes. L_E = Ligand in equatorial position, L_A = Ligand in axial position.

It was found earlier that the ligand in the axial position trans to a hard σ-donor in a trigonal bipyramidal complex is relatively stable towards substitution. The ligand in equatorial position in the same plane as the olefins; two π-acceptors, is more readily exchanged.[39]

However, prior work has established the lability of the axial ligand triphenylphosphine in axial position of the amide [Rh(trop$_2$N)(PPh$_3$)] **4**.[61] Analogous complexes with other phosphines showed the same behavior. In the crystal structure of [Rh(trop$_2$NH)(PPh$_2$Tol)] **4*** the Rh-P distance is 2.32 Å, slightly longer than in [Rh(trop$_2$NH)(PPh$_3$)]BArF **6** with a Rh-P distance of 2.28 Å (see Table 2). Elongation of the Rh-P bond is in agreement with the moderate lability of the axial ligand. The exchange of axial ligands in such complexes has been studied before.[61] Catalyst decomposition was investigated. Air sensitive ligands are easily oxidized when they leave the coordination sphere but more importantly the unsaturated metal complex formed can undergo a variety of decomposition reactions.

Directly related to this is the isomerisation of the equatorial hydride [Rh(eq-H)(trop$_2$NH)(PPh$_3$)] **5** to [Rh(ax-H)(trop$_2$NH)(PPh$_3$)] **5ax** with the hydride in axial position and triphenylphosphine in equatorial position first observed by Büttner[40] and later by Maire.[41] Hydride **5ax** is not catalytically active anymore. According to unpublished calculations of our group, complex **5ax** is 40 kcal mol^{-1}

more stable than **5**. This isomerisation reaction is catalyzed by excess base and/or accelerated by heat.



5 **5ax**

Scheme 7: Isomerisation of hydride **5** to hydride **5ax**

When hydride **5** was generated from [Rh(trop$_2$NH)(PPh$_3$)]OTf **3** in ethanol by addition of excess KO*t*Bu (10 eq.) **5** was stable for more than 2 days. Likely the isomerisation is kinetically inhibited under these conditions.

Unfortunately, due to the high dilution and low catalyst loading investigation of the fate of the catalyst is difficult. Büttner[40] found that if the transfer hydrogenation was performed in refluxing ethanol, **5ax** was the only product found after catalysis. It remains unclear if this is due to heating of the solution or excessive use of base. Furthermore it is uncertain if the same complex is formed at high substrate to catalyst ratios (S/C > 10'000) under transfer hydrogenation conditions.

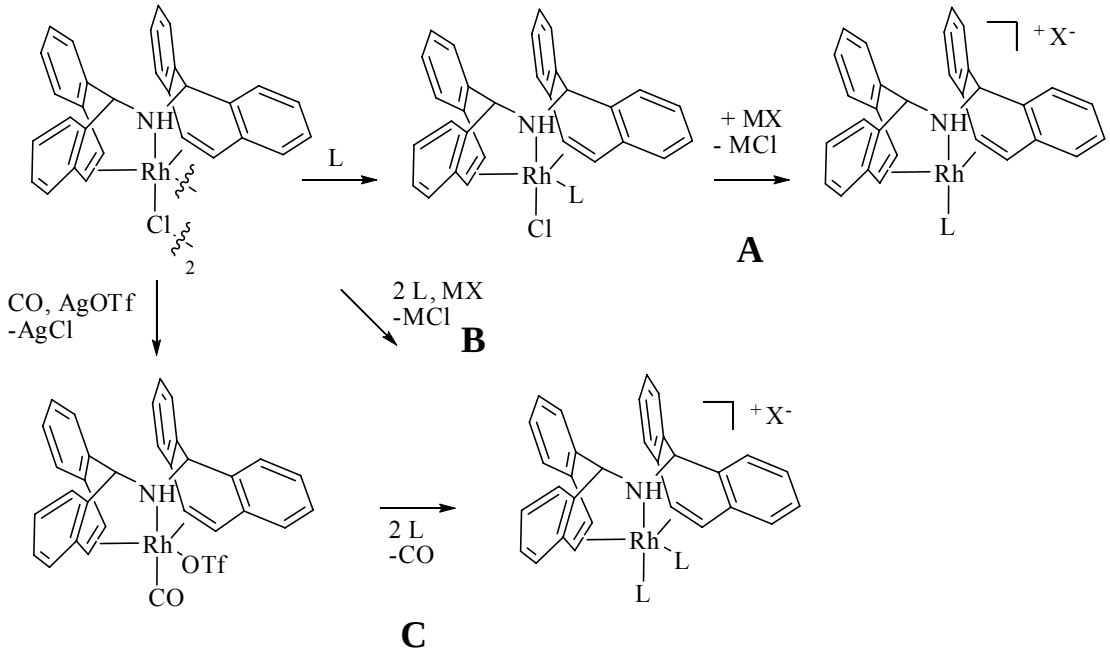
When air was allowed to enter the transfer hydrogenation reactions they stopped almost immediately. Surprisingly amide [Rh(trop$_2$N)(PPh$_3$)] **4** was stable in the presence of dry oxygen for a short time (minutes). After 5 min Amide **4** is the only substance found in ^{31}P-NMR. However, after 6 hours only triphenylphosphine oxide is observed. This is another clue that the triphenylphosphine ligand is not bound so well on amide **5**.

The hydride reacts readily with oxygen in solution to unidentified products. Water however is not a problem for the catalyst system. In the presence of primary alcohols the salt of the corresponding acid is formed as long as enough base is present and the system is essentially self drying (see section IV). Wet isopropanol was used without significant problems.[61]

2 Variation of ancillary ligands

On the basis of these results it was considered worthwhile to study the effect of the ancillary ligand(s) on catalytic activity and longevity. Several synthetic strategies to

introduce other ligands were applied. Starting from the chloro-bridged dimer $[Rh_2(\mu_2\text{-}Cl)_2(trop_2NH)_2]$ three approaches are possible. Splitting of the chloro-bridged dimer gives stable chloro complexes $[Rh(Cl)(trop_2NH)(L)]$ with many ligands. The chloride is normally coordinating in the axial position and is easily removed with common chloride abstraction reagents MX such as AgOTf, $TlPF_6$ or NaBArF, although NaBArF worked only in DCM (Method **A**). Another possibility with weakly coordinating or very bulky ligands is the direct synthesis of $[Rh(trop_2NH)(L)]X$ from the dimer, ligand L and a chloride abstraction reagent MX (Method **B**). Synthesis via the carbonyl compound $[Rh(trop_2NH)(CO)]OTf$ represents another alternative. Some ligands, for example small phosphites are strong enough to displace CO without the help of oxidizing reagents such as amine-N-oxides (Method **C**).



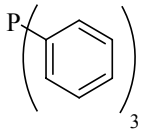
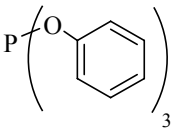
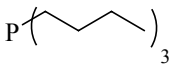
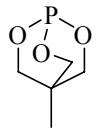
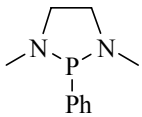
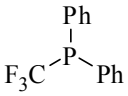
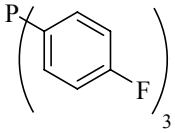
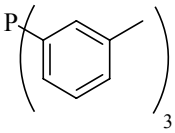
Scheme 8: Synthetic strategies for the synthesis of $[Rh(trop_2NH)(L)_n]X$ complexes

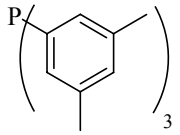
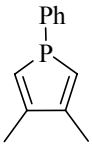
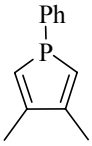
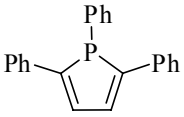
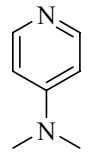
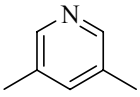
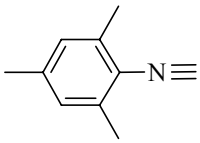
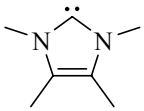
These strategies were applied to prepare precatalysts with various ancillary ligands. Complexes with phosphines, phospholes, phosphites, pyridines, a NHC carbene (1,3,4,5 tetramethylimidazole-2-ylidene, TMIY) complex (several others have been isolated in our group previously[62]) and an isonitrile complex have been prepared and evaluated in catalysis. NMR data and crystal structures are discussed in section III.4.

Several ideas to improve the catalyst guided the choice of ligands. One idea was to use more bulky phosphines not fitting into the equatorial coordination site in order to avoid or impede the isomerisation reaction. Aryl phosphines with methyl groups in

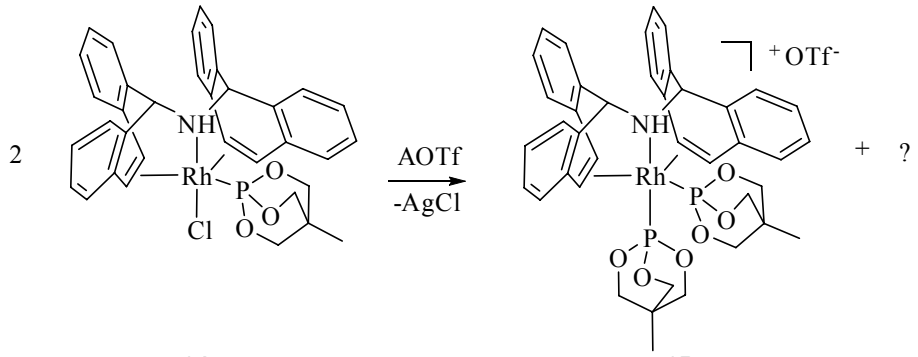
meta position were tested, because these are sterically not so demanding that they impede the catalytic reaction. The lability of the ligand in axial position is most likely essential for isomerisation and/or catalyst decomposition. Carbenes, phosphites, phospholes or electron poor phosphines form more stable metal ligand (M-L) bonds and were therefore also tested as ancillary ligands.

Table 3: Overview of the synthesized trop$_2$NH cationic complexes with various ancillary ligands, their abbreviation, and the synthesis method.

Ligand	Abbreviation	Complex	Synthesis
	PPh_3	[Rh(OTf)(trop$_2$NH)(PPh_3)] **3**	A
	$P(OPh)_3$	[Rh(trop$_2$NH)($P(OPh)_3$)]OTf **7**	A
	$P(n\text{Bu})_3$	[Rh(trop$_2$NH)($P(n\text{Bu})_3$)]OTf **11**	A
	PMe_3	[Rh(trop$_2$NH)(PMe_3)]OTf **13**	A
	$P(OCH_2)_3CCH_3$	[Rh(trop$_2$NH)($P(OCH_2)_3CCH_3)_2$]OTf **15**	C
	PN_2Ph	[Rh(trop$_2$NH)(PN_2Ph)]OTf **16**	A
	PPh_2CF_3	[Rh(trop$_2$NH)(PPh_2CF_3)]OTf **17**	A
	$P(p\text{FPh})_3$	[Rh(trop$_2$NH)($P(p\text{FPh})_3$)]OTf **18**	A
	$P(m\text{Tol})_3$	[Rh(trop$_2$NH)($P(m\text{Tol})_3$)]OTf **19**	A

	P(*m*Xyl)$_3$	[Rh(trop$_2$NH)(P(*m*Xyl)$_3$)]OTf **20**	A
	DMPP	[Rh(trop$_2$NH)(DMPP)]OTf **21**	A
	DMPP	[Rh(trop$_2$NH)(DMPP)$_2$]OTf **22**	C
	TPP	[Rh(TPP)(trop$_2$NH)]OTf **23**	B
	AsPh$_3$	[Rh(trop$_2$NH)(AsPh$_3$)]OTf **24**	A
	DMAP	[Rh(trop$_2$NH)(DMAP)$_2$]PF$_6$ **25**	B
	3,5DMP	[Rh(trop$_2$NH)(3,5DMP)$_2$]PF$_6$ **26**	B
	CNMes	[Rh(trop$_2$NH)(CNMes)]OTf **27**	A
	TMIY	[Rh(trop$_2$NH)(TMIY)]OTf **28**	A

Synthesis of these complexes was accompanied by few problems only. When [Rh(Cl)(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)] **14** was reacted with silver triflate always [Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$]OTf **15** and unidentified side products were obtained. Therefore complex **15** was synthesized by method **B** in good yield. No complex with only one phosphite of the type [Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$]X could be prepared by chloride abstraction from **14**.

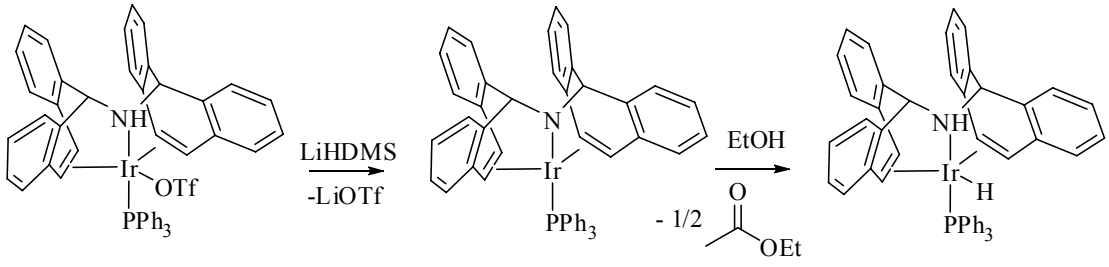


14 **15**

Scheme 9: Reaction of [Rh(Cl)(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)] **14** with silver triflate resulting in [Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$]OTf **15**.

3 Iridium complexes

The synthetic methods used to obtain iridium complexes of trop$_2$NH closely resemble the ones discussed for the rhodium complexes. An iridium complex akin to **3**, [Ir(trop$_2$NH)(PPh$_3$)]OTf **32**, was synthesized and studied in transfer hydrogenation. Heating [Ir$_2$(μ_2-Cl)$_2$(COE)$_4$] together with trop$_2$NH **1** in THF/toluene (1:1 v/v) gave [Ir$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] **30** analogous to [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$]. Subsequent addition of triphenylphosphine yielded [Ir(Cl)(trop$_2$NH)(PPh$_3$)] **31** without difficulties. Abstraction of the chloride was more difficult but successful with excess silver triflate and long reaction time (three days) in DCM. The complexes [Ir(trop$_2$N)(PPh$_3$)] **33** and [Ir(eq-H)(trop$_2$NH)(PPh$_3$)] **34** were identified as catalysts analogous to **4** and **5**. Amide **33** is obtained by deprotonation of **32** in THF with LiHDMS. Reaction of **33** with ethanol affords the hydride **34** and ethyl acetate analogous to **5**. Characteristic of the hydride is the ^{1}H-NMR signal at low frequency. (**34** ^{1}H-NMR δ = -11.92, d, $^2J_{PH}$ = 20.0 Hz; **5**: ^{1}H-NMR δ = –8.15, dd, $^1J_{RhH}$ = 23.0 Hz, $^2J_{PH}$ = 23.0 Hz). Iridium complex **32** is not very efficient in transfer hydrogenation (see Table 7). With heating TON's up to 5000 are possible in ethanol and acetophenone as substrate.

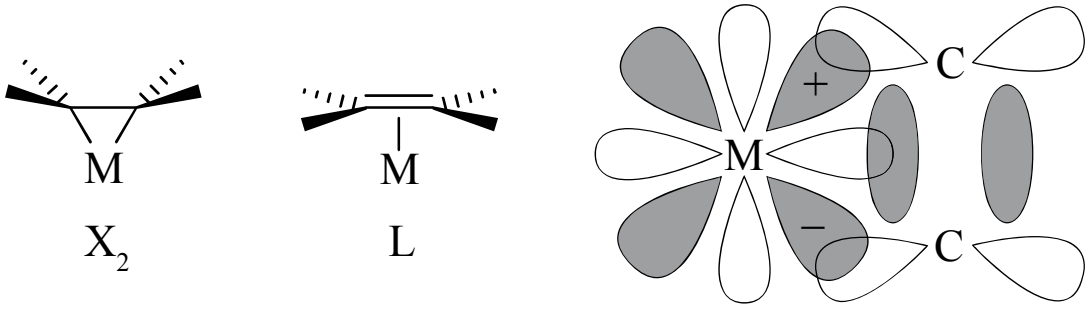


32 **33** **34**

Scheme 10: Reaction of iridium complex **32** to amide **33** and hydride **34**

4 Crystal structures and NMR data

Alkenes donate π-electrons to the metal rather than a σ-lone pair to form the metal-ligand bond. In the *Dewar-Chatt* model,[63-65] the C=C π electrons (the HOMO of the olefin) are donated into an empty d_σ-orbital on the metal and the electron pair delocalized over the three centers M, C and C'. This is accompanied by back donation from a metal d_π-orbital to the LUMO of the olefin, the C=C π* orbital. The C=C bond lengthens and weakens on binding, because the M-σ bond depletes the C=C π orbital. However, the determining factor in the lengthening of the C=C bond is the strength of the back donation from the metal filling the C=C π* orbital. This back donation depends on the π – basicity of the metal and can lower the C=C bond order significantly. In cases of strong backbonding interactions, transition metal complexes of alkenes may be thought of as a analogues of cyclopropanes (*metallacyclopropanes*). In the metallacyclopropane extreme, the substituents on carbon are strongly folded back, away from the metal as the carbons rehybridize from sp^2 to something more closely approaching sp^3. It is possible to think of the metallacyclopropane extreme as a cyclic dialkyl σ-donor, thereby increasing the oxidation state of the metal by two units. A good example of a metallacyclopropane-like complex is $[Pt(PPh_3)_2(C_2H_4)]$ with a C=C bond length of 1.43 Å.[66] In the *Dewar Chatt* extreme the ligand acts more like a simple ligand L as in Zeise's salt $K[PtCl_3(C_2H_4)]\cdot H_2O$ with a C=C bond length of 1.38 Å close to the one observed for the free olefine 1.34 Å.[67] The difference between Pt^0 and Pt^{II} is that the former is a much better π – base than Pt^{II}.



Scheme 11: The *metallacyclopropane* X_2 model, the *Dewar- Chatt* model of the metal olefin bond and the donation and back donation of an olefin to a metal cation (HOMO's grey, LUMO's white).

Electron withdrawing substituents on the olefin encourage back donation from the metal and the alkene binds stronger to the metal.[68] The phenyl rings of the trop moiety are slightly electron withdrawing thereby enhancing the binding of the olefin.

The decision with respect to where an alkene complex is situated on the continuum between these two extremes of the metal olefin bond is best tackled by structural studies and NMR.[69]

Crystal structures of some complexes discussed before were obtained. The C=C double bond lengths of the rhodium complexes characterized by X-ray diffraction were all around 1.40 Å. This value lies between the L and X_2 extremes with some amount of back bonding. Compared to the rhodium complexes the iridium complex [Ir(OTf)(trop$_2$NH)(PPh$_3$)] **32** has a longer C=C bond, about 1.45 Å (Figure 10). In general iridium is the stronger π-base and thus there is more back bonding.

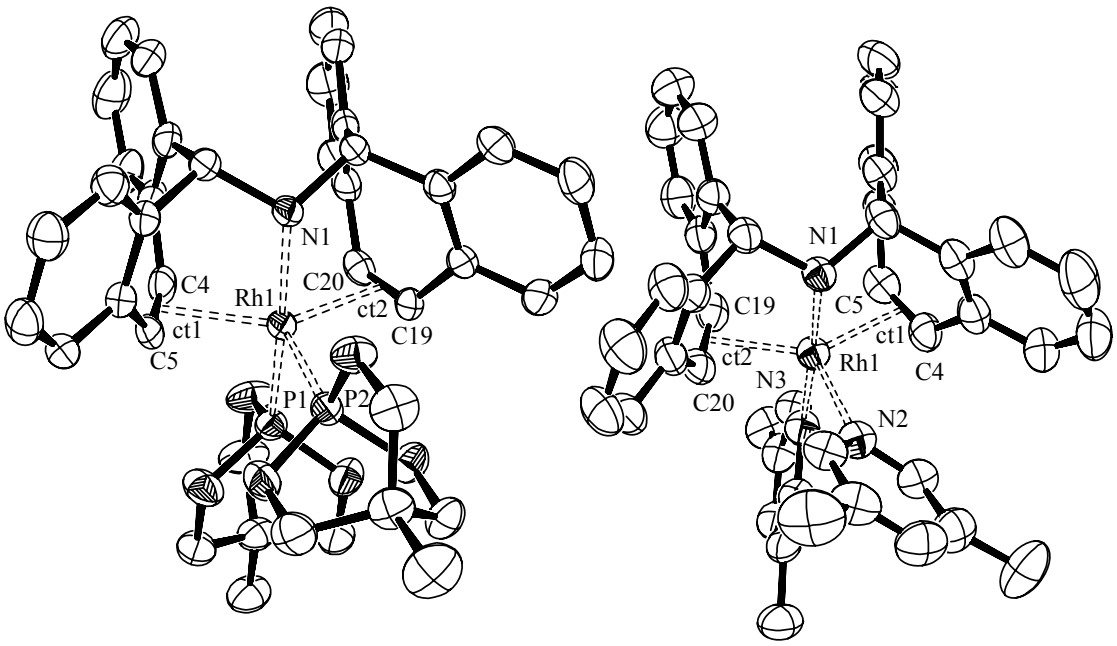


Figure 8: Ortep plot (at 50% ellipsoid probability) of the structures of [Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$]OTf **15** (left) and [Rh(trop$_2$NH)(3,5 Me-Py)$_2$]PF$_6$ **26** (right). The PF_6^- anions and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20) **15**: Rh1-N1 2.168(3), Rh1-P1 2.1932(10), Rh1-P2 2.2876(11), Rh1-ct1 2.078(4), Rh1-C4 2.209(4), Rh1-C5 2.182(4), Rh1-ct2 2.105(4), Rh1-C19 2.208(3), Rh1-C20 2.232(4), C4=C5 1.418(6), C19=C20 1.408(5), N1-Rh1-P1 174.20(9), ct1-Rh1-ct2 137.42(15); **26**: Rh1-N1 2.095(3), Rh1-N2 2.321(3), Rh1-N3 2.095(3), Rh1-ct1 2.082(4), Rh1-ct2 2.021(4), Rh1-C4 2.191(4), Rh1-C5 2.203(4), Rh1-C19 2.139(4), Rh1-C20 2.145(4), C4=C5 1.403(6), C19=C20 1.422(6), N1-Rh1-N3 176.85(12), ct1-Rh1-ct2 136.64(16).

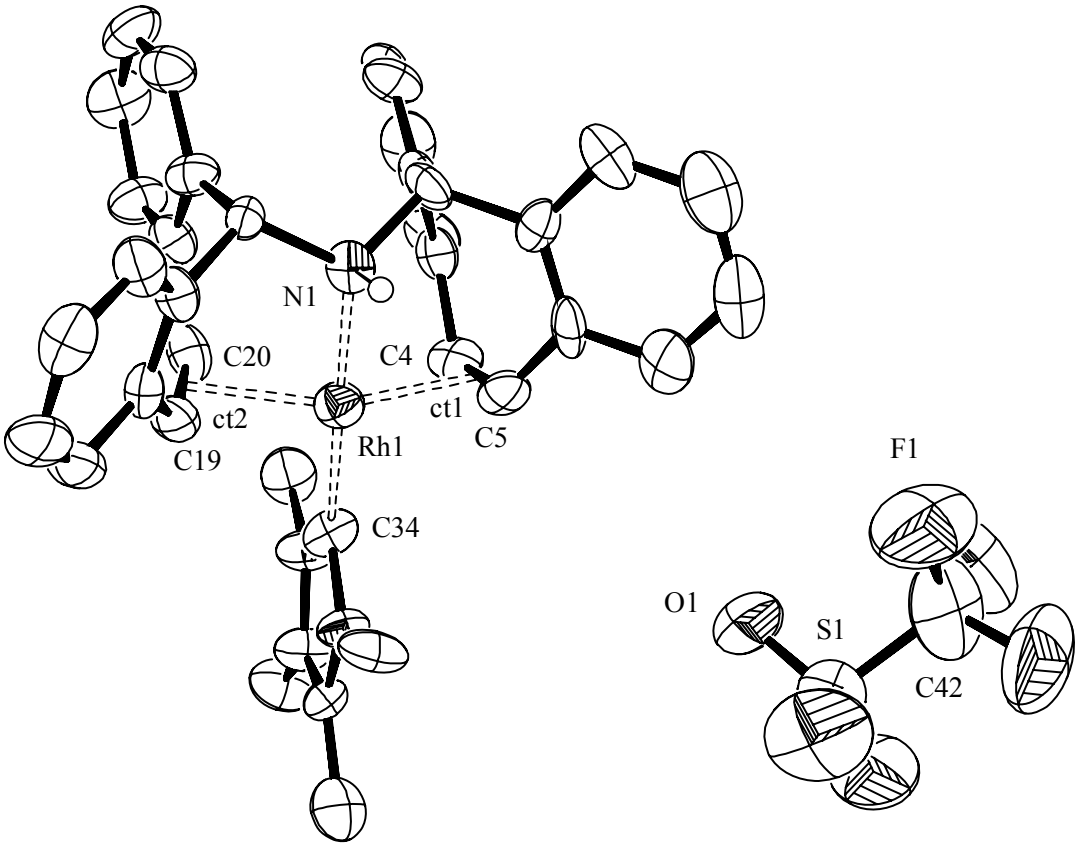


Figure 9: Ortep plot (at 50% ellipsoid probability) of the structure of [Rh(trop$_2$NH)(TMIY)]OTf **28**. Carbon bonded hydrogen atoms and non coordinating solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles[°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.130(4), Rh1-C34 1.993(5), Rh1-O1 5.995(9), Rh1-ct1 2.059(5), Rh1-C4 2.140(5), Rh1-C5 2.158(5), Rh1-ct2 2.033(5), Rh1-C19 2.159(5), Rh1-C20 2.193(5), C4=C5 1.408(6), C19=C20 1.393(5), N1-Rh1-C34 176.19(20), ct1-Rh1-ct2 149.43(21).

In the trigonal bipyramidal complexes of trop$_2$NH the distance M-L_A between the metal and the axial ligand is always shorter than the distance M-L_E between the equatorial ligand and the metal. This can be explained by the weaker bonding of the equatorial ligand to the metal, best seen if L_E and L_A are equivalent (Figure 8). The distance M-ct (ct = centroid of a double bond) is in a similar range of about 2.0-2.1 Å for all structures.

Complexes of trop$_2$NH adopt trigonal bipyramidal or – if the ligand in equatorial position is missing – saw-horse structures (see Scheme 6). A remarkable feature of the saw-horse structure [Rh(trop$_2$NH)(TMIY)]OTf **28** (the triflate anion does not coordinate in this complex, see Figure 9) is the distortion of the trop$_2$NH ligand. If a complex adopts an ideal trigonal bipyramidal or saw-horse structure, all olefinic carbon atoms should lie in the equatorial plane containing the metal cation. The distortion induced by the back bone of the trop$_2$NH ligand can be quantified by

measuring the angle θ between the two planes through the olefinic carbons and the metal. In structure **28** the angle θ between Rh1, C19, C20 and Rh1, C4, C5 is remarkably large: 17.2 °. This is the largest θ for all structures of trop$_2$NH complexes considered here (see Table 4). The metal carbon bond of the carbene in complex **28** is shorter than the metal phosphorus or nitrogen bonds in the other complexes. This may explain the distortion of the trop$_2$NH ligand.

However, from the data available it is not possible to conclude that the angle θ is largest for saw-horse structures. In [Rh(trop$_2$NH)(PPh$_3$)]BArF **6** and [Rh(trop$_2$N)(PPh$_2$tol)] **4***[41], two saw-horse structures, θ is in the range of the trigonal bipyramidal structures. Probably the distortion of the trop$_2$NH ligand and θ is more influenced by the nature of the ancillary ligand than by the geometry of the complex.

Table 4: Comparison of selected bond lengths [Å] and angles [°] from X-ray diffraction studies of rhodium and iridium trop$_2$NH complexes.

Compound	N1-M	M-L$_A$	N1-M-L$_A$	ct1-M-ct2	θ
[Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3**[40]	2.150(2)	2.279(1)	179.17(6)	139.90(9)	7.8
[Rh(trop$_2$NH)(PPh$_3$)]BArF **6**	2.155(2)	2.279(1)	173.1(2)	144.7(4)	4.7
[Rh(trop$_2$N)(PPh$_2$tol)] **4***[41]	2.007(1)	2.316(1)	166.18(5)	135.81(7)	2.4
[RhH(trop$_2$NH)(PPh$_2$tol)] **5***[41]	2.178(1)	2.230(1)	169.95(3)	132.54(5)	3.3
[Rh(trop$_2$NH)(P(OPh)$_3$)]OTf **7**	2.147(1)	2.203(1)	170.1(4)	145.5(5)	10.1
[Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$] OTf **15**	2.168(3)	2.193(1)	174.20(9)	137.42(15)	4.6
[Rh(trop$_2$NH)(3,5DMP)$_2$]PF$_6$ **26**	2.095(3)	2.095(3)	176.85(12)	136.64(16)	3.6
[Rh(trop$_2$NH)(TMIY)]OTf **28**	2.130(4)	1.993(5)	176.19(20)	149.43(21)	17.4
[Rh(trop$_2$NH)(DMPP)$_2$]OTf **22**[70]	2.195(3)	2.387(1)	176.75(12)	135.3(3)	5.7
[Rh(TPP)(trop$_2$NH)]OTf **23**[70]	2.135(2)	2.300(1)	179.01(6)	138.22(10)	15.2
[Ir(OTf)(trop$_2$NH)(PPh$_3$)] **32**	2.163(5)	2.284(2)	178.71(16)	138.5(3)	6.5

A structure of the iridium complex [Ir(OTf)(trop$_2$NH)(PPh$_3$)] **32** was obtained. The structure is remarkably similar (almost superimposable) to the structure of [Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3**. M-ct distances are slightly larger and the C=C double bond is longer by 0.05 Å compared to the rhodium complex. As in the structure of complex **3** the triflate anion is coordinated and forms a hydrogen bond with the NH proton.

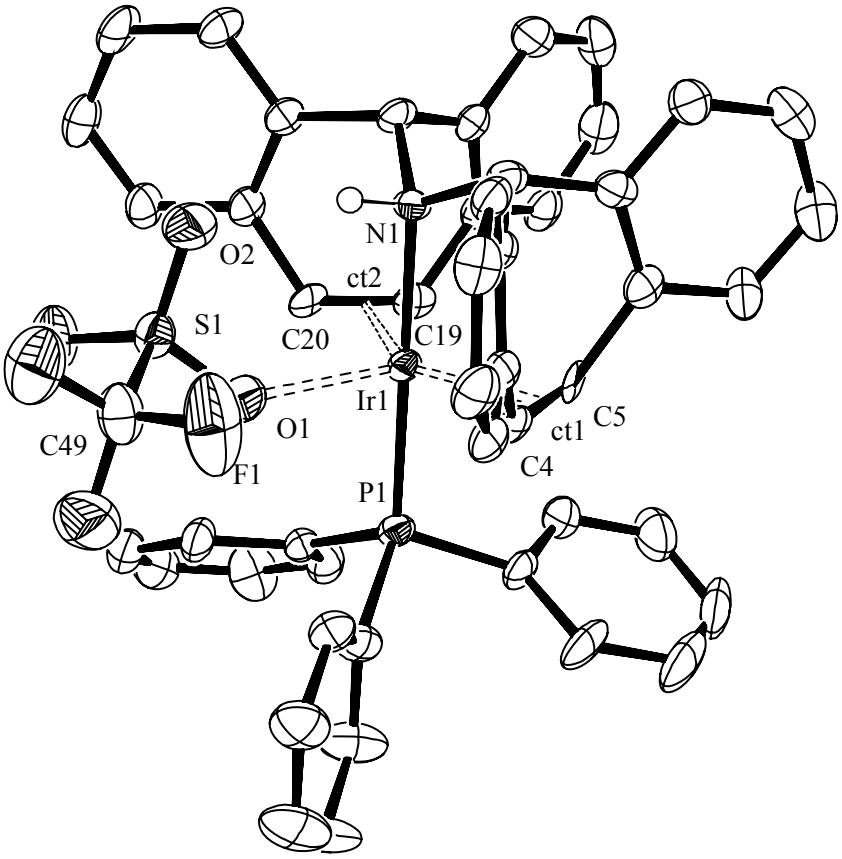


Figure 10: Ortep plot (at 50% ellipsoid probability) of the structure of **32**. Carbon bonded hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Ir1-N1 2.163(5), Ir1-P1 2.284(2), Ir1-ct1 2.038(6), Ir1-O1 2.332(6), Ir1-ct2 2.041(6), Ir1-C4 2.168(6), Ir1-C5 2.163(6), Ir1-C19 2.146(7), Ir-C20 2.183(6), C4=C5 1.463(10), C19=C20 1.440(10), N1-O2 3.017(12), N1-Ir1-P1 178.71(16), ct1-Ir1-ct2 138.5(3).

It is known that olefinic proton and carbon resonances in the ^{1}H- and ^{13}C-NMR correlate with the structure. The coordination shift is defined as shift difference of the resonance in the complex compared to the free olefin. In the metallacyclopropane X_2 extreme (see Scheme 11), the olefinic protons can resonate up to 5 ppm and the olefinic carbons up to 100 ppm to lower frequencies than the uncoordinated olefin bond. This is appropriate for a change of hybridization from sp^2 to sp^3. Coordination shifts are usually much lower in the Dewar-Chatt extreme where the olefin retains much of its alkene character.[69]

Table 5: Characteristic ^{1}H-NMR data of selected rhodium and iridium trop$_2$NH complexes.

Compound	Solvent	C*H*^{benzyl} δ[ppm]	C*H*^{olefin} A δ[ppm]	C*H*^{olefin} B δ[ppm]	N*H* δ [ppm]
trop$_2$NH **1** (*exo-exo*)	$CDCl_3$	4.37	7.06	-	3.43
[Rh(trop$_2$NH)(CO)]OTf [40]	$CDCl_3$	5.03	5.84	6.45	4.41
[Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3** [40]	$CDCl_3$	4.91	4.94	5.43	5.66
[Rh(trop$_2$NH)(PPh$_3$)]BArF **6**	$CDCl_3$	5.25	4.91	6.40	3.61
[Rh(trop$_2$N)(PPh$_3$)] **4**	[D_8]THF	4.92	4.69	5.62	-
[Rh(eq-H)(trop$_2$NH)(PPh$_3$)] **5**	[D_8]THF	4.56	3.55	3.91	5.56
[Rh(trop$_2$NH)(P(OPh)$_3$)]OTf **7**	$CDCl_3$	5.32	5.55	6.63	5.09
[Rh(trop$_2$N)(P(OPh)$_3$] **8**	[D_8]THF	4.85	5.94	-	-
[Rh(eq-H)(trop$_2$NH)(P(OPh)$_3$)] **9**	[D_8]THF	4.44	4.33	4.89	5.05
[Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$] OTf **15**	$CDCl_3$	4.82	5.30	5.38	4.15
[Rh(trop$_2$NH)(3,5DMP)$_2$]PF_6 **26**	CD_2Cl_2	4.76	4.86	5.65	2.75
[Rh(trop$_2$NH)(TMIY)]OTf **28**	CD_2Cl_2	5.41	5.13	6.60	3.42
[Rh(trop$_2$N)(TMIY)] **29**	[D_8]THF	4.77	4.78	6.02	-
[Rh(trop$_2$NH)(DMPP)]OTf **21**	$CDCl_3$	4.86	4.61	5.69	5.03
[Rh(trop$_2$NH)(DMPP)$_2$]OTf **22**	$CDCl_3$	4.62	4.90	4.90	2.55
[Rh(TPP)(trop$_2$NH)]OTf **23**	$CDCl_3$	5.02	5.27	5.64	5.89
[Ir(OTf)(trop$_2$NH)(PPh$_3$)] **32**	$CDCl_3$	5.10	4.38	5.23	6.23
[Ir(trop$_2$N)(PPh$_3$)] **33**	[D_8]THF	5.78	4.28	5.59	-
[Ir(eq-H)(trop$_2$NH)(PPh$_3$)] **34**	[D_8]THF	4.71	3.32	3.34	5.80

Table 6: Characteristic ^{13}C-NMR data of selected rhodium and iridium trop$_2$NH complexes.

Compound	Solvent	*C*H$_{benzyl}$ δ [ppm]	*C*H$_{olefin}$ A δ [ppm]	*C*H$_{olefin}$ B δ [ppm]
trop$_2$NH **1** (*exo-exo*)	$CDCl_3$	57.6	131.2	-
[Rh(trop$_2$NH)(CO)]OTf [40]	$CDCl_3$	73.3	75.9	76.4
[Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3** [40]	$CDCl_3$	72.7	74.0	74.2
[Rh(trop$_2$NH)(PPh$_3$)]BArF **6**	$CDCl_3$	73.8	81.7	91.4
[Rh(trop$_2$N)(PPh$_3$)] **4**	[D$_8$]THF	82.3	76.2	84.5
[Rh(eq-H)(trop$_2$NH)(PPh$_3$)] **5**	[D$_8$]THF	72.2	57.8	60.6
[Rh(trop$_2$NH)(P(OPh)$_3$)]OTf **7**	$CDCl_3$	72.0	75.1	79.8
[Rh(trop$_2$N)(P(OPh)$_3$] **8**	[D$_8$]THF	82.2	81.3	-
[Rh(eq-H)(trop$_2$NH)(P(OPh)$_3$)] **9**	[D$_8$]THF	72.3	55.3	58.8
[Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$]OTf **15**	$CDCl_3$	71.9	66.5	67.5
[Rh(trop$_2$NH)(3,5 Me-Py)$_2$]PF$_6$ **26**	CD_2Cl_2	71.9	71.7	73.6
[Rh(trop$_2$NH)(TMIY)]OTf **28**	CD_2Cl_2	72.4	81.0	87.1
[Rh(trop$_2$N)(TMIY)] **29**	[D$_8$]THF	81.3	75.7	81.3
[Rh(trop$_2$NH)(DMPP)]OTf **21**	$CDCl_3$	72.8	70.7	72.9
[Rh(trop$_2$NH)(DMPP)$_2$]OTf **22**	$CDCl_3$	70.9	64.3	65.8
[Rh(TPP)(trop$_2$NH)]OTf **23**	$CDCl_3$	72.5	73.5	76.1
[Ir(OTf)(trop$_2$NH)(PPh$_3$)] **32**	$CDCl_3$	72.5	50.2	57.8
[Ir(trop$_2$N)(PPh$_3$)] **33**	[D$_8$]THF	81.2	64.6	64.8
[Ir(eq-H)(trop$_2$NH)(PPh$_3$)] **34**	[D$_8$]THF	72.4	39.0	41.6

The most important trop$_2$NH complexes were chosen for discussion of their characteristic NMR data. Among others, the amide complexes (**4**, **8**, **29**, **33**), hydride complexes (**5**, **9**, **34**) as well as the corresponding amine complexes were selected (see Table 5 and Table 6).

The amide complexes have distinctly high frequency shifted benzylic carbon resonances ($\Delta\delta \approx 10$ ppm) compared to the amine complexes or the free ligand. For some of the compounds the same trend is observable in proton NMR. For the olefinic carbon and proton resonances no discernible pattern emerges, they are in a similar range compared to the amine complexes.

An analysis of the olefinic carbon and proton resonances of the hydrides on the other hand have a considerable low frequency shift ($\Delta\delta \approx$ -10 ppm to - 25 ppm) compared to the amine complexes. The hydride complexes are stabilized by a larger back bonding interaction of the olefins and the metal cation.

In the iridium complexes the carbon resonances of the olefins are shifted to low frequency ($\Delta\delta \approx$ -10 to -20 ppm) compared to the rhodium complexes. The same trend is found for the proton resonances although the observed shift differences are minor. This is in good agreement with the longer C=C double bonds in the iridium cation **32** compared to the rhodium cation **3** and is due to the larger π-basicity of iridium.

An interesting observation can be made comparing the compounds **3** and **6**. Even though they have the same cation the shift of the olefinic carbons are remarkably different. The $BArF^-$ salt **6** is shifted to high frequency by plus 10 ppm for one olefin and by plus 20 ppm for the other. Again the pattern is much less obvious but similar in proton NMR. This means there is complexation of the OTf anion on cation in **3** in chloroform.

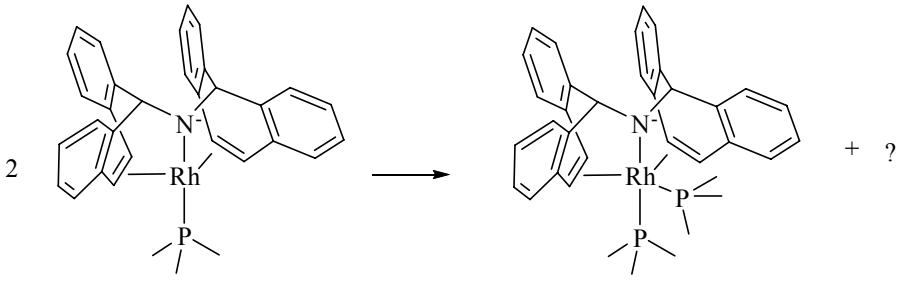
Both mono phosphole complexes [Rh($trop_2$NH)(DMPP)]OTf **21** and [Rh(TPP)($trop_2$NH)]OTf **23** have similar carbon NMR shift resonances. However the olefinic carbon resonances of bis phosphol complex [Rh($trop_2$NH)$(DMPP)_2$]OTf **22** are shifted to low frequency ($\Delta\delta \approx$ -7 ppm). Comparing the olefinic carbon resonances of bis-phosphite complex **15** with the bis pyridine complex **26** a low frequency shift is found ($\Delta\delta \approx$ -5ppm). Both observations are supported by weak but similar trends in the ^{1}H-NMR.

Coordinating a ligand in the fifth coordination site of a $trop_2$NH complex significantly enhances the back bonding of the metal cation to the olefins depending on the ligand. In the $trop_2$NH system the effect seems to depend mostly on the σ-donor strength. Hydrides are some of the best σ-donors and therefore the largest coordination shifts are observed for this class of complexes.

5 Ligand classes and their performance in catalysis

Turnover numbers (TON) were determined for all complexes by allowing the catalytic reaction to run for 2 days. The performance of the complexes was found to be highly dependent on the ancillary ligand (see Table 7).

For alkyl phosphines decomposition of the corresponding amides to form complexes with phosphines both in equatorial and axial position and unidentified side products was observed by ^{31}P-NMR. The amide complex [Rh(trop$_2$N)(P(*n*Bu)$_3$)] **12** synthesized by deprotonation of [Rh(Cl)(trop$_2$NH)(P(*n*Bu)$_3$)] **10** or optionally [Rh(trop$_2$NH)(P(*n*Bu)$_3$)]OTf **11** is stable enough to be characterized by NMR. However, the amide [Rh(trop$_2$N)(PMe$_3$)] of the trimethylphosphine complex [Rh(trop$_2$NH)(PMe$_3$)]OTf **13** decomposes very rapidly at room temperature and could not be fully characterized. Not surprisingly **13** is inferior as catalyst in transfer hydrogenation.



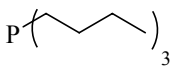
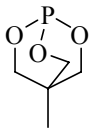
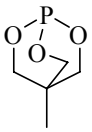
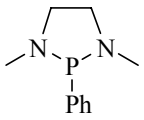
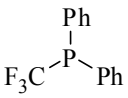
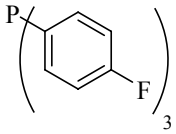
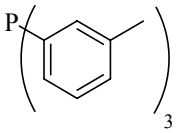
Scheme 12: Decomposition of the amide [Rh(trop$_2$NH)(PMe$_3$)] from [Rh(trop$_2$NH)(PMe$_3$)]OTf **13**

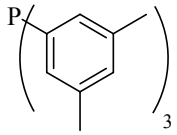
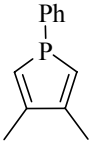
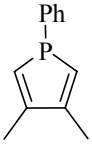
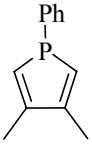
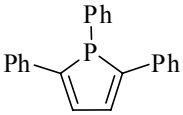
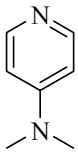
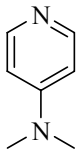
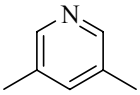
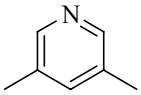
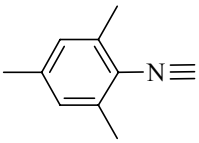
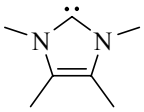
If the equatorial position is occupied by an additional ligand, e.g. a small phosphine or phosphite as in [Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$]OTf **15** and [Rh(trop$_2$NH)(DMPP)$_2$]OTf **22**, the activity in transfer hydrogenation decreases significantly. Complexes of weakly bound ligands with nitrogen donors like the two used pyridines dimethylaminopyridine (DMAP) and 3,5-dimethylpyrididine (3,5DMP) ([Rh(trop$_2$NH)(DMAP)$_2$]PF$_6$ **25** and [Rh(trop$_2$NH)(3,5DMP)$_2$]PF$_6$ **26**) were not efficient in catalysis, probably because they were too unstable under the reaction conditions. Also the complex of mesityl isocyanide [Rh(trop$_2$NH)(CNMes)]OTf **27** was not efficient in transfer hydrogenation. This ligand is easily attacked by nucleophiles like ethanolate and the complex therefore too unstable under the conditions of the catalysis. Carbene complex [Rh(trop$_2$NH)(TMIY)]OTf **28** is also disappointing in transfer hydrogenation, although turnover numbers over 5000 are

possible if the reaction is heated to 60°. Most likely the performance of the carbene complex suffers from unfavorable steric repulsion in the transition state caused by the carbene ligand (see Figure 9).

The best catalysts are complexes of aryl-phosphines. The triphenylphosphine complex **3** and the tri-m-tolylphosphine complex **19** reached turnover numbers of up to one million. It is not possible to conclude any influence on the performance and longevity of the catalyst of the methyl groups in the tris(3-methylphenyl)phosphine and tris(3,5-dimethylphenyl)phosphine since the observed differences are not significant enough.

Table 7: Assessment of $trop_2NH$ complexes with various ancillary ligands by determination of turnover numbers (TON). Conditions: Acetophenone 2 M in ethanol, 1 mol% K_2CO_3, 2 days.

Complex	Ligand in axial Position L_A	Ligand in equatorial Position L_E	S/C	TON
[Rh($trop_2NH$)(OTf)(PPh_3)] **3**	PPh_3	-	10^6	$9\cdot10^5$
[Rh($trop_2NH$)(P(OPh)$_3$)]OTf **7**	$P(OPh)_3$	-	10^6	$4\cdot10^5$
[Ir($trop_2NH$)(OTf)(PPh_3)] **32**	PPh_3	-	5000	4500
[Rh($trop_2NH$)(P(*n*Bu)$_3$)]OTf **11**		-	10^5	10^5
[Rh($trop_2NH$)(OTf)(PMe_3)] **13**		-	10^5	10’000
[Rh($trop_2NH$)(P(OCH_2)$_3$$CCH_3$)$_2$]OTf **15**			5000	3600
[Rh($trop_2NH$)(PN_2Ph)]OTf **16**		-	10^6	$4\cdot10^5$
[Rh($trop_2NH$)(PPh_2CF_3)]OTf **17**		-	10^5	10^5
[Rh($trop_2NH$)(P(*p*FPh)$_3$)]OTf **18**		-	10^5	10^5
[Rh($trop_2NH$)(P(*m*Tol)$_3$)]OTf **19**		-	10^6	10^6

[Rh(trop$_2$NH)(P(*m*Xyl)$_3$)]OTf **20**		-	10^6	$7.5\cdot10^5$
[Rh(trop$_2$NH)(DMPP)]OTf **21**		-	10^6	$3\cdot10^5$
[Rh(trop$_2$NH)(DMPP)$_2$]OTf **22**			5000	3500
[Rh(TPP)(trop$_2$NH)]OTf **23**		-	10^6	$2\cdot10^5$
[Rh(trop$_2$NH)(AsPh$_3$)]OTf **24**	AsPh$_3$	-	10^5	50’000
[Rh(trop$_2$NH)(DMAP)$_2$]PF$_6$ **25**			1000	200
[Rh(trop$_2$NH)(3,5DMP)$_2$]PF$_6$ **26**			5000	1000
[Rh(trop$_2$NH)(CNMes)]OTf **27**		-	1000	900
[Rh(trop$_2$NH)(TMIY)]OTf **28**		-	5000	700

6 Optimization of the transfer hydrogenation conditions

Having established that [Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3** is one of the best catalysts for transfer hydrogenation in ethanol, the reaction conditions were varied systematically to optimize the catalysis.

First the catalysis was run at different temperatures. The reaction was found to be faster at elevated temperatures, but catalyst decomposition was faster too. The optimum temperature was between 20 °C and 40 °C, but considerable activity of the catalyst was still found at 0 °C. Since running the catalytic reaction at room temperature is highly convenient, all further experiments were carried out at room temperature. For reactions on large scale warming of the reaction mixture was observed due to the exothermic nature of the reaction (see section II).

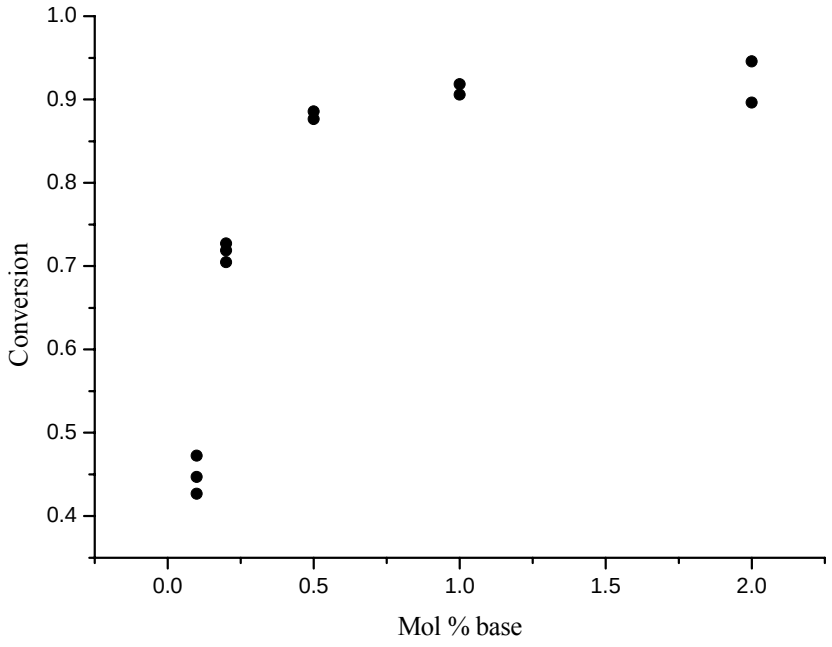


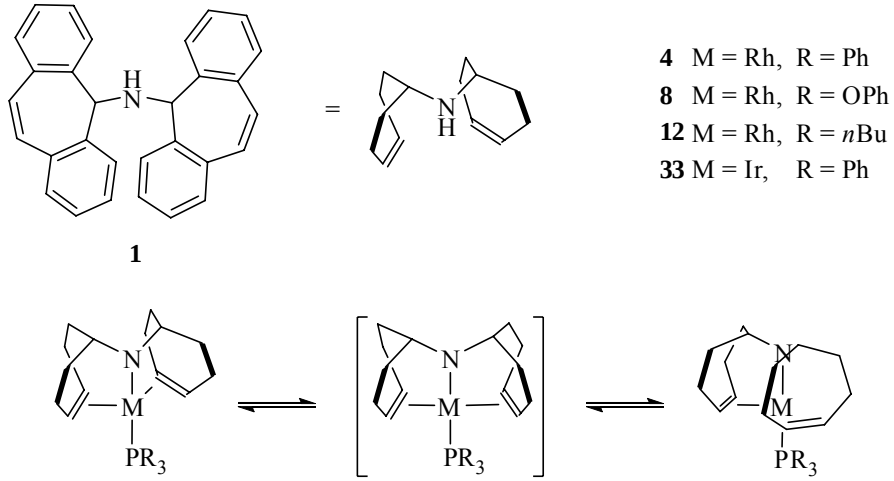
Figure 11: Conversion of transfer hydrogenation (S/C 10^5, acetophenone 2 M in ethanol) after 15 minutes in the presence of different mol% KO*t*Bu.

Furthermore, the effect of base on the catalytic reaction was studied. Several transfer hydrogenations were performed with S/C 10^5 and different amounts of KO*t*Bu added. The conversion was determined after 15 minutes (Figure 11). A certain amount of base is necessary that the transfer hydrogenation reaction proceeds at all. If between 0.5 mol% and 1 mol% KO*t*Bu were used the catalytic reaction proceeded as fast as possible. No further increase in reaction rate was found if additional base was added.

The effect of substrate concentration on catalyst efficiency was investigated. When the substrate concentration in ethanol was increased to more than 4 M, the catalytic reaction became inefficient. During the reaction a secondary alcohol is formed by ketone reduction. Since the transfer hydrogenation is reversible, ethanol has to compete with this secondary alcohol for the catalyst. If the reaction mixture is too concentrated, this competition is increasingly difficult for ethanol. Hence 2 M solutions of substrate in ethanol were found to be a suitable tradeoff and were used for all further experiments. Working in more dilute solutions did not increase the rate nor the efficiency of the catalytic reaction significantly.

7 Inversion of amide complexes

The inversion of the amide complex [Rh(trop$_2$N)(PPh$_3$)] **4** has been described previously.[40] The proton NMR spectrum of the deprotonated species **4** shows only one signal for the four olefinic protons and four signals for the 16 aromatic protons of the trop units. At first glance, these NMR observations suggest a square planar conformation of the complex. However, when an NMR sample of **4** is measured at low temperature all above mentioned signals are broadened and finally at –70 °C the familiar pattern of the trigonal bipyramidal coordination mode (two distinct signals for the olefinic protons) is revealed. The observation of a seemingly C_{2V} symmetric, planar complex was therefore only a result of a rapid exchange process.



Scheme 13: Rapid inversion process at the amide nitrogen leading to the observation of a seemingly planar complex at room temperature.

To study the effect of the ancillary ligand on this process variable temperature ^{1}H-NMR spectra were measured at temperatures between 56 °C and -78.4 °C of [Rh(trop$_2$NH)(PPh$_3$)] **4,** [Rh(trop$_2$NH)(P(OPh)$_3$)] **8**, [Ir(trop$_2$NH)(PPh$_3$)] **33** and [Rh(trop$_2$NH)(P(*n*Bu)$_3$] **12**. The obtained spectra were simulated using the MEXICO program package.[71, 72] The coupling constants of the relevant protons were determined in the low temperature case and afterwards used as input for the MEXICO program. Although, at high temperatures only the mean value of the shifts was accessible. Typically, ^{1}H chemical shifts reveal a linear dependence on the temperature. However, the proximity of the olefinic protons A and B to substituents on the phosphane ligands caused a non-linear dependence of their chemical shifts with

the temperature. The true shifts in the high temperature spectra were therefore estimated from the non-linearity observed in the low-temperature spectra. Even though this procedure is not entirely correct, only a minor additional uncertainty is added to the kinetic data.

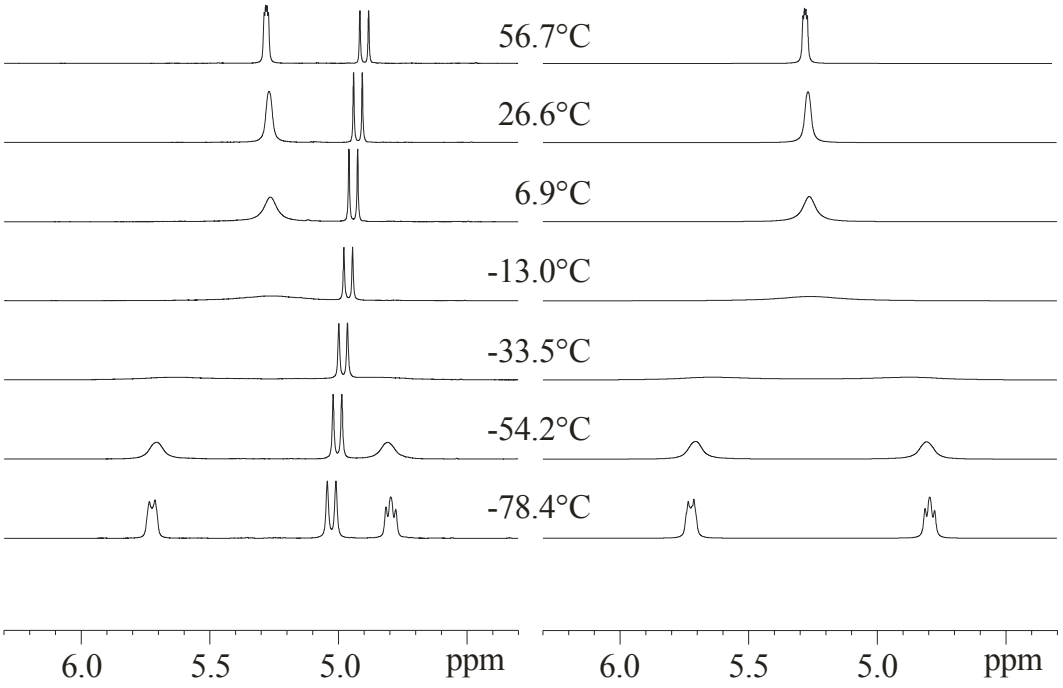


Figure 12: Experimental (left) vs. simulated (right) ^{1}H-NMR spectra of the olefine resonances of [Rh(trop$_2$N)(PPh$_3$)] **4**. In the experimental spectra the benzylic proton resonances are visible as additional signals.

The kinetic data were used to determine the activation parameters for the inversion process in **4**, **8**, **12** and **33** by an Eyring analysis (see Figure 13, equation *(i)* and *(ii)*).

Eyring equation:
$$k = \frac{k_B T}{h} e^{\frac{-\Delta H^{\neq}}{RT}} e^{\frac{\Delta S^{\neq}}{R}} \qquad (i)$$

k_B= 1.381*10^{-23} [JK^{-1}] Boltzmann constant, h= 6.626*10^{-34} [Js] Plank constant, R= 8.3145 [Jmol^{-1}K^{-1}] Universal Gas Constant, T= absolute temperature in K, $\Delta S^{\ddagger}$ = activation entropy [Jmol^{-1}K^{-1}], $\Delta H^{\ddagger}$ = activation enthalpy [kJmol^{-1}]

The equation can be reformulated to give equation *(ii)* for the Eyring plot:

Eyring plot: $$R\ln\frac{kh}{Tk_B} = -\Delta H^{\neq}\frac{1}{T} + \Delta S^{\neq} \qquad (ii)$$

When $R*\ln(khT^{-1}k_b^{-1})$ is plotted against T^{-1}, the slope directly affords the negative enthalpy of activation $-\Delta H^{\ddagger}$ and the intersect with the ordinate axis provides the entropy of activation $\Delta S^{\ddagger}$.

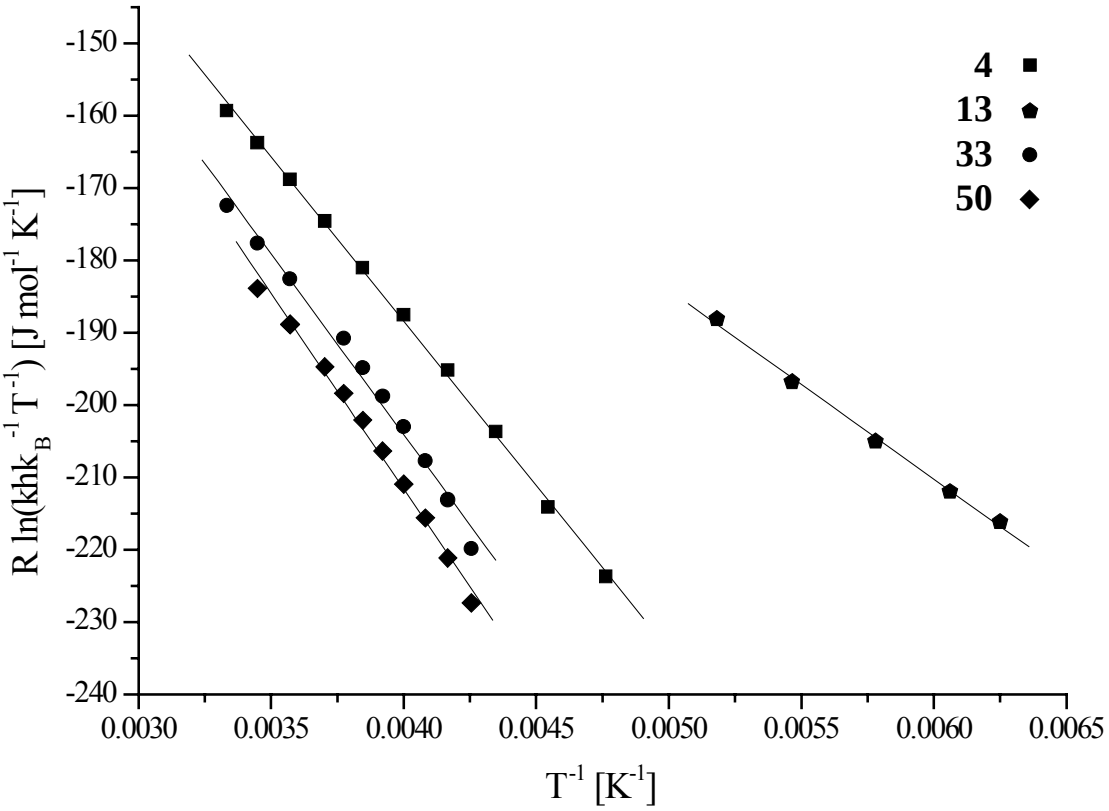


Figure 13: Eyring plots of amides **4**, **8**, **12** and **33** using the rate constants determined by NMR simulations.

The values obtained are given in Table 8. Notably the inversion in phosphite complex **8** is much faster than in all other complexes, possibly because $P(OPh)_3$ is the better acceptor than PPh_3 stabilizing the transition state. Complexes **12** and **33** invert slower at room temperature, the enthalpies of activation are in a similar range as for amide **4.**

For the inversion of the amide a planar transition state can be assumed. Therefore, the enthalpy of activation $\Delta H^{\ddagger}$ provides a good estimate for the stabilisation energy of the saw-horse conformation with respect to the square planar coordination mode ($\Delta H_{stab} = -\Delta H^{\ddagger} = -25 - 50$ kJ mol^{-1}).

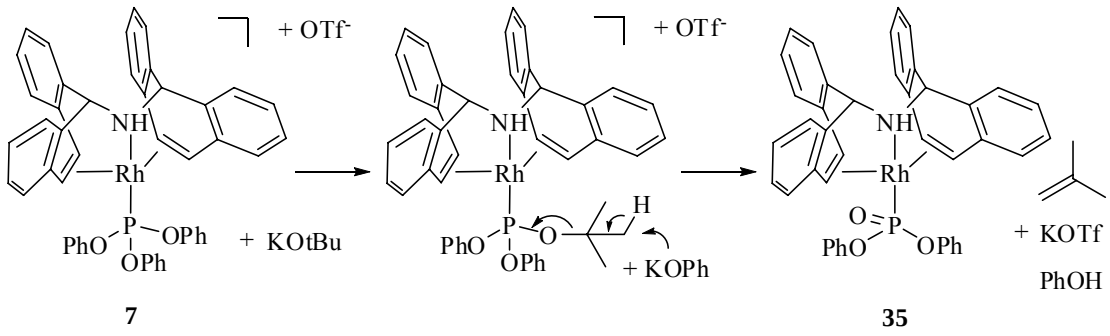
The small negative values determined for the entropies of activation are in agreement with a sterically less crowded planar transition state. The errors of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ compensate when $\Delta G^{\ddagger}$ is calculated.

Table 8: Enthalpies and entropies of activation for complexes **4, 8**, **12** and **33**

Complex	k (298 K) [s^{-1}]	$\Delta H^{\ddagger}$ [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [$Jmol^{-1}K^{-1}$]	$\Delta G^{\ddagger}$(220K) [kJ mol^{-1}]
[Rh($trop_2N$)(PPh_3)] **4**	30'000	43	-7	45
[Rh($trop_2N$)($P(OPh)_3$)] **8**	270'000	26	-53	38
[Rh($trop_2N$)($P(nBu)_3$] **12**	6'200	50	-4	51
[Ir($trop_2N$)(PPh_3)] **33**	3'300	52	-3	53

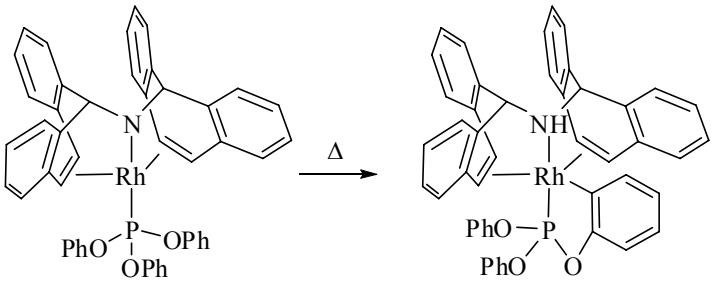
8 Side reactions of the amide [Rh(trop$_2$N)(P(OPh)$_3$] 8

When complex [Rh(trop$_2$NH)(P(OPh)$_3$)]OTf **7** was deprotonated with KO*t*Bu instead of LiHDMS an interesting decomposition reaction was observed. The green color of [Rh(trop$_2$N)(P(OPh)$_3$] **8** persists only for a short time. The triphenylphosphite ligand reacts with tert-butanolate to the diphenyl phosphonato ligand in complex Rh(trop$_2$NH)(PO(OPh)$_2$] **35**. The mechanism is most likely an organometallic variation of the Michaelis-Arbuzov reaction. The decomposition reaction of the rhodium tris- triphenylphosphite complex by KOH was reported and presumably has a similar mechanism.[73, 74] Phenol and 2-butene are observed as byproducts when the reaction is followed by NMR in [D$_8$]THF. A plausible mechanism explaining the observed formation of 2-butene and phenol is given in Scheme 14.



Scheme 14: Formation of the diphenyl phosphonato complex **35** from complex **7**.

Usually the amide **8** was prepared by deprotonation of **7** with LiHDMS in THF and was quite stable in the absence of water. However, when a solution of the amide was heated to 80 °C for six hours the green color of the amide vanished and formation of a new product was observed. The structure of the product formed was elucidated by NMR studies and was found to be the ortho metallated rhodium complex [Rh(trop$_2$NH)(P(OC$_6$H$_4$)(OPh)$_2$] **36** (see Scheme 15). Ortho metallation of the triphenylphosphite ligand is quite common.[75-81] However in this case the ortho metallation possibly occurs by C-H activation over the Rh-N$^-$ bond. CH activation over M-N$^-$ or M=N bonds is well known for early transition metals[82-88] but not for late transition metals like rhodium. The intramolecular C-H activation over the M-N$^-$ bond in late transition metals was investigated in our group.[62] Note how the phenyl rings in structure **7** (see Figure 3, section II) have already the correct conformation for the reaction with the M-N$^-$ bond in complex **8**.

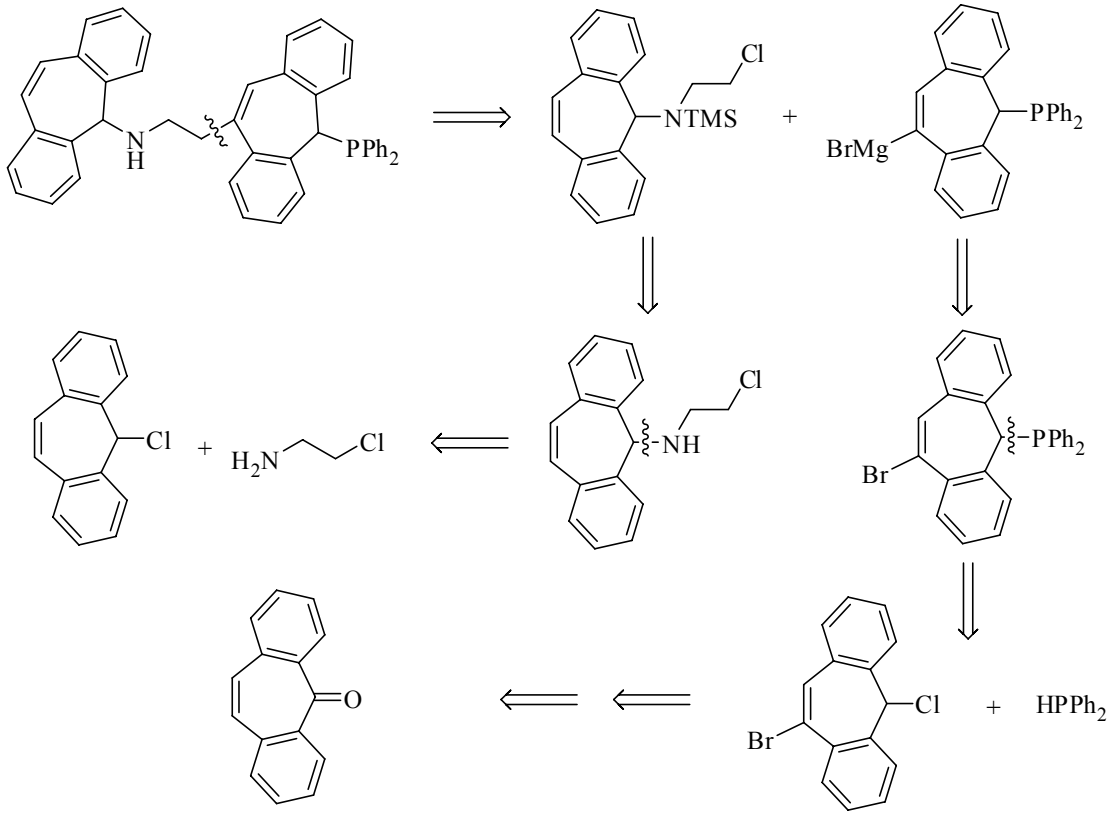


8 **36**

Scheme 15: Thermal rearrangement of amide **8** to the ortho metallated complex **36**.

9 Conclusion and Outlook

Synthesis of complexes with various ancillary ligands was achieved by convenient synthesis protocols. However with respect to the transfer hydrogenation reaction none of the new complexes was vastly superior to the triphenyl phosphine complex **3**. Likely other ways have to be found to further improve the catalyst, for example tetra-coordinating trop ligands (Scheme 16).



Scheme 16: Possible tetra coordinating diolefin phosphino amine ligand mimicking the coordination sphere found in **3**.

IV. Dehydrogenative Coupling of Primary Alcohols

1 Introduction

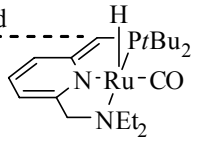
Fossil resources (petroleum, natural gas, coal) are widely used for the production of basic organic chemicals.[89] This increasingly limited feedstock is at the end of the chain converting CO_2 to hydrocarbons via photosynthesis and subsequent biological and slow geochemical processes,

$$n\ CO_2 + n\ H_2O + h\nu \rightarrow (CHOH)_n + n\ O_2 \rightarrow (CH_2)_n + n/2\ O_2.$$

From this oxygen-poor feedstock carbonyl compounds are mostly produced via oxygenation (oxidation) or carbonylation reactions. For both reaction types a wide range of rather efficient catalysts has been developed.[90] There is a need for replacing fossil resources by renewable ones ideally neutral in CO_2 consumption/production.[91] Plant biomass is a rapidly renewable feedstock and uses sun light as energy source for its formation. Compounds with relatively high oxygen content (sugars and other polyalcohols) are the main components.

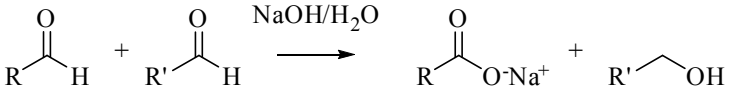
(1) $RCH_2OH + R'X \longrightarrow RCO(XR') + 2\ H_2$; X = O, NH

cooperative ligand
basic site

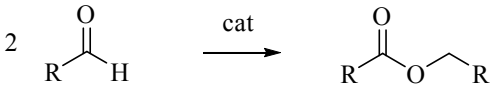


Milstein Catalyst

(2) Crossed Cannizzaro Reaction



(3) Tishchenko Reaction



Scheme 17: The DHC of primary alcohols to symmetrical esters as well as amides and the related Cannizzaro and Tishchenko reactions.

New catalysts and catalytic systems are needed to convert this biomass into fine-chemicals like carboxylic acid derivatives. Milstein et al. reported recently a Ru(II) complex with a "dearomatized" aminomethyl-phosphinomethyl-pyridine as pincer ligand (see Scheme 1) which allowed the *deh*ydrogenative *c*oupling (DHC) of primary alcohols to symmetrical esters[36] and of alcohols and amines to amides[38],

$$R\text{-}CH_2\text{-}OH + R'XH \rightarrow RCO(XR') + 2\ H_2,\ X = O,\ NH.$$

In this highly chemoselective new reaction, no hydrogen acceptor is needed and the ligand plays an active role in the hydrogen abstraction and liberation process.[27]

However, the reaction requires elevated temperatures (> 100 °C) to achieve high yields of products (>90%).

2 Cannizzaro-reaction

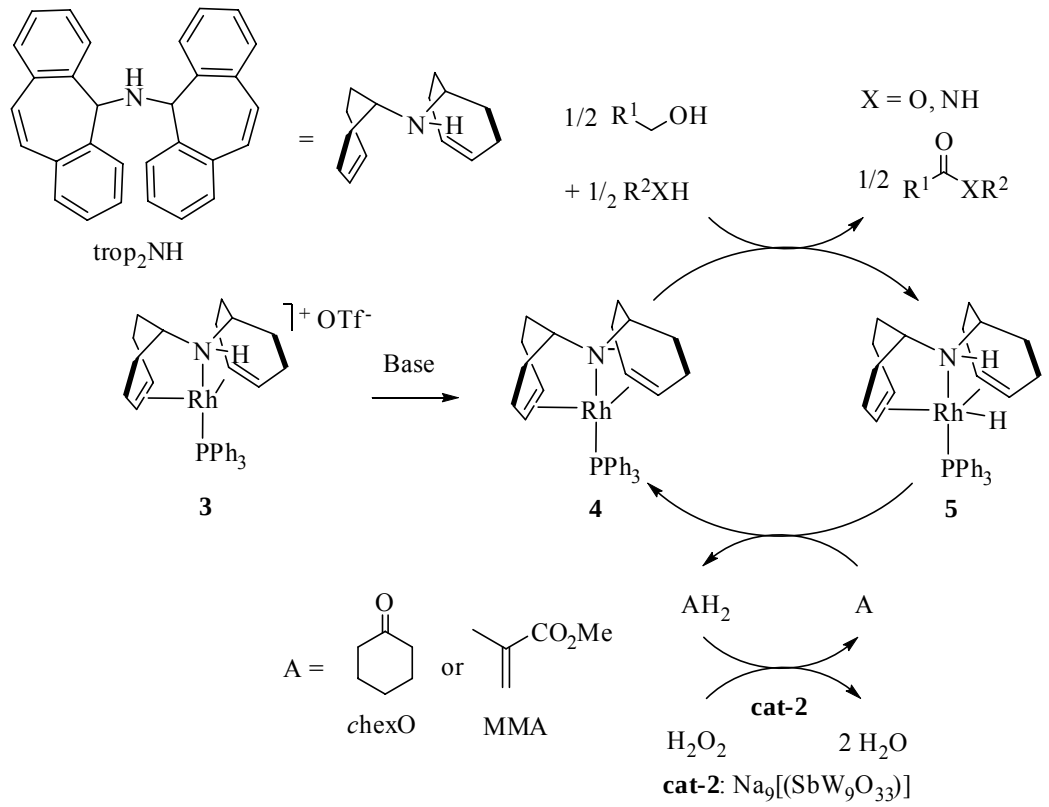
Related to this coupling reaction is the disproportionation of aldehydes to carboxylic acids and alcohols (Cannizzaro reaction, eq. *(2)* in Scheme 17) and the coupling of two aldehyde molecules to give one equivalent of a carboxylic acid ester (Tishchenko reaction, eq. *(3)* in Scheme 17). Both reactions are of industrial importance[89] and can be catalyzed with transition metal complexes. However, the efficiency is modest and the reaction conditions are harsh.

The previously described Rh(I) diolefin amido complex [Rh($trop_2N$)(PPh_3)] **4** ($trop_2N$ = bis(5-H-dibenzo[a,d]cyclohepten-5-yl)-amide) catalyzes with very high efficiency the transfer hydrogenation of ketones and activated olefins using ethanol as (renewable) hydrogen source. Computations indicated that in this reaction the amido complex **4** serves not only as catalyst for dehydrogenation of ethanol to acetaldehyde but also for the irreversible coupling of this aldehyde with another equivalent of ethanol to ethyl acetate (see section II).

Consequently we investigated the ability of **4** to catalyze the Cannizzaro-reaction. The amido complex **4** is very air-sensitive but its protonated form [Rh($trop_2NH$)(PPh_3)]OTF **3** can be conveniently handled and in our experiments **4** was often generated in situ with an alkoxide or hydroxide base (Scheme 18). When benzaldehyde was treated with 1.2 equivalents of aqueous sodium hydroxide (0.5 M) in the presence of 0.1 mol% of **3**, the disproportionation to benzyl alcohol and sodium benzoate is accelerated by a factor 10 compared to the reaction without catalyst (R = R' = Ph in Scheme 17).

More impressively, when the reaction was carried out in methanol instead of water, benzaldehyde was disproportionated to methyl benzoate and benzyl alcohol in the presence of only 0.001 mol% of **3** in 16 hours even when *no base* was added. Addition of 1 mol% K_2CO_3 resulted in to another 100 fold increase in reaction rate and complete conversion in 10 min.

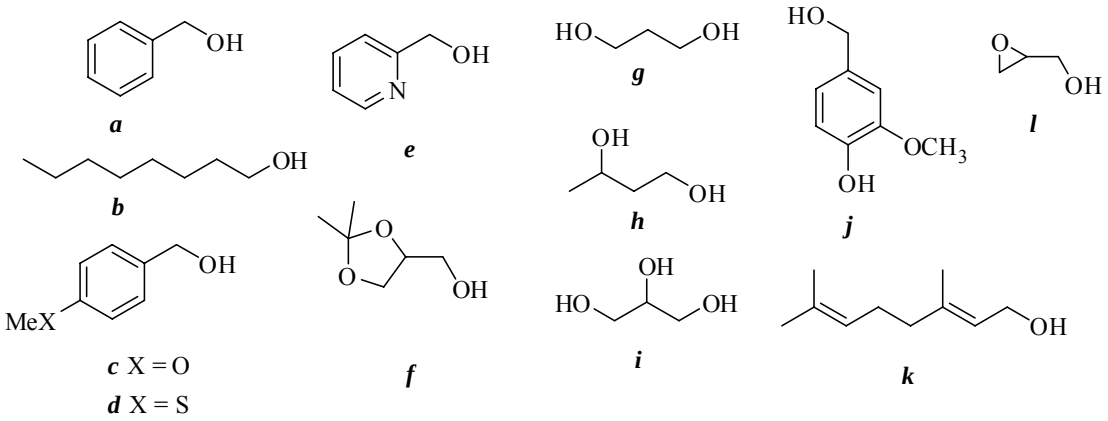
3 DHC to acids, methyl esters and amides



Scheme 18: Simplified DHC catalytic cycle giving acids, methyl esters and amides.

This unprecedented high activity of a catalyst for this type of reaction led us to investigate the possibility to use **4** as catalyst for the DHC of primary hydroxyl functions in ***a-k*** (Scheme 19) with water, methanol, or amines to furnish carboxylic acids, their methyl esters, or amides, respectively. A simplified catalytic cycle is shown in Scheme 18 and the products and reaction conditions are specified in Table 9 to 11.

This reaction requires a hydrogen acceptor **A** and cyclohexanone (cHexO) was used because it has a high heat of hydrogenation (18.4 kcal mol^{-1} vs. 16.6 kcal mol^{-1} for acetone).[34, 92, 93] More importantly it can be easily and almost quantitatively recycled with diluted hydrogen peroxide (3%) in presence of 0.1. mol% $Na_9[(SbW_9O_{33})]$ as catalyst **cat-2**.[94] Alternatively, methylmethacrylate (MMA) is a suitable hydrogen acceptor **A** especially for the synthesis of amides (Table 11).



Scheme 19: Substrates used for the DHC by catalyst **4** to acids, methyl esters and amides.

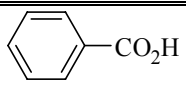
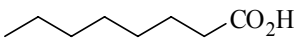
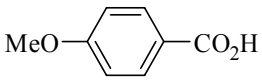
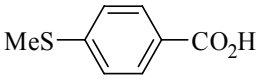
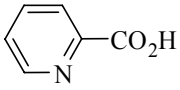
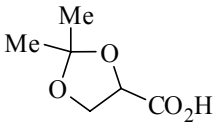
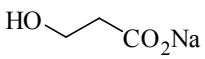
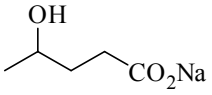
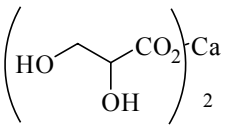
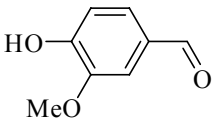
High reaction rates and catalytic turnover were achieved under mild conditions ($T \leq 25$ °C). In acid synthesis (or their sodium salts, respectively), a biphasic reaction mixture is obtained. The sodium salts of the carboxylic acids dissolve in the aqueous phase and can be conveniently isolated after the reaction is complete. The organic phase contains the generated cyclohexanol together with the cyclohexanone and is easily recycled with H_2O_2/ **cat-2**.

Various aryl and alkyl alcohols can be converted and a variety of functional groups like methoxy or methylthio groups (***c*** or ***d***) are tolerated. Especially remarkable is the highly chemoselective DHC of polyalcohols ***g*** - ***i*** without the necessity to apply protecting group strategies.[95]

For example, 2,3-dihydroxy-propanoic acid was isolated as calcium salt (Table 9, Entry 9) as sole product of the *DHC* reaction of glycerin ***i*** (the relatively low isolated yield is due to the difficulty to extract the product from the aqueous phase).

Disappointingly geraniol ***k*** could not be oxidized to the acid efficiently, only 50% conversion was achieved and the product contained also 5% citronellic acid, i.e. hydrogenation of the α C=C bond occurred also. When 4-hydroxy-3-methoxybenzyl alcohol ***j*** was dehydrogenated under slightly modified conditions (2.2 eq. sodium hydroxide) the sodium phenolate of vanillin was the only product (Table 9, Entry 10). Addition of water to the phenolate to give the acid instead of the aldehyde is disfavored because of its negative charge.

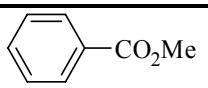
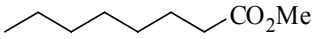
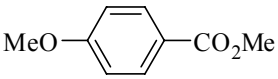
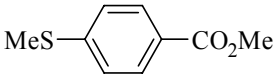
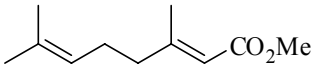
Table 9: Dehydrogenation of primary alcohols to their respective acids (and in one case to the aldehyde). Conditions: 0.1 mol% **3**, 66 eq. H_2O, 1.2 eq. NaOH, 5 eq. cyclohexanone. [a] as sodium salt of the acid; [b] as calcium salt of the acid; [c] 2.2 eq. NaOH were used, the aldehyde vanillin is the only product.

Entry	Alcohol	Product	Reaction time	Yield
1	Benzyl alcohol (***a***)		2 h	92%
2	Octanol (***b***)		4 h	89%
3	4-Methoxybenzyl alcohol (***c***)		4 h	88%
4	4-Methylthiobenzyl alcohol (***d***)		4 h	85%
5	2-(Hydroxymethyl) pyridine (***e***)		4 h	92%
6	2,2-Dimethyl-1,3-dioxolane-4-methanol (***f***)		12 h	89%
7	1,3-Propanediol (***g***)		12 h	67% [a]
8	1,3-Butanediol (***h***)		12 h	72% [a]
9	Glycerin (***i***)		12 h	63% [b]
10	4-Hydroxy-3-methoxybenzyl alcohol (***j***)		4 h	89% [c]

Catalyst **4** converts methanol only slowly to methyl formate, because the initial step, the dehydrogenation of methanol to formaldehyde, is significantly less favorable than with higher alcohols.[34] The latter can be very efficiently coupled with an excess of methanol in the presence of cHexO or, more efficiently, MMA as hydrogen acceptors

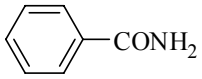
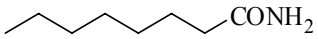
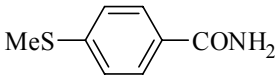
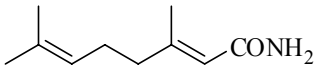
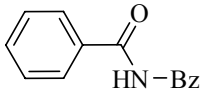
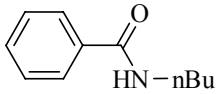
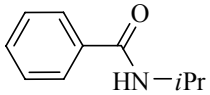
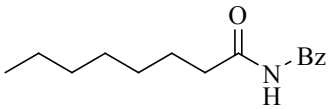
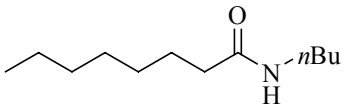
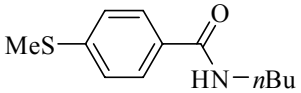
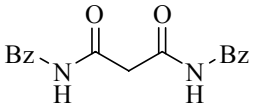
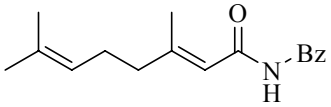
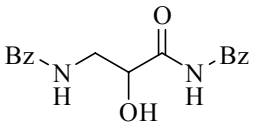
A to give methyl esters. Interestingly, in the dehydrogenation of geraniol ***k*** only the (*E*) isomer of methyl geranate is obtained, furthermore the reaction is considerably faster than for the other alcohols, even at 0 °C. At room temperature partial hydrogenation of the activated double bond is observed as in the DHC with water to the acid. Secondary alcohol groups (on polyols) as well as N-donor functionalities impede the catalytic reaction and only low conversion (~30%) to the desired products was observed with ***e***, ***g*** and ***i***. Steric hindrance seems to be detrimental for the reaction also, only 35% conversion was found for ***f***.

Table 10: Dehydrogenation of primary alcohols to their respective methyl esters. GC conversion was greater than 95% for all substrates. Dodecane was used as internal standard. Conditions: Method *cHexO*: 0.1 mol% **3**, 10 eq. methanol, 5 mol% K_2CO_3, 5 eq. cyclohexanone; Method *MMA*: 0.1 mol% **4**, 10 eq. methanol, MMA 3 eq., -30 °C to RT, 4 h; [a] at 0 °C.

Entry	Alcohol	Product	Reaction time	Yield *cHexO*	Yield *MMA*
1	Benzyl alcohol(***a***)		2 h	82%	95%
2	Octanol(***b***)		4 h	80%	93%
3	4-Methoxybenzyl alcohol (***c***)		4 h	77%	93%
4	4-Methylthio-benzyl alcohol(***d***)		4 h	86%	94%
5	Geraniol (***k***) [a]		20 min	79%	91%

Especially remarkably are the dehydrogenative coupling reactions with ammonia, NH_3, which lead to the amides (Table 11, Entry 1 – 4) in very high isolated yields. Even sterically demanding primary amines like iso-propylamine, iPrNH$_2$, can be employed. However, secondary amines, R_2NH, do not react. 1,3-Propanediol ***h*** is quantitatively converted to N, N'-dibenzylmalonamide (Table 11, Entry 11) and the epoxy alcohol ***l***, readily available through dehydration of glycerin, is converted to N-benzyl-3-(benzylamino)-2-hydroxypropanamide (Table 11, Entry 13) with benzylamine which is isolated as crystalline colorless material in almost quantitative yield.

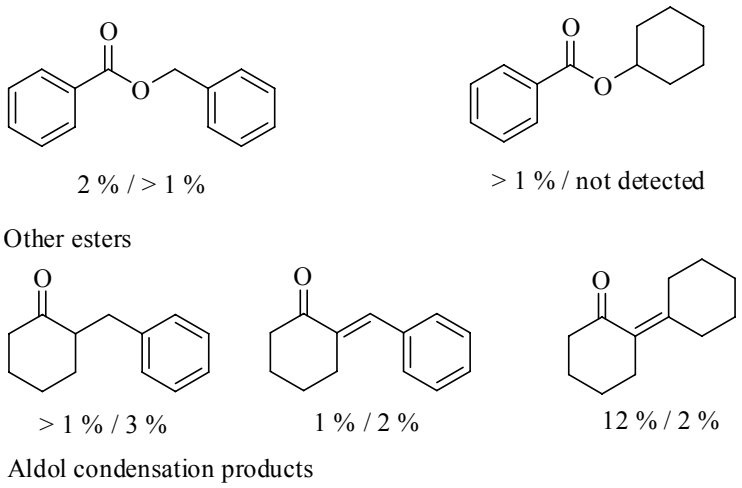
Table 11: Dehydrogenation of primary alcohols together with primary amines to their respective amides. GC conversion was greater than 95% for all substrates. Dodecane was used as internal standard. Conditions: 0.2 mol% **4**, 1.5 eq. amine, MMA 3 eq., -30 °C to RT, 4 h [a] xs NH_3, 5 eq. MMA, [b] 2.5 eq. amine.

Entry	Alcohol	Amine	Product	Yield
1	Benzyl alcohol (***a***)	NH_3		94% [a]
2	Octanol (***b***)	NH_3		92% [a]
3	4-Methylthio-benzyl alcohol (***d***)	NH_3		94% [a]
4	Geraniol (***k***)	NH_3		82% [a]
5	Benzyl alcohol (***a***)	$BzNH_2$		97%
6	Benzyl alcohol (***a***)	nBuNH$_2$		94%
7	Benzyl alcohol (***a***)	iPrNH$_2$		93%
8	Octanol (***b***)	$BzNH_2$		94%
9	Octanol (***b***)	nBuNH$_2$		96%
10	4-Methylthio-benzyl alcohol (***d***)	nBuNH$_2$		93%
11	1,3-Propanediol(***g***)	$BzNH_2$		90% [b]
12	Geraniol (***k***)	$BzNH_2$		89%
13	Glycidol (***l***)	$BzNH_2$		86% [b]

4 Side Products

Generally the catalytic reactions proceed very cleanly, especially the base free reactions with MMA yield only small amounts (1%) of the symmetric esters as byproducts.

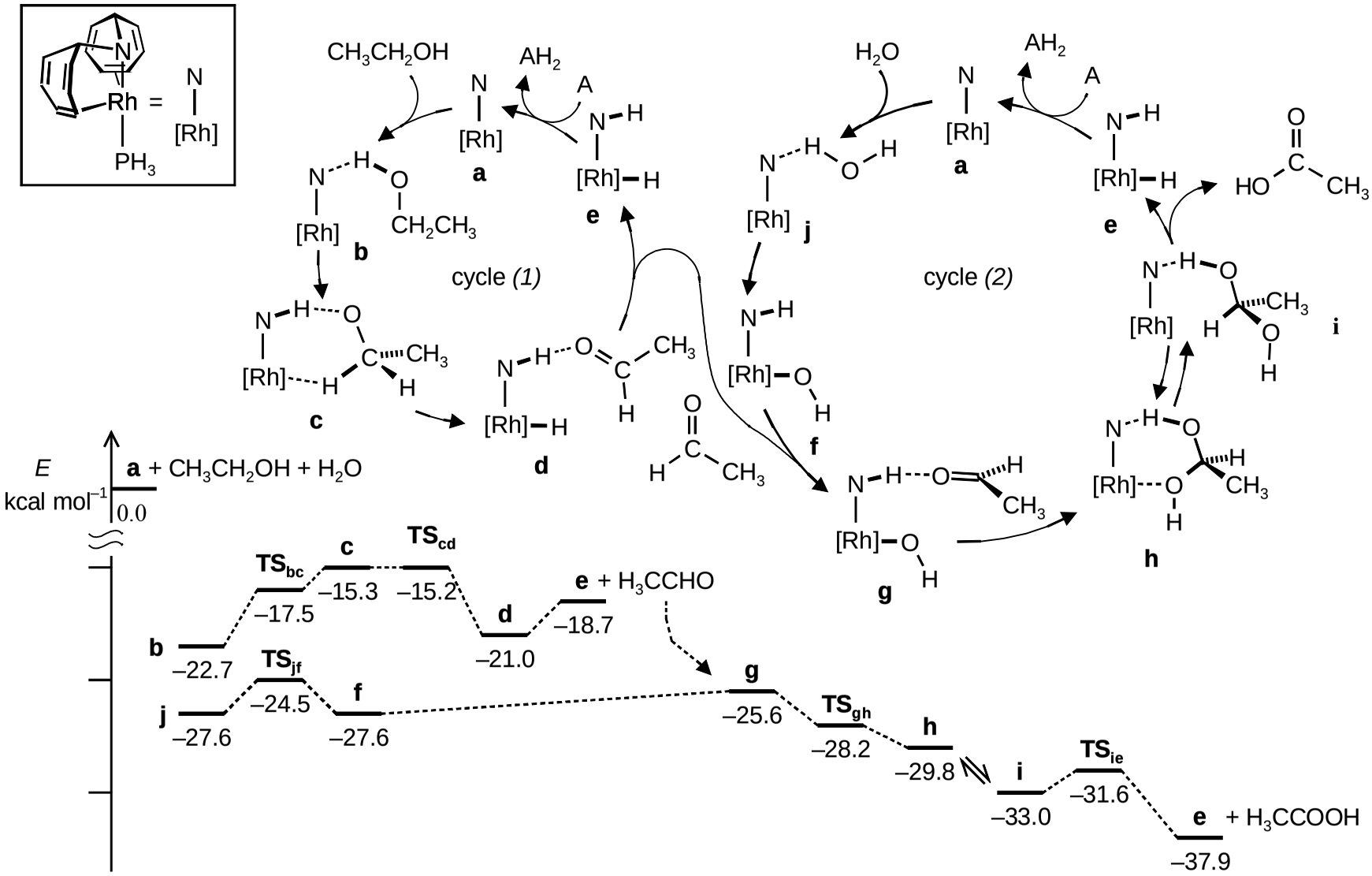
For the dehydrogenation of benzyl alcohol with cHexO the side products were identified by GC and GC-MS. Small amounts of aldol condensation products and other esters were found. We assume that the situation is similar for other alcohols.



Scheme 20: Side products of the DHC reaction of benzyl alcohol with methanol and water using cyclohexanone as hydrogen acceptor. The substances were identified by GC-MS and the amount was determined by GC with dodecane as internal standard. Values: DHC with methanol to methylester / DHC with water to acid

5 Computational investigation of the mechanism

The mechanism and especially the role of **4** as catalyst in the dehydrogenative coupling reaction $H_3C\text{-}CH_2\text{-}OH + H_2O + \mathbf{4\ a} \rightarrow H_3CCOOH + \mathbf{4\ e}$ was computed with Density Functional Theory (DFT) using the B3PW91 functional.[96] The benzo groups in the $trop_2N$ ligand were omitted and the phenyl groups of the phosphane ligand PPh_3 in **4** were replaced by hydrogen which gave the simplified model complexes **a** – **j** (Scheme 21). Amido complex **a** reacts exothermally either with ethanol [cycle *(1)*] or water [cycle *(2)*] to give adducts **b** and **j**, respectively. The former is converted by a Noyori-type mechanism[59] via the intermediates **c** and **d** to the amino hydride **e** and acetaldehyde, CH_3CHO. In the water adduct **j**, one O-H bond is broken to give the amino hydroxide complex **f** to which acetaldehyde is bonded to give **g**. In this adduct, the acetaldehyde molecule is activated and held via a NH···O=CHMe-bridge in proximity to the hydroxide which attacks the carbonyl group to form a hemiacetal complex **h**. The latter may easily rearrange into the isomer **i** which has as intermediate **c** the right conformation for the concerted heteropolar H_2 transfer from the NH^+ and CH^- groups which gives again the amino hydride **e** and the final product acetic acid, MeCOOH. In the reaction with the hydrogen acceptor **A**, the amino hydride **e** is converted back to the amide **a** by steps very similar to $\mathbf{e} \rightarrow \mathbf{d} \rightarrow \mathbf{c} \rightarrow \mathbf{b} \rightarrow \mathbf{a}$ in Scheme 21. The transition states $\mathbf{TS_{jf}}$ for cleavage of the O-H bond in **j**, and $\mathbf{TS_{ie}}$ for the hydrogen transfer in **i** are very low ($\leq$ 3 kcal mol^{-1}). At the employed level of theory and after inclusion of the Zero-Point-Energy (ZPE) the transition states $\mathbf{TS_{bc}}$, $\mathbf{TS_{cd}}$, and $\mathbf{TS_{gh}}$ are even lower than one of the intermediates to which they are connected. While this not meaningful, it indicates that the minimum energy reaction paths (MERP's) are very flat in this region and the activation barriers low. We therefore assume, that the highest barrier in this multi-step reaction is approximately given by the energy difference between **b** and **c** and in the range of 8 kcal mol^{-1}. We cannot exclude that the aldehydes formed catalytically in cycle *(1)* react with R^2XH in a non-metal assisted reaction to give intermediates $R^1CH(OH)(XR^2)$ (XR^2 = OH, OMe, NHR^3). However, the computations for the model reaction strongly imply that also the formation of these hemiacetals/aminals is efficiently catalyzed by the amido complex $[Rh(trop_2N)(PPh_3)]$ (**4**) as shown in cycle *(2)*.



Scheme 21: Computed reaction mechanism for the conversion of ethanol and water to acetic acid promoted by the model complex **a.**

This assumption is further bolstered by the observation that **4** catalyses with unmatched efficiency the reaction between benzaldehyde, PhCH=O, and methanol to give methyl benzoate, PhCO(OMe) and benzyl alcohol Ph-CH_2-OH as noted before.

6 Conclusion and Outlook

The amido ligand in **4** is a *cooperative ligand* actively participating in a reversible manner in the catalytic cycles leading to a variety of interesting products. Although many methods are available for the syntheses of carbonic acids, esters, and amides, dehydrogenative coupling reactions are less common. The reactions described here nicely complement the acceptorless DHC reactions reported by Milstein and stand out by the mild reaction conditions, low catalyst loadings, functional group tolerance, simple protocols, easy workup and especially their chemoselectivity. The proposed reaction mechanism may contribute to develop rationales to catalytically convert readily available low-cost materials from biomass into valuable fine chemicals. Emphasizing the role of the cooperating amido ligand may help to replace the expensive rhodium by cheaper metals, an important goal yet to be achieved.

V. Chiral Amine Diolefin Ligands

1 Introduction

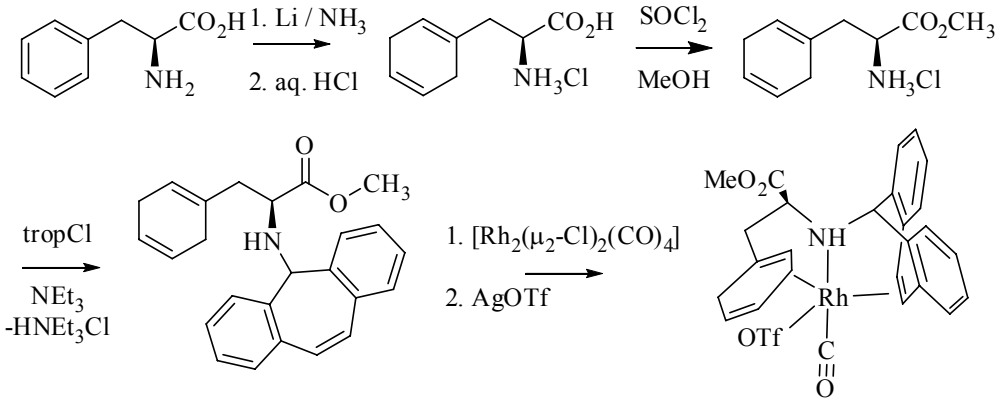
Chirality of organic molecules plays an significant role in areas ranging from medicine to material science. One of the most important strategies to introduce chirality involves the ability of a catalyst to differentiate between the enantiotopic faces of a prochiral functional group, for example a carbonyl group. For this differentiation the catalyst needs to be chiral itself.[97]

Asymmetric transfer hydrogenation has been the subject of intense research during the last two decades.[1-4, 98] Based on the success of the trop$_2$NH complexes chiral amine diolefin ligands were synthesized. Complexes with these new ligands were tested in catalysis and their ability to induce asymmetry in the transfer hydrogenation reaction was studied.

2 Synthesis of ligands and complexes

2.1 Phenylalanine as ligand building block

Phenylalanine was used for the synthesis of a chiral amino-diolefine ligand as previously described.[99] The phenyl group in phenylalanine was transformed via Birch reduction into the cyclohexa-1,4-dienyl derivative.[100] The subsequent esterification with thionyl chloride in methanol[101] and addition of a trop moiety was straightforward.



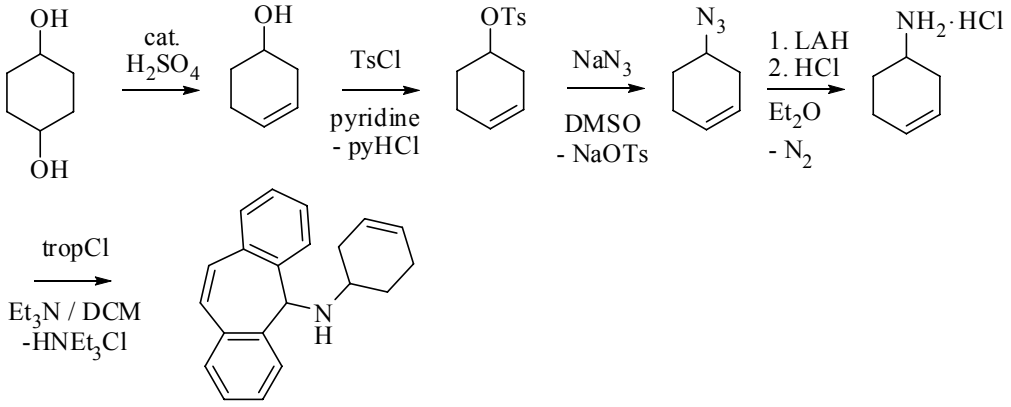
37 **39**

Scheme 22: Synthesis of (2*S*)-3-(Cyclohexa-1,4-dienyl)-2-(5*H*-dibenzo[*a,d*]cyclohepten-5-ylamino)-propionic acid methylester **37** and the rhodium complex [Rh((2H-Phe)tropNH)(CO)]OTf **39**.

As previously described[99] and confirmed in this study only $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ reacted cleanly with **37** to give [Rh(Cl)((2H-Phe)tropNH)(CO)] **38**. This complex was quantitatively converted to [Rh((2H-Phe)tropNH)(CO)]OTf **39** by addition of one equivalent of silver triflate. Several experiments to substitute the CO trans to NH on this complex were made, but none was successful. With triphenylphosphine always the free ligand **37** was observed in NMR experiments independently if **38** or **39** was used. Addition of **37** to the ethylene precursor $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ was not successful either. An ill defined product was obtained and upon addition of triphenylphosphine again the free ligand was observed. This means the metal-ligand bond in **38** and **39** is not very strong. Furthermore, from the crystal structure of **38** it is obvious that there is no space in the axial coordination site for a bulky ligand like triphenylphosphine (see Figure 14).

2.2 3-4-Cyclohexenylamine as replacement for the trop moiety

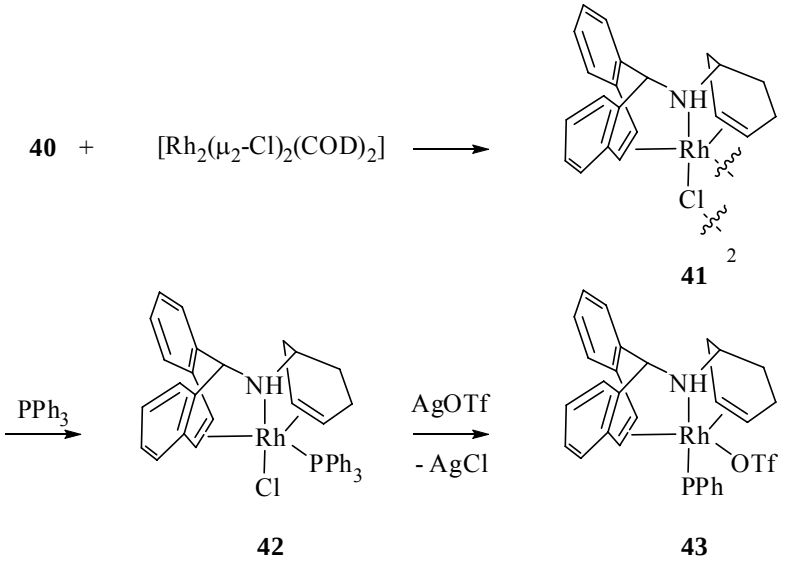
Since the trop moiety is cyclic, a more similar replacement was envisioned. However, cycloheptenyl moieties are difficult to synthesize, but cyclohexenyl moieties are relatively easy accessible by Diels-Alder reactions, Birch reductions and by other synthetic methods. Furthermore it was of interest if a cyclohexenyl moiety would be as good as a trop moiety as ligand for a transition metal. Starting from the known 3-4-cyclohexenylamine hydrochloride[102, 103] addition of a trop moiety was straightforward and the desired N-cyclohex-3'-en-1'-yl-5*H*-dibenzo[*a,d*]cycloheptene-5-amine (cyhtropNH) **40** was obtained in acceptable yield (69%). The two enantiomers of **40** were successfully separated on a preparative chiral HPLC column.



40

Scheme 23: Straightforward synthesis of cyhtropNH **40**.

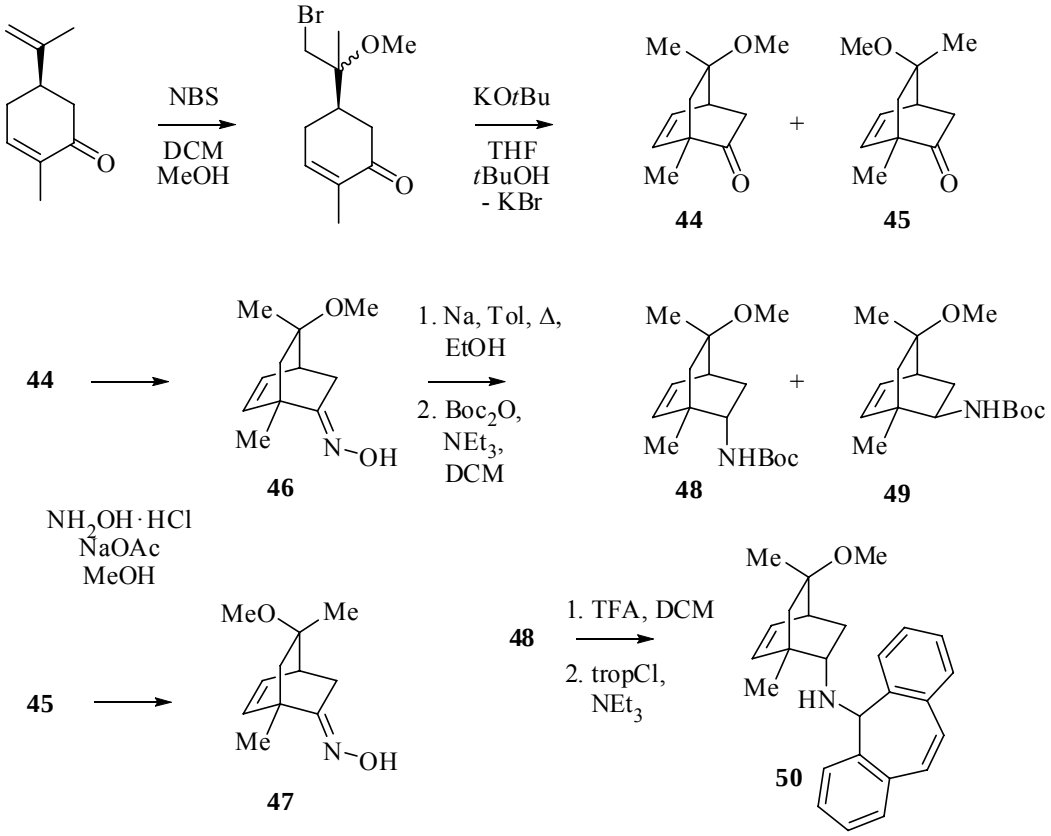
Rhodium complexes of the racemic mixture as well as the separated enantiomers of this ligand were obtained by standard methods. Ligand **40** reacted cleanly with $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$ and $[Rh_2(\mu_2\text{-}Cl)_2(cyhtropNH)_2]$ **41** was obtained. This dimer reacts with triphenyl-phosphine to give $[Rh(Cl)(cyhtropNH)(PPh_3)]$ **42**. The chloride is readily abstracted with silver triflate and $[Rh(OTf)(cyhtropNH)(PPh_3)]$ **43** analogous to **3** is obtained.



Scheme 24: Synthesis of rhodium complexes **41**, **42** and **43** with cyhtropNH **40**.

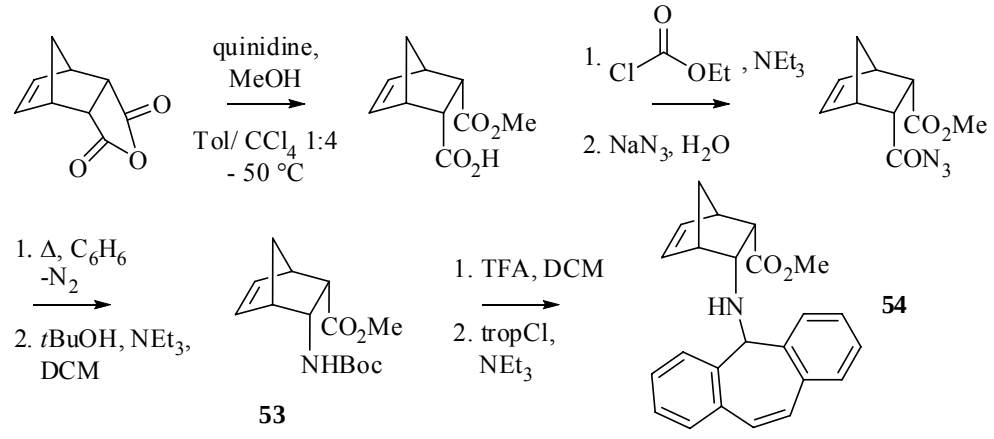
2.3 Asymmetric unsaturated bicyclic amines

Since the results in transfer hydrogenation obtained with **42** were encouraging (see V.4), chiral cyclohexenyl amines were sought. Inspired by the chiral bicyclo[2.2.2]octa-2,5-diene used in conjugate additions of boronic acids by Carreira et al.[104] an analogous bicyclo[2.2.2]oct-5-en-2-amine was envisioned. The synthesis started from (*R*)-carvone, a chiral pool substance to the known bicyclo[2.2.2]oct-5-en-2-ones **44** and **45**.[105] These were reacted with hydroxylamine hydrochloride to the bicyclo[2.2.2]oct-5-en-2-one oximes **46** and **47**. Reduction of **46** by sodium was successful and gave an excess of the desired diastereoisomer. Separation of these diastereoisomers was greatly simplified by protecting the free amines as *tert*-butyl carbamates. Thus the *tert*-butyl bicyclo[2.2.2]oct-5-en-2-yl carbamates **48** and **49** were obtained. **48** was deprotected and reaction with tropCl to 222tropNH **50** was then straightforward. Reduction of bicyclo[2.2.2]oct-5-en-2-one oxime **47** has not been tried yet but should be analogous to **46**.



Scheme 25: Synthesis of 222tropNH **50** from (*R*)-carvone.

(2*S*3*R*) - methyl 3-[(tert-butoxycarbonyl)amino]bicyclo[2.2.1]hept-5-ene-2-carboxylate **53** was obtained as a gift from the group of Prof. C. Bolm of RWTH Aachen.

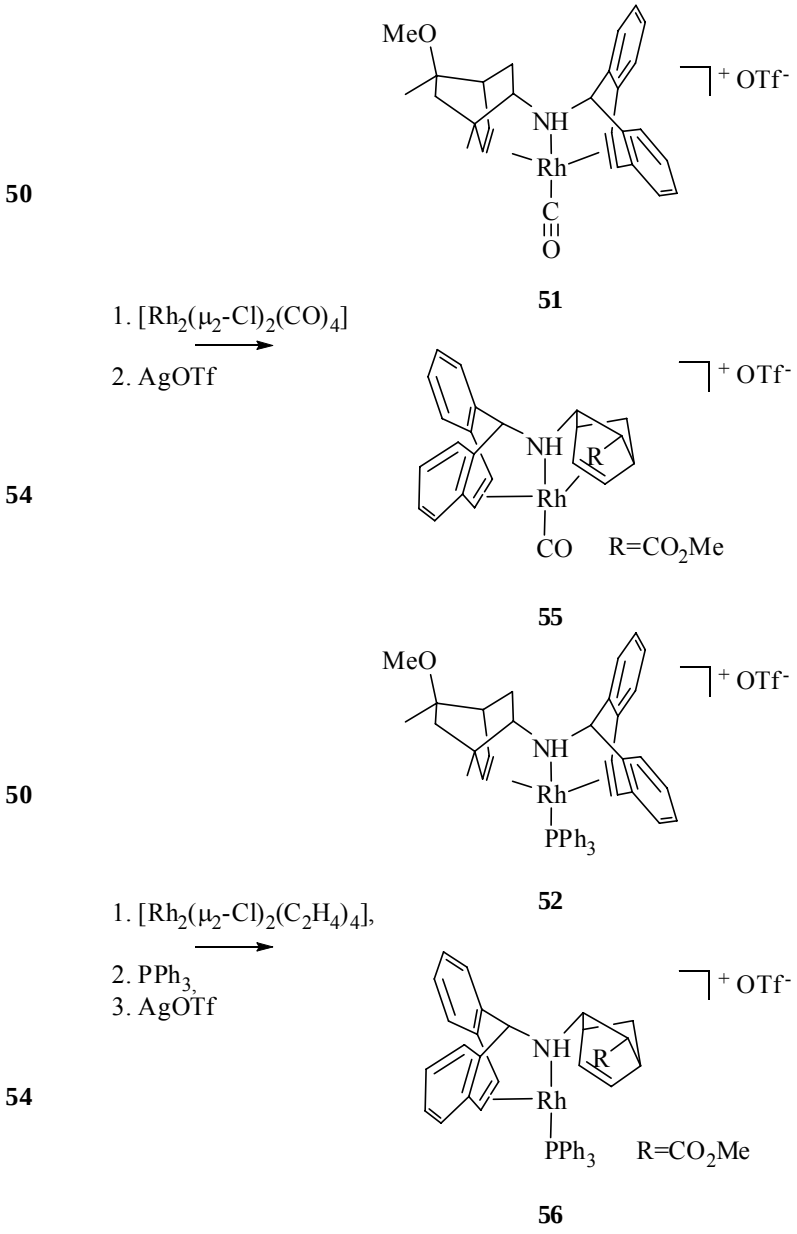


Scheme 26: Synthesis of 221tropNH **54** from *exo*-cis-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride by asymmetric ring opening.

The compound was synthesized by the procedure described for the stereo selective anhydride opening,[106, 107] but instead of benzyl alcohol *tert*-butanol was added to the isocyanate formed after Curtius reaction and a BOC moiety was obtained.

Deprotection of **53** and addition of a trop moiety to form 221tropNH **54** was straightforward.

222tropNH **50** and 221tropNH **54** did not coordinate to $[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$ but with $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ and $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ complexes **51**, **52**, **55**, and **56** were obtained in clean reactions.



Scheme 27: Synthesis of carbonyl complexes [Rh(222tropNH)(CO)]OTf **51** and [Rh(221tropNH)(CO)]OTf **55** and triphenylphosphine complexes [Rh(222tropNH)(PPh_3)]OTf **52** and [Rh(221tropNH)(PPh_3)]OTf **56** from 222tropNH **50** and 221tropNH **54**.

The chloro complexes of **50** and **54** were not isolated and the chloride directly abstracted with silver triflate. ^{1}H-NMR and – where applicable – ^{31}P-NMR indicated

very clean formation of the chloro complexes during the course of the synthesis. After separation of silver chloride the triflate complexes were obtained in good yields (>80%).

3 Crystal structures and NMR data

Crystal structures of complexes [Rh(OTf)(cyhtropNH)(PPh_3)] **43** and [Rh(222tropNH)(PPh_3)]OTf **52** were obtained. A crystal structure of [Rh(Cl)((2H-Phe)tropNH)(CO)] has been measured earlier.[99]

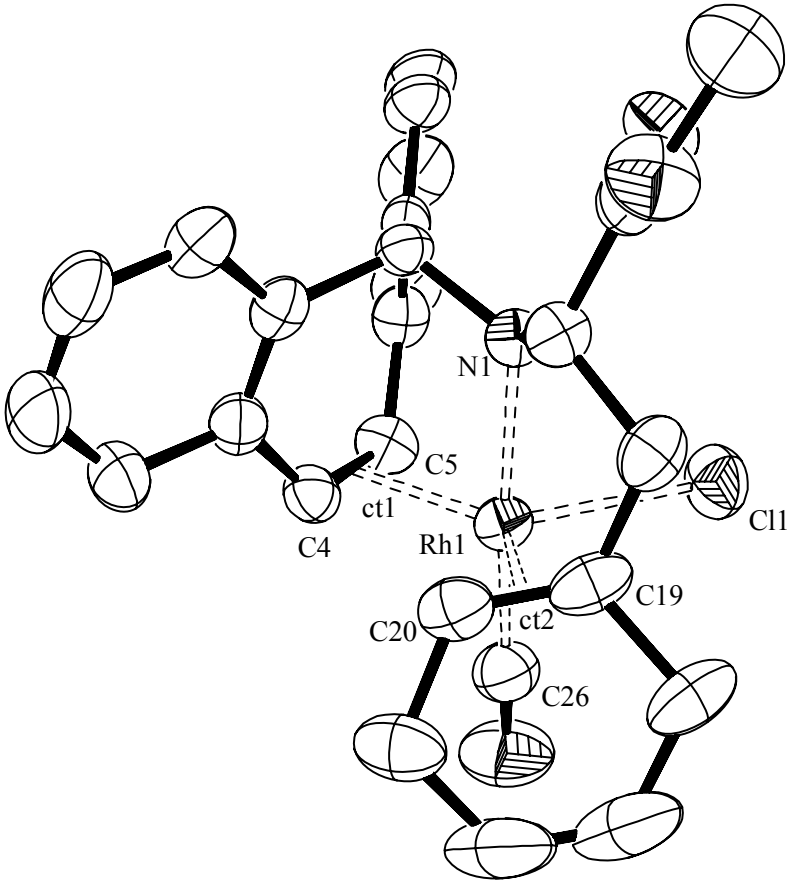


Figure 14: Ortep plot (at 50% ellipsoid probability) of structure [Rh(Cl)((2H-Phe)tropNH)(CO)] **38**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.151(3), Rh1-C26 1.867(4), Rh1-Cl 2.526(3), Rh1-ct1 2.074(4), Rh1-ct2 2.193(5), Rh1-C4 2.176(5), Rh1-C5 2.212(5), Rh1-C19 2.321(5), Rh-C20 2.282(5), C4=C5 1.430(6), C19=C20 1.396(7), N1-Rh1-C26 174.28(12), ct1-Rh1-ct2 129.18(18).

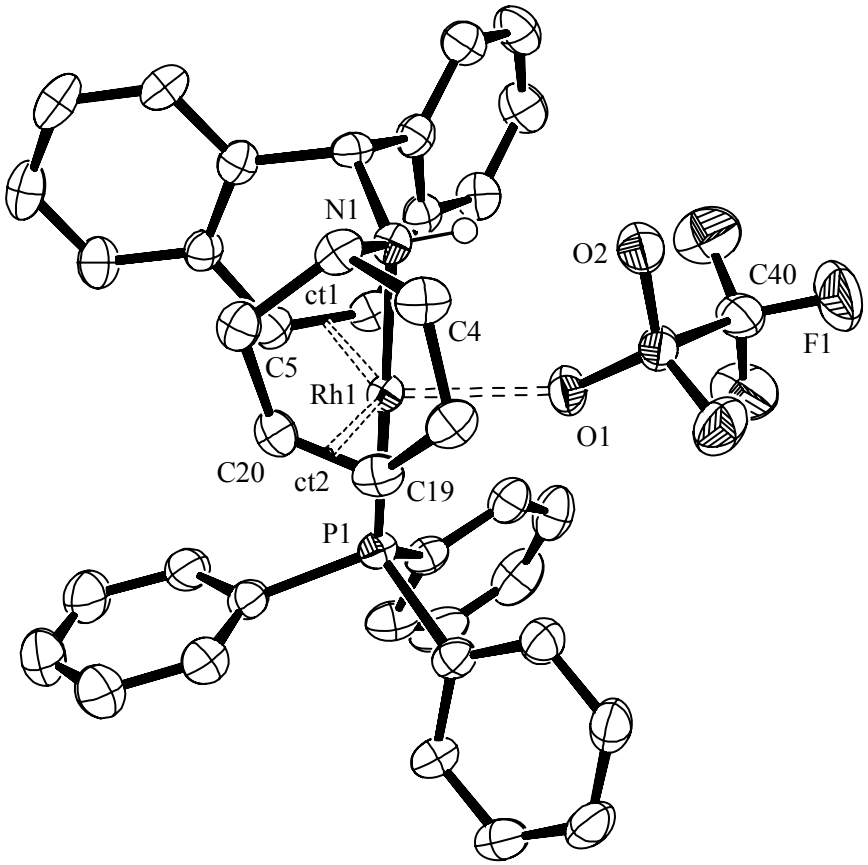


Figure 15: Ortep plot (at 50% ellipsoid probability) of structure **43**. Carbon bonded hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.135(3), Rh1-P1 2.075(4), Rh1-O1 2.347(3), Rh1-ct1 2.053(4), Rh1-ct2 2.075(4), Rh1-C4 2.182(4), Rh1-C5 2.161(4), Rh1-C19 2.210(4), Rh-C20 2.168(4), C4=C5 1.418(6), C19=C20 1.395(6), N1-O2 3.094(8), N1-Rh1-P1 177.62(9), ct1-Rh1-ct2 135.05(14).

Comparing structures **43**, **52** and **38** with [Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3** several observations can be made (Table 12). The N1-Rh and the ct1-Rh bond length between the olefin of the trop moiety and the rhodium do not change much. The ct1-Rh-ct2 angle and ct2-Rh bond length are dependent on the second olefin moiety. The ct2-Rh bond length is indicative of the rhodium olefin bond strength.

Complex **38** has a trigonal bipyramidal structure similar to **3**, however the second olefin binds not so well. The Rh1-ct2 distance is 2.193(5) Å, about 6% longer compared to Rh1-ct1 2.074(4) Å for the trop moiety. This is either due to the geometry of the ligand or due to steric interaction of the cyclohexadienyl moiety with the ancillary ligand CO (see Figure 14).

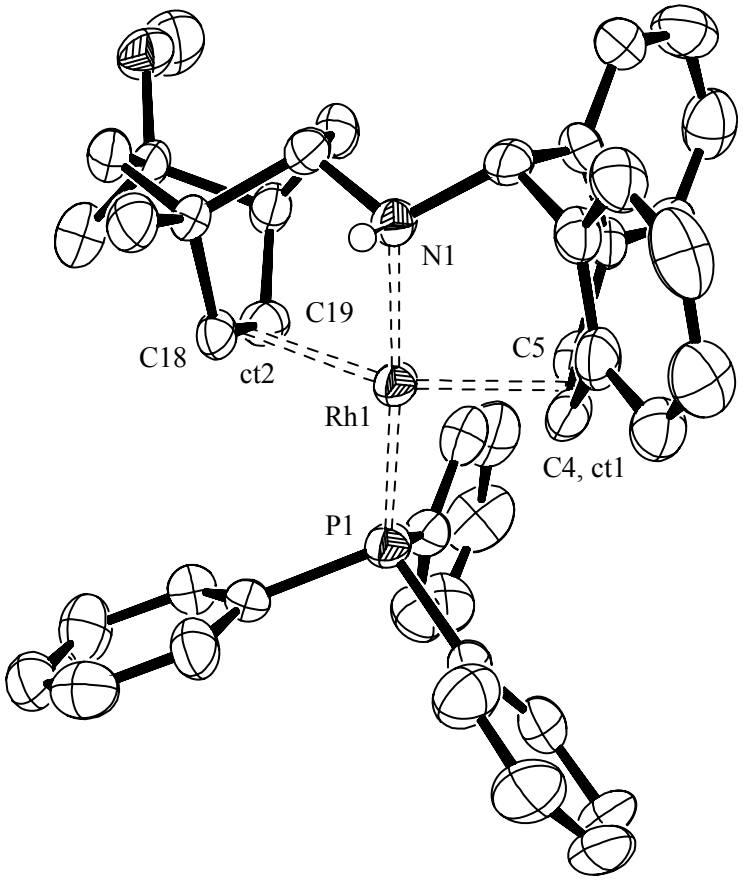


Figure 16: Ortep plot (at 50% ellipsoid probability) of structure **52**. Carbon bonded hydrogen atoms and the non coordinating disordered triflate anion are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C18=C19): Rh1-N1 2.114(4), Rh1-P1 2.2762(15), Rh1-ct1 2.073(5), Rh1-ct2 2.153(5), Rh1-C4 2.168(5), Rh1-C5 2.215(5), Rh1-C18 2.203(4), Rh-C19 2.320(6), C4=C5 1.418(8), C19=C20 1.393(7), N1-Rh1-P1 176.58(12), ct1-Rh1-ct2 153.22(21).

Structure **43** with cyhtropNH **40** as ligand is remarkably similar to structure **3**. As in **3** the triflate anion coordinates and there is a hydrogen bond between the amine proton of the ligand and the anion. The cyclohexenyl moiety binds well to the metal cation, the ct2-Rh bond length is in the same range as a common ct-Rh bond length of a complexed trop moiety (Table 12).

Structure **52** is more different from **3** in comparison. The ct2-Rh bond is significantly longer and the ct1-Rh-ct2 angle is larger than in structure **3**. Therefore, the structure is in between trigonal bipyramidal and planar. The largest angle θ (see III.4) is found in structure **52**, hence there is some amount of distortion.

Table 12: Comparison of selected bond lengths [Å] and angles [°] from X-ray diffraction studies of rhodium diolefin amine complexes.

Compound	N1-Rh	ct1-Rh	ct2-Rh	ct1-Rh-ct2	θ
[Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3**[40]	2.150(2)	2.040(3)	2.075(3)	139.90(9)	7.8
[Rh(Cl)((2H-Phe)tropNH)(CO)] **38**[99]	2.150(3)	2.074(4)	2.193(5)	129.18(18)	13.72
[Rh(OTf)(cyhtropNH)(PPh$_3$)] **43**	2.135(3)	2.053(4)	2.075(4)	135.05(14)	10.6
[Rh(222tropNH)(PPh$_3$)]OTf **52**	2.114(4)	2.073(5)	2.153(5)	153.22(21)	21.1

The size of the coordination shift (Δδ) in ^{13}C NMR, defined as shift difference of the resonance in the complex compared to the free olefin, correlates well with metal-olefin bond strength. The olefinic carbon resonances of all complexes and some ligands discussed are given in Table 13.

Table 13: Olefinic ^{13}C-NMR data of rhodium complexes with asymmetric amino diolefin ligands. *C*H$_{olefin}$ A, B: trop moiety, C, D: other olefin.

Compounds	Solvent	*C*H$_{olefin}$ A δ [ppm]	*C*H$_{olefin}$ B δ [ppm]	*C*H$_{olefin}$ D δ [ppm]	*C*H$_{olefin}$ E δ [ppm]
trop$_2$NH **1** (*exo-exo*)	$CDCl_3$	131.2	-	-	-
[Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3**[40]	$CDCl_3$	74.0	74.2	-	-
[Rh((2H-Phe)tropNH)(CO)]OTf **39**[99]	$CDCl_3$	66.7	67.2	84.3	101.4
cyhtropNH **40**	$CDCl_3$	131.0	-	125.5	127.5
[Rh(OTf)(cyhtropNH)(PPh$_3$)] **43**	$CDCl_3$	73.9	74.1	77.1	92.8
222tropNH **50**	$CDCl_3$	130.6	131.3	134.3	136.5
[Rh(222tropNH)(CO)]OTf **51**	CD_2Cl_2	79.4	79.8	98.7	100.7
[Rh(222tropNH)(PPh$_3$)]OTf **52**	CD_2Cl_2	82.5	87.2	103.3	107.6
221tropNH **54**	$CDCl_3$	125.6	131.1	132.4	138.5
[Rh(221tropNH)(CO)]OTf **55**	CD_2Cl_2	54.0	58.5	122.3	124.9
[Rh(221tropNH)(PPh$_3$)]OTf **56**	CD_2Cl_2	58.3	60.4	133.0	141.0

Of all new ligands cyhtropNH **40** binds best to the metal cation in good agreement with observations from the crystal structures. 222tropNH **50** binds much better than 221tropNH **54**, most likely because the carboxylic acid methyl ester moiety in **54** is

sterically demanding. Looking at the NMR data, ligand (2H-Phe)tropNH **37** seems to bind as well as ligand 222tropNH **50**.

Separation of ligand **50** from a rhodium cation with a good ligand like triphenylphosphine was never observed experimentally. However, ligand **37** is readily liberated when such a ligand is offered to complex **39**. Ligand **50** is less flexible compared to **37**, and shields the cation better, especially the equatorial coordination site. More importantly the cyclohexadienyl substituent in **37** is sterically crowding the axial coordination site, **37** is therefore only compatible with small ancillary ligands (see Figure 14). Therefore complexes of **50** are maybe kinetically more inert but not necessarily thermodynamically more stable than complexes of **37**.

4 Application in transfer hydrogenation

All catalysts were tested in transfer hydrogenation in ethanol. Mixed results were obtained. Especially the complexes of unsaturated bicyclic amines did not perform well. The results obtained can be explained partially by the structures of the catalysts. [Rh(OTf)(cyhtropNH)(PPh_3)] **43** performed very well. Turnover numbers of up to 400'000 were observed at S/C 10^6 after 48 hours. However, no enantiomeric excess (ee) was obtained anymore with low catalyst loadings and long reaction times. Structure **43** closely resembles the structure of the successful catalyst [Rh($trop_2NH$)(PPh_3)]OTf **3** (see Figure 15). [Rh((2H-Phe)tropNH)(CO)]OTf **39** was a less active catalyst precursor as expected for a carbonyl complex. Compared to **3** [Rh($trop_2NH$)(CO)]OTf was also found to be an inferior catalyst precursor.[40] [Rh(222tropNH)(PPh_3)]OTf **52** was not active in transfer hydrogenation at all. Probably the ligand is sterically too demanding and therefore inhibits the catalytic reaction (see Figure 16). Surprisingly [Rh(221tropNH)(PPh_3)]OTf **56** was much more active in transfer hydrogenation than **52** even though from NMR data we have to assume that the cyclohexenyl moiety is not coordinated (see Table 13). Both carbonyl complexes **51** and **56** were almost inactive in transfer hydrogenation and capable of only a few turnovers.

Table 14: Transfer hydrogenation with complexes of chiral amine diolefin ligands, 2 M acetophenone in EtOH and 1 mol% KO*t*Bu;

Catalyst precursor	S / C	t [h]	Conversion [%]	ee [%]
[Rh((2H-Phe)tropNH)(CO)]OTf **39**	1'000	0.8	83	30
39 [a]	1'000	1.5	75	58
[Rh(OTf)(cyhtropNH)(PPh_3)] **43**	10'000	0.05	96	33
43 [a]	10'000	0.25	91	44
[Rh(222tropNH)(CO)]OTf **51**	100	1.2	0	-
[Rh(222tropNH)(PPh_3)]OTf **52**	100	1.2	<1	0
[Rh(221tropNH)(CO)]OTf **55**	100	1.2	<1	0
[Rh(221tropNH)(PPh_3)]OTf **56**	100	1.2	66	42

[a] Acetophenone 0.5 M in *i*PrOH.

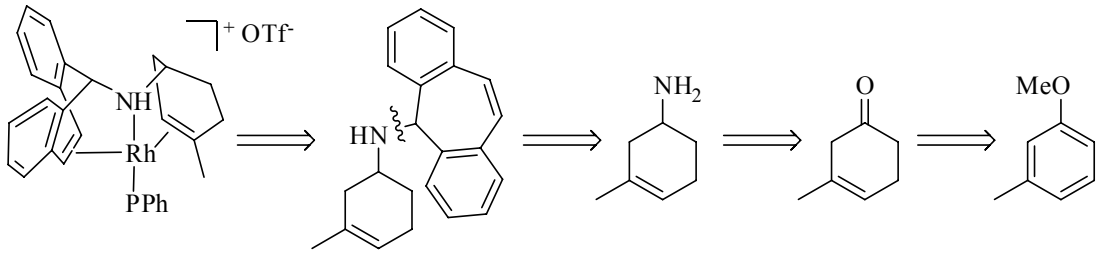
As expected the enantiomeric excess is influenced by the solvent. The diastereoisomeric transition states are differently stabilized by ethanol and isopropanol. Ethanol has a higher dipole moment. It interacts more with the transition states and less enantiomeric excess is observed (33 vs. 44% ee.).

5 Conclusion and outlook

The cyclohexenyl moiety seems to be a good replacement for the trop moiety. [Rh(OTf)(cyhtropNH)(PPh_3)] **43** performed very well and proved to be a remarkably stable catalyst. Turnover numbers of up to 400'000 were observed at S/C 10^6 after 48 h.

However, the bicyclic ligands performed disappointingly. Their cyclohexenyl moieties are probably too inflexible and ineptly substituted.

Some of the obtained results are promising and further research is necessary to optimize the system. Efficient asymmetric transfer hydrogenation may be possible with a suitably substituted cyclohexenyl amine (Scheme 28).

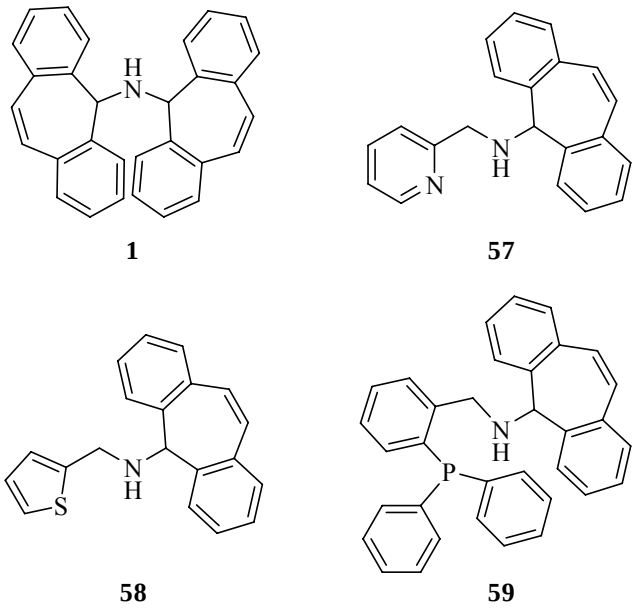


Scheme 28: Proposed methyl substituted cyclohexenyl amine to increase the obtained enantiomeric excess.

VI. Tridentate Amine Olefin Nitrogen, Sulfur and Phosphorous ligands

1 Introduction and Summary

It was found that rhodium and, to some extent, iridium complexes of $trop_2NH$ are efficient catalysts for transfer hydrogenation (see Section II and III). Taking bis-(trop)amine **1** (Scheme 29) as prototype, tridentate amine ligands with only one trop-moiety and other donor functionalities were synthesized.



1 **57**

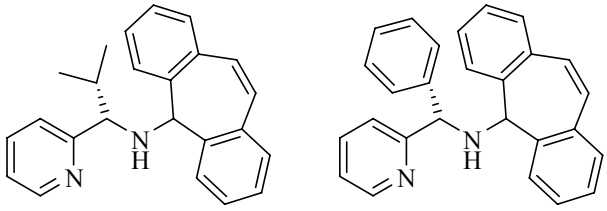
58 **59**

Scheme 29: New tridentate ligands based on $trop_2NH$ **1**: $pyCH_2tropNH$ **57**, $thioCH_2tropNH$ **58**, $Ph_2PPhCH_2tropNH$ **59**.

With the novel ligands (Scheme 29, compounds **57**, **58**, **59**) several different rhodium- and iridium-complexes were isolated. These were characterized, tested in transfer hydrogenation and compared with the previously discussed compounds.

Complexes of $trop_2NH$ **1** usually have a trigonal-bipyramidal or saw-horse structure (see section II and III, e.g. **3**, **6**, **7**). By changing the substituents the importance of the diolefin motif for catalytic activity and the influence on complex structure of other donors can be investigated.

Chiral derivatives (Scheme 30, compounds **60**, **61)** of $pyCH_2tropNH$ **57** were synthesized, but only low enatioselectivity in the transfer hydrogenation reaction was observed. Furthermore, chiral ancillary ligands were employed together with ligand **57** resulting in low to moderate enantioselectivity in the catalytic transfer hydrogenation.

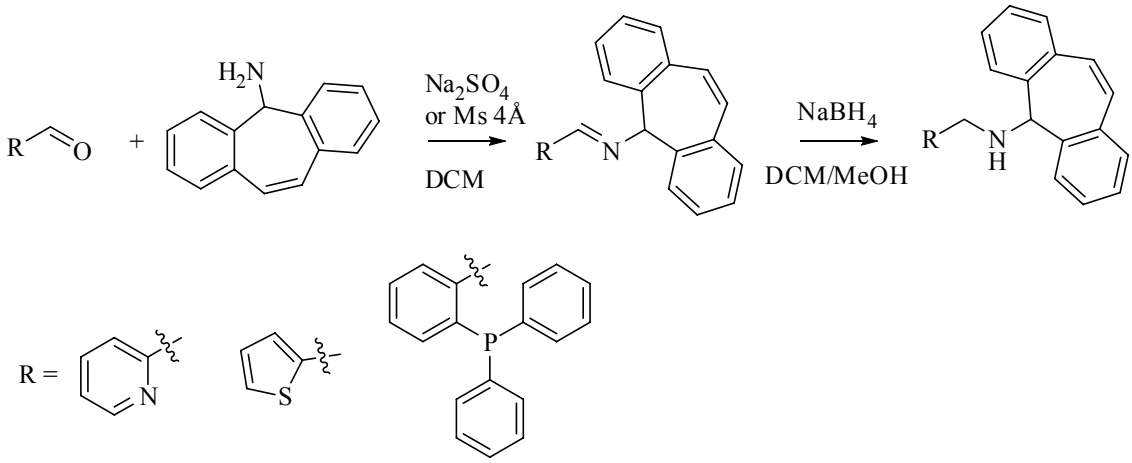


60 **61**

Scheme 30: Chiral derivatives of pyCH$_2$tropNH: py(*i*Pr)CHtropNH **60** and py(Ph)CHtropNH **61**.

2 Synthesis of the ligands

The ligands were synthesized from tropNH$_2$ and the corresponding aldehydes. The resulting imine was reduced to the amine using a modification of known literature methods.[108] The new ligands were purified by crystallization or chromatography, and good yields (70-90%) were obtained for all ligands. The aldehydes are commercially available, or in the case of triphenylphosphine carbaldehyde, easy to prepare.[109]



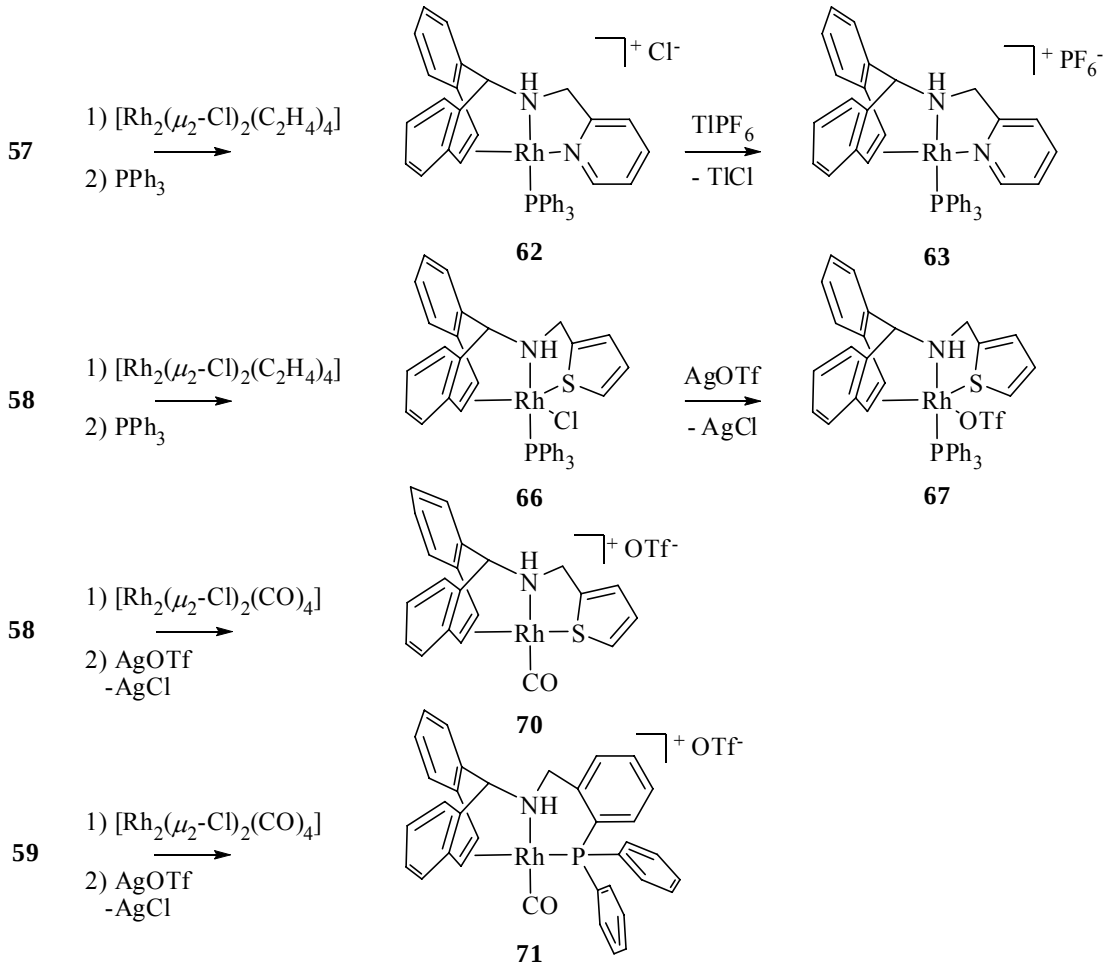
Scheme 31:Synthesis of the ligands pyCH$_2$tropNH **57**, thioCH$_2$tropNH **58**, Ph$_2$PPhCH$_2$tropNH **59**.

The chiral derivatives **60** and **61** were successfully synthesized by alkylation of the known (*S*)-1-(2-pyridyl)alkylamines [110] with tropCl, however yields obtained were only moderate (30-40%).

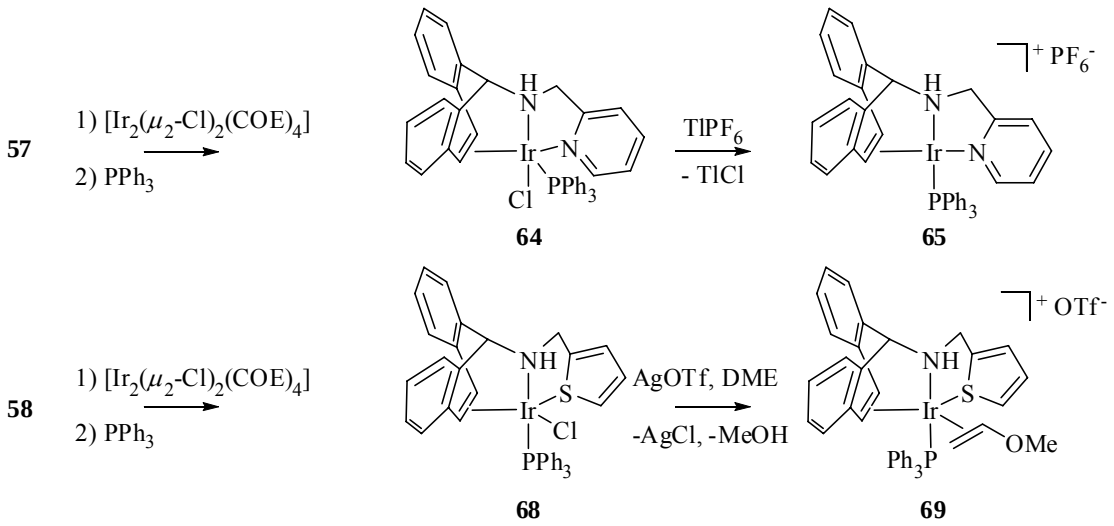
3 Synthesis of complexes

Isolation of complexes of ligands pyCH$_2$tropNH **57** and thioCH$_2$tropNH **58** was successful by a strategy closely resembling the synthetic method used for the synthesis of trop$_2$NH complexes. First, two equivalents of the ligand were complexed

to one equivalent of a dimeric metal precursor. In a second step an additional ligand was added and in a further reaction the chloride was abstracted with $TlPF_6$ or AgOTf. $TlPF_6$ was used if the silver cation oxidized the complexes.



Scheme 32: Synthesis of rhodium complexes of **57**, **58** and **59**.



Scheme 33: Synthesis of iridium complexes of **57** and **58**.

Remarkably no displacement of the ligands **57** and **58** from the complexes was observed when a stoichiometric amount of triphenylphosphine was used. The iridium complex **69** was found to be a remarkably strong Lewis acid able to split DME in methanol and methoxyethylene.

Synthesis of complexes analogous to **63** and **67** was attempted with the ligand $Ph_2PPhCH_2tropNH$ **59**. Addition of the ligand to the precursor $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ was successful. However upon addition of triphenylphosphine to the presumed dimer $[Rh_2(\mu\text{-}Cl)_2(Ph_2PPhtropNH)_2]$ **72** only broad signals were observed in ^{31}P-NMR, even after addition of $TlPF_6$ or AgOTf. Other phosphines were beyond the scope of this work, but with the precursor $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ carbonyl complex $[Rh(CO)(Ph_2PPhtropNH)]OTf$ **71** was obtained and characterized by standard spectroscopic methods and X-ray diffraction (see Figure 20).

4 Crystal structures

Crystal structures were obtained for complexes **63**, **65**, **67**, **69** and **71**. The observed geometry was dependent on the ligand and the ancillary ligand. The complexes **63**, **65** and **71** were found to be planar while the structures **67** and **69** were trigonal bipyramidal. The rhodium and iridium complexes **63** and **65** have a very similar geometry and are almost superimposable.

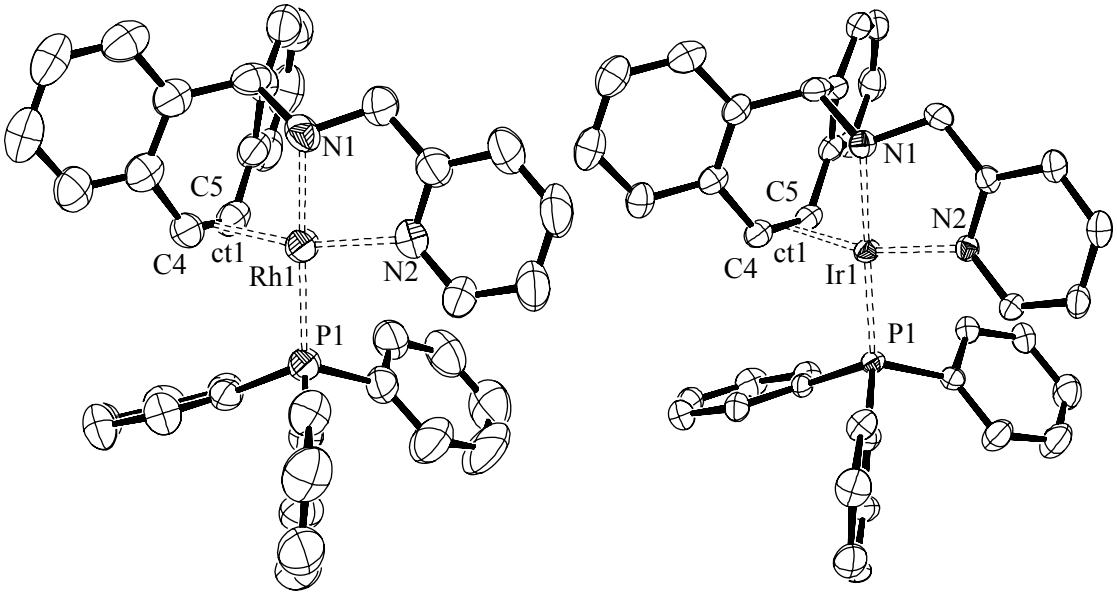


Figure 17: Ortep plots (at 50% ellipsoid probability) of the structures **63** (left) and **65** (right). The anions and (disordered) THF molecules included in the crystal are omitted. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5) **63**: N1-Rh1 2.119(5), N2-Rh1 2.115(4), P2-Rh1 2.2508(12), C4-Rh1 2.102(6), C5-Rh1 2.149(5), ct1-Rh1 2.005(6), C4=C5 1.411(9), N1-Rh1-N2 78.36(18), N2-Rh1-P1 98.32(12), P1-Rh1-ct 93.75(12), ct1-Rh1-N1 90.08(19), N1-Rh1-P1 174.46(15), ct1-Rh1-N2 164.40(15); **65**: N1-Ir1 2.116(4), N2-Ir1 2.108(4), P1-Ir1 2.2356(13), C4-Ir1 2.143(5), C5-Ir1 2.105(5), ct1-Ir1 2.000(5), C4=C5 1.434(8), N1-Ir1-N2 78.12(16), N2-Ir1-P1 98.85(11), P1-Ir1-ct 93.80(14), ct-Ir1-N1 89.68(18), N1-Rh1-P1 175.39(19), ct1-Rh1-N2 164.25(19).

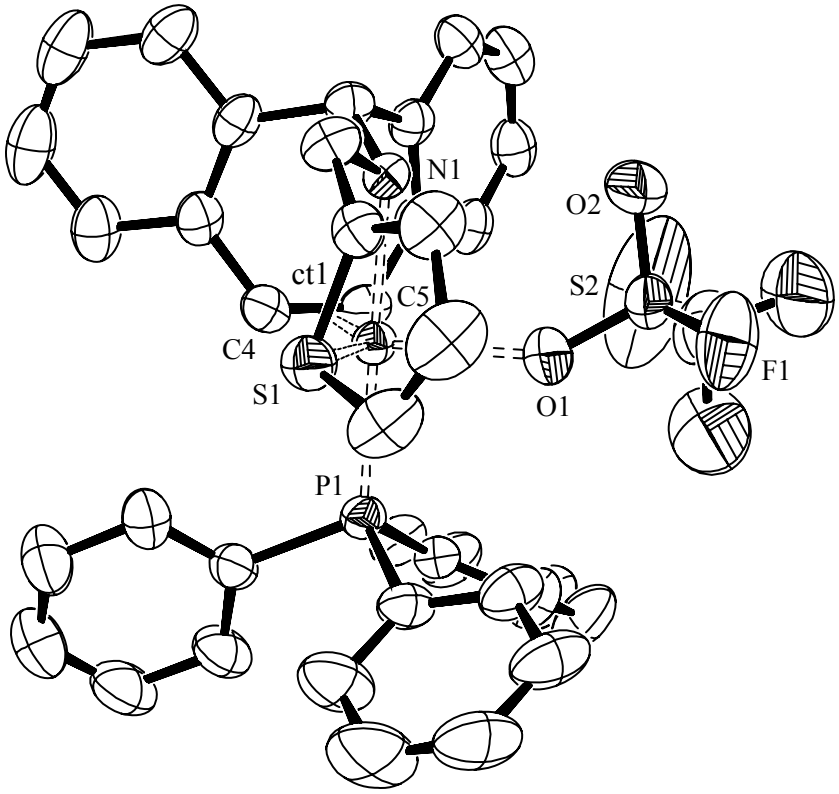


Figure 18: Ortep plot (at 50% ellipsoid probability) of the structure **67** Solvent molecules and hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5): N1-Rh1 2.160(3), S1-Rh1 2.536(1), P2-Rh1 2.287(1), C4-Rh1 2.101(4), C5-Rh1 2.106(4), O1-Rh1 2.337(3), ct1-Rh1 1.997(4), C4=C5 1.438(6), N1-O2 3.153(9), N1-Rh1-P1 177.35(8), ct1-Rh1-S1 137.95(12), N1-Rh1-S1 85.38(8), P1-Rh1-ct 93.61(11), ct-Rh1-N1 88.99(14).

Complexes **67** and **69** of thioCH_2tropNH **58** are much more different. Both structures are trigonal bipyramidal. However in structure **69** two olefins are present and the structures are therefore rather different. The most distinct feature is the angle between the metal, sulfur and the centroid of the double bond: 137.95(12)° in the rhodium complex **67** compared to 113.32(16)° in the iridium complex **69**.

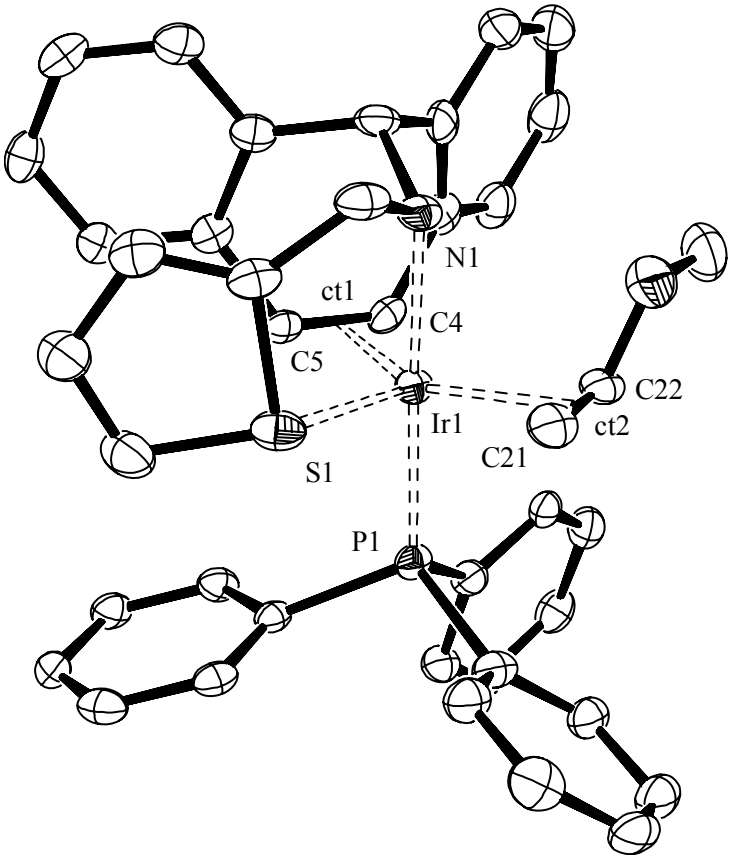


Figure 19: Ortep plot (at 50% ellipsoid probability) of the structure **69**. Solvent molecules and the non coordinating anion are omitted. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C21=C22): N1-Ir1 2.179(4), S1-Ir1 2.5083(13), P1-Ir1 2.2816(12), C4-Ir1 2.178(5), C5-Ir1 2.190(4), ct1-Ir1 2.064(5), C21-Ir1 2.156(5), C22-Ir1 2.226(5), ct2-Ir1 2.080, C4=C5 1.432(6), C21=C22 1.381(7), N1-Ir1-P1 177.92(11), ct1-Ir1-ct2 141.33(12), ct1-Rh1-S1 113.66(12), N1-Ir1-S1 84.30(12), S1-Ir1-P1 95.87(4).

Complex **71** obtained by coordination of $Ph_2PPhCH_2tropNH$ **59** on $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ has a planar structure. From the structure it is easily concluded that there is not very much space on the complex for stable coordination of an additional bulky phosphine like triphenylphosphine (see Figure 20), even though broad signals were observed when $[Rh_2(\mu\text{-}Cl)_2(Ph_2PPhtropNH)_2]$ **72** was treated with PPh_3.

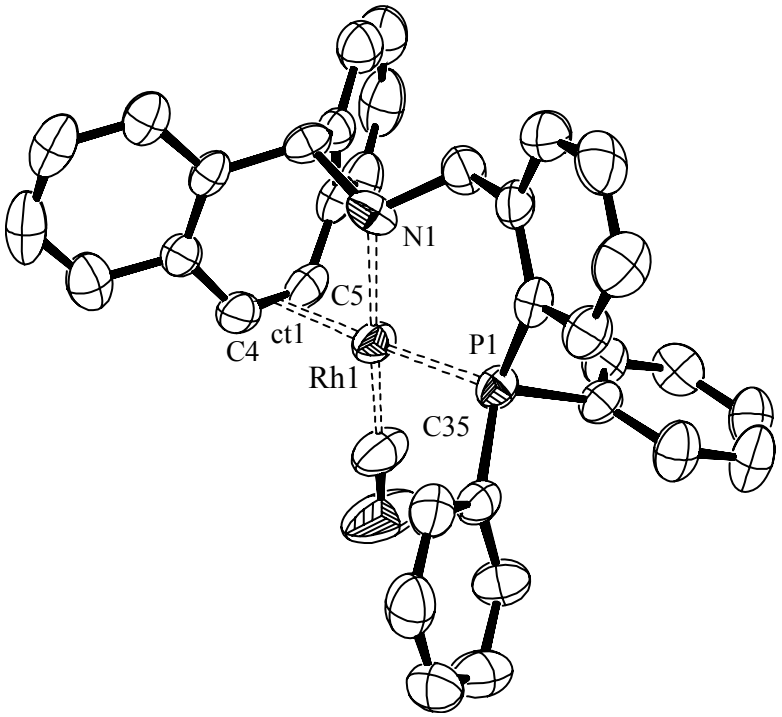


Figure 20: Ortep plots (at 50% ellipsoid probability) of the structure **71**. A disordered THF molecule and the non coordinating triflate anion are omitted. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5): Rh1-N1 2.108(3), Rh1-P1 2.307(1), Rh1-C4 2.230(3), Rh1-C5 2.260(3), Rh1-C35 1.837(5), C4=C5 1.390(5), ct1-Rh1 2.171(3), ct1-Rh1-N1 90.37(13), ct1-Rh1-C35 91.72(13), N1-Rh1-P1 89.78(8), P1-Rh-C35 88.09(13).

5 NMR data

Due to the dynamics of the seven-membered trop-ring, room temperature ^{1}H-NMR spectra of the ligands **57** and **58** show broad unresolved signals. At low temperature two conformers were detected, and the most important signals could be assigned to the *endo* and *exo* conformer. For comparison of the coordination shifts the NMR data of the *exo*-conformers are used; this geometry corresponds more closely to the geometries of the coordinated ligands.

While the rhodium complex **67** showed no peculiarities, NMR spectra of iridium complex **69** showed dynamic behavior in non-coordinating solvents like dichloromethane or chloroform. Even at low temperature only broad signals were observed. This is due to the dynamic methoxyethylene ligand preset in **69** which is labile and can rotate. The broadening of NMR signals vanished in coordinating solvents and complex **69** was successfully characterized by NMR in [D_6] DMSO. Likely DMSO displaces the methoxyethylene and therefore suppresses the dynamic behavior. Another possibility is that the sulfur moiety binds only weakly and the observed dynamic behavior is due to reversible coordination of the sulfur. Coordinating solvents would then lead to decoordination of the sulfur moiety. However the chelating nature of the ligand should favor coordination. In-depth investigations were beyond the scope of this work.

All complexes were characterized by ^{1}H, ^{13}C, ^{31}P NMR measurements. Selected data are given in Table 15 and Table 16. As discussed previously (see III.4), it is possible to draw conclusions about the strength of the olefin metal bond and the amount of back bonding present from the coordination shift.

Table 15: Selected ^{1}H-NMR data of complexes of tridentate amine olefin nitrogen, sulfur and phosphorous ligands.

Compound	Solvent	C*H*^{benzyl} δ [ppm]	C*H*^{olefin} A δ [ppm]	C*H*^{olefin} B δ [ppm]	N*H* δ [ppm]
trop$_2$NH **1** (*exo-exo*)	$CDCl_3$	4.37	7.06		3.43
pyCH_2tropNH **57** (*exo*)	$CDCl_3$	4.25	7.21		3.18
thioCH_2tropNH **58** (*exo*)	$CDCl_3$	4.26	7.23		2.43
Ph_2PPhtropNH **59** (*exo*)	$CDCl_3$	4.07	7.17		2.28
[Rh(trop$_2$NH)(PPh_3)]OTf **3**[40]	$CDCl_3$	4.91	4.94	5.43	5.66
[Ir(trop$_2$NH)(PPh_3)]OTf **32**	$CDCl_3$	5.10	4.38	5.23	6.23
[Rh(pyCH_2tropNH)(PPh_3)]PF_6 **63**	CD_2Cl_2	5.16	3.72	4.31	4.30
[Ir(pyCH_2tropNH)(PPh_3)]PF_6 **65**	CD_2Cl_2	5.36	3.62	3.95	4.72
[Rh(thioCH_2tropNH)(PPh_3)] OTf **67**	CD_2Cl_2	4.98	3.82	3.99	5.08
[Ir(thioCH_2tropNH)(PPh_3)] OTf **69**	[D_6] DMSO	5.28	3.44	3.54	6.10
[Rh(trop$_2$NH)(CO)]OTf [40]	$CDCl_3$	5.03	5.84	6.45	4.41
[Rh(thioCH_2tropNH)(CO)] OTf **70**	CD_2Cl_2	4.97	4.97	5.22	3.86
[Rh(Ph_2PPhtropNH)(CO)]OTf **71**	CD_2Cl_2	5.24	5.55	6.28	5.29

Table 16: Selected ^{13}C-NMR data of complexes of tridentate amine olefin nitrogen, sulfur and phosphorous ligands.

Compound	Solvent	CH_{benzyl} δ [ppm]	CH_{olefin} A δ [ppm]	CH_{olefin} B δ [ppm]
trop$_2$NH **1** (*exo-exo*)	$CDCl_3$	57.6	131.2	
pyCH_2tropNH **57** (*exo*)	$CDCl_3$	61.1	131.7	
thioCH_2tropNH **58** (*exo*)	$CDCl_3$	60.5	131.6	
Ph_2PPhtropNH **59** (*exo*)	$CDCl_3$	61.4	131.4	
[Rh(trop$_2$NH)(PPh_3)]OTf **3**[40]	$CDCl_3$	72.7	74.0	74.2
[Ir(trop$_2$NH)(PPh_3)]OTf **32**	$CDCl_3$	72.5	50.2	57.8
[Rh(pyCH_2tropNH)(PPh_3)]PF_6 **63**	CD_2Cl_2	67.0	60.8	68.2
[Ir(pyCH_2tropNH)(PPh_3)]PF_6 **65**	CD_2Cl_2	67.3	44.1	53.7
[Rh(thioCH_2tropNH)(PPh_3)]OTf **67**	CD_2Cl_2	68.0	56.7	56.7
[Ir(thioCH_2tropNH)(PPh_3)]OTf **69**	DMSO	66.7	32.7	42.5
[Rh(trop$_2$NH)(CO)]OTf [40]	$CDCl_3$	73.3	75.9	76.4
[Rh(thioCH_2tropNH)(CO)]OTf **70**	CD_2Cl_2	65.6	57.1	61.4
[Rh(Ph_2PPhtropNH)(CO)]OTf **71**	CD_2Cl_2	71.4	64.5	70.5

Not surprisingly, all the ligands have similar shifts for the characteristic protons and carbons of the trop moiety. In the complexes all benzylic protons and carbons are shifted similarly relative to the uncoordinated ligands. Compared to the rhodium complexes, the iridium complexes are shifted to lower frequencies in the ^{1}H and ^{13}C NMR ($\Delta\delta \approx 10$ ppm for ^{13}C-NMR). In the crystal structures this effect is small, the carbon bond of the complexed olefin is longer by 0.03-0.06 Å in the iridium complexes. As discussed previously iridium is the better π-base. In complexes of ligand pyCH_2tropNH **57** the olefinic carbon resonances have smaller coordination

shifts than complexes of thioCH_2tropNH **58**. This may be due to the different geometries of the complexes although the ligands and complexes, especially **69** are so different that it is difficult to draw a conclusion. In the carbonyl complexes a similar observation can be made. Of these three the olefinic carbon resonances have the largest coordination shift in complex **70** with thioCH_2tropNH **58** as ligand and the smallest with trop$_2$NH **1** as ligand. There seems to be more back bonding to the olefin in complexes of **58**.

6 Transfer hydrogenation

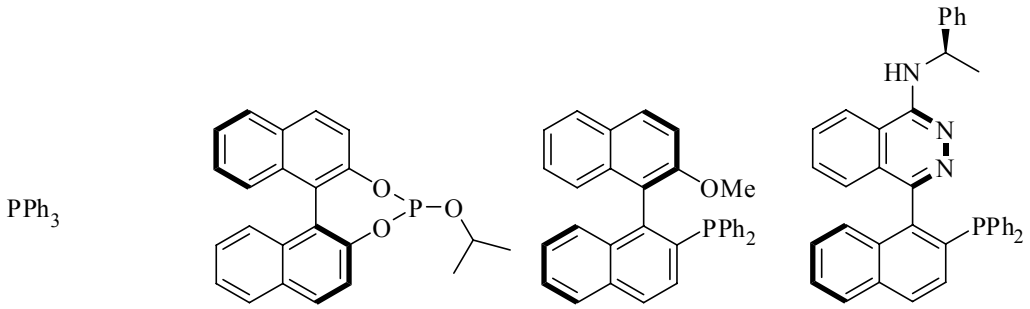
The obtained complexes were tested in transfer hydrogenation of acetophenone. 1 mol% of K_2CO_3 was used as base. The results of selected transfer hydrogenation experiments are presented in Table 17.

Table 17: Transfer hydrogenation with complexes of tridentate amine olefin nitrogen, sulfur and phosphorous ligands, 2 M substrate in ethanol or 0.5 M in *i*PrOH and 1 mol% K_2CO_3.

Catalyst precursor	S/ C	Alcohol	T [°C]	t [h]	Conv-ersion [%]	TOF [h^{-1}]
[Rh(pyCH_2tropNH)(PPh_3)]PF_6 **63**	1000	EtOH	40	48	7.4	1.5
[Rh(pyCH_2tropNH)(PPh_3)]PF_6 **63**	1000	*i*PrOH	40	20	100	5.0
[Ir(pyCH_2tropNH)(PPh_3)]PF_6 **65**	10000	EtOH	60	20	40.6	203
[Ir(pyCH_2tropNH)(PPh_3)]PF_6 **65**	1000	*i*PrOH	40	20	10	5.0
[Rh(thioCH_2tropNH)(PPh_3)] OTf **67**	1000	*i*PrOH	60	18	10	5.6
[Ir(thioCH_2tropNH)(PPh_3)]OTf **69**	1000	EtOH	20	1	0	0
[Ir(thioCH_2tropNH)(PPh_3)]OTf **69**	1000	*i*PrOH	20	1	>1%	>10
[Ir(thioCH_2tropNH)(PPh_3)]OTf **69**	1000	*i*PrOH	60	72	100%	13.9
[Rh(Ph_2PPhtropNH)(CO)]OTf **71**	1000	*i*PrOH	20	72	10%	1.4

Of the complexes discussed here, complex [Ir(pyCH_2tropNH)(PPh_3)]PF_6 **65** was found to be the best catalyst for transfer hydrogenation. It was more active in ethanol

than in isopropanol. The rhodium analog **63** on the other hand was more active in isopropanol, but could not match the performance of **65**. The complexes of thioCH_2tropNH **58**, **67** and **69** were performing better in isopropanol than in ethanol as catalyst precursors. Generally carbonyl complexes were inferior: [Rh(trop$_2$NH)(CO)]OTf is not a good transfer hydrogenation catalyst when compared to [Rh(trop$_2$NH)(PPh_3)]OTf **3**[40]. Therefore complex [Rh(Ph_2PPhtropNH)(CO)]OTf **71** was not a very good catalyst as expected. The new complexes were not active at room temperature and required heating (40 - 60 °C).



A B C D

Scheme 34: Ancillary ligands A: PPh_3, B: *S*-MONPOS, C: *R*-MOP, D: *R*-N-PINAP.

The ligands pyCH_2tropNH **57**, py(*i*Pr)CHtropNH **60** and py(Ph)CHtropNH **61** were tested together with chiral ancillary ligands in the enantioselective transfer hydrogenation.

Table 18: In situ catalysis: ligand, $[Ir_2(\mu_2\text{-}Cl)_2(COE)_4]$ stirred overnight, ancillary ligand, acetophenone 2 M in ethanol, 1 mol% K_2CO_3 added and warmed to 40 °C.

Ligand	Ancillary ligand	S / C	t [h]	Conversion [%]	ee [%]
pyCH_2tropNH **57**	B	1000	20	15	7S
pyCH_2tropNH **57**	C	100	20	53	10R
pyCH_2tropNH **57**	D	100	2	0	-
py(*i*Pr)CHtropNH **60**	A	1000	20	14	4R
py(*i*Pr)CHtropNH **60**	B	1000	20	16	12S
py(*i*Pr)CHtropNH **60**	C	1000	20	26	24R
py(*i*Pr)CHtropNH **60**	D	1000	20	3	9S
py(Ph)CHtropNH **61**	A	1000	20	16	2R
py(Ph)CHtropNH **61**	B	1000	20	18	11S
py(Ph)CHtropNH **61**	C	100	20	67	4R
py(Ph)CHtropNH **61**	D	100	20	30	1R

The active catalysts were prepared in situ. Based on the previous results only iridium complexes were used as catalysts. Low enantioselectivities along with a marked decrease in catalytic activity of the complexes were observed (Table 18).

7 Conclusion

It proved possible to prepare a series of complexes combining other donor functionalities with one olefin worked, but the catalytic performance of the new complexes was disappointing. No correlation between structure of the complexes and catalytic activity was found. The chiral ligands did not perform well which is not very surprising: they are too flexible, lack C2 symmetry and they can only block one quadrant.[111] However the new ligands may have other applications; for example in the preparation of complexes of coinage metals. The splitting of DME with **69** is a unique observation in the series of complexes observed, and may be employed in the future to catalyze related reactions, which could be highly interesting.

VII. $Trop_2NH$ Complexes of Coinage Metals

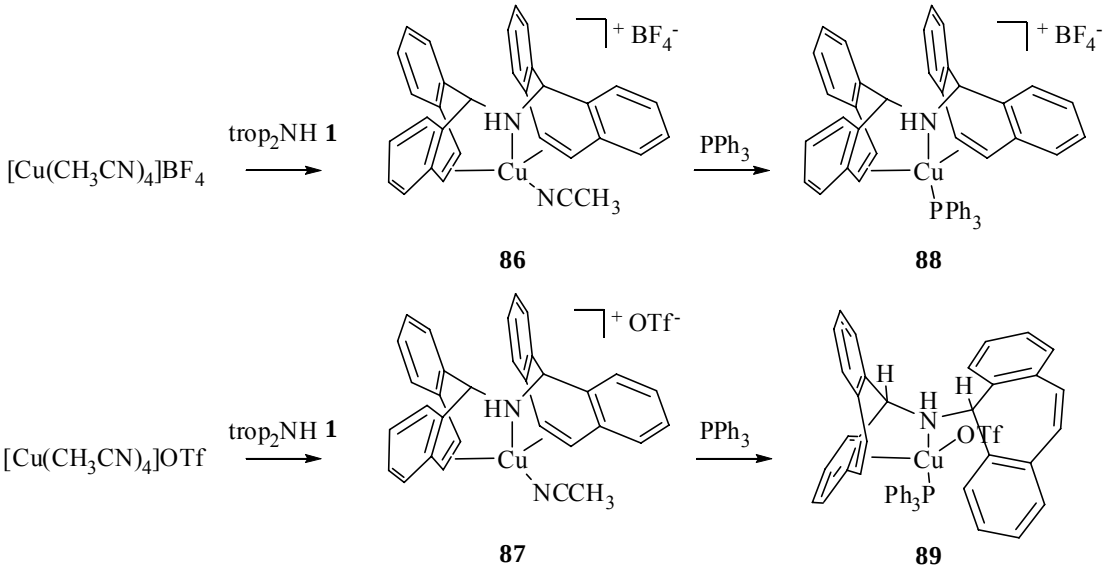
1 Summary

Complexes of coinage metals (Cu, Ag, Au) and alkenes are important in a number of applications.[112-115] Their use ranges from biochemistry,[116] chromatographic separations,[117] modern organic synthesis[118-120] to several industrial catalytic processes.[89] For example, copper–ethylene adducts are of interest as models for the ethylene (the smallest plant hormone) receptor site in plants.[121, 122] Silver-catalyzed oxidation of ethylene to ethylene oxide is a major industrial process.[122] Gold-based materials serve as excellent catalysts for the selective epoxidation of propene and other alkenes.[119, 123]

Therefore we were interested in the application of the $trop_2NH$ ligand in coordination of coinage metal complexes. Complexes of copper, silver and gold have been prepared and characterized by NMR and X-ray diffraction. It was found that the olefin donors in the $trop_2NH$ ligand coordinate to copper (I), weakly to silver (I), and not to gold (I).

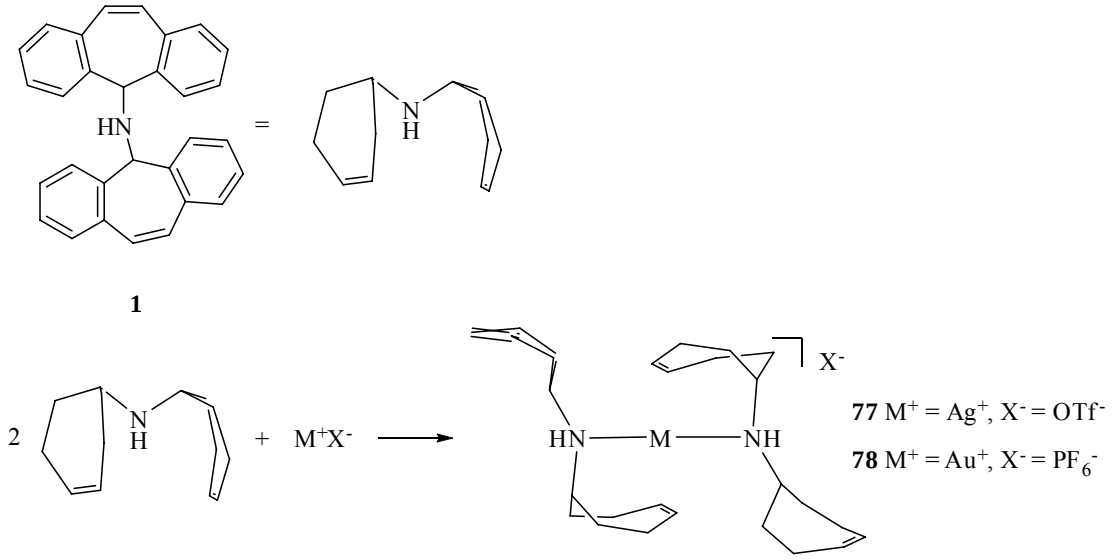
2 Synthesis of the complexes

The synthesis of the copper complexes was carried out by substitution of acetonitrile with $trop_2NH$ from the known $[Cu(CH_3CN)_4]BF_4$ and $[Cu(CH_3CN)_4]OTf$ precursor complexes[124]. The fourth acetonitrile could be replaced by adding a stoichiometric amount of triphenylphosphine.



Scheme 35: Synthesis of $trop_2NH$ copper complexes **73**, **74**, **75** and **76** with OTf^- and BF_4^- anions.

A silver complex was obtained by complexation of two equivalents of the trop$_2$NH ligand to silver triflate in an acetonitrile/ dichloromethane mixture. A gold complex was synthesized by reacting trop$_2$NH **1** with a solution of [Au(CH$_3$CN)$_4$]PF$_6$ [125, 126] in acetonitrile.



Scheme 36: Synthesis of Ag and Au complexes **77** and **78** of trop$_2$NH.

3 Results and discussion

With copper as metal one-to-one complexes of trop$_2$NH **1** were obtained. The olefins are coordinated but can be replaced by better ligands like phosphines. The new complexes are all air and moisture stable. They can be reduced to elemental copper by LiAlH$_4$ or by heating with 1 eq. KO*t*Bu in 1-4 butanediol. Crystal structures were obtained of complexes **74**, **75** and **76**.

The structure of **74** is best described as trigonal pyramid and not a tetrahedral structure (see Figure 21). The sum of angles between N2, ct1 and ct2 around Cu1 is 356.8° approaching 360° expected for a trigonal pyramidal structure compared to the 327° for a tetrahedral structure. The structure could also be interpreted as trigonal planar as is often found in copper (I) with only the olefins and the acetonitrile coordinated. However the distance between the copper cation and the nitrogen atom of the trop$_2$NH ligand is short enough (2.114(2) Å) to be considered a bond. Structures **75** and **76** are both tetrahedral. Compared to **74** the olefin is more weakly bound in the triphenylphosphine complexes (Cu1-ct1 2.130(5) and Cu1-ct2 2.166(5) in **75** vs. Cu1-ct1 2.109(2) and Cu1-ct2 2.075(2) in **74**). The triflate anion coordinates in **76** instead of the olefine.

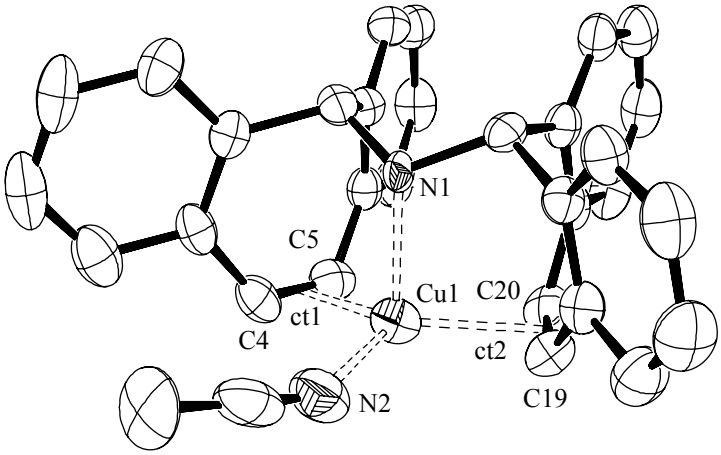


Figure 21: Ortep plot (at 50% ellipsoid probability) of the structure **74**: Solvent molecules and the anion are omitted. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Cu1-N1 2.114(2), Cu1-N2 1.981(2), Cu1-ct1 2.109(2), Cu1-ct2 2.075(2), Cu1-C4 2.136(2), Cu1-C5 2.234(22), C4=C5 1.364(3), Cu1-C19 2.203(22), Cu1-C20 2.230(21), C21=C22 1.375(3), ct1-Cu-ct2 128.92(9), ct1-Cu-N1 94.82(9), ct2-Cu-N1 93.63(9), ct2-Cu-N2 120.54(9), ct1-Cu-N2 107.37(9), N1-Cu-N2 99.84 (8).

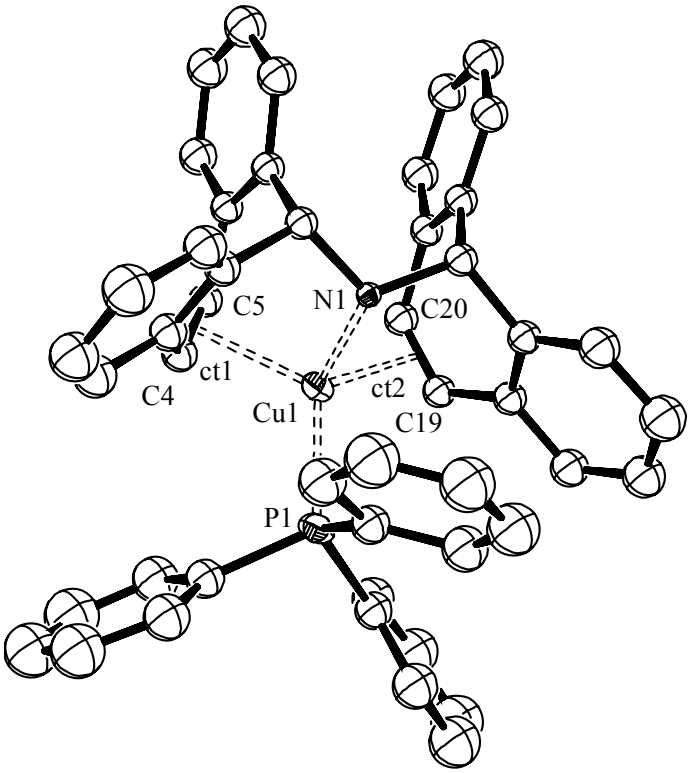


Figure 22: Ortep plot (at 50% ellipsoid probability) of the structure **75** Solvent molecules and the anion are omitted. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Cu1-N1 2.141(3), Cu1-P1 2.2943(12), Cu1-C4 2.212(5), Cu1-C5 2.260(4), Cu1-ct1 2.130(5), Cu1-C19 2.343(4), Cu1-C20 2.194(4), Cu1-ct2 2.166(5), C4=C5 1.365(6), C19=C20 1.359(7), ct1-Cu-ct2 124.30(16), ct1-Cu-N1 93.08(15), ct2-Cu-N1 90.49(14), ct2-Cu-P1 113.77(12), ct1-Cu-P1 116.94(13), N1-Cu-P1 109.77(10);

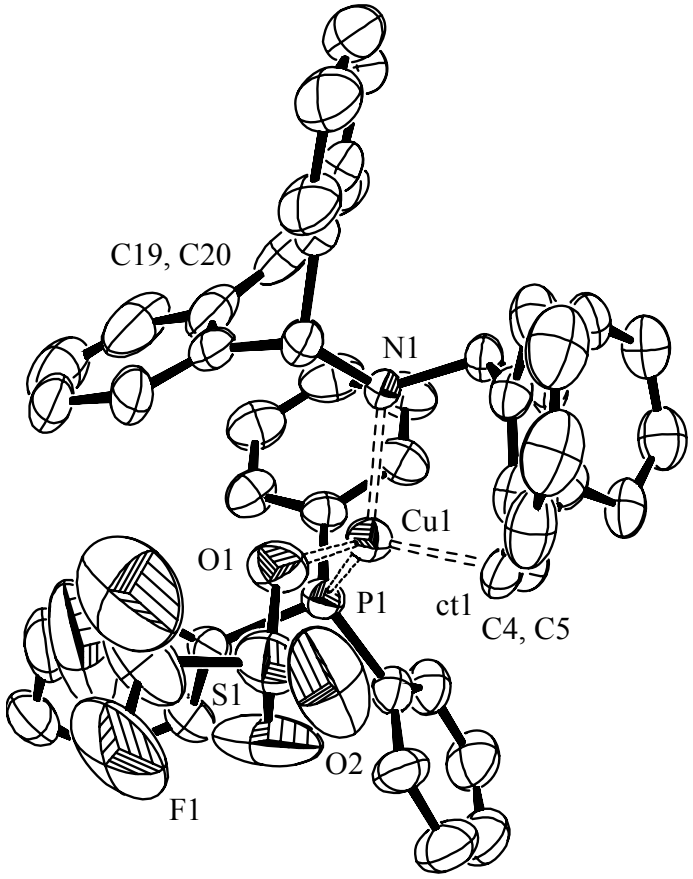


Figure 23: Ortep plot (at 50% ellipsoid probability) of the structure **76**: Solvent molecules are omitted. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5): Cu1-N1 2.118(3), Cu1-P1 2.2261(14), Cu1-C4 2.270(3), Cu1-C5 2.272(3), Cu1-ct1 2.164(3), Cu1-O1 2.101(2), C4=C5 1.375(5), C19=C20 1.374(6), ct1-Cu-O1 106.85(12), ct1-Cu-N1 94.69(11), O1-Cu-N1 98.95(10), O1-Cu-P1 115.85(8), ct1-Cu-P1 117.52(12), N1-Cu-P1 119.60(8).

The coordinated double bond has the same length as the non coordinating one (C4=C5 1.375(5) vs. C19=C20 1.374(6)). Therefore the olefine acts mostly as σ-donor and not as π-acceptor in these complexes as in the Dewar-Chatt L model of the metal olefin bond (see III.4).

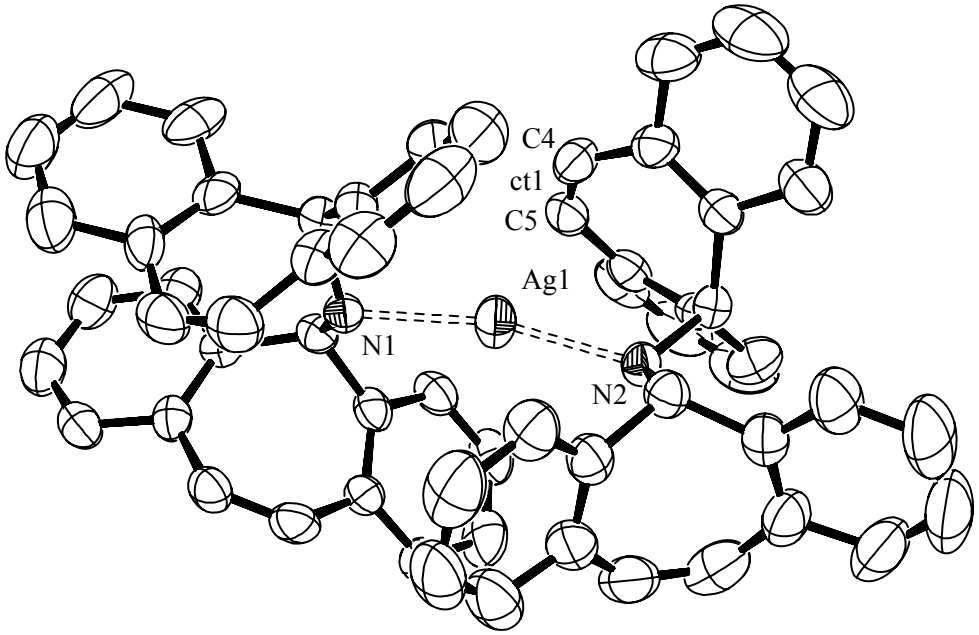


Figure 24: Ortep plot (at 50% ellipsoid probability) of the structure **77**: Solvent molecules and the anion are omitted. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5): Ag1-N1 2.233(3), Ag1-N2 2.227(3), Ag-ct1 2.866(5), C4=C5 1.344(6), N1-Ag1-N2: 166.53(10).

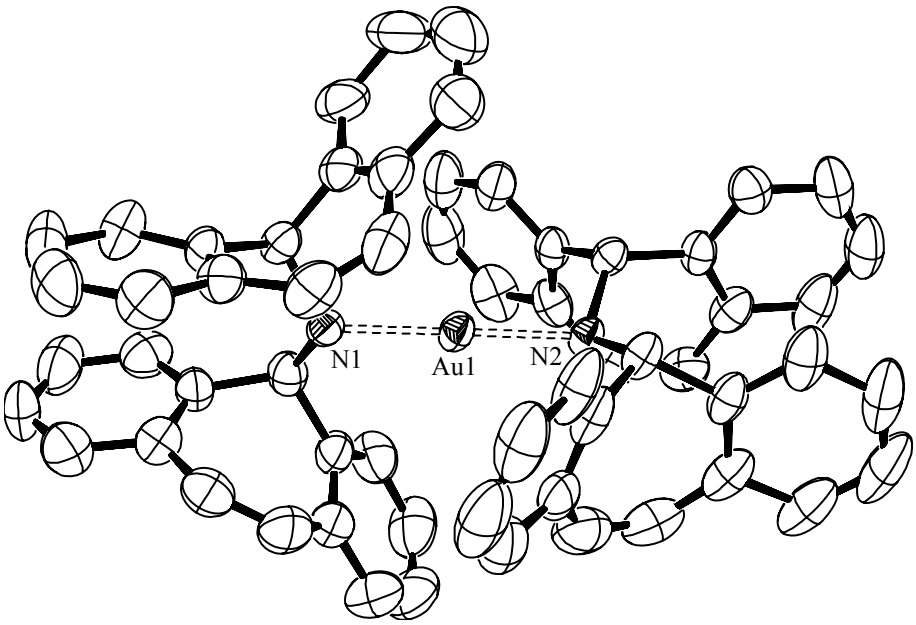


Figure 25: Ortep plot (at 50% ellipsoid probability) of the structure **78**: Solvent molecules and the anion are omitted. Selected bond lengths [Å] and angles [°]: Au1-N1 2.071(3), Au1-N2 2.083(3), N1-Au1-N2: 178.40(13).

Coordination of $trop_2NH$ to silver and gold led to bis amine type complexes in which only the N-atoms coordinate. With non coordinating anions it was impossible to obtain complexes with only one ligand. The use of coordinating anions as additional ligands, e.g. chloride, was beyond the scope of this work.

Interestingly the structure **77** (Figure 24) is not linear, but this could be due to accidental crystallization of this conformer. Interaction of the olefin with the metal seems unlikely or must be very weak since the distance is rather long: 2.866 Å. In the crystal structures of the two complexes the ligands adopt different conformations. In the structure of gold complex **78** both $trop_2NH$ are *exo-exo* whereas in the structure of silver complex **77** one ligand is *endo-exo* and the other *exo-exo*. This could be interpreted as an additional evidence for the supposed interaction of the olefin with the silver cation.

Table 19: Selected ^{1}H-NMR data for the complexes of $trop_2NH$ with coinage metals in CD_2Cl_2. [a] $trop_2NH$ was measured in $CDCl_3$.

Complex	C*H*$_{benzyl}$ δ [ppm]	C*H*$_{olefin}$ A δ [ppm]	C*H*$_{olefin}$ B δ [ppm]	N*H* δ [ppm]
$trop_2NH$ **1** (*exo-exo*) [a]	4.37	7.06		3.43
$[Cu(CH_3CN)(trop_2NH)]BF_4$ **73**	5.34	6.76	6.77	2.61
$[Cu(CH_3CN)(trop_2NH)]OTf$ **74**	5.27	6.80	6.81	2.79
$[Cu(trop_2NH)(PPh_3)]BF_4$ **75**	5.08	6.75	6.76	2.96
$[Cu(trop_2NH)(PPh_3)]OTf$ **76**	4.79	6.54	6.75	3.89
$[Ag(trop_2NH)_2]OTf$ **77**	4.36	6.38	6.68	3.61
	4.69	6.93	6.96	
$[Au(trop_2NH)_2]PF_6$ **78**	4.42	6.49	6.66	5.20
	4.67	6.69	6.73	

As expected considering the relativistic contraction of the s-electrons of gold (I) versus silver (I) the N-M bonds are shorter in the structure **78** than in structure **77**. This is also observed in the ^{1}H-NMR data: the amine proton resonance of the amine is shifted to higher frequency in the gold complex **78** relative to the silver complex **77** ($\Delta\delta$ = 1.6 ppm, see Table 19).

Table 20: Selected ^{13}C-NMR data for the complexes of $trop_2NH$ with coin metals in CD_2Cl_2 [a] $trop_2NH$ was measured in $CDCl_3$.

Complex	CH_{benzyl} δ [ppm]	CH_{olefin} A δ [ppm]	CH_{olefin} B δ [ppm]
$trop_2NH$ **1** (*exo-exo*) [a]	57.6	131.2	
$[Cu(CH_3CN)(trop_2NH)]BF_4$ **73**	70.1	110.6	112.1
$[Cu(CH_3CN)(trop_2NH)]OTf$ **74**	70.7	109.4	112.3
$[Cu(trop_2NH)(PPh_3)]BF_4$ **75**	69.5	117.9	119.31
$[Cu(trop_2NH)(PPh_3)]OTf$ **76**	67.6	123.6	125.1
$[Ag(trop_2NH)_2]OTf$ **77**	69.0	127.9	128.7
	69.9	129.4	130.8
$[Au(trop_2NH)_2]PF_6$ **78**	74.3	128.6	130.2
	74.9	130.7	131.2

The silver complex shows dynamic behavior and broad NMR signals at room temperature, but cooling to 200 K leads to well resolved spectra.

The olefinic carbon resonances of silver complex **77** are slightly broadened and weakly shifted to lower frequency compared to the uncoordinated ligand ($\Delta\delta \approx 2$ ppm). Those of the gold complex **78** in comparison show no coordination shift at all (Table 20). In solution the silver and gold complexes **77** and **78** adopt a similar structure, both ligands are bound in an *endo-exo* conformation unlike in the crystal structures. For the copper complexes a similar trend as observed in the crystal structures is visible. The olefinic carbon resonances in **73** and **74** are shifted to lower frequency compared to the free ligand ($\Delta\delta \approx 20$ ppm). This shift is less pronounced in the triphenylphosphine complexes **75** and **76** ($\Delta\delta \approx$ 5-10 ppm). Although in the crystal structure of **76** one olefin is not coordinated anymore, in solution both olefins are coordinated on average. Coordination of the triflate in solution can be inferred from the smaller extent of shift to lower frequency for **76** compared to **75** ($\Delta\delta \approx$ -5 ppm). Also observable in the ^{13}C NMR is a broadening of the resonances of the olefinic carbons in **76** compared to **75**.

The copper complexes **73** – **75** were tested in transfer hydrogenation but only low turnover numbers (TON) at 80 °C under standard conditions with cyclohexanone

were found. The triphenylphosphine complexes worked best and 50% conversion was found at substrate to catalyst ratio 1:100. Precipitation of red Cu_2O was observed. Because the results were not very promising no further experiments were made.

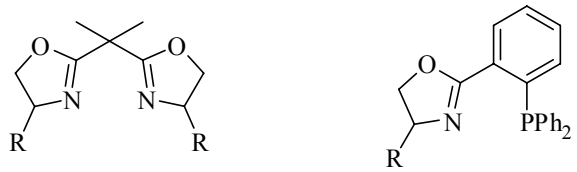
4 Conclusion

$Trop_2NH$ forms interesting complexes with coinage metals. Other than gold complex **78** which is sensitive to humidity all complexes were air stable. Trop complexes of copper could be of further interest, perhaps for the synthesis of copper coordination polymers with the already described ligands **57** and **58** (Section VI) or derivatives thereof.

VIII. A New Oxazoline Olefine Ligand

1 Introduction

Oxazolines represent an important and relatively young class of ligands and have found extensive use in asymmetric catalysis.[127-130] Especially important are C2 symmetric chiral bis-oxazolines as the BOX ligand and mixed phosphines-oxazoline ligands as for example the PHOX ligand developed by Pfalz and Helmchen.[131] Chelating oxazolines with other donors have been successfully prepared and used in asymmetric catalysis.[132]



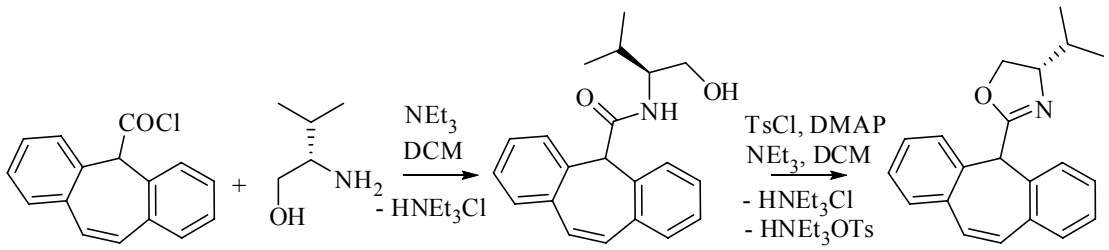
BOX PHOX

Scheme 37: The BOX and the PHOX ligand class

Hayashi et al. and Carreira et al. developed the efficient rhodium catalyzed asymmetric 1,4-addition of arylboronic acids with chiral dienes.[104, 133, 134] Phosphane alkene as steering ligand was described by us and Hayashi.[135-137] The use of a phosphane alkene with a trop backbone in the same reaction was reported by our group.[138] Inspired by this the new oxazoline ligand tropOxaz$^{i\text{-}Pr}$ **80** was developed. The complex [Rh(tropOxaz$^{i\text{-}Pr}$)$_2$]BArF **82** obtained with **80** has interesting electrochemical properties and may be of further use.

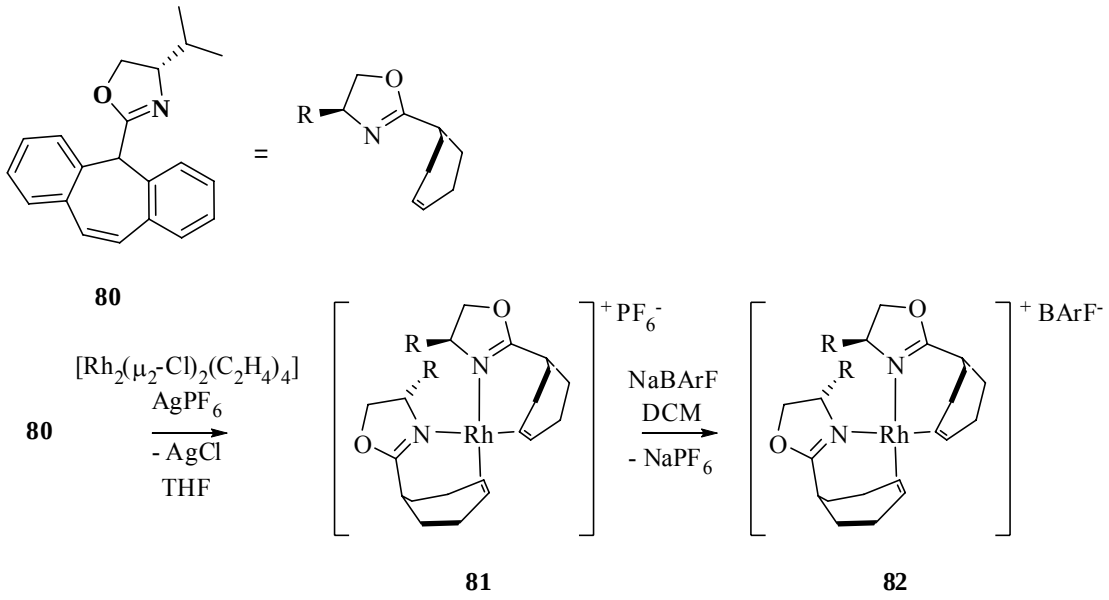
2 Synthesis of the ligand and complexes

Synthesis of 5*H*-dibenzo[*a,d*]cycloheptene-4-(S)-isopropyl-4,5-dihydro-oxazole (tropOxaz$^{i\text{-}Pr}$) **80** was accomplished by reaction of the known 5*H*-dibenzo[*a,d*]cycloheptene-5-carbonyl chloride[139, 140] with S-valinol and subsequent cyclization of the amide **79** by reaction with tosylchloride as described by Evans.[141] A Rhodium complex of tropOxaz$^{i\text{-}Pr}$ was obtained by complexation of the ligand to ethene complex [Rh$_2$(μ_2-Cl)$_2$(C_2H_4)$_4$] and addition of $AgPF_6$. The PF_6^- anion was exchanged with the $BArF^-$ anion to enhance the solubility of the complex. This made measuring cyclic voltammetry in THF feasible.



79 **80**

Scheme 38: Synthesis of the ligand tropOxaz$^{i\text{-Pr}}$ **80**.



81 **82**

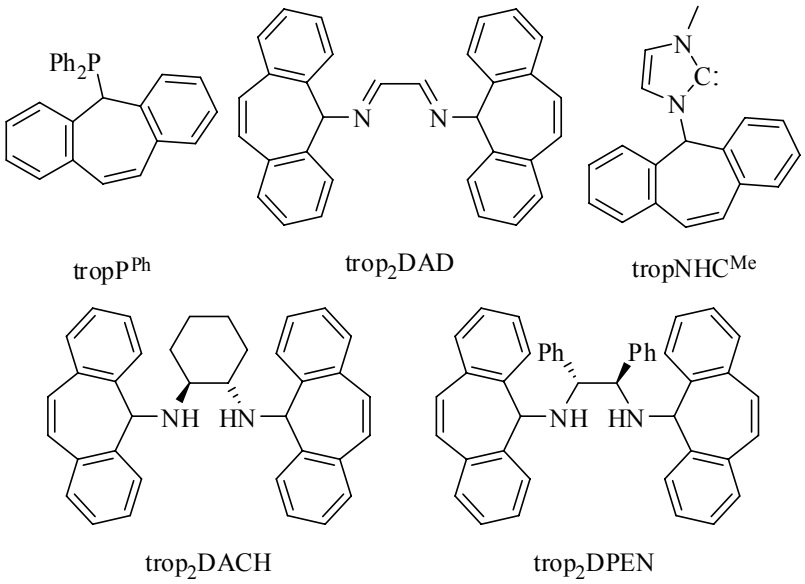
Scheme 39: Synthesis of [Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]PF$_6$ **81** and [Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]BArF **82**.

3 Catalysis, cyclic voltammetry measurements and preliminary ESR experiments

The ligand tropOxaz$^{i\text{-Pr}}$ **80** was tested in the rhodium catalyzed 1,4-addition of arylboronic acids, following the reported protocol of Hayashi[133] (Phenylboronic acid, 2 cyclohexen-1-one, 3 mol% [Rh$_2$(μ$_2$-Cl)$_2$(C$_2$H$_4$)$_4$], 3.3 mol% tropOxaz$^{i\text{-Pr}}$ **80** and 50 mol% KOH as 1.5 M aqueous solution. Dioxane was used as solvent, water/ dioxane 1:10). In this protocol the active catalytic species is formed in situ, however only low yields of the 1,4 addition product and no enantioselectivity was observed. This may be due to the fact that the ligand is not stable enough towards hydrolysis and the protocol used employs potassium hydroxide in water as base.

Due to the similarity of the synthesized complexes to other trop ligand complexes obtained in our group, most notably the [Rh(tropP^{Ph})$_2$]PF$_6$ **85** [142] cyclic voltammetry

measurements of [Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]BArF **82** were made. Similar to other complexes containing two ligands of the type trop-donor two reversible reduction waves were observed at 298 K.



Scheme 40: Selected trop-ligands related to tropOxaz$^{i\text{-Pr}}$.

The reduction potentials of **82** can be compared to selected related compounds.

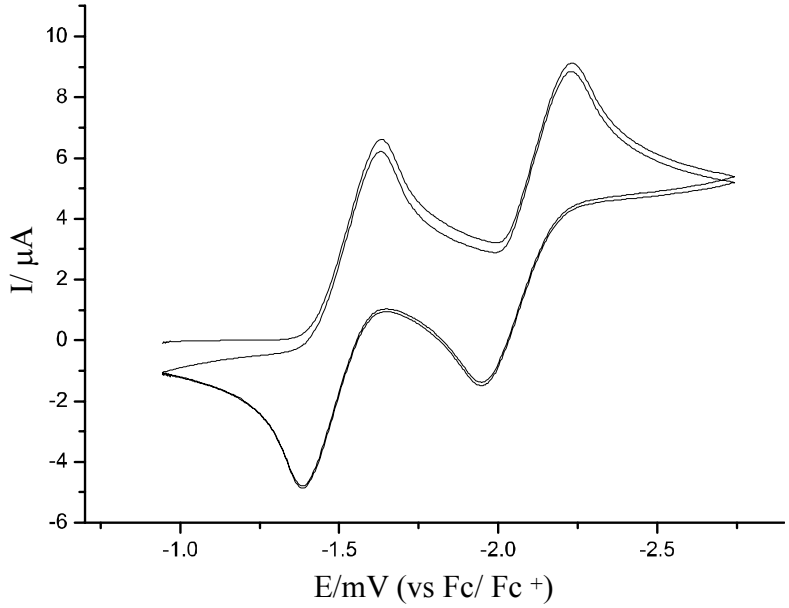


Figure 26: Cyclic voltammogramm of [Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]BArF **82**, 0.1 M [nBu$_4$N]$^+$PF6$^-$, THF, T 298 K, Pt working electrode, Ag/AgCl reference, versus Fc/Fc$^+$ scan rate 100 mVs^{-1}.

Table 21: Reduction potentials of selected complexes related to [Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]BArF **82**, 0.1 M [nBu$_4$N]$^+$PF6$^-$, THF, Pt working electrode, versus Fc/Fc$^+$, scan rate 100 mVs^{-1}.

Compound	$E^1_{red1/2}$ (V)	$E^2_{red1/2}$ (V)
[Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]BArF **82**	-1.509	-2.090
[Rh(tropNHC^{Me})$_2$]BArF **83** [143]	-1.541	-2.041
[Rh(trop$_2$DAD)]OTf **84** [144]	-0.915	-1.646
[Rh(tropP^{Ph})$_2$]PF$_6$ **85** [142]	-1.269	-1.660
[Rh(trop$_2$DACH)]OTf **86** [145]	-1.83	-2.27
[Rh(trop$_2$DPEN)]OTf **87** [145]	-1.78	-2.24

Obviously [Rh(trop$_2$dad)]OTf **84** is more easily reduced than [Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]BArF **82** or [Rh(tropP^{Ph})$_2$]PF$_6$ **85** because of the non-innocent nature of the trop$_2$DAD ligand. Phosphorus is a stronger σ-donor and a better π-acceptor when compared to amine or imine donor centers. It is therefore not surprising that the complex **82** has a higher reduction potential. The similarity in the reduction potential of **82** and [Rh(tropNHC^{Me})$_2$]BArF **83** indicates that N-heterocyclic carbenes and imines or amines have similar electronic properties.

[Rh(trop$_2$DACH)]OTf **86** and [Rh(trop$_2$DPEN)]OTf **87** are even harder to reduce; the first and second reduction potential of these complexes are more negative by about 0.3 V. This is best understood noting that amine-ligands have only σ-donor character whereas imines and carbenes are also weak π-acceptors.

A small sample of **82** was reduced in an ESR tube by decamethyl cobaltocene. The resulting paramagnetic species were quite persistent and an ESR signal could still be detected after standing for 2 days. The ESR spectra (see Figure 27) show that there are two paramagnetic species in a rapid equilibrium at room temperature. The two species could be the cis and trans isomers of a paramagnetic Rh^0 complex. From the spectra in frozen THF (at 164 K and 143 K) it is possible to conclude that the two paramagnetic species are quite anisotropic.

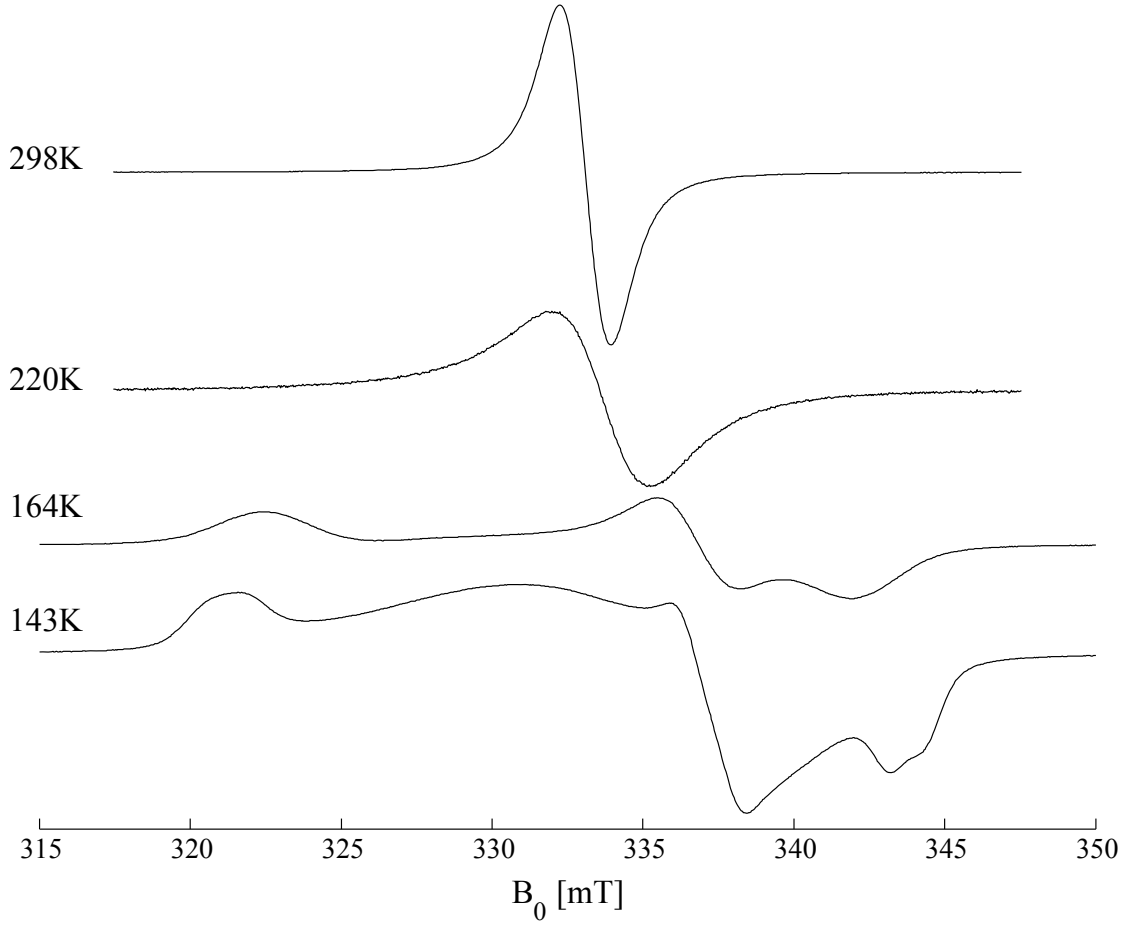


Figure 27: ESR spectra at various temperatures of **82** reduced by decamethyl-cobaltocene in THF. The top two spectra were recorded in liquid THF, the two lower ones in frozen THF.

4 Crystal structure and NMR-data

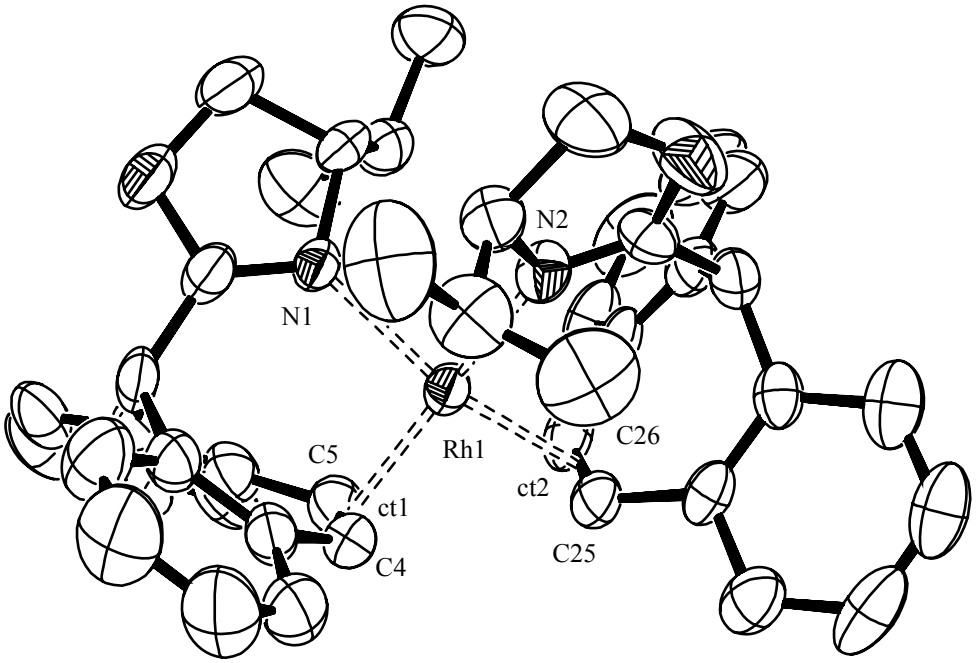


Figure 28: Ortep plot (at 50% ellipsoid probability) of the structure **81**: The anion and the second molecule of **81** found are omitted. They adopt similar conformations. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C25=C26, ct3 = centroid C46=C47, ct4 = centroid C88=C89, φ1 = angle between the plains ct1,Rh1,N1 and ct2,Rh1,N2, φ2 = angle between the plains ct3,Rh2,N3 and ct4,Rh2,N4) *Conformer 1*: Rh1-N1 2.116(3), Rh1-N2 2.110 (3), Rh1-C4 2.113(4), Rh1-C5 2.184(4), Rh1-ct1 2.046(4), Rh1-C25 2.206(4), Rh1-C26 2.111(4), Rh1-ct2 2.048(4), ct1-Rh1-ct2 92.81(15), N1-Rh1-N2 85.22(12), ct1-Rh1-N1 95.94(15), ct2-Rh1-N2 96.42(15), ct1-Rh1-N2 155.81(15), ct2-Rh1-N1 154.43(15), φ1 33.2; *Conformer 2*: Rh2-N3 2.110(3), Rh2-N4 2.093(3), Rh2-C46 2.1158(3), Rh2-C47 2.230(3), Rh2-ct3 2.059(3), Rh2-C88 2.118(3), Rh2-C89 2.243(3), Rh2-ct4 2.068(3), ct3-Rh2-ct4 92.13(13), N3-Rh2-N4 83.00 (11), ct3-Rh2-N3 95.11(12), ct4-Rh2-N4 95.42(12), ct3-Rh2-N4 161.66(15), ct4-Rh2-N3 161.47(15), φ2 = 24.2.

A crystal structure of [Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]PF$_6$ **81** containing two slightly different conformers was obtained. The complex is a tetracoordinate tetrahedrally distorted 16-electron rhodium complex. Such a distortion is best quantified by the dihedral angle φ between the intersection of the planes spanned by the rhodium atom, the nitrogen atom and the centroid of the double bond of each bidentate ligand (see Figure 28). In the complex **81** two dihedral angles were measured: φ1 = 33.2° and φ2 = 24.2°.

Compared to complex [Rh(tropNHC^{Me})$_2$]BArF **83** which has a dihedral angle φ = 22.7° the distortion is similar and is mostly determined by the geometry of the ligand. The complexes [Rh(trop$_2$DACH)]OTf **86** and [Rh(trop$_2$DPEN)]OTf **87** described earlier[145] have similar dihedral angles: φ = 22.2° and φ = 20.1° respectively.

[Rh(trop$_2$dad)]OTf **84** has a square planar geometry whereas in [Rh(tropP^{Ph})$_2$]PF_6 **85** the *cis*- and *trans*- coordinated forms are in an equilibrium via a five membered trigonal bipyramidal transition state. In contrast to this [Rh(trop$Oxaz^{i\text{-}Pr}$)$_2$]BArF **82** and [Rh(tropNHC^{Me})$_2$]BArF **83** were only observed in the *cis*-form.

Table 22: Selected ^{1}H-NMR data of compounds related to [Rh(trop$Oxaz^{i\text{-}Pr}$)$_2$]BArF **82**.

Compound	Solvent	C*H*^{benzyl} δ[ppm]	C*H*^{olefin} A δ[ppm]	C*H*^{olefin} B δ[ppm]
trop$Oxaz^{i\text{-}Pr}$ **80**	$CDCl_3$	4.98	6.98	-
[Rh(trop$Oxaz^{i\text{-}Pr}$)$_2$]BArF **82**	$CDCl_3$	4.89	3.03	5.50
tropNHC^{Me}·HCl [143]	CD_2Cl_2	6.58	6.95	-
[Rh(tropNHC^{Me})$_2$]BArF **83** [143]	CD_2Cl_2	6.29	4.16	6.25
[Rh(trop$_2$dad)]OTf **84** [144]	CD_2Cl_2	5.94	5.47	-
tropP^{Ph} [146]	C_6D_6	4.78	6.76	-
[Rh(tropP^{Ph})$_2$]PF_6 **85** [142]	$CDCl_3$	4.68	5.19	-
[Rh(trop$_2$DACH)]OTf **86** [145]	CD_3CN	5.10	4.16	5.38
[Rh(trop$_2$DPEN)]OTf **87** [145]	CD_3CN	4.39	4.36	5.54

Table 23: Selected ^{13}C-NMR data of compounds related to [Rh(trop$Oxaz^{i\text{-}Pr}$)$_2$]BArF **82**.

Compound	Solvent	*C*H$_{benzyl}$ δ[ppm]	*C*H$_{olefin}$ A δ[ppm]	*C*H$_{olefin}$ B δ[ppm]
trop$Oxaz^{i\text{-}Pr}$ **80**	$CDCl_3$	51.9	130.7	131.4
[Rh(trop$Oxaz^{i\text{-}Pr}$)$_2$]BArF **82**	$CDCl_3$	53.9	65.6	83.0
tropNHC^{Me}·HCl [143]	[D_6]DMSO	67.5	123.9	122.2
[Rh(tropNHC^{Me})$_2$]BArF **83** [143]	CD_2Cl_2	72.6	76.4	91.7
[Rh(trop$_2$dad)]OTf **84** [144]	CD_2Cl_2	75.9	85.3	-
tropP^{Ph} [146]	C_6D_6	57.4	132.7	-
[Rh(tropP^{Ph})$_2$]PF_6 **85** [142]	$CDCl_3$	n.a.	88.2	-
[Rh(trop$_2$DACH)]OTf **86** [145]	CD_3CN	61.7	70.1	83.4
[Rh(trop$_2$DPEN)]OTf **87** [145]	CD_3CN	64.5	71.5	84.5

As expected the PF_6^- salt **81** and the $BArF^-$ salt **82** of the [Rh(trop$Oxaz^{i\text{-}Pr}$)$_2$]$^+$ cation have very similar NMR shifts and the spectra are superimposable despite the two

different solvents used: DCM and $CDCl_3$. The complexes [Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]BArF **82** and [Rh(tropNHC^{Me})$_2$]BArF **83** have two distinct ^{1}H and ^{13}C olefin resonances due to their geometry. Complex **82** shows a larger coordination shift of the olefinic proton and carbon resonances to lower frequency than the carbene complex **83**, which could be due to a larger trans influence of the nitrogen donor in the oxazoline ligand **80**. This is supported by the coordination shifts of complexes **86** and **87** which are rather similar to the ones observed for **83**.

5 Conclusion and Outlook

The ligand tropOxaz$^{i\text{-Pr}}$ **80** is able to stabilize rhodium in low oxidation states, although probably the ligand is reduced and not the metal itself. It may be possible to isolate the d^9 and d^{10} Rhodium complexes. Eventually such species could be applied as chiral radicals or even as chiral radical catalysts.

A substituent could be added to the double bond of the ligand tropOxaz$^{i\text{-Pr}}$ **80** or a related molecule by – for example – a Heck reaction. It is conceivable that such a reaction should proceed with some diastereoselectivity. Application of such a ligand in carefully chosen catalytic reactions could be interesting.

IX. Experimental Section

1 General Comments

General techniques

All manipulations of air or moisture sensitive compounds were performed on a standard vacuum line in flame-dried flasks under an atmosphere of argon. The argon was provided by *PANGAS* and further purified with an *MBraun 100 HP* gas purification system. Solvents were distilled under argon from sodium/benzophenone (THF, diethyl ether), sodium/benzophenone/tetraglyme (*n*-hexane, DME) or calcium hydride (methylene chloride). Acetone and DMSO were sequentially dried over 4Å molecular sieves and acetone was additionally distilled afterwards. Air sensitive compounds were stored and weighted in a glovebox (*M Braun: lab master 130* or *150B-G*). Reactions in small quantities were performed within a glovebox. Substances are classified as: air sensitive: decompose rapidly on air, in seconds to minutes; slightly air sensitive: decompose on air in solution in hours and as solid in hours to days, air stable: stable on air in solution and as solid (in the period observed, usually days).

Chemicals

Basic chemicals were ordered at *ABCR*, *Acros*, *Aldrich*, *Fluka*, *Lancaster*, or *STREM*. Chemicals used for catalysis were purified as described in the corresponding section. The following organic compounds and metal precursors were prepared by literature methods: 5*H*-dibenzo[*a*,*d*]cycloheptene-5-carbonyl chloride[139, 140], tropCl[147], tropNH$_2$[148, 149], [Rh$_2$(μ_2-Cl)$_2$(C$_2$H$_4$)$_4$][150, 151], [Rh$_2$(μ_2-Cl)$_2$(COD)$_2$][152], [Rh$_2$(μ_2-Cl)$_2$(CO)$_4$][153], [Ir$_2$(μ_2-Cl)$_2$(COE)$_4$][154], P(OCH$_2$)$_3$CCH$_3$[155], 1,3,4,5 tetramethylimidazol-2-ylidene (TMIY)[156], [Cu(CH$_3$CN)$_4$]BF$_4$[124], [Cu(CH$_3$CN)$_4$]OTf[124], Au(CH$_3$CN)$_4$PF$_6$[125, 126], (2*S*)-2-amino-3-cyclohexa-1,4-dien-1-ylpropanoate [99], 3-4-Cyclohexenylamine hydrochloride[102, 103], (*S*)-2-Amino-3-methyl-1-butanol[157], (1*S*)-2-methyl-1-pyridin-2-ylpropylamine[110], (*S*)-1-phenyl-1-pyridin-2-ylmethanamine[110], 2-Diphenylphosphine benzaldehyde[109], [Rh(trop2NH)(CO)]OTf [40], [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] [39-41], 3,4-dimethyl-1-phenylphosphole (DMPP)[158], 1,2,5-Triphenylphosphole (TPP)[159].

NMR spectra

NMR spectra were recorded on *Bruker Avance 700, 500, 400, 300*, and *250* spectrometers. The chemical shifts (δ) are measured according to IUPAC[160, 161] and expressed in ppm relative to TMS, CD_3NO_2, $CFCl_3$, H_3PO_4, and Rh(acac)$_3$ for ^{1}H, ^{2}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P and ^{103}Rh respectively. Coupling constants *J* are given in Hertz [Hz] as absolute values, unless specifically stated. The multiplicity of the signals is indicated as *s*, *d*, *t*, *q*, or *m* for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. Quaternary carbon atoms are indicated as C^{quart}, aromatic units as CH^{ar} and CH^{ar} when not noted otherwise. The olefinic protons and ^{13}C atoms of the C=C$_{trop}$ unit in the central seven-membered ring are indicated as CH^{olefin} and CH^{olefin}. The benzylic protons and ^{13}C atoms in the central seven-membered ring are indicated as CH^{benzyl} and CH^{benzyl}.

IR spectra

IR spectra were recorded on a *Perkin-Elmer-Spectrum 2000* FT-IR-Raman spectrometer with KBr beam splitter (range 500-4000 cm^{-1}). For solid compounds the ATR technique was applied. The absorption bands are described as follows: strong (*s*), very strong (*vs*), middle (*m*), weak (*w*), or broad (*br*).

UV/Vis-spectra

UV/Vis-spectra were measured with a *Perkin Elmer Lambda 19* spectrometer in 5 mm quartz cuvettes (200-1000 nm).

Optical rotation

Optical rotation was measured at 589 nm (Na/Hal) and room temperature (22 °C) on a Perkin Elmer 341 polarimeter using a 10 cm cell and a concentration of 1 mg/ 1 mL (*c*=1.0) in the given solvent where not stated otherwise.

Gas chromatography

Gas chromatography was performed on a *Hewlett Packard HP 6890 Series* GC system equipped with a EPC split/splitless injector. Most measurements were done with a inlet pressure of 4.88 psi, a 50:1 split resulting in a slit flow of 108 mL/min and a *HP-5* Crosslinked 5% PH ME Siloxane column (30 m x 0.32 mm, film thickness 0.25 μm), flow rate 27.2 mL/min at 4.88 psi. and temperature program: initial temperature 80 °C (hold 1 min), increase to 180 °C at a rate of 4 °C/min and hold for 40 min. Further details are provided in IX.0 and 2.

Cyclic voltammetry

Cyclic voltammetry investigations were performed using a *Princeton Applied Research* potentiostat/galvanostat model *263A* or model *283*. The measurements were performed on an apparatus designed by Heinze et al.[162, 163] Working electrode: planar platinum electrode (approximate surface area 0.785 mm^2); reference electrode: silver; counter electrode: platinum wire. At the end of each measurement, ferrocene was added as internal standard for calibration (+0.352 V vs. Ag/AgCl).

Elemental Analysis

Elemental analyses were performed by the microanalytical laboratory of the ETH Zürich.

Mass Spectrometry (MS) and GC-MS

Mass Spectra were recorded on a *Finnigan MAT SSQ 7000* mass spectrometer in EI mode (70 eV) equipped with a solid probe inlet. Alternatively the attached GCQ Gas

chromatograph with a *Macherey Nagel Optima 5 Accent* (30 m x 0.32 mm x 0.25 µm) column and helium as carrier gas was used as inlet for the MS device.

High resolution MALDI MS (HiRes MS)

High resolution MALDI MS was measured by the mass spectroscopy service of ETH Zürich.

X-Ray diffraction

X-Ray diffraction was measured on an *Oxford XCalibur* or *Bruker SMART Apex* diffractometer with CCD area detector; $Mo_{K\alpha}$ radiation (0.71073 Å) at T = 293 K. where not noted otherwise. The refinement against full matrix (versus F^2) was done with SHELXTL (ver. 6.12) and SHELXL-97. Empirical absorption correction was done with SADABS (ver. 2.03). All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model.

Computational Methods

A simplified model **4'** was used to represent the catalysts **4**. All calculations were carried out within the framework of DFT. For optimizations, we used the B3PW91 functional. This functional employs a combination of exchange terms: exact HF, the Becke 1988 nonlocal gradient correction[164, 165], and the original Slater local exchange functional.[166] In addition, it uses the Perdew-Wang 1991 local correlation functional.[167]

We have evaluated the impact of several combinations of basis set on the geometry of **4'**. The combination of basis set **BS1** showed a good agreement between geometry of **4'** and X-Ray data of **4*** (**Table 2**, page 16). **BS1** consisted of the 6-311G(d) basis set for all atoms directly connected to the metal or directly involved in the chemical reaction. The 6-31G(d) basis was employed for all other atoms, except the Rh atom. The Lanl2dz basis functions, which included a double-zeta valence basis set (8s5p5d)/[3s3p2d] with the Hay and Wadt effective core potential (ECP)[168] replacing core electrons up to 3p was used for the Rh atom. Full geometry optimizations were carried out followed by vibrational frequency calculations. All transition state structures reported in this paper are characterized by only one imaginary frequency. The transition state structures were slightly distorted along the normal mode of the imaginary frequency and geometry minimizations using the transition structure force constants as the initial Hessian were performed in order to obtain the two minimum structures attached to it. All reasonable possible conformations were inspected for each species and the results for the most stable conformations are given. The energies of all structures were improved by performing single point calculations with an extended basis set, B3PW91/**BS2**. The basis set **BS2** consisted of 6-311+G(d,p) for all atoms except Rh which is calculated with the Lanl2dz basis set. All energies were corrected for zero point energies.

All calculations were carried out with the Gaussian 03 program.[96] Molecular drawings and cartesian coordinates of structures are given in the supporting information of the published paper[169].

Transferhydrogenation (Section II, V and VI)

Purification of substrates: Ethanol used for transfer hydrogenation was dried by in situ generation of sodium ethanolate from sodium (7 g/l), refluxing of this solution with diethyl phthalate (30 g/l) for 4 h and subsequent distillation. All ketones were freshly distilled or in the case of 3-Nitroacetophenone and 4-Nitroacetophenone recrystallized from ethanol. Dimethyl itaconate was recrystallized from methanol. Acrylic acid methyl ester was distilled from 4Å molecular sieves. Propionic acid methyl ester was distilled from calcium hydride.

General method – ethanol: A 2 M solution of the substrate in dry ethanol was prepared in a Schlenk tube under argon. The catalyst was added either as solid or as solution in THF or ethanol. For low catalyst loadings (> 0.01 mol%) the solution was degassed by three pump-freeze-thaw cycles. Then 1 mol% of the base (K_2CO_3 or KO*t*Bu) was added under a stream of argon. The reaction was followed by NMR spectroscopy or CG by taking samples periodically.

General method – isopropanol: A 0.5 M solution of the substrate in dry isopropanol was prepared in a Schlenk tube under argon. The catalyst was added either as solid or as solution in THF or isopropanol. For low catalyst loadings (> 0.1 mol%) the solution was degassed by three pump-freeze-thaw cycles. Then 1 mol% of the base (K_2CO_3 or KO*t*Bu) was added under a stream of argon. The reaction was followed by NMR spectroscopy or CG by taking samples periodically.

Method A: A solution of Rh(trop$_2$NH)(PPh$_3$)OTf **3** or Rh(trop$_2$NH)(PPh$_3$)BARF **6** in ethanol was added to a Schlenk-tube containing a 2 M solution of the substrate in ethanol. The solution was degassed by three pump-freeze-thaw cycles. Then 1 mol% of KO*t*Bu was added as solid under a stream of argon. The reaction was followed by NMR spectroscopy. For cyclohexanone and acetophenone the reaction was also followed by GC. TOF values were determined after 50% conversion. Depending on the scale of the reaction, gentle warming of the reaction solution was observed indicating an exothermic reaction.

As example, the protocol with acetophenone as substrate is given (S/C= 100000): To a solution of acetophenone (7.2 mL, 62 mmol) in ethanol (30 mL, 525 mmol) [Rh(trop$_2$NH)(PPh$_3$)]BARF **6** (1 mg, 0.62 μmol) was added as solution in ethanol. The solution was degassed by three freeze-pump-thaw cycles and KO*t*Bu (70 mg, 62 mmol) was added. The reaction was followed by NMR and GC.

Distilled as well as commercially available absolute ethanol may be employed successfully for this reaction.

Method B: A solution of [Rh(trop$_2$NH)(P(OPh)$_3$)]OTf **7** in ethanol (1 mg/mL, 1.04 mM) was added to a Schlenk-tube containing a 2 M solution of the substrate in ethanol. For the solid substrates 3-nitroacetophenone and 4-nitroacetophenone, a 1 M

solution in THF/ethanol 1:1 was prepared. The solution was degassed by three freeze-pump-thaw cycles. Then 1 mol% of solid K_2CO_3 was added under argon. The suspension was warmed to 40 °C and the reaction followed by NMR spectroscopy. TOF values were determined after 50% conversion.

As example, the protocol with 3-nitroacetophenone as substrate is given (S/C= 10000): 3-Nitroacetophenone (1720 mg, 10.42 mmol) was dissolved in a mixture of ethanol (4.2 mL, 71.7 mmol) and THF (5.2 mL, 64.2 mmol). [Rh(trop$_2$NH)(P(OPh)$_3$)]OTf **7** (1 mg, 1.04 μmol) was added dissolved in 1 mL of ethanol and the solution degassed. K_2CO_3 (15 mg, 0.1 mmol) was added and the suspension warmed to 40 °C.

Method C: A 2 M solution of the substrate in ethanol was prepared. To this solution [Rh(trop$_2$N)(PPh$_3$)] **4** dissolved in THF (1 mg/mL, 1.1 mM) was added. The reaction was followed by GC and NMR. TOF values were determined after 50% conversion.

As example, the protocol with dimethyl itaconate as substrate is given (S/C= 10000): Dimethyl itaconate (1037 mg, 6.6 mmol) was suspended in ethanol (3.25 mL, 55.9 mmol). [Rh(trop$_2$N)(PPh$_3$)] **4** (0.5 mg, 0.6 μmol) was added as THF solution. The reaction was quantitative after 10 min.

Method D: A solution of [Rh(trop$_2$NH)(PPh$_3$)]OTf **3** in isopropanol (1 mg/mL, 1.10 mM) was added to a Schlenk-tube containing a 0.5 M solution of the substrate in isopropanol. The solution was degassed by three freeze-pump-thaw cycles. The solution was degassed by three pump-freeze-thaw cycles. Then 1 mol% of KO*t*Bu was added as solid under a stream of argon. The reaction was followed by NMR spectroscopy and GC.

Experiments in [D$_5$]ethanol: Method C was used at S/C= 1000 in [d$_5$]ethanol for acetophenone and dimethyl itaconate. All solvents where removed under reduced pressure after 30 min.

Influence of triphenylphosphine: Method C was used to transfer hydrogenate acetophenone, dimethyl itaconate and acrylic acid methyl ester at S/C= 10'000 with and without the addition of triphenylphosphine (100 eq.) with respect to [Rh(trop$_2$N)(PPh$_3$)] **4**. Reactions where followed by GC. The addition of triphenylphosphine did not affect the rate of the reaction.

Chromatographic conditions for the products of the transfer hydrogenation:

A) Separation of cyclohexanol from cyclohexanone: Column: *Machery-Nagel Permabond CW20M-DF-0.25* (25 m x 0.32 mm x 0.21 μm); temperature: 80 °C isotherm; H_2 pressure: 0.34 bar; retention times: cyclohexanone: 1.62 min; cyclohexanol: 1.98 min.

B) Separation of 1-phenyl-ethanol from acetophenone: Column: *Machery-Nagel Permabond CW20M-DF-0.25* (25 m x 0.32 mm x 0.21 μm); temperature: 120 °C isotherm; H_2 pressure: 0.34 bar; retention times: acetophenone: 1.95 min; 1-phenylethanol: 2.63 min.

C) Separation of dimethyl itaconate from methylsuccinic acid dimethyl ester: Column: *Hewlett-Packard HP-5 phenyl methyl siloxane* (30 m x 0.32 mm x 0.25 µm); temperature: 1min 80 °C then 4 °C/min to 180 °C; H_2 pressure: 0.50 bar; retention times: Methylsuccinic acid dimethyl ester: 5.30 min; Dimethyl itaconate 6.00 min.

D) Separation of (R)- and (S)-1-phenyl-ethanol from acetophenone: Column: *Machery-Nagel Lipodex E* (25 m x 0.32 mm x 0.25 µm); temperature: 1min 70 °C then 1 °C/min to 110 °C; H_2 pressure: 0.50 bar; retention times: Acetophenone: 26.0 min; (S)-1-Phenylethanol 31.0 min; (S)-1-Phenylethanol 31.7 min.

Identification of the products of transfer hydrogenation:

Isopropanol (from acetone): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.14 (d, $^3J_{HH}$ = 6.5 Hz, 6H, C*H*$_3$), 4.03 (7, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*OH);

Cyclohexanol (from cyclohexanone): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.1- 1.5 (m, 5H, C*H*), 1.54 (m, 1H, C*H*), 1.6-1.7 (m, 3H, C*H*), 1.90 (m, 1H, C*H*), 3.61 (7, $^3J_{HH}$ = 4.8 Hz, 1H, C*H*OH);

1-Phenylethanol (from acetophenone): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.52 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$), 4.92 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*OH), 7.25-7.40 (m, 5H, C*H*^{ar});

1-(Pyridin-2-yl)ethanol (from 2-acetylpyridine): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.48 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$), 4.88 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*OH), 7.18 (td, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, C*H*^{ar}), 7.33 (d, $^3J_{HH}$ = 7.9 Hz, 1H, C*H*^{ar}), 7.68 (t, $^3J_{HH}$ = 7.9 Hz, 1H, C*H*^{ar}), 8.49 (d, $^3J_{HH}$ = 4.8 Hz, 1H, C*H*^{ar});

1-(4-Nitrophenyl)ethanol (from 4-nitroacetophenone): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.55 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$), 5.00 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*OH), 7.55 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C*H*^{ar}), 8.21 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C*H*^{ar});

1-(3-Nitrophenyl)ethanol (from 3-nitroacetophenone): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.56 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$), 5.03 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*OH), 7.54 (t, $^3J_{HH}$ = 7.9 Hz, 1H, C*H*^{ar}), 7.74 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C*H*^{ar}), 8.15 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.3 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, C*H*^{ar}) 8.28 (m, 1H, C*H*^{ar});

1-(2-Nitrophenyl)ethanol (from 2-nitroacetophenone): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.58 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$), 5.43 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*OH), 7.43 (t, $^3J_{HH}$ = 7.9 Hz, C*H*^{ar}), 7.66 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C*H*^{ar}), 7.87 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C*H*^{ar}), 7.90 (d, $^3J_{HH}$ = 7.9 Hz, 1H, C*H*^{ar});

1-(2-Bromophenyl)ethanol (from 2-bromoacetophenone): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.51 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$), 5.26 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*OH), 7.15 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, C*H*^{ar}), 7.32 (t, $^3J_{HH}$ = 7.9 Hz, 1H, C*H*^{ar}), 7.50 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C*H*^{ar}), 7.61 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C*H*^{ar});

Methylsuccinic acid dimethyl ester (from dimethyl itaconate): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.25 (d, $^3J_{HH}$ = 7.1 Hz, 3H, C*H*$_3$), 2.43 (dd, $^2J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 6.0

Hz, 1H, CH_2), 2.77 (dd, $^2J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, CH_2), 2.95 (6, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*), 3.70 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3);

Propanoic acid methyl ester (from Acrylic acid methyl ester): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3), 2.36 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 3.70 (s, 3H, OCH_3);

[D_1]Phenylethanol: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.52 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 7.25-7.40 (m, 5H, CH^{ar}); ^{2}H-NMR (46.1 MHz, $CHCl_3$) δ = 4.88 (s, 1D);

[D_1]Methylsuccinic acid dimethyl ester:^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.25 (d, $^3J_{HH}$ = 7.1 Hz, 2H, CH_3), 2.43 (dd, $^2J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, CH_2), 2.77 (dd, $^2J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, CH_2), 2.95 (6, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*), 3.70 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3); ^{2}H-NMR (46.1 MHz, $CHCl_3$) δ = 1.15 (s, 1D);

2 Dehydrogenation (Section IV)

Purification of substrates: Methanol was dried over magnesium and distilled. Cyclohexanone was fractionally distilled from mol sieves taking the middle fraction. Methyl methacrylate was carefully distilled from mol sieves. Alcohols used for the synthesis of methyl esters or amides were distilled from their respective sodium alcoholates which were generated in situ by addition of sodium to the alcohol or mol sieves. The amines used for amide synthesis were distilled from calcium hydride. The alcohols for the synthesis of acids were used as received.

A.1 Acids

Alcohol (5.5 mmol, 1 eq.), cyclohexanone (2.8 mL, 27.5 mmol, 5 eq.), water (6.5 mL, 362 mmol, 66 eq.) and sodium hydroxide (263 mg, 6.6 mmol, 1.2 eq.) were combined in a Schlenk tube. Optionally (0.68 mL, 3 mmol, 0.54 eq.) dodecane as internal standard was added. The biphasic solution was degassed by purging with argon for 15 min. Rh(trop$_2$NH)(PPh$_3$)(OTf) **3** (5 mg, 5.5 µmol, 0.1 mol%) was added under a stream of argon and the mixture stirred at room temperature (RT) for 4 h unless otherwise noted. The reaction was monitored by GC if possible (alcohol vs dodecane as internal standard).

Isolation and recycling of cyclohexanone/cyclohexanol:

All volatile materials (aqueous and organic) were removed under reduced pressure. A clean mixture of cyclohexanone, cyclohexanol and water was obtained. This mixture was reoxidized by a modification of the method of Manikandan [94]: 3%$_{wt}$ hydrogen-peroxide (22.5 mL, 22 mmol, 1.5 eq.), $Na_9[SbW_9O_{33}]$ (37 mg, 0.015 mmol, 0.1 mol%) and methyltricapryl ammonium chloride (63 mg, 0.15 mmol, 1 mol%) were added. This mixture was refluxed for 3 h. After cooling to RT the product was extracted three times with small portions (10 mL) of diethyl ether. The organic phase was dried over sodium sulfate and the diethyl ether removed under reduced pressure. Distillation of the crude product afforded 76% (2.04 g, 20.9 mmol) of pure cyclohexanone (GC, NMR).

Isolation of the acids (unless otherwise noted)

The non-volatile residue containing the sodium salt of the carboxylic acid was dissolved in water (10 mL) and the aqueous phase extracted once with a small portion (2-3 mL) of diethyl ether. The aqueous solution was acidified by addition of 1 M hydrochloric acid and the crude acid was extracted from the aqueous phase with small portions (5 mL) of diethyl ether three times. The organic phase was dried over sodium sulfate and the diethyl ether removed under reduced pressure. The crude acid was distilled or washed with pentane if it was a solid.

A.2 Methyl esters

A.2.a Methyl methacrylate as hydrogen acceptor

Alcohol (5.25 mmol, 1 eq.), methanol (2.1 mL, 52 mmol, 10 eq.) and methyl methacrylate (1.7 mL, 15.75 mmol, 3 eq.) were cooled to -30 °C. The amide $Rh(trop_2N)(PPh_3)$ **4** (4 mg, 5.2 µmol, 0.1 mol%) dissolved in 4 mL THF was cooled to -30 °C and added to the first solution. The solution was left at -30 °C for 2 h then warmed to RT for 2 h. The reaction was monitored by GC. All volatile materials were removed under reduced pressure and the residue bulb to bulb distilled unless otherwise noted.

A.2.b Cyclohexanone as hydrogen acceptor

Alcohol (5.25 mmol, 1 eq.), methanol (2.2 mL, 55 mmol, 10 eq.), cyclohexanone (2.8 mL, 27.5 mmol, 5 eq.) and (5 mg, 5.5 µmol, 0.1 mol%) of $Rh(trop_2NH)(PPh_3)(OTf)$ **3** were combined in a Schlenk tube. Optionally dodecane (0.68 mL, 3 mmol, 0.54 eq.) was added as internal standard. Subsequently solid K_2CO_3 (38 mg, 0.27 mmol, 5 mol%) was added under a stream of argon and the mixture was stirred at RT for 4 h unless otherwise noted. The reaction was monitored by GC. All volatile materials were removed under reduced pressure and the residue dissolved in ethyl acetate. The organic phase was washed with a saturated NH_4Cl solution, dried over $MgSO_4$ and flash-chromatographed on silica gel with *n*-hexane/ethyl acetate (20:1).

B.3 Amides

A.3.a Ammonia

Alcohol (1.31 mmol, 1 eq.), methyl methacrylate (0.70 mL, 6.5 mmol, 5 eq.) and 1 mL THF were added to a 20 mL Schlenk bomb. In a dry ice bath, ammonia (ca. 1 mL, xs) was condensed in. Then the amide $Rh(trop_2N)(PPh_3)$ **4** (2 mg, 2.6 µmol, 0.2 mol%) dissolved in 1 mL THF were added. The solution was warmed to -20 °C for 2 h then warmed to RT for 2 h. The Schlenk bomb was cooled to dry ice temperature again, opened and the ammonia slowly evaporated. In the end the reaction was checked by GC. All volatile materials were removed under reduced pressure and the residue recrystallized from hot *n*-hexane unless otherwise noted.

A.3.b Other amines

Alcohol (1.31 mmol, 1 eq.), amine (2 mmol, 1.5 eq.) and methyl methacrylate (0.42 mL, 4 mmol, 3 eq.) were cooled to -30 °C. The amide $Rh(trop_2N)(PPh_3)$ **4** (2 mg, 0.0026 mmol, 0.2 mol%) dissolved in 2 mL THF was cooled to -30 °C and

added to the first solution. The solution was left at -30 °C for 2 h then warmed to RT for 2 h. The reaction was monitored by GC. All volatile materials were removed under reduced pressure and the residue bulb to bulb distilled unless otherwise noted.

A.4 Cannizzaro reaction

A.4.a with water

NaOH (263 mg, 6.58 mmol, 1.2 eq.) was dissolved in water (3.2 mL, 180 mmol, 33 eq.) and benzaldehyde (0.58 mL, 5.48 mmol, 1 eq.) added. The mixture was degassed by purging with argon for 15 min. [Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3** (5 mg, 0.005 mmol, 0.1 mol%) was added. The reaction was followed by GC.

A.4.a with methanol

11.2 mL (109.7 mmol, 1 eq.) benzaldehyde were dissolved in 45 mL (1.01 mol, 10 eq.) dry methanol. The mixture was degassed by purging with argon for 15 min. [Rh(OTf)(trop$_2$NH)(PPh$_3$)] **3** (1 mg, 0.001 mmol, 0.001 mol%) and K_2CO_3 (151 mg, 1.1 mmol, 1 mol%) were added. The reaction was followed by GC.

B. Isolation and identification of products

B.1 Chromatographic conditions

Separation of alcohols and esters: Column: *Hewlett-Packard HP-5 phenyl methyl siloxane* (30 m x 0.32 mm x 0.25 µm); temperature: 1 min 80 °C then 4 °C/min to 180 °C; H_2 pressure: 0.50 bar; retention times: Benzaldehyde: 3.68 min; Benzyl alcohol: 4.83 min; Methyl benzoate: 5.91 min; Octanol: 5.43 min; Methyl octanoate: 6.55 min; (2E)-3,7-Dimethyl-2,6-octadien-1-ol: 10.33 min; (E)- 3,7-Dimethyl- 2,6 - octadienoic acid methyl ester: 12.19 min; 4-Methylthiobenzyl alcohol: 16.70 min; Methyl 4-methylthiobenzoate: 19.05 min; 4-Methoxybenzyl alcohol: 11.09 min; Methyl 4-methoxybenzoate: 13.79; 2,2-Dimethyl-1,3-dioxolane-4-methanol:3.32 min; 4-Hydroxy-3-methoxybenzyl alcohol: 16.28 min; 2-(Hydroxymethyl)pyridine: 5.24 min; benzamide: 12.37 min; N-benzyloctanamide: 35.18 min; N-butyl-4-(methylthio)benzamide: 39.96 min; (E)-N-benzyl-3,7-dimethylocta-2,6-dienamide: 50.91 min; N-benzylbenzamide: 35.02 min; N-butyloctanamide: 21.67 min; N-butylbenzamide: 21.38 min; Benzamide: 12.90 min; Octanamide: 13.32 min; Dodecane: 8.58 min;

Glycerine, Butane-1,3-diol and 1-3 Propanediol gave rise to very broad peaks in the GC trace and could not be measured.

B.2 Acids

Benzoic acid (from benzyl alcohol): The catalytic reaction is complete after 2 h. Isolated by method A.1, washed with pentane. Yield: 94%, 635 mg, 5.2 mmol as colorless solid. – M.p.: 120 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (t, $^3J_{HH}$ = 7.8 Hz, 2H, CH^{ar}), 7.65 (t, $^3J_{HH}$ = 7.8 Hz, 1H, CH^{ar}), 8.16 (d, $^3J_{HH}$ = 7.2 Hz, 1H, CH^{ar}); –

$^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$): δ = 128.9 (s, 2C, CH^{ar}), 129.8 (s, 1C, C^{quart}), 130.6 (s, 2C, CH^{ar}), 134.2 (s, 1C, CH^{ar}), 172.7 (s, 1C, C^{quart});

Octanoic acid (from octanol): Isolated by method A.1 and distilled. Yield: 89%, 703 mg, 4.9 mmol, as colorless oil. – ^1H-NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3), 1.32 (m, 8H, CH_2), 1.66 (tt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2), 2.37 (t, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2); – $^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$): δ = 14.4 (s, 1C, CH_3), 23.0 (s, 1C, CH_2), 25.1 (s, 1C, CH_2), 29.3 (s, 1C, CH_2), 29.4 (s, 1C, CH_2), 32.0 (s, 1C, CH_2), 34.4 (s, 1C, CH_2), 180.1 (s, 1C, C^{quart});

4-Methoxybenzoic acid (from 4-methoxybenzyl alcohol): Isolated by method A.1, washed with pentane. Yield: 88%, 817 mg, 4.8 mmol as colorless solid. – M.p.: 184 °C – ^1H-NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3H, OCH_3), 6.97 (d, $^3J_{HH}$ = 8.9 Hz, 2H, CH^{ar}), 8.10 (d, $^3J_{HH}$ = 8.9 Hz, 2H, CH^{ar}); – $^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$): δ = 55.9 (s, 1C, OCH_3), 114.2 (s, 2C, CH^{ar}), 122.0 (s, 1C, C^{quart}), 132.8 (s, 2C, CH^{ar}), 164.5 (s, 1C, CH^{ar}), 171.8 (s, 1C, C^{quart});

4-Methylthiobenzoic acid (from 4-methylthiobenzyl alcohol): Isolated by method A.1, washed with pentane. Yield: 85%, 781 mg, 4.65 mmol as colorless solid. – M.p.: 190 °C – ^1H-NMR (400 MHz, $CDCl_3$): δ = 2.56 (s, 3H, SCH_3) 7.30 (d, $^3J_{HH}$ = 8.9 Hz, 2H, CH^{ar}), 8.03 (d, $^3J_{HH}$ = 8.9 Hz, 2H, CH^{ar}); – $^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$): δ = 15.2 (s, 1C, SCH_3), 125.3 (s, 2C, CH^{ar}), 125.6 (s, 1C, C^{quart}), 130.9 (s, 2C, CH^{ar}), 147.2 (s, 1C, CH^{ar}), 171.8 (s, 1C, C^{quart});

2-Pyridinecarboxylic acid (from 2-(hydroxymethyl)pyridine): Catalysis was performed as described in A.1, but required 16 h to reach completion. All volatile materials (aqueous and organic) were removed under reduced pressure. The residue was dissolved in water and washed twice with small portions of diethyl ether. This solution was acidified with 2 M hydrochloric acid and the water removed under reduced pressure. The residue was recrystallized from hot toluene. Yield: 96%, 657 mg, 5.3 mmol, as off-white solid. – M.p.: 136 °C – ^1H-NMR (400 MHz, D_2O): δ = 8.10 (t, $^3J_{HH}$ = 6.8 Hz, 1H, CH^{ar}), 8.39 (d, $^3J_{HH}$ = 7.7 Hz, 1H, CH^{ar}), 8.63 (t, $^3J_{HH}$ = 8.3 Hz, 1H, CH^{ar}), 8.72 (t, $^3J_{HH}$ = 5.5 Hz, 1H, CH^{ar}); – $^{13}C\{^1H\}$-NMR (101.6 MHz, D_2O): δ = 127.6 (s, 1C, CH^{ar}), 130.0 (s, 1C, CH^{ar}), 142.0 (s, 1C, CH^{ar}), 143.4 (s, 1C, C^{quart}), 148.4 (s, 1C, CH^{ar}), 162.7 (s, 1C, C^{quart});

2,2-Dimethyl-1,3-dioxolane-4-carboxylic acid (from 2,2-dimethyl-1,3-dioxolane-4-methanol): Catalysis was performed as described in A.1, but required 16 h to reach completion. The work up was adapted from the literature.[170] All volatile materials (aqueous and organic) were removed under reduced pressure. The residue was dissolved in water and washed twice with small portions of diethyl ether. The aqueous solution was cooled in an ice bath and 4 mL 2 M Phosphoric Acid in water were added. The free acid was extracted three times with small portions of diethyl ether and the organic phase dried over sodium sulfate. The diethyl ether was removed under reduced pressure without heating and the acid stored in the freezer. Yield: 89%, 715 mg, 4.9 mmol as colorless oil. – ^1H-NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 4.21 (dd, $^2J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, CH_2), 4.31 (dd, $^2J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, CH_2), 4.31 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 4.8 Hz, 1H,

C*H*); – $^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$): δ = 25.6 (s, 1C, *C*H_3), 26.3 (s, 1C, *C*H_3), 67.7 (s, 1C, *C*H_2), 74.0 (s, 1C, *C*H), 112.3 (s, 1C, C^{quart}), 175.7 (s, 1C, C^{quart});

Sodium-3-hydroxypropionate (from 1,3-propanediol): Catalysis was performed as described in A.1 but required 16 h to reach completion. All volatile materials (aqueous and organic) were removed under reduced pressure. The residue was dissolved in water and washed twice with small portions of diethyl ether. Then the water was removed under reduced pressure and the residue recrystallized from hot ethanol. Yield: 72%, 4.0 mmol, 444 mg as off-white solid – M.p.: 136 °C – ^{1}H-NMR (400 MHz, D_2O): δ = 2.34 (t, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*$_2$), 3.70 (t, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*$_2$); – $^{13}C\{^1H\}$-NMR (101.6 MHz, D_2O): δ = 40.3 (s, 1C, *C*H_2), 59.4 (s, 1C, *C*H_2), 181.1 (s, 1C, C^{quart}); – EA found% (calc%) for$C_3H_5O_3Na$: C: 32.45 (32.15) H: 4.71 (4.50);

Sodium 3-hydroxybutanoate (from 1-3 butanediol): similar to sodium-3-hydroxypropionate. Yield: 67%, 3.7 mmol, 465 mg as white solid – M.p.: 160 °C – ^{1}H-NMR (400 MHz, D_2O): δ = 1.11 (d, $^3J_{HH}$ = 6.4 Hz, 3H, C*H*$_3$), 2.21 (dd, $^2J_{HH}$ = 17.4, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*$_2$), 2.32 (dd, $^2J_{HH}$ = 17.4, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*$_2$), 4.06 (6, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*); – $^{13}C\{^1H\}$-NMR (101.6 MHz, D_2O): δ = 21.1 (s, 1C, *C*H_3), 46.9 (s, 1C, *C*H_2), 46.9 (s, 1C, *C*H_2), 180.9 (s, 1C, C^{quart}); – EA found% (calc%) for$C_4H_7O_3Na$: C: 37.82 (38.10) H: 5.45 (5.60);

Glyceric acid calcium salt (from glycerine): Catalysis was performed as described in A.1 but required 16 h to reach completion. The work up was adapted from the literature.[171] All volatile materials (aqueous and organic) were removed under reduced pressure. The residue was dissolved in water and washed twice with small portions of diethyl ether. Anhydrous $CaCl_2$ (424 mg, 3.6 mmol, 0.65 eq.) was added to the aqueous solution and the solution warmed. It was filtered while still warm and placed in the fridge. The glyceric acid calcium salt precipitated overnight. Yield: 63%, 1.8 mmol, 495 mg as colorless solid. – M.p.: >220 °C – ^{1}H-NMR (400 MHz, D_2O): δ = 3.68 (m, 1H, C*H*$_2$), 3.75 (m, 1H, C*H*$_2$), 4.08 (m, 1H, C*H*); – $^{13}C\{^1H\}$-NMR (101.6 MHz, D_2O): δ = 64.5 (s, 1C, *C*H_2), 73.9 (s, 1C, *C*H), 179.2 (s, 1C, C^{quart}); – EA found% (calc%) for $C_6H_{10}CaO_8$(2 H_2O): C: 25.00 (25.18) H: 4.68 (4.93);

4-Hydroxy-3-methoxybenzaldehyde (from 4-(Hydroxymethyl)-2-methoxyphenol): 2.2 eq. NaOH were used, otherwise the catalysis was performed as described in A.1. All volatile materials (aqueous and organic) were removed under reduced pressure. The residue was dissolved in water and washed twice with small portions of diethyl ether. The aqueous solution was cooled in an ice bath and 1 g of ammonium chloride added. The organic product was extracted three times with small portions of diethyl ether. The diethyl ether was removed under reduced pressure and the residue recrystallized from hot *n*-hexane. Yield: 89%, 4.9 mmol, 744 mg as colorless solid. – M.p.: 81 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 3H, C*H*$_3$), 6.23 (s, 1H, C*H*^{ar}), 7.07 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C*H*^{ar}), 7.44 (m, 2H, C*H*^{ar}), 9.85 (s, 1H, C*H*O); – $^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$): δ = 56.5 (s, 1C, *C*H_3), 109.2 (s, 1C, *C*H^{ar}), 114.8 (s, 1C, *C*H^{ar}), 127.9 (s, 1C, *C*H^{ar}), 130.3 (s, 1C, C^{quart}), 147.5 (s, 1C, C^{quart}), 152.0 (s, 1C, C^{quart}), 191.2 (s, 1C, C^{quart});

B.3 Esters

Methyl benzoate (from benzyl alcohol): Method A.2.a: Yield: 95%, 693 mg, 5.0 mmol; Method A.2.b: flash-chromatographed on silica gel with *n*-hexane/ethyl acetate 20:1, R_f= 0.31. Yield: 82%, 614 mg, 5.2 mmol as colorless oil. – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3H, OC*H*$_3$), 7.44 (t, $^3J_{HH}$ = 7.8 Hz, 2H, C*H*^{ar}), 7.65 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C*H*^{ar}), 8.06 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*^{ar}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 52.4 (s, 1C, O*C*H$_3$), 128.7 (s, 2C, *C*H^{ar}), 130.0 (s, 2C, *C*H^{ar}), 130.6 (s, 1C, *C*^{quart}), 133.3 (s, 1C, *C*H^{ar}), 167.5 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)):51.2 (24%), 77.2 (66%), 105.1 (100%), 136.1 (38%, M^+);

Methyl octanoate (from octanol): Method A.2.a: Yield: 93%, 788 mg, 4.9 mmol; Method A.2.b: flash-chromatographed on silica gel with *n*-hexane/ethyl acetate 10:1, R_f= 0.47. Yield: 80%, 697 mg, 4.4 mmol as colorless oil. – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{HH}$ = 6.7 Hz, 3H, C*H*$_3$), 1.30 (m, 8H, C*H*$_2$), 1.63 (tt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*$_2$), 2.32 (t, $^3J_{HH}$ = 7.6 Hz, 2H, C*H*$_2$), 3.68 (s, 3H, OC*H*$_3$); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 14.4 (s, 1C, *C*H$_3$), 23.0 (s, 1C, *C*H$_2$), 25.1 (s, 1C, *C*H$_2$), 29.3 (s, 1C, *C*H$_2$), 29.4 (s, 1C, *C*H$_2$), 32.0 (s, 1C, *C*H$_2$), 34.4 (s, 1C, *C*H$_2$), 180.1 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)): 74.2 (100%), 87.2 (37%), 127.2 (15%), 158.2 (4%, M^+);

(2E)- 3,7-Dimethyl- 2,6 -octadienoic acid methyl ester (from (2E)-3,7-Dimethyl-2,6-octadien-1-ol): Method A.2.a: Yield: 91%, 882 mg, 4.8 mmol; Method A.2.b: Catalysis was performed at 0 °C, otherwise under standard conditions. The reaction was complete after 20 min. Isolated by flash-chromatography on silica gel with *n*-hexane/ethyl acetate 20:1, R_f= 0.34. Yield: 79%, 791 mg, 4.3 mmol as colorless oil. – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.63 (s, 3H, C*H*$_3$), 1.70 (s, 3H, C*H*$_3$), 2.18 (m, 2H, C*H*$_2$), 2.18 (s, 3H, C*H*$_3$), 2.19(m, 2H, C*H*$_2$), 3.71 (s, 3H, OC*H*$_3$), 5.09 (br, 1H, C*H*^{olefin}), 5.69 (s, 1H, C*H*^{olefin}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 18.1 (s, 1C, *C*H$_3$), 19.2 (s, 1C, *C*H$_3$), 26.1 (s, 1C, *C*H$_3$), 26.4 (s, 1C, *C*H$_2$), 41.3 (s, 1C, *C*H$_2$), 51.2 (s, 1C, O*C*H$_3$), 115.6 (s, 1C, *C*H^{olefin}), 116.2 (s, 1C, *C*^{quart}), 123.4 (s, 1C, *C*H$_2$), 132.9 (s, 1C, *C*^{quart}), 160.4 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)):69.0 (100%), 83.0 (18%), 113.8 (40%), 122.9 (32%), 150.8 (15%), 182.1 (11%, M^+);

Methyl 4-methoxybenzoate (from 4-Methoxybenzyl alcohol): Method A.2.a: Yield: 93%, 825 mg, 4.9 mmol; Method A.2.b: flash-chromatographed on silica gel with *n*-hexane/ethyl acetate 20:1, R_f= 0.20, Yield: 77%, 703 mg, 4.2 mmol as colorless solid. – M.p.: 48 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3H, OC*H*$_3$), 3.90 (s, 3H, OC*H*$_3$), 6.94 (d, $^3J_{HH}$ = 8.9 Hz, 2H, C*H*^{ar}), 8.01 (d, $^3J_{HH}$ = 8.9 Hz, 2H, C*H*^{ar}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 52.2 (s, 1C, O*C*H$_3$), 55.8 (s, 1C, O*C*H$_3$), 114.0 (s, 2C, *C*H^{ar}), 123.0 (s, 1C, *C*^{quart}), 132.0 (s, 2C, *C*H^{ar}), 163.7 (s, 1C, *C*H^{ar}), 167.2 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)):64.2 (15%), 77.2 (25%), 92.1 (20%), 107.2 (12%), 135.1 (100%), 166.2 (33%, M^+);

Methyl 4-methylthiobenzoate (from 4-Methylthiobenzyl alcohol): Method A.2.a: Yield: 94%, 912 mg, 4.9 mmol; Method A.2.b: flash-chromatographed on silica gel with *n*-hexane/ethyl acetate 20:1, R_f= 0.26, Yield: 86%, 862 mg, 4.7 mmol as colorless solid. – M.p.: 79 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3H, SC*H*$_3$), 3.91 (s, 3H, OC*H*$_3$), 7.27 (d, $^3J_{HH}$ = 8.9 Hz, 2H, C*H*^{ar}), 7.95 (d, $^3J_{HH}$ = 8.9 Hz, 2H,

C*H*^{ar}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 15.2 (s, 1C, S*C*H$_3$), 52.4 (s, 1C, O*C*H$_3$), 125.4 (s, 2C, *C*H^{ar}), 126.7 (s, 1C, *C*^{quart}), 130.3 (s, 2C, *C*H^{ar}), 145.8 (s, 1C, *C*H^{ar}), 167.2 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)):108.1 (16%), 151.1 (100%), 182.1 (67%, M$^+$);

B.3 Amides

Benzamide (from benzyl alcohol and ammonia): Recrystallized from toluene, washed with *n*-hexane. Yield: 94%, 154 mg, 1.23 mmol as colorless solid. – M.p.: 125 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.22 (br, 2H, N*H*$_2$), 7.46 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H, C*H*^{ar}), 7.56 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, C*H*^{ar}), 7.85 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 127.8 (s, 2C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 132.4 (s, 1C, *C*H^{ar}), 133.8 (s, 1C, *C*^{quart}), 170.0 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)): 51.1 (30%), 77.1 (90%), 105.1 (95%) 121.1 (100%, M$^+$);

Octanamide (from octanol and ammonia): Recrystallized from *n*-hexane. Yield: 94%, 181 mg, 1.2 mmol, as colorless solid. – M.p.: 105 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, C*H*$_3$), 1.32 (m, 8H, C*H*$_2$) 1.65 (m, 2H, C*H*$_2$), 2.23 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, C*H*$_2$), 5.55 (s, 1H, CON*H*$_2$), 5.84 (br s, 1H, N*H*$_2$); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 14.4 (s, 1C, *C*H$_3$) 23.0 (s, 1C, *C*H$_2$), 26.0 (s, 1C, *C*H$_2$), 29.4 (s, 1C, *C*H$_2$) 29.6 (s, 1C, *C*H$_2$), 32.1 (s, 1C, *C*H$_2$) 36.4 (s, 1C, *C*H$_2$), 176.2 (s, 1C, C^{quart});– MS (EI, m/z, (%)): 59.0 (100%), 72.1 (53%), 86.1 (16%), 114.1 (7%), 144.1 (100%, M$^+$);

4-Methylthiobenzamide (from 4-Methylthiobenzyl alcohol and ammonia): The obtained solid was washed with diethyl ether. Yield: 92%, 207 mg, 1.2 mmol as colorless solid. – M.p.: 185 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.55 (s, 3H, SC*H*$_3$), 5.68 (br s, 1H, N*H*$_2$), 5.99 (br s, 1H, N*H*$_2$), 7.30 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, C*H*^{ar}) 7.76 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, C*H*^{ar}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 15.4 (s, 1C, S*C*H$_3$), 125.9 (s, 2C, *C*H^{ar}), 128.2 (s, 2C, *C*H^{ar}), 129.8 (s, 1C, *C*^{quart}), 144.7 (s, 1C, *C*^{quart}), 169.1 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)): 108.0 (24%), 122.9 (27%), 150.8 (100%) 167.0 (99%, M$^+$);

(2E)-3,7-dimethylocta-2,6-dienamide (from (2E)-3,7-Dimethyl-2,6-octadien-1-ol and ammonia: Isolated by flash-chromatography on silica gel with *n*-hexane/ethyl acetate 1:1, R$_f$= 0.25. Yield: 82%, 183 mg, 1.07 mmol as colorless solid. – M.p.: 64 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.62 (s, 3H, C*H*$_3$), 1.70 (s, 3H, C*H*$_3$), 2.14 (s, 2H, C*H*$_2$), 2.16 (s, 2H, C*H*$_2$), 2.16 (s, 3H, C*H*$_3$), 5.09 (s, 1H, C*H*^{olefin}), 5.42 (br s, 1H, NH$_2$), 5.62 (s, 1H, C*H*^{olefin}), 5.62 (s, 1H, N*H*$_2$); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 18.1 (s, 1C, *C*H$_3$), 18.8 (s, 1C, *C*H$_3$), 26.1 (s, 1C, *C*H$_3$), 26.5 (s, 1C, *C*H$_2$), 41.2 (s, 1C, *C*H$_2$), 117.4 (s, 1C, *C*H^{olefin}), 123.5 (s, 1C, *C*H^{olefin}), 132.8 (s, 1C, *C*^{quart}), 156.3 (s, 1C, *C*^{quart}), 169.6 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)):69.0 (75%), 99.0 (100%), 123.1 (20%), 167.2 (7%, M$^+$);

N-benzylbenzamide (from benzyl alcohol and benzyl amine): Recrystallized from toluene, washed with *n*-hexane. Yield: 97%, 272 mg, 1.3 mmol as colorless solid – M.p.: 104 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.61 (d, 2H, $^{3}J_{HH}$ = 5.7 Hz, C*H*$_2$), 6.22 (br, 1H, N*H*), 7.25 – 7.38 (m, 5H, C*H*^{ar}), 7.41 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, C*H*^{ar}), 7.50 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, C*H*^{ar}), 7.82 (t, $^{3}J_{HH}$ = 7.32 Hz, 2H, C*H*^{ar}); – ^{13}C{^{1}H}-NMR

(101.6 MHz, $CDCl_3$): δ = 44.6 (s, 1C, *C*H_2), 127.5 (s, 2C, *C*H^{ar}), 127.9 (s, 1C, *C*H^{ar}), 128.3 (s, 2C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 131.9 (s, 1C, *C*H^{ar}), 134.8 (s, 1C, *C*^{quart}), 138.7 (s, 1C, *C*^{quart}), 167.9 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)): 51.1 (13%), 77.1 (38%), 105.1 (48%), 211.1 (100%, M^+);

N-butylbenzamide (from benzyl alcohol and *n*-butyl amine): Bulb to bulb distilled at 220 °C, 0.05 mm Hg. Yield: 94%, 221 mg, 1.2 mmol as colorless oil. – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, $^3J_{HH}$ = 7.3 Hz, 3H, C*H*$_3$), 1.38 (6, $^3J_{HH}$ = 7.6 Hz, 2H, C*H*$_2$), 1.58 (5, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*$_2$), 3.41 (5, $^3J_{HH}$ = 5.9 Hz, 2H, C*H*$_2$), 6.23 (br, 1H, N*H*), 7.38 (t, $^3J_{HH}$ = 7.8 Hz, 2H, C*H*^{ar}), 7.56 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C*H*^{ar}), 7.85 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*^{ar}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 14.2 (s, 1C, *C*H$_3$), 20.6 (s, 1C, *C*H$_2$), 32.1 (s, 1C, *C*H$_2$), 40.2 (s, 1C, *C*H$_2$), 127.3 (s, 2C, *C*H^{ar}), 128.8 (s, 2C, *C*H^{ar}), 131.6 (s, 1C, *C*H^{ar}), 135.3 (s, 1C, *C*^{quart}), 168.0 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)):51.1 (11%), 77.1 (32%), 105.1 (100%), 134.1 (22%), 177.2 (14%, M^+);

N-isopropylbenzamide (from benzyl alcohol and isopropyl amine): Bulb to bulb distilled at 220 °C, 0.05 mm Hg. Yield: 93%, 203 mg, 1.2 mmol as colorless solid. – M.p.: 101 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.27 (d, $^3J_{HH}$ = 6.5 Hz, 6H, C*H*$_3$), 4.29 (7, $^3J_{HH}$ = 7.7 Hz, 1H, C*H*), 6.10 (br, 1H, N*H*), 7.41 (t, $^3J_{HH}$ = 7.6 Hz, 2H, C*H*^{ar}), 7.56 (t, $^3J_{HH}$ = 7.3 Hz, 1H, C*H*^{ar}), 7.76 (d, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*^{ar}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 23.2 (s, 1C, *C*H$_3$), 42.3 (s, 1C, *C*H), 127.2 (s, 2C, *C*H^{ar}), 128.9 (s, 2C, *C*H^{ar}), 131.6 (s, 1C, *C*H^{ar}), 135.4 (s, 1C, *C*^{quart}), 167.1 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)): 51.0 (23%), 77.1 (61%), 105.1 (100%), 163.1 (48%, M^+);

N-benzyloctanamide (from octanol and benzyl amine): Recrystallized from *n*-hexane, washed with *n*-hexane. Yield: 94%, 291 mg, 1.2 mmol as colorless solid. – M.p.: 66 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, $^3J_{HH}$ = 7.0 Hz, 3H, C*H*$_3$), 1.30 (m, 8H, C*H*$_2$), 1.67 (5, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*$_2$), 2.22 (t, $^3J_{HH}$ = 7.7 Hz, 2H, C*H*$_2$), 4.44 (d, $^3J_{HH}$ = 5.8 Hz, 2H, C*H*$_2$), 5.90 (br, 1H, N*H*), 7.25 – 7.39 (m, 5H, C*H*^{ar}); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 14.5 (s, 1C, *C*H$_3$), 23.0 (s, 1C, *C*H$_2$), 26.2 (s, 1C, *C*H$_2$), 29.4 (s, 1C, *C*H$_2$), 29.7 (s, 1C, *C*H$_2$), 32.1 (s, 1C, *C*H$_2$), 37.2 (s, 1C, *C*H$_2$), 44.0 (s, 1C, *C*H$_2$), 127.9 (s, 1C, *C*H^{ar}), 128.2 (s, 2C, *C*H^{ar}), 129.1 (s, 2C, *C*H^{ar}), 138.9 (s, 1C, *C*^{quart}), 173.4 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)) 57.2 (18%), 91.1 (100%), 106.1 (43%), 149.2 (89%), 162.1 (30%), 233.3 (67%, M^+);

N-butyloctanamide (from octanol and *n*-butyl amine): Bulb to bulb distilled at 250 °C, 0.05 mm Hg. Yield: 96%, 255 mg, 1.3 mmol as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, $^3J_{HH}$ = 7.3 Hz, 3H, C*H*$_3$), 0.90 (t, $^3J_{HH}$ = 7.3 Hz, 3H, C*H*$_3$), 1.2 – 1.4 (m, 10H, C*H*$_2$), 1.46 (5, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*$_2$), 1.60 (5, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*$_2$), 2.14 (t, $^3J_{HH}$ = 7.9 Hz, 2H, C*H*$_2$), 3.21 (d, $^3J_{HH}$ = 5.8 Hz, 2H, C*H*$_2$), 5.84 (br, 1H, N*H*); – ^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$): δ = 14.1 (s, 1C, *C*H$_3$), 14.4 (s, 1C, *C*H$_3$), 20.5 (s, 1C, *C*H$_2$), 23.0 (s, 1C, *C*H$_2$), 26.3 (s, 1C, *C*H$_2$), 29.4 (s, 1C, *C*H$_2$), 29.7 (s, 1C, *C*H$_2$), 32.1 (s, 1C, *C*H$_2$), 32.1 (s, 1C, *C*H$_2$), 37.2 (s, 1C, *C*H$_2$), 39.5 (s, 1C, *C*H$_2$), 173.6 (s, 1C, *C*^{quart}); – MS (EI, m/z, (%)): 57.2 (82%), 73.2 (53%), 100.2 (32%), 115.2 (100%), 128.2 (32%), 199.19 (17%, M^+);

(E)-N-benzyl-3,7-dimethylocta-2,6-dienamide (from (2E)-3,7-Dimethyl-2,6-octadien-1-ol and benzyl amine): Flash-chromatographed on silica gel with *n*-hexane/ethyl acetate 3:1, R_f= 0.45, Yield: 89%, 302 mg, 4.7 mmol as colorless oil. ^{1}H-NMR (400

MHz, $CDCl_3$): δ = 1.62 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.05-2.15 (m, 4H, CH_2), 2.19 (s, 3H, CH_3), 4.46 (d, $^3J_{HH}$ = 5.8 Hz, 2H, CH_2), 5.09 (br, 1H, CH^{olefin}), 5.60 (s, 1H, CH^{olefin}) 5.95, (br, 1H, N*H*), 7.25 – 7.39 (m, 5H, CH^{ar}); – $^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$): δ = 18.1 (s, 1C, *C*H_3), 18.8 (s, 1C, *C*H_3), 26.1 (s, 1C, *C*H_3), 26.6 (s, 1C, *C*H_2), 41.2 (s, 1C, *C*H_2), 43.7 (s, 1C, *C*H_2), 118.3 (s, 1C, *C*H^{olefin}), 123.7 (s, 1C, *C*H^{olefin}), 127.7 (s, 1C, *C*H^{ar}), 128.2 (s, 2C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 132.7 (s, 1C, C^{quart}), 139.1 (s, 1C, C^{quart}), 155.0 (s, 1C, C^{quart}), 167.4 (s, 1C, C^{quart}); – MS (EI, m/z, (%)):69.2 (47%), 91.1 (86%), 106.1 (42%), 174.1 (100%), 189.1 (32%), 257.2 (17%, M^+);

N-butyl-4-(methylthio)benzamide (from 4-Methylthiobenzyl alcohol and *n*-butyl amine): Recrystallized from toluene/*n*-hexane, washed with *n*-hexane. Yield: 93%, 276 mg, 1.2 mmol as colorless solid. – M.p.: 93 °C – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3), 1.42 (6, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 1.61 (7, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2), 2.52 (s, 3H, SCH_3), 3.46 (q, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2), 6.13 (br, 1H, N*H*), 7.26 (d, $^3J_{HH}$ = 8.4 Hz, 2H, CH^{ar}), 7.69 (d, $^3J_{HH}$ = 8.4 Hz, 2H, CH^{ar}); – $^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$): δ = 14.2 (s, 1C, *C*H_3), 15.5 (s, 1C, *C*H_3), 20.6 (s, 1C, *C*H_2), 32.2 (s, 1C, *C*H_2), 40.2 (s, 1C, *C*H_2), 125.9 (s, 2C, *C*H^{ar}), 127.6 (s, 2C, *C*H^{ar}), 131.4 (s, 1C, C^{quart}), 143.5 (s, 1C, C^{quart}), 167.3 (s, 1C, C^{quart}); – MS (EI, m/z, (%)):79.1 (9%), 108.0 (12%), 151.0 (100%), 167.1 (24%), 223.2 (29%, M^+);

N-benzyl-3-(benzylamino)-2-hydroxypropanamide (from glycidol and benzyl amine): Catalysis was done as described in A.3, except that 2.5 eq. benzyl amine were used. Recrystallized from THF/*n*-hexane, washed with *n*-hexane. Yield 86%, 325 mg, 1.13 mmol. – M.p.: 128 °C – ^{1}H-NMR (700 MHz, $CDCl_3$) δ = 3.02 (dd, $^2J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, CH_2NH), 3.07 (dd, $^2J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, CH_2NH), 3.79 (d, ^3J = 5.5 Hz, 2H, PhCH_2), 4.09 (t, *J* = 6.0 Hz, 1H, C*H*OH), 4.48 (d, *J* = 5.80 Hz, 2H, PhCH_2) 7.24-7.35 (m, 1H, CH^{ar}), 7.58 (s, 1H, CON*H*); – $^{13}C\{^1H\}$-NMR (176 MHz, $CDCl_3$) δ = 43.2 (s, 1C, Ph*C*H_2), 51.3 (s, 1C, *C*HOH), 53.5 (s, 1C, Ph*C*H_2), 69.2 (s, 1C, *C*H_2), 127.4 (s, 1C, *C*H^{ar}), 127.5 (s, 1C, *C*H^{ar}), 127.7 (s, 1C, *C*H^{ar}), 128.1 (s, 1C, *C*H^{ar}), 128.6 (s, 1C, *C*H^{ar}), 128.7 (s, 1C, *C*H^{ar}), 138.1 (s, 1C, C^{quart}), 139.3 (s, 1C, C^{quart}), 172.9 (s, 1C, C^{quart}); – MS (EI, m/z, (%)):65.2 (10%), 91.1 (100%), 120.1 (70%), 150.1 (5%), 165.1 (4%), 175.1 (3%), 266.1 (4%), 284.1 (1%, M^+);

N, *N*'-dibenzyl-malonamide (from 1-3 propanediol and benzyl amine): Catalysis was done as described, except that 2.5 eq. benzyl amine were used. Recrystallized from THF/*n*-hexane, washed with *n*-hexane. Yield 90%, 337 mg, 1.18 mmol. – M.p.: 140 °C – ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 3.24 (s, 2H, CH_2), 4.43 (d, $^3J_{HH}$ = 5.8 Hz, 4H, CH_2), 7.25-7.35 (m, 10H, CH_{ar}), 7.41 (br s, 2H, N*H*); – $^{13}C\{^1H\}$-NMR (101.6 MHz, $CDCl_3$) δ = 43.5 (s, 1C, *C*H_2), 44.1 (s, 2C, *C*H_2), 128.0 (s, 2C, *C*H_{ar}), 128.1 (s, 4C, *C*H_{ar}), 129.1 (s, 4C, *C*H_{ar}), 138.1 (s, 2C, C_{quart}), 167.6 (s, 2C, C_{quart}); – MS (EI, m/z, (%)):65.1 (10%), 91.1 (53%), 106.1 (100%), 107.1 (15%), 282.1 (23%, M^+);

3 Preparation and Characterization

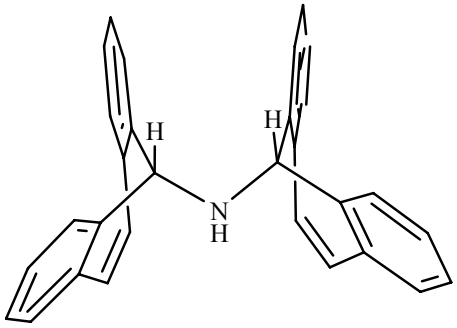
Compounds of section II and IV

bis(5-H-dibenzo[a,d]cycloheptен-5-yl)-amine ($trop_2NH$) (**1**)

MF = $C_{30}H_{23}N$

MW = 397.91 g/mol

MP = 167 °C
Air stable



The corrected synthesis is given for completeness and future reference [39, 40, 172]. TropCl (32.6 g, 144 mmol, 1 eq.) was dissolved in 300 mL toluene and 1,1,1,3,3,3-hexamethyldisilazane (20.2 mL, 15.3 g, 95.0 mmol, 0.66 eq.) was added. The solution was refluxed for 4 h. The solution became yellowish while refluxing. After cooling of the solution to room temperature the solvent was removed under reduced pressure and 200 mL *n*-hexane was added to the obtained oil. The resulting suspension was refluxed for 30 min and filtered off. The filter cake was washed with *n*-hexane and dried under high vacuum yielding an off white solid which can be further purified by column chromatography on silica gel with DCM as eluent. Yield: 90%, 25.91 g, 65.1 mmol.

exo-exo conformer:
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 3.43 (t, $^3J_{HH}$ = 6.0 Hz, 1H, N*H*), 4.37 (d, $^3J_{HH}$ = 6.0 Hz, 2H, C*H*^{5}), 7.06 (s, 4H, C*H*^{10,11}), 7.26 (m, 4H, C*H*^{2,8}), 7.34 (m, 4H, C*H*^{1,9}), 7.44, (m, 4H, C*H*^{3,7}), 7.78 (m, 4H, C*H*^{4,6});

^{13}C{^{1}H}-NMR (176.1 MHz, $CDCl_3$) δ = 57.6 (s, 2C, *C*H^5), 122.0 (s, 4C, *C*H^{4,6}), 125.5 (s, 4C, *C*H^{2,8}), 127.9 (s, 4C, *C*H^{1,9}), 128.7 (s, 4C, *C*H^{3,7}), 131.2 (s, 4C, *C*H^{10,11}), 134.1 (s, 4C, *C*$^{9a, 11a}$), 140.2 (s, 4C, *C*^{4a,6a});

^{15}N-NMR (71 MHz, $CDCl_3$) δ = 44.7 (s);

endo-exo conformer
^{1}H-NMR (700 MHz, $CDCl_3$), δ = 3.04 (d, $^3J_{HH}$ = 12.0 Hz, 1H, N*H*), 3.74 (s, 1H, 5-C*H*^{5}), 5.00 (d, $^3J_{HH}$ = 12.0 Hz, 1H, C*H*$^{5'}$), 7.04 (s, 2H, C*H*^{10,11}), 7.07 (s, 2H, C*H*$^{10',11'}$), 7.21 (m, 2H, C*H*$^{4',6'}$), 7.23 (m, 2H, C*H*^{2,8}), 7.31 (m, 2H, C*H*^{1,9}), 7.33 (m, 2H, 2',8'-C*H*$^{2',8'}$), 7.35 (m, 2H, C*H*$^{3',7'}$), 7.43 (m, 2H, C*H*^{3,7}), 7.45 (m, 2H, C*H*$^{1',9'}$), 7.66 (m, 2H, C*H*^{4,6});

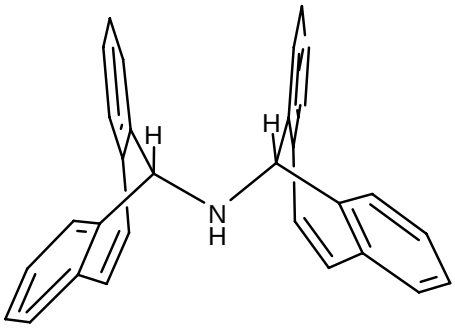
^{13}C{^{1}H}-NMR (176.1 MHz, $CDCl_3$) δ = 57.2 (s, 1C, *C*H^5), 65.74 (s, 1C, *C*H$^{5'}$), 122.6 (s, 2C, *C*H^{4,6}), 125.5 (s, 2C, *C*H^{2,8}), 127.1 (s, 2C, *C*H$^{2',8'}$), 127.6 (s, 2C, *C*H^{1,9}), 128.6 (s, 2C, *C*H^{3,7}), 128.6 (s, 2C, *C*H$^{3',7'}$), 129.6 (s, 2C, *C*H$^{4',6'}$), 130.1 (s, 2C, *C*H$^{1',9'}$), 130.7 (s, 2C, *C*H$^{10',11'}$), 130.8 (s, 2C, *C*H^{10,11}), 133.4 (s, 2C, *C*$^{9a',11a'}$), 133.9 (s, 2C, *C*^{9a,11a}), 140.0 (s, 2C, *C*H^{4a,6a}), 140.0 (s, 2C, *C*$^{4a',6a'}$);

^{15}N-NMR (71 MHz, $CDCl_3$) δ = 37.7 (s);

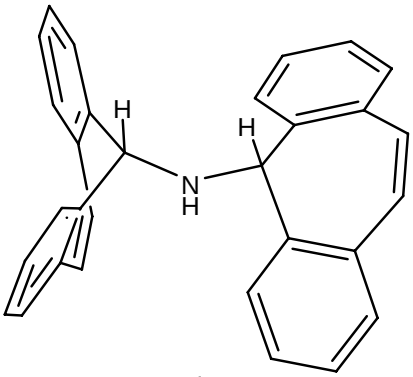
endo-endo conformer
^{1}H-NMR (700 MHz, $CDCl_3$), δ = 2.59 (s, 1H, N*H*), 4.66 (s, 2H, C*H*^{5}), 6.88 (s, 4H, C*H*^{10,11}), 7.14 (m, 4H, C*H*^{4,6}), 7.24 (m, 4H, C*H*^{2,8}), 7.27 (m, 4H, C*H*^{3,7}), 7.29 (m, 4H, C*H*^{1,9});

^{13}C{^{1}H}-NMR (176.1 MHz, $CDCl_3$) δ = 67.5 (s, 2C, *C*H^{5}), 126.6 (s, 4C, *C*H^{2,8}), 128.3 (s, 4C, *C*H^{3,7}), 129.3 (s, 4C, *C*H^{4,6}), 129.6 (s, 4C, *C*H^{1,9}), 130.4 (s, 4 C, *C*H^{10,11}), 133.7 (s, 4C, *C*^{9a,11a}), 139.8 (s, 4C, *C*^{4a,6a});

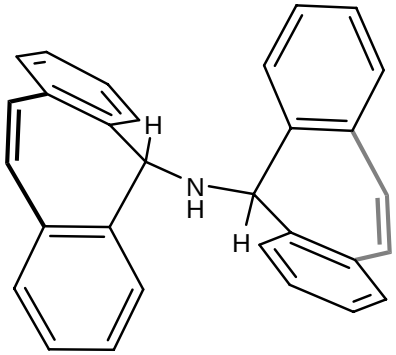
ATR IR (ν in cm^{-1}): 3018 m, 1596 w, 1484 m, 1452 m, 1438 w, 1344 w, 1289 w, 1266.98 w, 1242 w, 1125 w, 1109 w, 1077 w, 944 w, 902 w, 888 w, 875 w, 845 w, 824 w, 794 w, 765 m, 755.08 s, 737 m, 724 m, 697 m, 666 w, 642 w, 628 w;



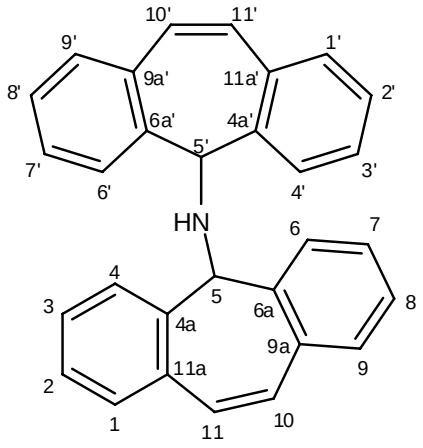
exo-exo



exo-endo

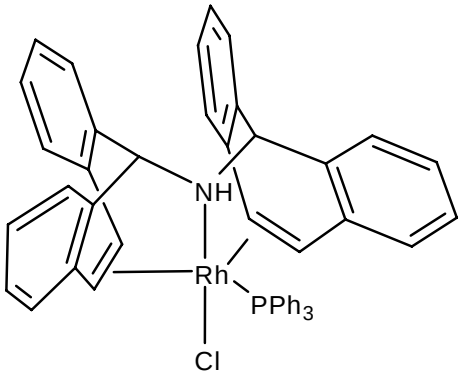


endo-endo



Scheme 41: The three conformers of trop$_2$NH: *exo-exo*, *exo-endo* and *endo-endo* conformer. Numbering of the atoms of trop$_2$NH used for assigning the NMR-signals. For the *exo-endo* conformer the numbers with the superscript prime are assigned to the carbon atoms of the *endo*-part of the molecule.

[Rh(Cl)(trop$_2$NH)(PPh$_3$)] (**2**) [41]



MF = $C_{48}H_{38}ClNPRh$

MW = 798.15 g/mol

MP >260 °C (dec.)
Air stable

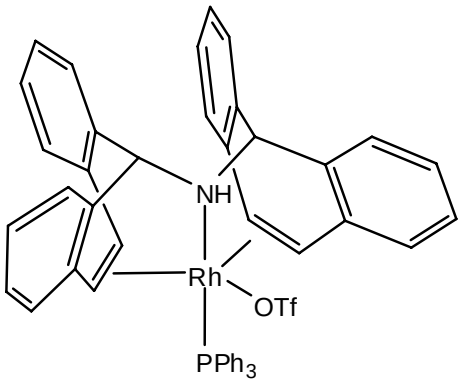
To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (500 mg, 0.467 mmol, 1 eq.) in DCM (40 mL) PPh$_3$ (260 mg, 0.99 mmol, 2.12 eq.) was added and a yellow solution formed immediately. Addition of *n*-hexane precipitated the product complex [RhCl(trop$_2$NH)(PPh$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 90%, 670 mg, 0.841 mmol.

^{1}H-NMR (300.1 MHz, $CDCl_3$): δ = 1.59 (br., 1H, N*H*), 3.85 (s, 2H, C*H*^{benzyl}), 5.27 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, C*H*^{ar}), 5.42 (dd, $^3J_{HH}$ = 9.4 Hz, $^3J_{PH}$ = 7.4 Hz, 2H, C*H*^{olefin}), 5.66 (ddd, $^3J_{HH}$ = 9.4 Hz, $^3J_{PH}$ = 5.8 Hz, $^2J_{RhH}$ = 1.3 Hz, 2H, C*H*^{olefin}), 6.53 (d, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*^{ar}), 6.63-6.97 (m, 14H, C*H*^{ar}), 7.09 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, C*H*^{ar}), 7.18 (d, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*^{ar}), 7.32-7.38 (m, 6H, C*H*^{ar}), 8.11-8.17 (m, 4H, C*H*^{ar});

^{31}P{^{1}H}-NMR (101.2 MHz, $CDCl_3$) δ = 7.7 (d, $^1J_{RhP}$ = 111 Hz);

ATR IR (ν in cm^{-1}): 3188 m, 3038 w, 1599 m, 1489 m, 1472 m, 1434 s, 1275 m, 1187 m, 1087 m, 970 w, 937 m, 746 s, 695 s.

[Rh(trop$_2$NH)(PPh$_3$)]OTf (**3**) [169]



MF = $C_{49}H_{38}F_3NO_3PRhS$

MW = 911.77 g/mol

MP >260 °C (dec.)
Air stable

[RhCl(trop$_2$NH)(PPh$_3$)] **2** (500 mg, 0.63 mmol, 1 eq.) and AgOTf (166 mg, 0.65 mmol, 1.03 eq.) were suspended in DCM (15 mL) and stirred for 12 h. The formed AgCl was removed by filtration over a plug of celite. Addition of *n*-hexane precipitated the orange product complex [Rh(trop$_2$NH)(PPh$_3$)]OTf. The mother liquor was decanted off and the product dried under vacuum. A second fraction was obtained from the mother liquor upon recrystallization from DCM/*n*-hexane. Yield: 95%, 542 mg, 0.6 mmol.

^{1}H-NMR (400.1 MHz, $CDCl_3$) δ = 4.91 (d, $^4J_{PH}$ =8.4 Hz, 2 H, C*H*^{benzyl}), 4.94 (ddd, $^3J_{HH}$ = 9.3 Hz, $^3J_{PH}$ = 2.7 Hz, $^2J_{RhH}$ = 1.8 Hz, 2 H, C*H*^{olefin}), 5.43 (ddd, $^3J_{HH}$ = 9.3 Hz, $^2J_{RhH}$ = 3.3 Hz, $^3J_{PH}$ = 2.8 Hz, 2 H, C*H*^{olefin}), 5.66 (dd, $^3J_{PH}$ = 5.8 Hz, $^2J_{RhH}$ = 2.1 Hz, 1 H, N*H*), 6.7-6.85 (m, 4H, C*H*^{ar}), 6.85-7.00 (m, 4H, C*H*^{ar}), 7.15-7.40 (m, 8H, C*H*^{ar}), 7.55-7.70 (m, 9H, C*H*^{ar}), 7.84 (m, 6H, C*H*^{ar});

^{13}C{^{1}H}-NMR (101.6 MHz, $CDCl_3$) δ = 72.7 (d, $^3J_{PC}$ = 1.4 Hz, 2 C, *C*H^{benzyl}), 74.0 (d, $^1J_{RhC}$ = 6.9 Hz, 2 C, *C*H^{olefin}), 74.2 (d, $^1J_{RhC}$ = 13.3 Hz, 2 C, *C*H^{olefin}), 119.8 (q, $^1J_{FC}$ = 321.1 Hz, C, *C*F_3), 126.4 (s, 2 C, *C*H^{ar}), 126.4 (s, 2 C, *C*H^{ar}), 127.0 (s, 2 C, *C*H^{ar}), 127.5 (s, 2 C, *C*H^{ar}), 128.2 (s, 2 C, *C*H^{ar}), 128.5 (s, 2 C, *C*H^{ar}), 128.7 (d, $^3J_{PC}$ = 10.1 Hz, 6 C, *C*H^{ar}), 129.0 (d, $^1J_{PC}$ = 46.4 Hz, 3 C, *C*^{quart}), 129.5 (s, 2 C, *C*H^{ar}), 129.6 (s, 2 C, *C*H^{ar}), 131.0 (d, $^4J_{PC}$ = 2.3 Hz, 3 C, *C*H^{ar}), 134.5 (d, $^2J_{PC}$ = 9.2 Hz, 6 C, *C*H^{ar}), 134.6 (s, 2 C, *C*^{quart}), 134.6 (s, 2 C, *C*^{quart}), 135.5 (d, $^2J_{RhC}$ = 1.8 Hz, 2 C, *C*^{quart}), 136.9 (s, 2 C, *C*^{quart});

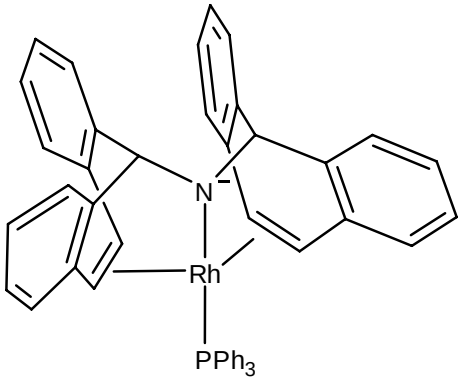
^{19}F-NMR (376.5 MHz, $CDCl_3$) δ = –78.9 (s);

^{31}P{^{1}H}-NMR (162.0 MHz, $CDCl_3$) δ = 40.6 (d, $^1J_{RhP}$ = 137.7 Hz);

^{1}H, ^{103}Rh-NMR (12.7 MHz, $CDCl_3$) δ = -6797 (d, $^1J_{RhP}$ = 138 Hz);

ATR IR (ν in cm^{-1}): 3149 s, 3052 w, 2889 w, 1602 w, 1482 s, 1437 w, 1299 s, 1217 s, 1158 s, 1024 s, 748 s, 700 s, 632 s.

[Rh(trop$_2$N)(PPh$_3$)] (**4**) [41]



MF = $C_{48}H_{37}NPRh$

MW = 761.69 g/mol

MP >260 °C (dec.)
Air sensitive

To a suspension of [RhCl(trop$_2$NH)(PPh$_3$)] **2** (150 mg, 0.188 mmol, 1 eq.) in THF (2 mL) potassium *tert*-butoxide (21.1 mg, 0.188 mmol, 1 eq.) was added. After 30 min of stirring toluene (1 mL) was added to the resulting deep green solution and the solvents were removed under vacuum. The dark green residue was dissolved in THF (2 * 3 mL) and filtered over Celite. The volume of the solution was reduced under vacuum to approximately 1 mL. Dark green micro-crystals of [Rh(trop$_2$N)(PPh$_3$)] grew upon layering of this solution with toluene (1 mL) and *n*-hexane (10 mL). Yield: 77%, 110 mg, 0.144 mmol.

^{1}H-NMR (400.1 MHz, [D$_8$] THF, 200 K): δ = 4.69 (ddd, $^3J_{HH}$ = 9.0 Hz, $^3J_{PH}$ = 6.2 Hz, $^2J_{RhH}$ = 1.2 Hz, 2H, C*H*^{olefin}), 4.92 (d, $^4J_{PH}$ = 13.5 Hz, 2H, C*H*^{benzyl}), 5.62 (ddd, $^3J_{HH}$ = 9.0 Hz, $^2J_{RhH}$ = 3.3 Hz, $^3J_{PH}$ = 2.9 Hz, 2H, C*H*^{olefin}), 6.57 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 6.67 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*^{ar}), 6.79 (d, $^3J_{HH}$ =7.6 Hz, 2H, C*H*^{ar}), 6.90 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 6.95 (d, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*^{ar}), 7.03 (m, 4H, C*H*^{ar}), 7.22 (d, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*^{ar}), 7.56 (m, 9H, C*H*^{ar}), 7.63 (m, 6H, C*H*^{ar});

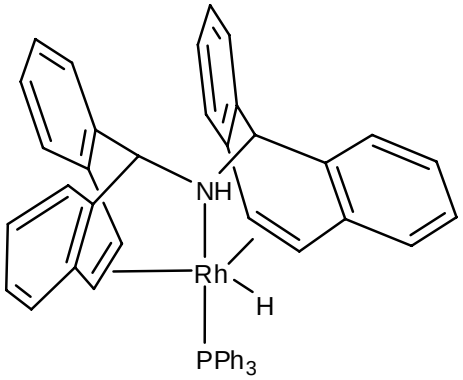
^{13}C{^{1}H}-NMR (100.6 MHz, [D$_8$] THF, 200 K): δ = 76.2 (d, $^1J_{RhC}$ = 6.7 Hz, 2C, *C*H^{olefin}), 82.3 (s, 2C, *C*H^{benzyl}), 84.5 (d, $^1J_{RhC}$ = 14.7 Hz, 2C, *C*H^{olefin}), 125.8 (s, 2C, *C*H^{ar}), 126.0 (s, 2C, *C*H^{ar}), 126.3 (s, 2C, *C*H^{ar}), 126.4 (s, 2C, *C*H^{ar}), 126.4 (s, 2C, *C*H^{ar}), 127.3 (s, 2C, *C*H^{ar}), 127.9 (s, 2C, *C*H^{ar}), 128.7 (s, 2C, *C*H^{ar}), 129.5 (d, $^3J_{RhC}$ = 8.6 Hz, 6C, *C*H^{ar}), 131.1 (s, 3C, *C*H^{ar}), 132.1 (d, $^1J_{RhP}$ = 35.5 Hz, 3C, *C*^{quart}), 135.5 (d, $^2J_{RhC}$ = 11.0 Hz, 6C, *C*H^{ar}), 136.6 (s, 2C, *C*^{quart}), 137.7 (s, 2C, *C*^{quart}), 143.7 (s, 2C, *C*^{quart}), 146.8 (s, 2C, *C*^{quart});

^{31}P{^{1}H}-NMR (162.0 MHz, [D$_8$] THF, 200K): δ = 40.8 (d, $^1J_{RhP}$ =124 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, [D$_8$] THF, 200K): δ = -7469 (d, $^1J_{RhP}$ =124 Hz);

UV/Vis (THF): λ_{max} (ε) = 301 (20000), 352 (10000), 438 (3000), 662 (1000).

[Rh(eq-H)(trop$_2$NH)(PPh$_3$)] (**5**) [41]



MF = $C_{48}H_{39}NPRh$

MW = 763.69 g/mol

Air sensitive

This hydride was prepared *in situ* in a Young-NMR tube in [D$_8$] THF. [Rh(trop$_2$NH)(Cl)(PPh$_3$)] (8 mg) was reacted with an small excess of KO*t*Bu. The resulting green solution was frozen in liquid nitrogen, evacuated and filled with 2 bar of dihydrogen gas. A yellow solution was obtained immediately in which the hydride is the only product. Under these conditions, the hydride remains stable at room temperature for about 30 minutes but subsequently isomerizes completely to the axial hydride upon standing.

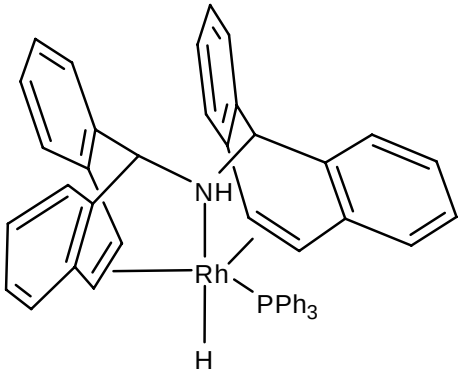
^{1}H-NMR (400.1 MHz, [D$_8$] THF, 230 K): δ = –8.15 (dd, $^1J_{RhH}$ = 23.0 Hz, $^2J_{PH}$ = 23.0 Hz, 1H, Rh*H*), 3.55 (d, $^3J_{HH}$ = 9.3 Hz, 2H, C*H*$_{olefin}$), 3.91 (dd, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 4.7 Hz, 2H, C*H*$_{olefin}$), 4.56 (d, $^4J_{PH}$ = 7.8 Hz, 2H, C*H*$_{benzyl}$), 5.56 (d, $^3J_{PH}$ = 4.9 Hz, 1H, N*H*), 6.1–7.9 (31H, C*H*$_{ar}$);

^{13}C{^{1}H}-NMR (100.6 MHz, [D$_8$] THF, 230 K): δ = 57.8 (d, $^1J_{RhC}$ = 8.0 Hz, 2C, *C*H$_{olefin}$), 60.6 (d, $^1J_{RhC}$ = 8.6 Hz, 2C, *C*H$_{olefin}$), 72.2 (s, 2C, *C*H$_{benzyl}$), 119.9–144.1 (*C*H$_{ar}$ and *C*$_{quart}$);

^{31}P{^{1}H}-NMR (162.0 MHz, [D$_8$] THF, 230 K): δ = 65.4 (d, $^1J_{RhP}$ = 144 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, [D$_8$] THF, 230K): δ = –187 (d, $^1J_{RhP}$ =144 Hz).

[Rh(ax.-H)(trop$_2$NH)(PPh$_3$)] (**5ax**) [41]



MF = $C_{48}H_{39}NPRh$

MW = 763.69 g/mol

MP >150 °C (dec.)
Air sensitive

The axial hydride **5ax** is the only product formed upon isomerisation of **5**. It was characterized by NMR spectroscopy and was isolated as pale yellow micro-crystals upon addition of *n*-hexane.

^{1}H-NMR (400.1 MHz, [D$_8$] THF, 230 K): δ = –21.37 (dd, $^1J_{RhH}$ = 17.4 Hz, $^2J_{PH}$ = 17.4 Hz, 1H, Rh*H*), 0.82 (s, 1H, N*H*), 4.21 (s, 2H, CH_{benzyl}), 4.40 (dd, $^3J_{HH}$ = 9.0 Hz, $^3J_{PH}$ = 7.8 Hz, 2H, CH_{olefin}), 5.15 (dd, $^3J_{HH}$ = 9.0, $^3J_{PH}$ = 5.1 Hz, 2H, CH_{olefin}), 6.1–7.9 (m, 31H, CH_{ar});

^{13}C{^{1}H}-NMR (100.6 MHz, [D$_8$] THF, 230 K): δ = 57.1 (dd, $^2J_{PC}$ = 14.7 Hz, $^1J_{RhC}$ = 9.8 Hz, 2C, *C*H$_{olefin}$), 61.2 (dd, $^1J_{RhC}$ = 8.6 Hz, $^2J_{PC}$ = 4.90 Hz, 2C, *C*H$_{olefin}$), 70.7 (s, 2C, *C*H$_{benzyl}$), 119.9–144.1 (*C*H$_{ar}$ and C_{quart});

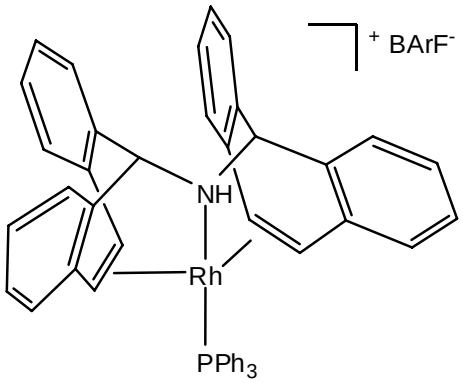
^{31}P{^{1}H}-NMR (162.0 MHz, [D$_8$] THF, 230 K): δ = 47.3 (d, $^1J_{RhP}$ = 138 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, [D$_8$] THF, 230K): δ = –38 (d, $^1J_{RhP}$ = 138 Hz);

ATR IR (υ cm^{-1}): 3229 w, 3017 m, 2852 w, 2028 m, 1598 m, 1573 w, 1487 m, 1467 s, 1434 m, 1091 w, 738 s.

Compounds of section II

[Rh(trop$_2$NH)(PPh$_3$)]BArF (**6**)



MF = $C_{80}H_{50}BF_{24}NPRh$

MW = 1625.91 g/mol

MP = 205 °C (dec.)
Air stable

[Rh(trop$_2$NH)(PPh$_3$)]OTf **3** (103 mg, 0.113 mmol, 1 eq.) and NaBArF (100 mg, 0.11 mmol, 1 eq.) were dissolved in DCM (10 mL). The solution was stirred for 2 h. The formed NaOTf was removed by filtration over celite. DCM was removed under reduced pressure, the product washed with pentane and dried under vacuum. Crystals could be obtained from $CDCl_3$/*n*-hexane. Yield: 90%, 165 mg, 0.10 mmol.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.61 (dd, $^3J_{PH}$ = 5.7 Hz, $^2J_{RhH}$ = 2.2 Hz, 1 H, N*H*), 4.91 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{PH}$ = 2.5 Hz, $^2J_{RhH}$ = 0.2 Hz, 2 H, C*H*^{olefin}), 5.25 (dd, $^3J_{RhH}$ = 1.4 Hz, $^4J_{PH}$ =7.3 Hz, 2 H, C*H*^{benzyl}), 6.40 (ddd, $^3J_{HH}$ = 8.9 Hz, $^2J_{RhH}$ = 3.7 Hz, $^3J_{PH}$ = 2.8 Hz, 2 H, C*H*^{olefin}), 6.98-7.07 (m, 6H, C*H*^{ar}), 7.08-7.14 (m, 4H, C*H*^{ar}), 7.29-7.36 (m, 4H, C*H*^{ar}), 7.37-7.42 (m, 2H, C*H*^{ar}), 7.52-7.57 (m, 4H, C*H*^{ar}), 7.60-7.82 (m, 23H, C*H*^{ar}),

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 73.8 (s, 2 C, *C*H^{benzyl}), 81.7 (d, $^1J_{RhC}$ = 7.3 Hz, 2 C, *C*H^{olefin}), 91.4 (d, $^1J_{RhC}$ = 12.5 Hz, 2 C, *C*H^{olefin}), 117.8 (q, $^3J_{FC}$ = 4.1 Hz, 4 C, *C*H^{ar}), 125.0 (q, $^1J_{FC}$ = 272.7 Hz, 8C, *C*F$_3$) 127.3 (s, 2 C, *C*H^{ar}), 127.5 (d, $^1J_{PC}$ = 49.1 Hz, 3 C, *C*^{quart}), 128.3 (s, 2 C, *C*H^{ar}), 129.3 (qq, $^2J_{FC}$ = 31.3 Hz $^4J_{FC}$ = 2.7 Hz, 8C, *C*^{quart}), 129.6 (s, 2 C, *C*H^{ar}), 129.7 (s, 2 C, *C*H^{ar}), 129.7 (s, 2 C, *C*H^{ar}), 129.8 (s, 2 C, *C*H^{ar}), 129.9 (d, $^3J_{PC}$ = 10.1 Hz, 6 C, *C*H^{ar}), 130.0 (s, 2 C, *C*H^{ar}), 130.7 (s, 2 C, *C*H^{ar}), 132.8 (d, $^4J_{PC}$ = 2.5 Hz, 3 C, *C*H^{ar}), 134.1 (d, $^2J_{RhC}$ = 0.9 Hz, 2 C, *C*^{quart}), 134.3 (s, 2 C, *C*^{quart}), 134.6 (d, $^2J_{PC}$ = 9.6 Hz, 6 C, *C*H^{ar}), 135.2 (s br, 8C, *C*H^{ar}), 135.6 (s, 2 C, *C*^{quart}), 136.2 (d, $^2J_{RhC}$ = 2.3 Hz, 2 C, *C*^{quart}), 162.1 (q, $^1J_{BC}$ = 49.8 Hz, 4C, C^{quart});

^{19}F-NMR (183 MHz, $CDCl_3$): δ = - 62.3 (s);

^{31}P{^{1}H}-NMR (162.0 MHz, $CDCl_3$): δ = 40.3 (d, $^1J_{RhP}$ = 143.5 Hz);

^{1}H, ^{103}Rh-NMR (15.8 MHz, $CDCl_3$): δ =-7256 (d, $^1J_{RhP}$ = 144 Hz);

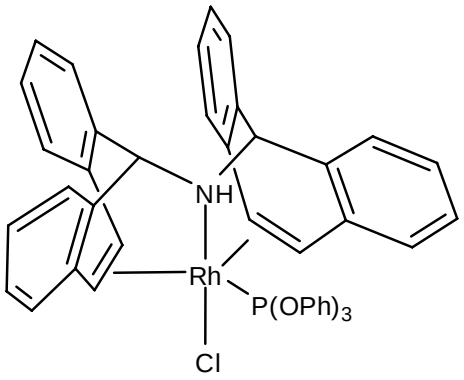
ATR IR (ν in cm^{-1}): 3244 w, 3073 w, 3015 w, 1610 m, 1490 m, 1435 m, 1352 s, 1275 s, 1154 s, 1122 s, 888 m, 837 m, 822 w, 765 m, 748 m, 714 m, 692 m, 681 m, 667 m;

[Rh(Cl)(trop$_2$NH)(P(OPh)$_3$)]

MF = $C_{50}H_{44}ClNO_3PRh$

MW = 875.18 g/mol

MP > 240 °C
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (100 mg, 0.09 mmol, 1 eq.) in DCM (4 mL) P(OPh)$_3$ (80 mg, 0.26 mmol, 2.8 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [RhCl(trop$_2$NH)(P(OPh)$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 95%, 150 mg, 0.177 mmol.

^{1}H-NMR (300.1 MHz, $CDCl_3$): δ = 3.85 (br., 1H, N*H*), 4.32 (s, 2H, C*H*^{benzyl}), 5.30-5.55 (m, 4H, C*H*^{olefin}), 6.60-7.30 (m, 31H, C*H*^{ar});

^{31}P{^{1}H}-NMR (121.5 MHz, $CDCl_3$) δ = 115.5 (d, $^1J_{RhP}$ = 199.0 Hz);

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 66.5 (dd, $^1J_{RhC}$ = 8.0 Hz, $^2J_{PC}$ = 8.0 Hz, 2C, *C*H^{olefin}) 71.1 (dd, $^1J_{RhC}$ = 8.4 Hz, $^2J_{PC}$ = 30.9 Hz, 2C, *C*H^{olefin}), 72.8 (s, 2C, *C*H^{benzyl}), 121.4 (d, $^3J_{PC}$ = 3.2 Hz, 6C, *C*H^{ar}), 124.4 (d, $^5J_{PC}$ = 0.6 Hz, 3C, *C*H^{ar}), 124.5 (d, *J* = 3.5 Hz, 2C, *C*H^{ar}), 125.2 (s, 2C, *C*H^{ar}), 126.4 (s, 2C, *C*H^{ar}), 128.2 (s, 2C, *C*H^{ar}), 128.3 (d, *J* = 8.7 Hz, 2C, *C*H^{ar}), 128.4 (s, 2C, *C*H^{ar}), 128.9 (d, *J* = 3.4 Hz, 2C, *C*H^{ar}), 129.0 (d, *J* = 2.4 Hz, 2C, *C*H^{ar}), 129.2 (s, 6C, *C*H^{ar}), 132.3 (d, *J* = 4.1 Hz, 2C, *C*^{quart}), 135.2 (d, *J* = 8.3 Hz, 2C, *C*^{quart}), 135.6 (s, 2C, *C*^{quart}), 140.5 (d, *J* = 5.2 Hz, 2C, *C*^{quart}) 151.5 (d, $^2J_{PC}$ = 11.6 Hz, 3C, *C*^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6636 (d, $^1J_{RhP}$ = 199 Hz);

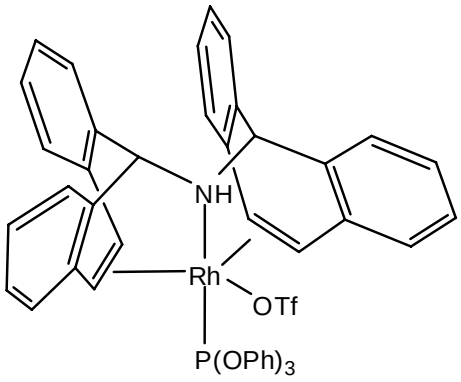
ATR IR (ν in cm^{-1}): 3221 w, 3017 w, 1585 m, 1487 s, 1472 m, 1419 m, 1290 m, 1271 m, 1232 m, 1179 m, 1152 m, 1109 m, 1069 m, 924 m, 906 m, 882 s, 773 m, 686 s;

[Rh(trop$_2$NH)(P(OPh)$_3$)]OTf (**7**)

MF = $C_{49}H_{38}F_3NO_6PRhS$

MW = 959.77 g/mol

MP > 240 °C
Air stable



Preparation is analogous to **3**. [RhCl(trop$_2$NH)(P(OPh)$_3$)] (150 mg, 0.18 mmol, 1 eq.) and AgOTf (47 mg, 0.18 mmol, 1.03 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. DCM (5 mL) was added and the resulting suspension was stirred for 12 h. The solution was filtered over a plug of celite. DCM was removed under reduced pressure and the resulting red solid recrystallized from acetone/*n*-hexane and dried under vacuum. Yield: 95%, 162 mg, 0.169 mmol.

Crystals suitable for X-Ray diffraction were obtained by layering a solution of the complex in DCM with *n*-hexane, but could also be obtained from THF/*n*-hexane and from acetone/*n*-hexane.

^{1}H-NMR (300.1 MHz, $CDCl_3$): δ = 5.09 (dd, $^3J_{PH}$ = 7.3 Hz, $^2J_{RhH}$ = 1.0 Hz, 1H, N*H*), 5.32 (dd, $^4J_{PH}$ = 13.0 Hz, $^2J_{RhH}$ = 0.8 Hz, 2H, C*H*^{benzyl}), 5.55 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{PH}$ = 1.2 Hz, 2H, C*H*^{olefin}), 6.63 (ddd, $^3J_{HH}$ = 8.6 Hz, $^2J_{RhH}$ = 3.8 Hz, $^3J_{PH}$ = 2.9 Hz, 2H, C*H*^{olefin}) 6.8-7.5 (m, 31H, C*H*^{ar});

^{31}P{^{1}H}-NMR (121.5 MHz, $CDCl_3$): δ = 105.7 (d, $^1J_{RhP}$ = 227.0 Hz);

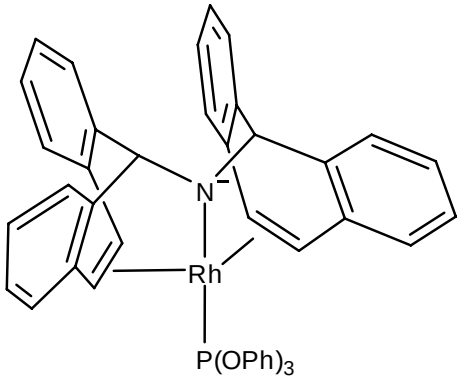
^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 72.0 (s, 2C, *C*H^{benzyl}), 75.1 (s, br, 2C, *C*H^{olefin}), 79.8 (d, $^1J_{RhC}$ = 11.7 Hz, 2C, *C*H^{olefin}), 120.0 (d, $^3J_{PC}$ = 4.6 Hz, 6C, *C*H^{ar}), 120.3 (q, $^1J_{FC}$ = 321.1 Hz, C, *C*F$_3$), 126.0 (s, 3C, *C*H^{ar}), 127.2 (s, 2C, *C*H^{ar}), 127.9 (s, 2C, CH^{ar}), 128.1 (s, 2C, *C*H^{ar}), 128.3 (s, 2C, *C*H^{ar}), 128.4 (s, 4C, *C*H^{ar}), 129.5 (s, 2C, *C*H^{ar}), 130.3 (s, 2C, *C*H^{ar}), 130.5 (s, 6C, *C*H^{ar}), 134.9 (d, *J* = 2.1 Hz, 2C, *C*^{quart}), 135.0 (s, 2C, *C*^{quart}), 135.1(d, *J* = 0.5 Hz, 2C, *C*^{quart}) 135.3(s, 2C, *C*^{quart}), 151.1 (d, $^2J_{PC}$ = 10.6 Hz, 3C, *C*^{quart});

^{19}F NMR (376.5 MHz, $CDCl_3$) δ = –78.9 (s);

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -7178 (d, $^1J_{RhP}$ =227.0 Hz);

ATR IR (ν in cm^{-1}): 3188 m, 3038 w, 1599 m, 1489 m, 1472 m, 1434 s, 1275 m, 1187 m, 1087 m, 970 w, 937 m, 746 s, 695 s.

[$Rh(trop_2N)(P(OPh)_3]$ (**8**)



MF = $C_{48}H_{37}NO_3PRh$

MW = 809.69 g/mol

Air sensitive

The highly air-sensitive amide was prepared *in situ* in a young-NMR tube in [D_8] THF. [$Rh(trop_2NH)(P(OPh)_3)$]OTf **7** (10 mg, 0.01 mmol, 1 eq.) was deprotonated by addition of LiHMDS (2 mg, 0.01 mmol, 1.1 eq.) to give a dark green solution containing a small portion (>3%) of an unknown byproduct.

^{1}H-NMR (300.1 MHz, [D_8] THF, 298 K): δ = 4.85 (d, $^4J_{PH}$ = 23.0 Hz, 2H, CH^{benzyl}), 5.94 (m, 4H, CH^{olefin}), 6.75-7.4 (m, 31H, CH^{ar});

^{31}P{^{1}H}-NMR (121.5 MHz, [D_8] THF, 298 K): δ = 120.0 (d, $^1J_{RhP}$ = 206.0 Hz);

^{13}C{^{1}H}-NMR (75.5 MHz, [D_8] THF, 298 K): δ = 81.3 (d, $^1J_{RhC}$ = 10.5 Hz, 4C, CH^{olefin}) 82.2 (d, $^3J_{PC}$ = 2.4 Hz 2C, CH^{benzyl}), 120.4 (d, $^3J_{PC}$ = 5.0 Hz, 6C, CH^{ar}), 124.5 (d, $^5J_{PC}$ = 0.5 Hz 3C, CH^{ar}), 125.3 (s, 4C, CH^{ar}), 125.7 (s, 4C, CH^{ar}), 126.6 (s, 4C, CH^{ar}), 126.8 (s, 4C, CH^{ar}), 129.7 (s, 6C, CH^{ar}), 135.4 (d, $^2J_{RhC}$ = 1.5 Hz, 4C, C^{quart}), 144.9 (s, 4C, C^{quart}), 151.8 (d, $^2J_{PC}$ = 7.0 Hz, 3C, C^{quart});

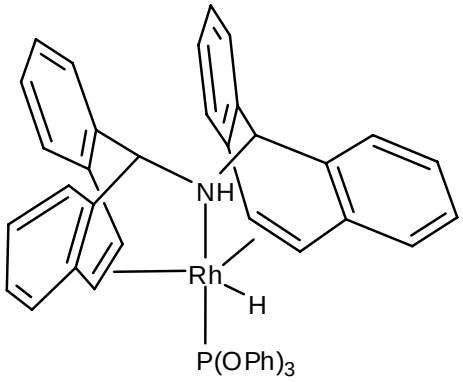
^{1}H, ^{103}Rh-NMR (12.6 MHz, [D_8] THF, 298 K): δ = -7731 (d, $^1J_{RhP}$ = 206 Hz);

[Rh(eq-H)(trop$_2$NH)(P(OPh)$_3$)] (**9**) and
[Rh(ax-H)(trop$_2$NH)(P(OPh)$_3$)] (**9ax**)

MF = $C_{48}H_{39}NO_3PRh$

MW = 811.71 g/mol

Air sensitive



A previously prepared solution of [Rh(trop$_2$N)(P(OPh)$_3$)] **8** in [D$_8$] THF was frozen in liquid nitrogen and filled with 2 bar H_2. A yellow solution was obtained after warming to room temperature. The equatorial hydride is the main product (90%). As byproduct the axial hydride is observed (5-10%).

Alternatively ethanol (10 µl, approx. 3 eq.) was added to a solution of Rh(trop$_2$N)(P(OPh)$_3$)] (10 mg) in [D$_8$] THF to give the equatorial hydride and byproducts in about the same ratio. 0.5 eq of the added ethanol is converted to ethyl acetate.

^{1}H-NMR (400.1 MHz, [D$_8$] THF): δ = -7.79 (dd, $^1J_{RhH}$ = 24.4 Hz, $^2J_{PH}$ = 6.9 Hz, 1H, Rh*H*) 4.33 (d, $^3J_{HH}$ = 9.4 Hz, 2H, C*H*^{olefin}), 4.44 (d, $^4J_{PH}$ = 12.8 Hz, 2H, C*H*^{benzyl}), 4.89 (dd, $^3J_{HH}$ = 9.4 Hz, $^2J_{RhH}$ = 2.7 Hz, 2H, C*H*^{olefin}) 5.05 (d, $^3J_{PH}$ = 8.6 Hz, 1H, N*H*), 6.4-7.5 (m, 31H, C*H*^{ar});

^{31}P{^{1}H}-NMR (162.0 MHz, [D$_8$] THF): δ = 120.0 (d, $^1J_{RhP}$ = 244 Hz);

^{13}C{^{1}H}-NMR (75.5 MHz, [D$_8$] THF): δ =55.3 (d, $^1J_{RhC}$ = 7.7 Hz, 2C, *C*H^{olefin}), 58.8 (d, $^1J_{RhC}$ = 8.2 Hz, 2C, *C*H^{olefin}), 72.3 (s, 2C, *C*H^{benzyl}), 119.9–152.5 (*C*H^{ar} and *C*^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, [D$_8$] THF): δ = -8565 (d, $^1J_{RhP}$ = 244 Hz

[Rh(ax-H)(trop$_2$NH)(P(OPh)$_3$)]:

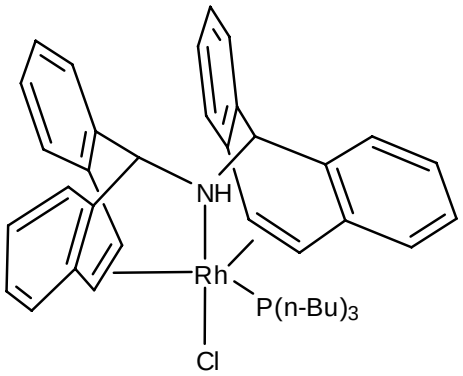
^{1}H-NMR (400.1 MHz, [D$_8$] THF): δ = -7.23 (dd, $^1J_{RhH}$ = 31.1 Hz, $^2J_{PH}$ = 12.0 Hz, 1H, Rh*H*) 4.15 (d, $^3J_{HH}$ = 8.3 Hz, 2H, C*H*^{olefin}), 4.32 (s, 2H, C*H*^{benzyl}), 4.77 (m, 2H, C*H*^{olefin}) 5.34 (br, 1H, N*H*), 6.4-7.5 (m, 31H, C*H*^{ar});

^{31}P{^{1}H}-NMR (162.0 MHz, [D$_8$] THF): δ = 98.4 (d, $^1J_{RhP}$ = 214 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, [D$_8$] THF): δ = -8541 (d, $^1J_{RhP}$ = 214 Hz);

Compounds of section III

[Rh(Cl)(trop$_2$NH)(P(*n*Bu)$_3$)] (**10**)



MF = $C_{42}H_{50}ClNPRh$

MW = 738.19 g/mol

MP = 209-211 °C (dec)

Air stable

Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (200 mg, 0.16 mmol, 1 eq.) in DCM (3 mL) tris *n*-butylphosphine (94 mg, 0.47 mmol, 2.5 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH) (P(*n*-Bu)$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 85%, 234 mg, 0.32 mmol.

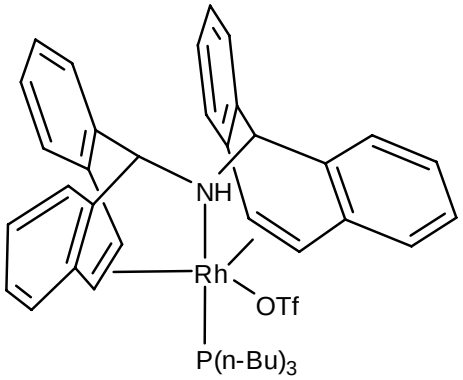
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.2 Hz, 9H, C*H*$_3$), 1.00 (s, 6H, C*H*$_2$), 1.27 (m, 6H, C*H*$_2$), 1.42 (m, 6H, C*H*$_2$), 2.89 (s, 1H, N*H*), 4.32 (s, 2H, C*H*^{benzyl}), 4.96 (t, *J* = 7.5 Hz, 2H, C*H*^{olefin}), 5.22 (t, *J* = 9.0 Hz, 2H, C*H*^{olefin}), 6.67 (d, *J* = 7.2 Hz, 2H, C*H*^{ar}), 6.77-6.95 (m, 4H, C*H*^{ar}), 7.02 (d, *J* = 4.14 Hz, 4H, C*H*^{ar}), 7.07-7.30 (m, 4H, C*H*^{ar}), 7.54 (d, *J* = 7.54 Hz, 2H, C*H*^{ar});

^{13}C{^{1}H}-NMR (63 MHz, $CDCl_3$): δ = 13.8 (s, 3C, *C*H$_3$), 20.4 (d, $^1J_{PC}$ = 12.8 Hz, 3C, *C*H$_2$), 24.6 (d, $^2J_{PC}$ = 10.1 Hz, 3C, *C*H$_2$), 25.1 (d, $^3J_{PC}$ = 3.7 Hz, 3C, *C*H$_2$), 63.7 (dd, *J* = 8.5 Hz, *J* = 5.8 Hz, 2C, *C*H^{olefin}), 66.8 (dd, *J* = 18.6 Hz, *J* = 8.8 Hz, 2C, *C*H^{olefin}), 72.8 (s, 2C, *C*H^{benzyl}), 123.8 (d, *J* =1.8 Hz, 2C, *C*H^{ar}), 124.7 (s, 2C, *C*H^{ar}), 126.8 (s, 2C, *C*H^{ar}), 127.8 (s, 2C, *C*H^{ar}), 128.1 (d, *J* = 4.9 Hz, 2C, *C*H^{ar}), 128.6 (s, 2C, *C*H^{ar}), 128.8 (d, *J* = 1.8 Hz, 2C, *C*H^{ar}), 129.1 (s, 2C, *C*H^{ar}), 131.6 (d, *J* = 2.1 Hz, 2C, *C*^{quart}), 135.5 (s, 2C, *C*^{quart}), 136.3 (d, *J* = 5.2 Hz, 2C, *C*^{quart}), 141.9 (d, *J* = 4.0 Hz, 2C, *C*^{quart});

^{31}P{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = -13.0 (d, $^1J_{RhP}$ = 116.3 Hz);

ATR IR (ν in cm^{-1}): 3013 w, 2956 w, 2928 w, 2862 w, 1600 m 1488 m, 1467 br, 1398 w, 1377 w, 1304 w, 1273 w, 1255 w, 1219 w, 1192 br, 1158 w, 1124 w, 1091 w, 1058 w, 1043 w, 1021 w, 996 w, 964 br, 937 w, 903 w, 873 w, 826 w, 780 w, 747 s, 729 m, 670 w.

[Rh(trop$_2$NH)(P(*n*Bu)$_3$)]OTf (**11**)



MF = $C_{43}H_{50}F_3NO_3PRhS$

MW = 851.80 g/mol

MP = 135-140 °C (dec)

Slightly air sensitive

[Rh(Cl)(trop$_2$NH)(P(*n*-Bu)$_3$)] **10** (265 mg, 0.36 mmol, 1 eq.) and AgOTf (97 mg, 0.36 mmol, 1.05 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. THF (5 mL) was added and the resulting suspension was stirred overnight. The THF was removed under reduced pressure, the complex dissolved in DCM and filtered over celite. The DCM was removed under reduced pressure and the red solid recrystallized from THF/*n*-hexane and dried under vacuum. Yield: 76%, 232 mg, 0.27 mmol.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.11 (t, $^3J_{HH}$ = 7.1 Hz, 9H, CH_3), 1.62 (m, 12 H, CH_2), 1.86 (m, 6H, CH_2), 4.87 (d, $^4J_{PH}$ = 7.6 Hz, 2H, CH^{benzyl}), 5.01 (d, $^3J_{HH}$ =8.8 Hz, 2H, CH^{olefin}), 5.17 (d, $^3J_{PH}$ = 4.4 Hz, 1H, N*H*), 5.65 (d, *J* = 8.8 Hz, 2H, CH^{olefin}), 6.80-6.95 (m, 8H, CH^{ar}), 7.15-7.30 (m, 6H, CH^{ar}), 7.35-7.40 (m, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 13.9 (s, 3C, *C*H$_3$), 21.2 (d, $^1J_{PC}$ = 27.1 Hz, 3C, *C*H$_2$), 24.6 (d, $^2J_{PC}$ = 12.5 Hz, 3C, *C*H$_2$), 25.9 (d, $^3J_{PC}$ = 3.0 Hz, 3C, *C*H$_2$), 69.4 (d, $^1J_{RhC}$ = 12.8 Hz, 2C, *C*H^{olefin}), 70.2 (d, $^1J_{RhC}$ = 7.0 Hz, 2C, *C*H^{olefin}), 72.5 (s, 2C, *C*H^{benzyl}), 119.7 (d, *J* = 320.7 Hz, 1C, *C*F$_3$), 126.2 (s, 2C, *C*H^{ar}), 126.7 (s, 2C, *C*H^{ar}), 126.7 (s, 2C, *C*H^{ar}), 127.4 (s, 2C, *C*H^{ar}), 128.4 (s, 2C, *C*H^{ar}), 128.5 (s, 2C, *C*H^{ar}), 129.5 (s, 2C. *C*H^{ar}), 129.7 (s, 2C, *C*H^{ar}), 134.5 (s, 2C, *C*^{quart}) 134.7 (s, 2C, *C*^{quart}) 135.8 (s, 2C, *C*^{quart}) 137.5 (s, 2C, *C*^{quart});

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ = 21.5 (d, $^1J_{RhP}$ = 133.3 Hz);

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = -78.0 (s, CF_3);

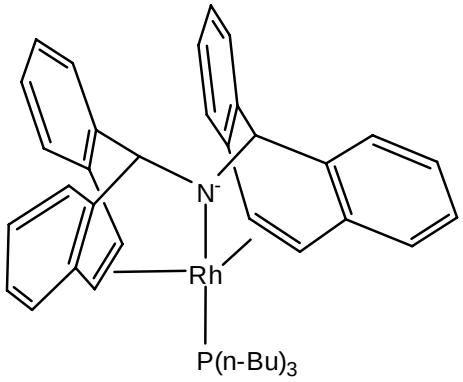
^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6886 (d, J_{RhP} = 133.3 Hz);

ATR IR (ν in cm^{-1}): 3190 w, 3049 w, 2934 w, 2870 w, 2030 br, 1977 br, 1600 w, 1493 br, 1425 w, 1380 w, 1341 w, 1291 w, 1261 s, 1238 w, 1223 m, 1148 br, 1095 w, 1082 w, 1048 w, 1028 s, 994 br, 909 m, 890 m, 822 m, 785 m, 770 w 748 s, 727 w, 699 w, 665 w, 645 w, 636 s.

[Rh(trop$_2$N)(P(*n*-Bu)$_3$] (**12**)

MF = $C_{42}H_{49}NPRh$

MW = 701.72 g/mol



Air sensitive

The highly air-sensitive amide was prepared *in situ* in a young-NMR tube in [D_8] THF. [Rh(Cl)(trop$_2$NH)(P(*n*-Bu)$_3$)] **10** (10 mg, 0.03 mmol, 1 eq.) was deprotonated by addition of KO*t*Bu (3.3 mg, 0.03 mmol, 1.1 eq.) to give a dark green solution. The product decomposes on standing at RT in 2 h to about 10% side product with two phosphines in axial and equatorial position but is stable at low temperatures.

^{1}H-NMR (400 MHz, [D_8] THF, 200 K): δ = 1.04 (br s, 9H, CH_3), 1.55 (br s, 12H, CH_2), 1.86 (s, 6H, CH_2), 4.84 (d, $^4J_{PC}$ = 13.1 Hz, 2H, CH^{benzyl}), 5.12 (t, J = 6.4 Hz, 2H, CH^{olefin}), 5.90 (d, J = 7.9 Hz, 2H, CH^{olefin}), 6.62 (t, J = 7.3 Hz, 4H, CH^{ar}), 6.71 (t, J = 7.2 Hz, 4H, CH^{ar}), 6.88 (d, J = 7.31 Hz, 4H, CH^{ar}), 6.95-7.09 (m, 4H, CH^{ar}), 7.12-7.24 (m, 2H, CH^{ar}), 7.24-7.32 (m, 2H. CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, [D_8] THF, 200 K): δ = 14.2 (s, 3C, CH$_3$), 21.6 (d, $^1J_{PC}$ = 21.2 Hz, 3C, CH$_2$), 25.3 (s, 3C, CH$_2$), 26.9 (s, 3C, CH$_2$), 73.2 (d, $^1J_{RhC}$ = 6.1 Hz, 2C, CH^{olefin}), 80.9 (d, $^1J_{RhC}$ = 15.2 Hz, 2C, CH^{olefin}), 81.5 (s, 2C, CH^{benzyl}), 125.2 (s, 2C, CH^{ar}), 125.4 (s, 2C, CH^{ar}), 125.6 (s, 2C, CH^{ar}), 125.9 (s, 4C, CH^{ar}), 126.9 (s, 2C, CH^{ar}) 127.4 (s, 2C, CH^{ar}), 128.3 (s, 2C, CH^{ar}), 136.8 (s, 2C, C^{quart}), 138.0 (s, 2C, C^{quart}), 143.3 (s, 2C, C^{quart}), 146.4 (s, 2C, C^{quart});

^{31}P{^{1}H}-NMR (162 MHz, [D_8] THF, 200 K): δ =11.9 (d, $^1J_{RhP}$ = 120.9 Hz)

^{1}H, ^{103}Rh-NMR (12.6 MHz, [D_8] THF, 200 K): δ = -7385 (d, $^1J_{RhP}$ = 206 Hz);

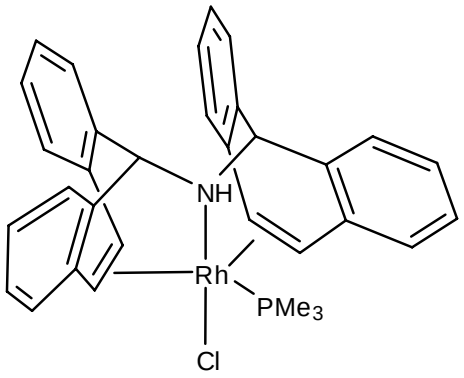
Side product: ^{31}P{^{1}H}-NMR (162 MHz, [D_8] THF, 298 K): δ = -9.4 (dd, $^1J_{RhP}$ = 122.9 Hz, $^2J_{PP}$ = 35.7 Hz), 0.6 (dd, $^1J_{RhP}$ = 99.8 Hz, $^2J_{PP}$ = 33.7 Hz);

[Rh(Cl)(trop$_2$NH)(PMe$_3$)]

MF = $C_{33}H_{32}ClNPRh$

MW = 611.94 g/mol

MP > 220 °C (dec)
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (290 mg, 0.27 mmol, 1 eq.) in 4 mL THF a small excess of a 1 M PMe$_3$ solution in THF (600 µl, 0.6 mmol, 2.1 eq.) was added, and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(PMe$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 94%, 310 mg, 0.51 mmol.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.96 (d, $^2J_{PH}$ = 8.1 Hz, 9H, C*H*$_3$), 2.50 (s, 1H, N*H*), 4.30 (s, 2H, C*H*^{benzyl}), 4.83 (t, *J* = 8.6 Hz, 2H, C*H*^{olefin}), 5.18 (t, *J* = 7.5 Hz, 2H, C*H*^{olefin}), 6.68 (d, $^3J_{HH}$ = 7.1 Hz, 2H, C*H*^{ar}), 6.80-6.90 (m, 4H, C*H*^{ar}), 7.00-7.15 (m, 6H, C*H*^{ar}), 7.17-7.30 (m, 6H, C*H*^{ar}), 7.54 (d, *J* = 7.8 Hz, 2H, C*H*^{ar});

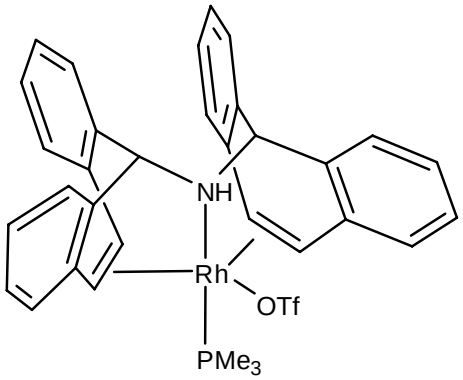
^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 11.4 (d, $^1J_{PC}$ = 18.3 Hz, 3C, *C*H$_3$), 65.0 (dd, *J* = 8.7 Hz, *J* = 5.6 Hz, 2C, *C*H^{olefin}), 65.9 (dd, *J* = 19.8 Hz, *J* = 8.8 Hz, 2C, *C*H^{olefin}), 72.9 (s, 2C, *C*H^{benzyl}), 123.7 (d, *J* = 2.1 Hz, 2C, *C*H^{ar}), 124.8 (s, 2C, *C*H^{ar}), 126.6 (s, 2C, *C*H^{ar}), 127.9 (d, *J* = 1.2 Hz, 2C *C*H^{ar}), 128.0 (d, *J* = 5.2 Hz, 2C, *C*H^{ar}), 128.6 (s, 2C, *C*H^{ar}), 129.0 (d, *J* = 2.1 Hz, 2C, *C*H^{ar}), 129.2 (d, *J* = 1.5 Hz, 2C, *C*H^{ar}), 131.3 (dd, *J* = 2.7 Hz, *J* = 0.9 Hz, 2C, *C*^{quart}), 135.5 (s, 2C, *C*^{quart}), 136.3 (dd, *J* = 5.6 Hz, *J* = 0.8 Hz, 2C, *C*^{quart}), 141.5 (dd, *J* = 4.7 Hz, *J* = 1.1 Hz, 2C, *C*^{quart});

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ = -22.8 (d, $^1J_{RhP}$ = 123.0 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6603 (d, $^1J_{RhP}$ = 123.0 Hz);

ATR IR (ν in cm^{-1}): 3039 w, 2908 w, 1598 m, 1487 m, 1467 m, 1433 w, 1396 w, 1298 w, 1280 m, 1250 w, 1214 w, 1192 w, 1160 m, 1124 m, 1086 m, 1044 w, 944 s, 874 m, 839 m, 780 m, 759 m, 740 s, 730 s, 688 m, 669 m, 646 m;

[Rh(trop$_2$NH)(PMe$_3$)]OTf (**13**)



MF = $C_{34}H_{32}F_3NO_3PRhS$

MW = 725.56 g/mol

MP = 203-205 °C (dec)
Slightly air sensitive

[Rh(Cl)(trop$_2$NH)(PMe$_3$)] (243 mg, 0.40 mmol, 1 eq.) and AgOTf (102 mg, 0.40 mmol, 1 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. THF (5 mL) was added and the resulting suspension was stirred overnight. The THF was removed under reduced pressure, the complex dissolved in DCM and filtered over celite. The DCM was removed under reduced pressure and the red solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 65%, 178 mg, 0.25 mmol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.53 (d, $^2J_{PH}$ = 10.0 Hz, 9H, CH_3), 4.80 (d, $^3J_{PH}$ = 6.1 Hz, 1H, NH), 4.86 (d, $^4J_{PH}$ = 8.2 Hz, 2H, CH^{benzyl}), 5.03 (d, $^3J_{HH}$ = 9.1 Hz, 2H, CH^{olefin}), 5.56 (dt, *J* = 9.14 Hz, *J* = 3.05 Hz, 2H, CH^{olefin}), 6.80-6.87 (m, 4H, CH^{ar}), 6.90-6.98 (m, 4H, CH^{ar}), 7.15-7.20 (m, 2H, CH^{ar}), 7.22 – 7.30 (m, 4H, CH^{ar}), 7.44 (d, *J* = 7.61 Hz, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 12.9 (d, $^1J_{PH}$ = 30.6 Hz, 3C, CH_3), 69.9 (d, $^1J_{RhC}$ = 13.2 Hz, 2C, CH^{olefin}), 70.9 (d, $^1J_{RhC}$ = 7.3 Hz, 2C, CH^{olefin}), 72.8 (d, $^3J_{PC}$ = 1.8 Hz, 2C, CH^{benzyl}), 120.3 (q, $^1J_{FC}$ = 321.1 Hz, C, CF_3), 126.7 (s, 2C, CH^{ar}), 127.1 (s, 2C, CH^{ar}), 127.5 (s, 2C, CH^{ar}), 127.7 (s, 2C, CH^{ar}), 128.8 (s, 2C, CH^{ar}), 128.9 (s, 2C, CH^{ar}), 130.0 (s, 2C, CH^{ar}), 130.4 (s, 2C, CH^{ar}), 135.0 (s, 2C, C^{quart}), 135.0 (s, 2C, C^{quart}), 136.0 (d, *J* = 2.3 Hz, 2C, C^{quart}), 137.9 (s, 2C, C^{quart});

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = -78.1 (s, SCF_3);

^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$): δ = 8.5 (d, $^1J_{RhP}$ = 134.6 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6950 (d, $^1J_{RhP}$ = 134.6 Hz);

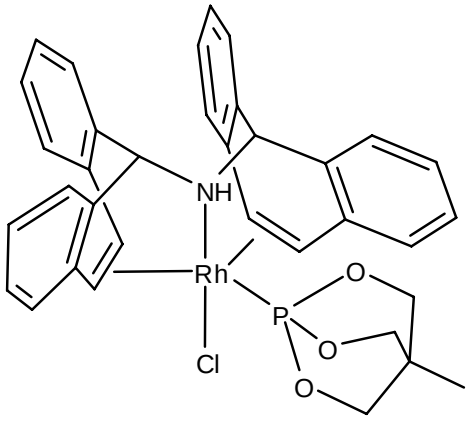
ATR IR (ν in cm^{-1}): 3159 w, 1600 w, 1491 m, 1473 m, 1426 w, 1290 s, 1230 s, 1219 s, 1174 m, 1152 m, 1026 s, 997 m, 952 s, 886 w, 868 s, 854 w, 823 m, 781 w, 748 s, 728 s, 696 m, 677 m, 630 s, 607 w;

[Rh(Cl)(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)]
(**14**)

MF = $C_{35}H_{32}ClNO_3PRh$

MW = 683.97 g/mol

MP > 220 °C (dec)
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ$_2$-Cl)$_2$(trop$_2$NH)$_2$] (100 mg, 0.09 mmol, 1 eq.) in DCM (4 mL) 4-methyl-2,6,7-trioxa-1-phospha-bicyclo[2.2.2]octane (35 mg, 0.23 mmol, 2.5 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 92%, 117 mg, 0.17 mmol.

Reaction of chloride abstracting reagents MX with this complex give only [Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$]X like **15** in solvents like THF and DCM.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.59 (s, 3H, C*H*$_3$) 3.29 (s, 1H, N*H*), 3.76 (d, $^3J_{PH}$ = 3.7 Hz, 6H, C*H*$_2$), 4.30 (s, 2H, C*H*^{benzyl}), 5.24 (t, *J* = 8.0 Hz, 2H, C*H*^{olefin}), 5.30 (t, *J* = 8.5 Hz, 2H, C*H*^{olefin}), 6.72 (d, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*^{ar}), 6.86 (m, 4H, C*H*^{ar}), 7.03 (d, $^3J_{HH}$ = 4.0 Hz, 4H, C*H*^{ar}), 7.10 (d, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*^{ar}), 7.21 (ddd, $^3J_{HH}$ = 8.0 Hz, *J* = 4.2 Hz, *J* = 4.1 Hz, 2H, C*H*^{ar}), 7.62 (d, $^3J_{HH}$ = 7.6 Hz, 2H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 15.5 (s, 1C, C*H*$_3$), 32.9 (d, $^3J_{PC}$ = 28.3 Hz, 1C, *C*^{quart}), 66.8 (t, *J* = 7.9 Hz, 2C, *C*H^{olefin}), 69.2 (dd, *J* = 31.1 Hz, *J* = 8.2 Hz, 2C, *C*H^{olefin}), 73.0 (s, 2C, *C*H^{benzyl}), 74.4 (d, $^2J_{PC}$ = 6.4 Hz, 3C, *C*H$_2$O), 124.0 (d, *J* = 3.7 Hz, 2C, *C*H^{ar}), 124.9 (s, 2C, *C*H^{ar}), 126.4 (s, 2C, *C*H^{ar}), 128.0 (s, 2C, *C*H^{ar}), 128.0 (d, *J* = 7.9 Hz, 2C, *C*H^{ar}), 128.2 (d, *J* = 0.9 Hz, 2C, *C*H^{ar}), 129.1 (d, *J* = 4.9 Hz, 2C, *C*H^{ar}), 129.1 (s, 2C, *C*H^{ar}), 131.8 (d, *J* = 4.0 Hz, 2 C, *C*^{quart}), 135.4 (s, 2 C, *C*^{quart}), 135.5 (d, *J* = 8.8 Hz, 2C, *C*^{quart}), 140.8 (d, *J* = 5.8 Hz, 2C, *C*^{quart});

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ = 112.5 (d, $^1J_{RhP}$ = 206.8 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6814 (d, $^1J_{RhP}$ = 206.8 Hz);

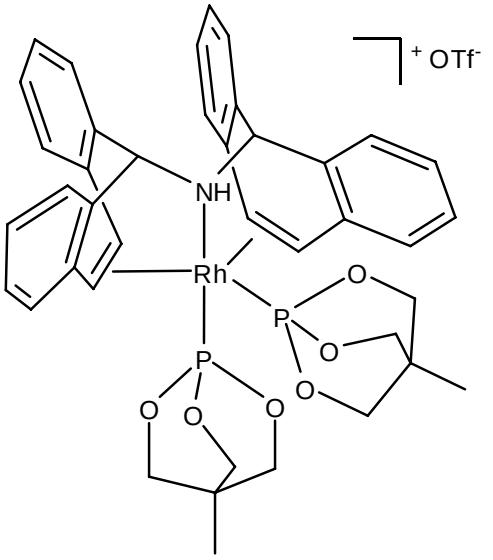
ATR IR (ν in cm^{-1}): 3215 w, 3041 w, 2934 w, 2882 w, 1599 w, 1489 m, 1461 m, 1392 w, 1341 w, 1317 w, 1268 w, 1255 m, 1221 w, 1176 m, 1159 m, 1127 w, 1110 w, 1013 s, 951 s, 922 s, 891 s, 858 s, 832 w, 775 s, 764 s, 749 s, 740 s, 704 m, 674 m, 650.90 s;

[Rh(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)$_2$]OTf (**15**)

MF = $C_{41}H_{41}F_3NO_9P_2RhS$

MW = 945.68 g/mol

MP > 220 °C (dec)
Air stable



[Rh(trop$_2$NH)(CO)]OTf (100 mg, 0.15 mmol, 1 eq.) was dissolved in 2 mL DCM. P(OCH$_2$)$_3$CCH$_3$ (43 mg, 0.5 mmol, 2 eq.) was added. The yellow solution was filtered over celite and the product precipitated with *n*-hexane. The product was recrystallized from DCM/*n*-hexane to give the product as yellow crystals. Yield: 91%, 127 mg, 0.13 mmol.

The PF_6^- salt of the substance was first obtained by accident from reaction of [Rh(Cl)(trop$_2$NH)(P(OCH$_2$)$_3$CCH$_3$)] **14** with $TlPF_6$. Crystals of the PF_6^- salt were obtained from this reaction in THF.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 0.62 (s, 3H, C*H*$_3$), 0.93 (s, 3H, C*H*$_3$), 3.74 (d, $^3J_{PH}$ = 4.4 Hz, 6H, C*H*$_2$O), 4.15 (s, 1H, N*H*), 4.42 (d, $^3J_{PH}$ = 4.8 Hz, 6H, C*H*$_2$O), 4.82 (d, $^4J_{PH}$ = 12.8 Hz, 2H, C*H*^{benzyl}), 5.30 (t, *J* = 10.3 Hz, 2H, C*H*^{olefin}), 5.38 (t, *J* = 10.3 Hz, 2H, C*H*^{olefin}), 6.90-7.05 (m, 8H, C*H*^{ar}), 7.20 (t, *J* = 6.8 Hz, 2H, C*H*^{ar}), 7.25-7.35 (m, 4H, C*H*^{ar}), 7.53 (d, *J* = 7.34 Hz, 2H, C*H*^{ar});

^{13}C{^{1}H}-NMR (125 MHz, CD_2Cl_2): δ = 14.5 (d, $^4J_{PC}$ = 2.1 Hz, 1C, *C*H$_3$), 14.8 (s, 1C, *C*H$_3$), 33.0 (d, $^4J_{PC}$ = 30.5 Hz, 1C, *C*^{quart}), 33.4 (d, $^4J_{PC}$ = 34.4 Hz, 1C, *C*^{quart}), 66.5 (t, *J* = 7.2 Hz, 2C, *C*H^{olefin}), 67.5 (dd, *J* = 23.0 Hz, *J* = 7.2 Hz, 2C, *C*H^{olefin}) 71.9 (s, 2C, *C*H^{benzyl}), 75.0 (d, $^2J_{PC}$ = 6.7 Hz, 3C, *C*H$_2$O), 77.3 (d, $^2J_{PC}$ = 7.3 Hz, 3C, *C*H$_2$O), 121.2 (q, $^1J_{CF}$ = 321.3 Hz, 1C, *C*F$_3$), 126.0 (d, *J* = 3.0 Hz, 2C, *C*H^{ar}), 127.0 (s, 2C, *C*H^{ar}), 127.3 (s, 2C, *C*H^{ar}), 128.2 (s, 2C, *C*H^{ar}), 129.0 (d, *J* = 7.3 Hz, 2C, *C*H^{ar}), 129.1 (s, 2C, *C*H^{ar}), 129.2 (s, 2C, *C*H^{ar}), 129.7 (d, *J* = 2.7 Hz, 2C, *C*H^{ar}), 132.8 (d, *J* = 7.0 Hz, 2C, *C*^{quart}), 133.1 (d, *J* = 4.0 Hz, 2C, *C*^{quart}), 136.6 (s, 2C, *C*^{quart}), 137.1 (d, *J* = 4.6 Hz, 2C *C*^{quart});

^{19}F-NMR (188.3 MHz, CD_2Cl_2): δ = -78.9 (s, SC*F*$_3$);

^{31}P{^{1}H}-NMR (203 MHz, CD_2Cl_2): δ = 110.1 (dd, $^1J_{RhP}$ = 190.1 Hz, $^2J_{PP}$ = 78.8 Hz), 114.3 (dd, $^1J_{RhP}$ = 200.7 Hz, $^2J_{PP}$ = 79.0 Hz);

^{1}H, ^{103}Rh-NMR (15.8 MHz, $CDCl_3$): δ = -8359 (dd, $^1J_{RhP}$ = 200.7 Hz, $^1J_{RhP}$ = 190.1 Hz);

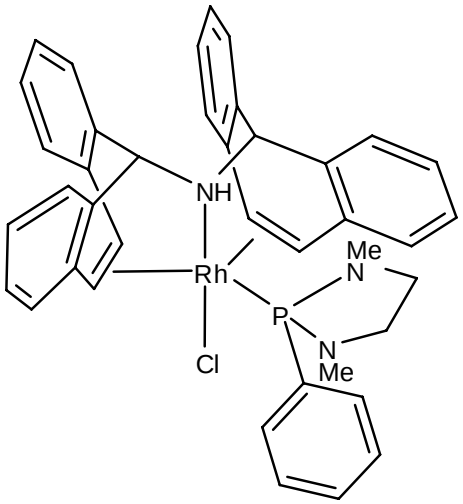
ATR IR (ν in cm^{-1}): 3228 w, 2939 w, 1601 w, 1491 w, 1477 w, 1464 w, 1394 w, 1318 w, 1259 m, 1222 w, 1150 m, 1023 s, 1002 s, 947 m, 930 m, 867 m, 857 m, 812 m, 798 s, 775 s, 752 s, 662 s, 650 s, 635 s;

[Rh(Cl)(trop$_2$NH)(P(Ph)(NMeCH$_2$)$_2$)]

MF = $C_{40}H_{38}ClN_3PRh$

MW = 730.08 g/mol

MP > 220 °C (dec)
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ$_2$-Cl)$_2$(trop$_2$NH)$_2$] (200 mg, 0.19 mmol, 1 eq.) in DCM (4 mL) 1,3-Dimethyl-2-phenyl-1,3,2-diazaphospholidine (110 mg, 0.56 mmol, 3 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(P(Ph)(NMeCH$_2$)$_2$)] which was isolated by filtration followed by drying under vacuum. Yield: 81%, 221 mg, 0.30 mmol.

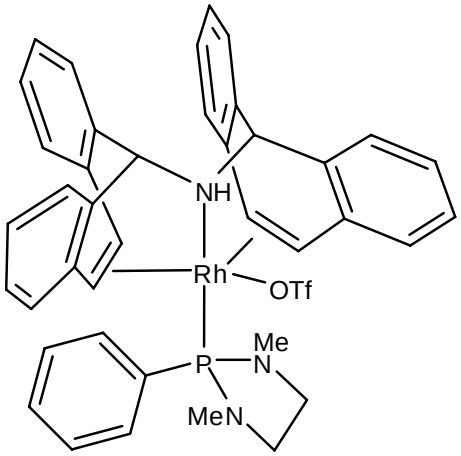
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.0-2.4 (br m, C*H*$_2$), 2.67 (br s, 6H, C*H*$_3$), 3.33 (s, 1H, N*H*), 4.30 (s, 2H, C*H*^{benzyl}), 5.27 (m, 4H, C*H*^{olefin}), 7.23 (m, 21H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 34.5 (br s, 2C, N*C*H$_3$), 52.4 (s, 2C, N*C*H$_2$), 65.3 (br s, 2C, *C*H^{olefin}), 69.7 (dd, J = 25.0 Hz, J = 6.4 Hz, 2C, *C*H^{olefin}), 73.1 (s, 2C, *C*H^{benzyl}), 123.5 – 137 (m, 30C, CH^{ar} and C^{quart});

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ = 110.9 (d, $^1J_{RhP}$ = 149.2 Hz);

ATR IR (ν in cm^{-1}): 3018 w, 2921 w, 2872 m, 2811 m, 1598 m, 1480 m, 1468 s, 1432 m, 1413 m, 1398 m, 1379 m, 1334 w, 1303 w, 1272 w, 1253 m, 1219 s, 1199 m, 1150 s, 1123 m, 1086 s, 1043 m, 1030 s, 1013 m, 970 m, 935 s, 905 s, 886 m, 871 m, 856 m, 827 w 780 m, 759 m, 747 s, 739 m, 728 s, 698 s, 675 s, 647 s, 618 m;

[Rh(trop$_2$NH)(P(Ph)(NMeCH$_2$)$_2$)]OTf (**16**)



MF = $C_{41}H_{38}F_3N_3O_3PRhS$

MW = 843.70 g/mol

MP = 190 – 210 °C (dec)
Slightly air sensitive

[Rh(Cl)(trop$_2$NH)(P(Ph)(NMeCH$_2$)$_2$)] (108 mg, 0.15 mmol, 1 eq.) and AgOTf (42 mg, 0.16 mmol, 1.1 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. THF (5 mL) was added and the resulting suspension was stirred 12 h. The THF was removed under reduced pressure, the complex dissolved in DCM and filtered over celite. The DCM was removed under reduced pressure and the red solid recrystallized from THF/*n*-hexane and dried under vacuum. Yield: 90%, 112 mg, 0.13 mmol.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 3.06 (s, 3 H, NC*H*$_3$), 3.09 (s, 3H, NC*H*$_3$), 3.00-3.15 (m, 2H, NC*H*$_2$), 3.38 (m, 2H, NC*H*$_2$), 5.06 (d, $^3J_{HH}$ = 9.1 Hz, 2H, C*H*^{olefin}), 5.18 (d, $^4J_{PH}$ = 8.8 Hz, 2H, C*H*^{benzyl}), 5.80 (d, $^3J_{HH}$ = 7.9 Hz, 2H, C*H*^{olefin}), 6.85-7.80 (m, 21H, CH^{ar});

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 34.8 (d, $^2J_{PC}$ = 8.2 Hz, 2C, NC*H*$_3$), 52.13 (d, $^2J_{PC}$ = 2.3 Hz, 2C NC*H*$_2$), 73.2 (s, 2C, *C*H^{benzyl}), 73.6 (d, $^1J_{RhC}$ = 9.6 Hz, 2C, *C*H^{olefin}), 77.5 (d, $^1J_{RhC}$ = 6.0 Hz, 2C *C*H^{olefin}), 126 – 138 (m, 31C, CH^{ar} and C^{quart});

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = -78.1 (s, SC*F*$_3$);

^{31}P{^{1}H}-NMR (203 MHz, CD_2Cl_2): δ = 118.7 (d, $^1J_{RhP}$ = 158.5 Hz);

^{1}H, ^{103}Rh-NMR (15.8 MHz, $CDCl_3$): δ = -7075(d, $^1J_{RhP}$ = 158.5 Hz);

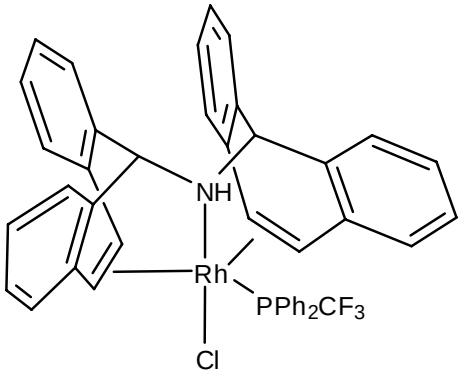
ATR IR (ν in cm^{-1}): 3048 w, 2859 w, 1600 w, 1490 m, 1435 m, 1259 m, 1222 s, 1150 s, 1093 s, 1025 s, 935 s, 859 m, 823 m, 804 m, 782 m, 749 s, 731 m, 711 m, 701 m, 686 m, 633 s;

[Rh(Cl)(trop$_2$NH)(PPh$_2$CF$_3$)]

MF = $C_{43}H_{33}ClF_3NPRh$

MW = 790.06 g/mol

MP > 220 °C (dec)
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (257 mg, 0.24 mmol, 1 eq.) in DCM (4 mL) PPh$_2$CF$_3$ (128 mg, 0.5 mmol, 2.1 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(PPh$_2$CF$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 97%, 367 mg, 0.46 mmol.

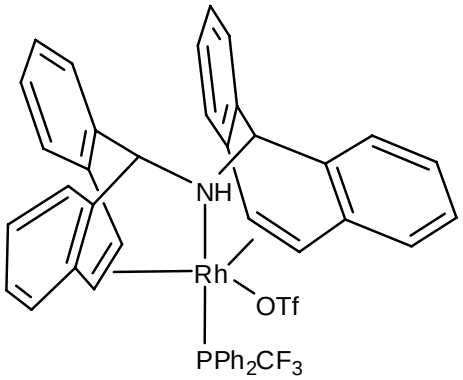
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.47 (br s, 1H, N*H*), 3.96 (br s, 2H, CH^{benzyl}), 5.68 (br s, 4H, CH^{olefin}), 6.50-7.50 (m, 26H, CH^{ar});

^{31}P{^{1}H}-NMR (283 MHz, $CDCl_3$): δ = 32.5 (dq, $^1J_{RhP}$ = 117.0 Hz, $^2J_{FP}$ = 52.7 Hz);

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = - 53.5 (d, $^2J_{FP}$ = 52.7 Hz, CF_3);

ATR IR (ν in cm^{-1}): 3199 w, 1599 w, 1488 w, 1439 w, 1314 w, 1189 w, 1149 m, 1127 m, 1110 m, 968 w, 938 w, 908 w, 828 w, 779 w, 730 m, 696 m, 645 w;

[Rh(trop$_2$NH)(PPh$_2$CF$_3$)]OTf (**17**)



MF = $C_{44}H_{33}F_6NO_3PRhS$

MW = 903.67 g/mol

MP = 208-212 °C (dec)
Air stable

Preparation is analogous to **3**. [Rh(Cl)(trop$_2$NH)(PPh$_2$CF$_3$)] (367 mg, 0.46 mmol, 1 eq.) and AgOTf (125 mg, 0.49 mmol, 1 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. DCM (5 mL) was added and the resulting suspension was stirred 12 h. The solution was filtered over a plug of celite. DCM was removed under reduced pressure and the resulting red solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 95%, 162 mg, 0.169 mmol.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.86 (dd, $^3J_{HH}$ = 9.3 Hz, $^2J_{RhH}$ = 1.22 Hz, 2H, C*H*^{olefin}), 5.07 (d, $^4J_{PH}$ = 9.0 Hz, 2H, C*H*^{benzyl}), 5.73 (d, $^3J_{PH}$ = 5.9 Hz, 1H, N*H*), 6.17 (dt, $^3J_{HH}$ = 9.5 Hz, $^2J_{RhH}$ = $^3J_{PH}$ = 2.8 Hz, 2H, C*H*^{olefin}), 6.85 -7.15(m, 10H, C*H*^{ar}), 7.20-7.30 (m, 4H, C*H*^{ar}), 7.35-7.40 (m, 2H, C*H*^{ar}), 7.55-7.75 (m, 6H, C*H*^{ar}), 7.85-7.97 (m, 4H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 72.6 (d, $^3J_{PC}$ = 1.2 Hz, 2C, *C*H^{benzyl}), 74.4 (d, $^1J_{RhC}$ = 12.2 Hz, 2C, *C*H^{olefin}), 74.7 (d, $^1J_{RhC}$ = 7.0 Hz, 2C, *C*H^{olefin}), 119.8 (q, $^1J_{CF}$ = 320.4 Hz, 1C, *C*F$_3$), 121.2 (q, $^1J_{CF}$ = 321.3 Hz, 1C, SO$_3$*C*F$_3$), 124.1 (d, $^1J_{PC}$ = 46.6 Hz, 2C, *C*^{quart}), 126.9 (s, 2C, *C*H^{ar}), 127.0 (d, *J* = 1.8 Hz, 4C, *C*H^{ar}), 127.4 (s, 2C, *C*H^{ar}), 128.4 (d, *J* = 2.1 Hz, 4C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 129.2 (s, 2C, *C*H^{ar}), 129.7 (s, 2C, *C*H^{ar}), 129.8 (s, 2C, *C*H^{ar}), 132.5 (d, *J* = 2.4 Hz, 2C, *C*H^{ar}), 134.4 (s, 2C, *C*H^{ar}), 134.5 (s, 2C, *C*H^{ar}), 134.6 (s, 2C, *C*^{quart}), 134.7 (s, 2C, *C*^{quart}), 135.0 (d, *J* = 1.8 Hz, 2C, *C*^{quart}), 136.4 (s, 2C, *C*^{quart});

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = -53.1 (d, $^2J_{FP}$ = 59.1 Hz, PC*F*$_3$), -78.0 (s, SC*F*$_3$);

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ = 59.4 (dq, $^1J_{RhP}$ = 148.5 Hz, $^2J_{FP}$ = 59.1 Hz);

^{1}H, ^{103}Rh-NMR (22.3 MHz, $CDCl_3$): δ = -6900 (d, $^1J_{RhP}$ = 148.5 Hz,);

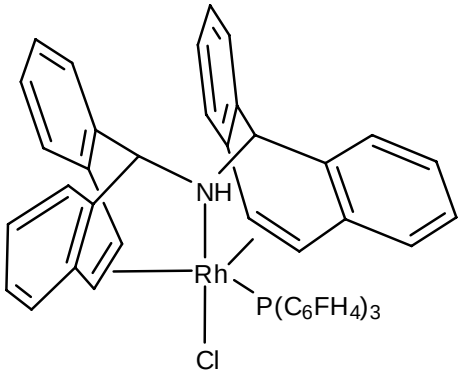
ATR IR (ν in cm^{-1}): 3148 w, 1627 w, 1601 w, 1486 w, 1436 m, 1290 m, 1229 s, 1160 s, 1134 s, 1113 s, 1096 s, 1025 s, 973 m, 943 w, 914 w, 883 w, 825 m, 780 w, 747 s, 696 s, 631 s;

[Rh(Cl)(trop$_2$NH)(P(*p*-FPh)$_3$)]

MF = $C_{48}H_{35}ClF_3NPRh$

MW = 852.13 g/mol

MP = 120-125 °C (dec)
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (154 mg, 0.14 mmol, 1 eq.) in DCM (3 mL) tris(4-fluorophenyl)phosphine (100 mg, 0.32 mmol, 2.2 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(P(*p*-FPh)$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 89%, 219 mg, 0.26 mmol.

^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.50 (s, 1H, N*H*), 3.93 (s, 2H, C*H*^{benzyl}), 5.22 (d, *J* = 5.5 Hz, 2H, C*H*^{ar}), 5.34 (t, *J* = 8.5Hz, 2H, C*H*^{olefin}), 5.69 (dd, $^3J_{HH}$ = 9.2 Hz, 6.10 Hz, 2H, C*H*^{olefin}), 6.5-7.8 (m, 28H, C*H*^{ar});

^{13}C{^{1}H}-NMR (176 MHz, $CDCl_3$): δ = 66.2 (t, *J* = 6.6 Hz, 2C, *C*H^{olefin}), 71.34 (dd, *J* = 18.4 Hz, *J* = 8.7 Hz, 2C, *C*H^{olefin}), 72.52 (s, 2C, *C*H^{benzyl}), 115.5 – 164.5 (m, 42C, *C*H^{ar} and *C*^{quart});

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ =-110.0 (s, 4F, C*F*^{ar}), - 110.3 (s, 2F, C*F*^{ar});

^{31}P{^{1}H}-NMR (283 MHz, $CDCl_3$): δ = 5.8 (d, $^1J_{RhH}$ = 112.9 Hz);

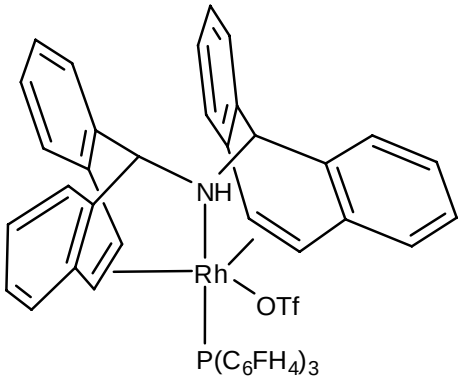
ATR IR (ν in cm^{-1}): 3204 w, 3026 w, 1655 m, 1587 w, 1493 m, 1447 m, 1395 m, 1317 m, 1276 m, 1227 s, 1161 s, 1117 m, 1088 m, 1014 m, 970 m, 941 m, 908 m, 889 w, 827 s, 814 s, 779 w, 765 s, 748 s, 730 s, 702 s, 672 m, 638 s, 606 w;

[Rh(trop$_2$NH)(P(*p*-FPh)$_3$)]OTf (**18**)

MF = $C_{49}H_{35}F_6NO_3PRhS$

MW = 965.74 g/mol

MP = 200- 205 °C (dec)
Air stable



Preparation is analogous to **3**. [Rh(Cl)(trop$_2$NH)(P(*p*-FPh)$_3$)] (219 mg, 0.26 mmol, 1 eq.) and AgOTf (70 mg, 0.27 mmol, 1.05 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. DCM (5 mL) was added and the resulting suspension was stirred for 12 h. The solution was filtered over a plug of celite. DCM was removed under reduced pressure and the resulting red solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 88%, 218 mg, 0.23 mmol.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.89 (d, $^3J_{HH}$ = 8.6 Hz, 2H, C*H*^{olefin}), 4.97 (d, $^4J_{PH}$ = 8.6 Hz, 2H, C*H*^{benzyl}), 5.38 (dt, $^3J_{HH}$ = 9.4 Hz, *J* = 3.0 Hz, 2H, C*H*^{olefin}), 5.67 (d, $^3J_{PH}$ = 5.9 Hz, 1H, N*H*), 6.70 -6.97 (d, *J* = 6.9 Hz, 8H, C*H*^{ar}), 7.15-7.35 (m, 13H, C*H*^{ar}), 7.75-7.87 (m, 6H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 72.6 (s, 2C, *C*H^{benzyl}), 73.9 (d, *J* = 18.0 Hz, 2C, *C*H^{olefin}), 73.9 (d, *J* = 1.2 Hz, 2C, *C*H^{olefin}), 116.4 (dd, $^2J_{FC}$ = 21.0 Hz, $^3J_{PC}$ = 11.0 Hz, 6C, *C*H^{ar}), 124.5 (dd, $^1J_{PC}$ = 48.3 Hz, $^4J_{FC}$ = 3.5 Hz, 3C, *C*^{quart}), 126.4 (s, 2C, *C*H^{ar}), 126.6 (s, 2C, *C*H^{ar}), 126.9 (s, 2C, *C*H^{ar}), 127.4 (s, 2C, *C*H^{ar}), 128.3 (s, 2C, *C*H^{ar}), 128.5 (s, 2C, *C*H^{ar}), 129.4 (s, 2C, *C*H^{ar}), 129.7 (s, 2C, *C*H^{ar}), 134.6 (d, *J* = 0.9 Hz, 2C, *C*^{quart}), 134.7 (s, 2C, *C*^{quart}), 135.1 (d, *J* = 2.1 Hz, 2 C, *C*^{quart}), 136.5 (s, 2C, *C*^{quart}), 136.7 (dd, $^2J_{PC}$ = 8.5 Hz, $^3J_{FC}$ = 2.4 Hz, 6C, *C*H^{ar}), 164.5 (dd, $^1J_{FC}$ = 254.8 Hz, $^4J_{PC}$ = 2.6 Hz, 3C, *C*^{quart});

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = -78.3 (s, SC*F*$_3$), -107.0 (s, C*F*^{ar});

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ = 38.6 (d, $^1J_{RhP}$ = 138.8 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6905 (d, $^1J_{RhP}$ = 138.8 Hz);

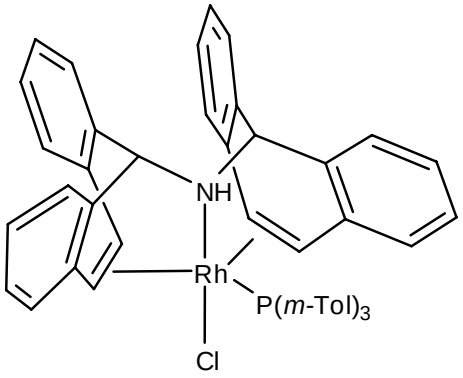
ATR IR (ν in cm^{-1}): 3140 w (NH), 1590 m, 1495 m, 1398 w, 1296 m, 1229 m, 1170 m, 1161 m, 1090 w, 1025 m, 978 w, 944 w, 885 w, 848 w, 824 m, 781 w, 750 m, 731 w, 713 w, 670 w, 629 s;

[Rh(Cl)(trop$_2$NH)(P(*m*-Tol)$_3$)]

MF = $C_{51}H_{44}ClNPRh$

MW = 840.23 g/mol

MP = 128-132 °C (dec)
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (170 mg, 0.16 mmol, 1 eq.) in DCM (3 mL) tri-m-tolylphosphine (97 mg, 0.32 mmol, 2 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(P(*m*-Tol)$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 81%, 215 mg, 0.26 mmol.

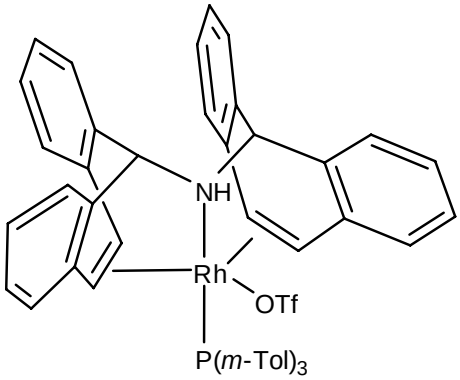
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.93 (s, 1H, N*H*), 2.06 (s, 3H, CH_3), 2.38 (s, 6 H, CH_3), 3.92 (s, 2H, CH^{benzyl}), 5.04 (t, *J* = 7.8 Hz, 1H, CH^{ar}), 5.36 (d, *J* = 7.3 Hz, 11H, CH^{ar}), 5.39 (dd, $^3J_{HH}$ = 9.5 Hz, *J* = 7.6 Hz, 2H, CH^{olefin}), 5.64 (dd, *J* = 9.8, 5.8 Hz, 2H, CH^{olefin}), 6.54 (d, *J* = 7.0 Hz, 2H, CH^{ar}), 6.67 (d, *J* = 7.3 Hz, 5H, CH^{ar}), 6.79 (t, *J* = 7.3 Hz, 2H, CH^{ar}), 6.85 (t, *J* = 7.2 Hz, 2H, CH^{ar}), 6.87–6.95 (m, 5H, CH^{ar}), 7.18 (d, *J* = 7.9 Hz, 2H, CH^{ar}), 7.21 (d, *J* = 7.6 Hz, 2H, CH^{ar}), 7.27 (dt, *J* = 7.6 Hz, *J* = 2.1 Hz, 2H, CH^{ar}), 7.85 (t, *J* = 8.7 Hz, 2H, CH^{ar}), 7.89 (d, *J* = 9.8 Hz, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (176 MHz, $CDCl_3$): δ = 21.6 (s, 2C, *C*H$_3$), 22.0 (s, 1C, *C*H$_3$), 66.2 (t, *J* = 6.7 Hz, 2C, *C*H^{olefin}), 70.6 (dd, *J* = 18.0 Hz, *J* = 8.3 Hz, 2C, *C*H^{olefin}), 72.6 (s, 2C, *C*H^{benzyl}), 124.0-140.5 (m, 42C, *C*H^{ar} and *C*^{quart});

^{31}P{^{1}H}-NMR (283 MHz, $CDCl_3$): δ = 7.6 (d, *J* = 109.9 Hz);

ATR IR (ν in cm^{-1}): 3139 w, 3052 w, 2883 w, 1977 w, 1591 w, 1491 w, 1477 m, 1402 w, 1313 w, 1291 m, 1277 m, 1262 w, 1216 s, 1179 s, 1158 s, 1134 m, 1107 m, 1046 w, 1020 s, 1007 m, 987 m, 937 w, 909 w, 870 w, 854 w, 823 w, 794 w, 779 m, 763 m, 748 m, 701 s, 632 s;

[Rh(trop$_2$NH)(P(*m*-Tol)$_3$)]OTf (**19**)



MF = $C_{52}H_{44}F_3NO_3PRhS$

MW = 953.85 g/mol

MP > 220 °C (dec)
Air stable

Preparation is analogous to **3**. [Rh(Cl)(trop$_2$NH)(P(*m*-Tol)$_3$)] (190 mg, 0.23 mmol, 1 eq.) and AgOTf (64 mg, 0.25 mmol, 1.1 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. DCM (5 mL) was added and the resulting suspension was stirred overnight. The solution was filtered over a plug of celite. DCM was removed under reduced pressure and the resulting red solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 89%, 192 mg, 0.20 mmol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.51 (s, 9H, CH_3,) 4.95 (d, $^4J_{PH}$ = 8.2 Hz, 2H, CH^{benzyl}), 4.99 (d, $^3J_{HH}$ = 9.1 Hz, 2H, CH^{olefin}), 5.45 (dt, $^3J_{HH}$ = 9.3 Hz, J = 2.78 Hz, 2H, CH^{olefin}), 5.66 (d, $^3J_{PH}$ = 5.5 Hz, 1 H) 6.69 (d, J = 7.31 Hz, 2H, CH^{ar}), 6.78 (td, J = 7.31 Hz, J = 1.52 Hz, 2H, CH^{ar}), 6.85-6.95 (m, 4H, CH^{ar}), 7.15-7.35 (m, 8H, CH^{ar}), 7.40-7.55 (m, 9H, CH^{ar}), 7.82 (d, J = 10.97 Hz, 3H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 21.9 (s, 3C, CH_3), 73.0 (s, 2C, CH^{benzyl}), 74.6 (d, J = 21.0 Hz, 2C, CH^{olefin}), 74.6 (s, 2C, CH^{olefin}), 120.2 (q, $^1J_{FC}$ = 320.3 Hz, 1C, CF_3), 126.7 (s, 2C, CH^{ar}), 126.8 (s, 2C, CH^{ar}), 127.2 (s, 2C, CH^{ar}), 127.9 (s, 2C, CH^{ar}), 128.6 (s, 2C, CH^{ar}), 128.8 (d, $^3J_{PC}$ = 1.8 Hz, 3C, CH^{ar}), 128.9 (s, 2C, CH^{ar}), 129.5 (d, $^1J_{PC}$ = 46.1 Hz, 3C, C^{quart}), 130.0 (s, 2C, CH^{ar}), 130.0 (s, 2C, CH^{ar}), 131.6 (d, $^2J_{PC}$ = 7.3 Hz, 3C, CH^{ar}), 132.2 (d, $^4J_{PC}$ = 2.7 Hz, 3C, CH^{ar}), 135.0 (s, 2 C, C^{quart}), 135.1 (s, 2 C, C^{quart}), 135.7 (d, $^2J_{PC}$ = 11.0 Hz, 3C, CH^{ar}), 136.0 (d, J = 2.3 Hz, 2C, C^{quart}), 137.5 (s, 2C, C^{quart}), 139.1 (d, $^3J_{PC}$ = 10.5 Hz, 3C, C^{quart});

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = -78.0 (s, CF_3);

^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$): δ = 39.6 (d, J_{RhP} = 136.7 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6781 (d, J_{RhP} = 136.7 Hz);

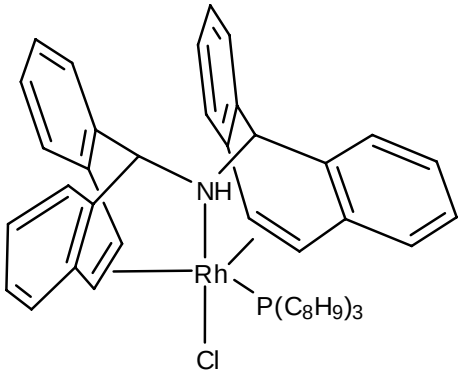
ATR IR (ν in cm^{-1}): 3190 w, 3021 w, 1592.37 w, 1488 m, 1473 m, 1400 m, 1313 w, 1272 w, 1253 w, 1217 w, 1197 w, 1174 w, 1159 w, 1105 m, 1042 w, 971 w, 936 w, 907 m, 827 w, 778 m, 765 m, 747 s, 729 s, 698 s, 645 m;

[Rh(Cl)(trop$_2$NH)(P(*m*-Xyl)$_3$)]

MF = $C_{54}H_{50}ClNPRh$

MW = 882.31 g/mol

MP > 220 °C (dec)
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (130 mg, 0.12 mmol, 1 eq.) in DCM (3 mL) tri-m-xylyl phosphine (84 mg, 0.24 mmol, 2 eq.) and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(P(*m*-Xyl)$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 84%, 180 mg, 0.20 mmol.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.01 (s, 6H, C*H*$_3$), 2.26 (s, 1H, N*H*), 2.34 (s, 12H, C*H*$_3$), 3.97 (s, 2H, C*H*^{benzyl}), 5.12 (d, $^3J_{HH}$ = 7.7 Hz, 2H, C*H*^{ar}), 5.34 (dd, $^3J_{HH}$ = 9.4 Hz, *J* = 7.7 Hz, 2H, C*H*^{olefin}), 5.61 (dd, $^3J_{HH}$ = 9.5 Hz, *J* = 5.87 Hz, 2H, C*H*^{olefin}), 6.54 (d, *J* = 7.3 Hz, 2H, C*H*^{ar}), 6.65 – 6.70 (m, 4H, C*H*^{ar}), 6.73 (s, 1H, C*H*^{ar}), 6.78 (t, *J* = 7.5 Hz, 2H, C*H*^{ar}), 6.80-6.90 (m, 6H, C*H*^{ar}), 7.04 (s, 2H, C*H*^{ar}), 7.16 (d, *J* = 7.7 Hz, 2H, C*H*^{ar}), 7.58 (d, *J* = 9.9 Hz, 4H, C*H*^{ar});

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 21.9 (s, 4C, *C*H$_3$), 22.1 (s, 2C, *C*H$_3$), 66.8 (dd, *J* = 8.4 Hz, *J* = 5.5 Hz, 2C, *C*H^{olefin}), 70.7 (dd, *J* = 17.8 Hz, *J* = 9.1 Hz, 2C, *C*H^{olefin}), 73.1 (s, 2C, C*H*^{benzyl}), 124.7-140.6 (m, 42C, *C*H^{ar} and *C*^{quart});

^{31}P{^{1}H}-NMR (203 MHz, $CDCl_3$): δ = 8.8 (d, $^1J_{RhP}$ = 109.9 Hz);

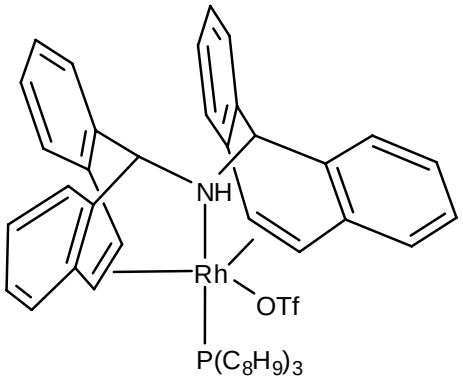
ATR IR (ν in cm^{-1}): 3192 w, 3172 w, 3022 w, 2914 w, 1599 w, 1583 w, 1488 m, 1470 m, 1413 w, 1374 w, 1314 w, 1270 w, 1218 w, 1197 w, 1158 w, 1126 m, 1042 m, 993 w, 973 w, 960 w, 937 w, 887 w, 869 w, 847 m, 778 m, 765 m, 747 s, 738 s, 693 s, 674 m, 618 w;

[Rh(trop$_2$NH)(P(*m*-Xyl)$_3$)]OTf (**20**)

MF = $C_{55}H_{50}F_3NO_3PRhS$

MW = 995.93 g/mol

MP = 180- 185 °C (dec)
Air stable



Preparation is analogous to **3**. [Rh(Cl)(trop$_2$NH)(P(*m*-Xyl)$_3$)] (148 mg, 0.17 mmol, 1 eq.) and AgOTf (48 mg, 0.18 mmol, 1.1 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. DCM (5 mL) was added and the resulting suspension was stirred overnight. The solution was filtered over a plug of celite. DCM was removed under reduced pressure and the resulting red solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 81%, 136 mg, 0.14 mmol.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.45 (s, 18H, C*H*$_3$), 5.00 (d, $^4J_{PH}$ = 8.4 Hz, 2H, C*H*^{benzyl}), 5.02 (d, $^3J_{HH}$ = 9.9 Hz, 2H, C*H*^{olefin}), 5.46 (ddd, $^3J_{HH}$ = 9.4 Hz, *J* = 2.8 Hz, *J* = 2.6 Hz, 2H, C*H*^{olefin}), 5.59 (d, $^3J_{PH}$ = 5.1 Hz, 1H, N*H*), 6.69 (d, *J* = 7.3 Hz, 2H, C*H*^{ar}), 6.79 (td, *J* = 7.3, *J* = 1.5 Hz, 2H, C*H*^{ar}), 6.85 – 6.95 (m, 4H, C*H*^{ar}), 7.17 (d, *J* = 6.24 Hz, 2H, C*H*^{ar}), 7.20-7.30 (m, 7H, C*H*^{ar}), 7.36 (d, *J* = 7.3 Hz, 2H, C*H*^{ar}), 7.47 (d, *J* = 10.6 Hz, 6H, C*H*^{ar});

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 21.9 (s, 6C, *C*H$_3$), 72.8 (s, 2C, *C*H^{benzyl}), 74.8 (d, $^1J_{RhH}$ = 7.2 Hz, 2C, *C*H^{olefin}), 75.1 (d, $^1J_{RhH}$ = 13.0 Hz, 2C, *C*H^{olefin}), 120.3 (q, $^1J_{CF}$ = 319.6 Hz, 1C, *C*F$_3$), 126.7 (s, 2C, *C*H^{ar}), 126.7 (s, 2C, *C*H^{ar}), 126.7 (s, 2C, *C*H^{ar}), 127.8 (s, 2C, *C*H^{ar}), 128.5 (s, 2C, *C*H^{ar}), 128.6 (s, 2C, *C*H^{ar}), 129.4 (d, $^1J_{PC}$ = 46.1 Hz, 3C, *C*^{quart}), 130.0 (s, 2C, *C*H^{ar}), 130.1 (s, 2C, *C*H^{ar}),132.4 (d, *J* = 9.1 Hz, 6C, *C*H^{ar}), 133.1 (d, *J* = 2.4 Hz, 3C, *C*H^{ar}), 135.0 (s, 2C, *C*^{quart}), 135.2 (s, 2C, *C*^{quart}), 136.1 (s, 2C, *C*^{quart}), 137.7 (s, 2C, *C*^{quart}), 138.7 (d, *J* = 10.6 Hz, 6C, *C*^{quart});

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = -78.0 (s, C*F*$_3$);

^{31}P{^{1}H}-NMR (203 MHz, $CDCl_3$): δ = 38.5 (d, $^1J_{RhP}$ = 135.8 Hz);

^{1}H, ^{103}Rh-NMR (15.8 MHz, $CDCl_3$): δ = -6769 (d, J_{RhP} = 136.7 Hz);

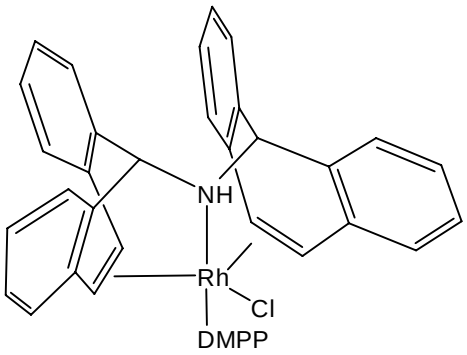
ATR IR (ν in cm^{-1}): 3047 w, 2922 w, 1978 w, 1598 w, 1489 w, 1380 w, 1295 m, 1222 m, 1163 m, 1126 m, 1022 m, 944 w, 849.69 w, 825 w, 788 w, 747 m, 696 m, 633 s;

[RhCl(DMPP)(trop$_2$NH)]

MF = $C_{44}H_{43}ClNPRh$

MW = 754.19

MP > 220 °C
Air stable



To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (200 mg, 0.19 mmol, 1 eq.) in DCM (10 mL) DMPP (86 µl, 89 mg, 0.47 mmol, 2.5 eq.) was added. The solid particles were dissolved within seconds yielding an intensively orange solution. Addition of *n*-hexane precipitated the orange product complex [Rh(Cl)(DMPP)(trop$_2$NH)] which was isolated by filtration followed by drying under high vacuum. Yield: 73%, 210 mg, 0.28 mmol.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.95 (6H, s, CH_3 ^{phosphole}), 2.42 (1H, s, N*H*), 4.14 (2H, s, CH^{benzyl}), 5.04 (2H, m, CH^{olefin}), 5.29 (2H, m, CH^{olefin}), 6.29 (1H, s, CH^{ar}), 6.39-6.45 (3H, m, CH^{ar}), 6.60-6.62 (2H, m, CH^{ar}), 6.77-7.32 (16H, m, CH^{ar}).

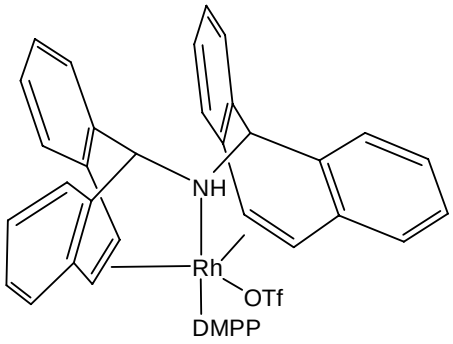
^{13}C{^{1}H}-NMR (62.9 MHz, $CDCl_3$) δ = 17.8 (2C, d, $^3J_{PC}$ = 9.5 Hz, *C*H$_3$ ^{phosphole}), 65.7 (2C, dd, *J* = 4.4 Hz, *J* = 8.6 Hz, *C*H^{olefin}), 67.5 (2C, dd, *J* = 9.2 Hz, *J* = 16.0 Hz, *C*H^{olefin}), 72.5 (2C, s, *C*H^{benzyl}), 122.8 (1C, s, *C*H^{ar}), 123.3 (1C, s, *C*H^{ar}), 124.0 (2C, d, *J* = 1.9 Hz, *C*H^{ar}), 124.6 (2C, s, *C*H^{ar}), 126.8 (2C, s, *C*H^{ar}), 127.8 (2C, s, *C*H^{ar}), 128.1 (2C, d, *J* = 3.3 Hz), 128.2 (2C, s, *C*H^{ar}), 128.3 (2C, s, *C*H^{ar}), 128.8 (2C, d, *J* = 1.8 Hz, *C*H^{ar}), 129.0 (2C, s, *C*H^{ar}), 129. 1 (2C, s, *C*^{quart}), 129.6 (2C, s, *C*^{quart}), 131.1 (2C, d, *J* = 8.4 Hz, *C*H^{ar}), 131.5 (2C, d, *J* = 4.4 Hz, *C*^{quart}), 132.0 (1C, s, *C*H^{ar}), 135.3 (1C, s, *C*H^{ar}), 136.1 (1C, d, *J* = 5.0 Hz, *C*H^{ar}), 136.5 (2C, d, *J* = 3.8 Hz, *C*^{quart}), 140.8 (1C, d, *J* = 3.3 Hz, *C*H^{ar}), 151.4 (1C, d, *J* = 6.9 Hz, *C*H^{ar}).

^{31}P{^{1}H}-NMR (101.2 MHz, $CDCl_3$) δ = 19.2 (d, $^1J_{RhP}$ = 107 Hz).

ATR IR (ν in cm-1): 3196 w, 2911 w, 1598 m, 1486 m, 1469 m, 1433 m, 1398 w, 1327 w, 1256 w, 1220 w, 1195 w, 1158 w, 1125 w, 1042 w, 982 br, 939 w, 873 w, 815 w, 789 m, 748 s, 737 s, 698 m, 689 m, 672 w.

EA found% (calc%) for $C_{42}H_{36}ClNPRh \cdot H_2O$: C: 69.02 (67.98), H: 5.19 (5.16), N: 1.87 (1.89).

[Rh(DMPP)(trop$_2$NH)]OTf (**21**)



MF = $C_{45}H_{43}F_3NO_3PRhS$

MW = 868.17

MP > 220 °C
Slightly air sensitive

To a solution of [Rh(Cl)(DMPP)(trop2NH)] (50 mg, 0.069 mmol, 1 eq.) in DCM AgOTf (19.5 mg, 0.076 mmol, 1.1 eq.) was added. After 1 h of stirring, the resulting suspension was filtrated through a plug of celite. Addition of *n*-hexane precipitated the orange-red product complex [Rh(DMPP)(trop$_2$NH)]OTf which was isolated by filtration followed by drying under high vacuum. Yield: 43%, 26 mg, 0.030 mmol.

^{1}H-NMR (250 MHz, $CDCl_3$) δ = 2.26 (6H, s, CH_3 ^{phosphole}), 4.61 (2H, d, $^3J_{HH}$ = 9.0 Hz, CH^{olefin}), 4.86 (2H, d, $^4J_{PH}$ = 7.8 Hz, CH^{benzyl}), 5.03 (1H, d, $^3J_{PH}$ = 5.0 Hz, NH), 5.69 (2H, ddd, $^3J_{HH}$ = 9.0 Hz, $^2J_{RhH}$ = 3.0 Hz, $^3J_{PH}$ = 3.0 Hz, CH^{olefin}), 6.74-6.96 (10H, m, CH^{ar}, C$H^{phosphole}$), 7.10-7.18 (8H, m, CH^{ar}), 7.49-7.51 (3H, m, C$H^{phosphole,ar}$), 7.79-7.85 (2H, m, C$H^{phosphole,ar}$).

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$) δ = 17.7 (2C, d, $^3J_{PC}$ = 12.2 Hz, CH$_3$ ^{phosphole}), 70.7 (2C, d, J = 12.2 Hz, CH^{olefin}), 72.8 (2C, s, CH^{benzyl}), 72.9 (2C, d, J = 8.3 Hz, CH^{olefin}), 122.0 (1C, s, C$H^{phosphole}$), 122.5 (1C, s, C$H^{phosphole}$), 125.6 (2C, s, C^{quart}), 125.9 (2C, d, J = 4.5 Hz, C^{quart}), 126.2 (2C, s, CH^{ar}), 126.7 (2C, s, CH^{ar}), 126.9 (2C, s, CH^{ar}), 127.2 (2C, s, CH^{ar}), 127.3 (2C, s, CH^{ar}), 128.1 (2C, s, CH^{ar}), 128.3 (1C, s, CH^{ar}), 128.8 (1C, m, CH$^{ar,\ phosphole}$), 128.9 (2C, d, J_{PC} = 10.1 Hz, $C^{ar,\ phosphole}$), 129.5 (2C, s, C^{quart}), 129.6 (1C, s, CH^{ar}), 129.9 (1C, s, CH^{ar}), 130.8 (1C, m, CH$^{ar,\ phosphole}$), 132.5 (2C, d, J_{PC} = 8.5 Hz, CH$^{ar,\ phosphole}$), 134.1 (2C, s, C^{quart}), 134.4 (2C, m, CH^{ar}), 135.6 (1C, s, CH^{ar}), 137.4 (1C, s, CH^{ar}), 153.2 (2C, d, $^2J_{PC}$ = 8.8 Hz, CMe^{phosphole}).

^{19}F-NMR (188.3 MHz, $CDCl_3$) δ = -78.2 (s) (s, CF_3).

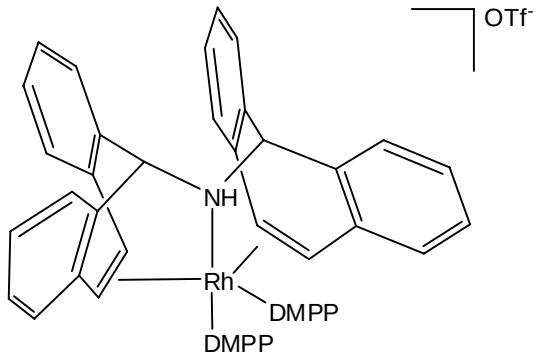
^{31}P{^{1}H}-NMR (121.5 MHz, $CDCl_3$) δ = 44.6 (d, $^1J_{RhP}$ = 129 Hz).

^{1}H, ^{103}Rh-NMR (22.1 MHz, $CDCl_3$) δ = -6921 (d, $^1J_{PRh}$ = 129 Hz).

ATR IR (ν in cm-1): 3053 w, 1600 w, 1491 w, 1436 w, 1275 m, 1259 m, 1232 s, 1155 br, 1103 w, 1028 s, 986 w, 877 w, 822 br, 781 w, 750 s, 695 m, 671 w, 635 s.

EA found% (calc%) for $C_{43}H_{36}F_3NO_3PRhS \cdot 2\ H_2O$: C: 59.49 (59.11), H: 4.67 (4.61), N: 1.57 (1.60);

[Rh(DMPP)$_2$(trop$_2$NH)]OTf (**22**)



MF = $C_{58}H_{61}F_3NO_3P_2RhS$

MW = 1073.29

MP > 220 °C
Air stable

To a solution of [Rh(CO)(trop$_2$NH)]OTf (200 mg, 0.30 mmol, 1 eq.) in THF (20 mL) DMPP (0.2 mL, 207 mg, 1.1 mmol, 3.6 eq.) was added. The resulting solution was heated to 70 °C for 6 h. After cooling the solution to room temperature, its volume was reduced to about 5 mL. Addition of *n*-hexane precipitated the orange-red product complex [Rh(DMPP)$_2$(trop$_2$NH)]OTf which was isolated by filtration followed by drying under high vacuum. Yield: 96%, 310 mg, 0.29 mmol.

Crystals suitable for X-ray diffraction were obtained by layering a solution of [Rh(DMPP)$_2$(trop$_2$NH)]OTf in THF with *n*-hexane.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 2.10 (6H, s, CH_3 ^{phosphole}), 2.15 (6H, s, CH_3 ^{phosphole}), 2.55 (1H, s, N*H*), 4.62 (2H, d, *J* = 9.9 Hz, CH^{benzyl}), 4.86-4.94 (4H, m, CH^{olefin}), 5.38 (2H, dd, *J* = 9.9 Hz, *J* = 9.9 Hz, CH^{ar}), 6.49 (2H, d, $^3J_{PH}$ = 4.2 Hz, C$H^{phosphole}$), 6.62 (2H, d, $^3J_{PH}$ = 4.8 Hz, C$H^{phosphole}$), 6.72-6.84 (10H, m, CH^{ar}), 7.06-7.11 (3H, m, CH^{ar}), 7.20 (2H, dd, *J* = 7.2 Hz, *J* = 7.5 Hz, CH^{ar}), 7.36-7.62 (9H, m, CH^{ar}).

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$) δ = 17.9 (2C, s, *C*H$_3$ ^{phosphole}), 18.0 (2C, s, *C*H$_3$ ^{phosphole}), 64.2-64.4 (2C, m, *C*H^{olefin}), 65.7-66.0 (2C, m, *C*H^{olefin}), 70.9 (2C, s, *C*H^{benzyl}), 121.5 (2C, d, $^1J_{PC}$ = 3.8 Hz, *C*H^{phosphole}), 122.2 (2C, d, $^1J_{PC}$ = 3.0 Hz, *C*H^{phosphole}), 124.6 (1C, s, *C*H^{ar}), 125.0 (1C, s, *C*H^{ar}), 125.9 (2C, d, *J* = 1.5 Hz, *C*H^{ar}), 126.7 (2C, d, *J* = 3.0 Hz, *C*^{quart}), 126.9 (2C, s, *C*H^{ar}), 127.3 (4C, m, *C*^{quart}), 128.1 (2C, s, *C*H^{ar}), 128.6-128.9 (7C, m, *C*H^{ar}, *C*^{quart}), 129.1 (2C, d, J = 1.5 Hz, *C*^{quart}), 129.2 (2C, s, *C*H^{ar}), 129.6 (2C, d, *J* = 1.5 Hz, *C*H^{ar}), 130.5 (2C, d, *J* = 8.3 Hz, *C*H^{ar}), 131.1 (1C, d, *J* = 3.0 Hz, *C*H^{ar}), 132.0 (2C, d, *J* = 7.6 Hz, *C*H^{ar}), 132.9 (1C, dd, *J* = 4.5 Hz, *J* = 1.5 Hz, *C*H^{ar}), 133.6 (1C, d, *J* = 2.3 Hz, *C*H^{ar}), 136.3 (1C, s, *C*H^{ar}), 138.0 (1C, d, *J* = 3.0 Hz, *C*H^{ar}), 152.8 (2C, d, $^2J_{PC}$ = 6.0 Hz, *C*Me^{phosphole}), 153.5 (2C, d, $^2J_{PC}$ = 9.0 Hz, *C*Me^{phosphole}).

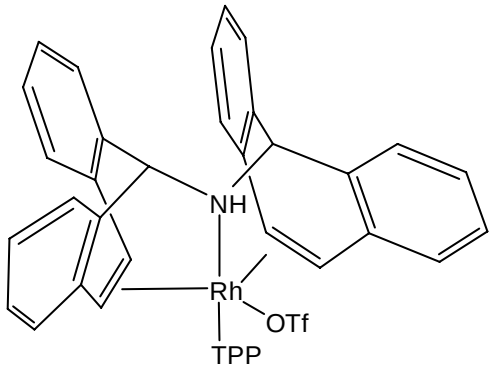
^{19}F-NMR (188.3 MHz, $CDCl_3$) δ = -77.8 (s).

^{31}P{^{1}H}-NMR (101.2 MHz, $CDCl_3$) δ = 17.2 (1P, dd, $^1J_{RhP}$ = 108 Hz, $^2J_{PP}$ = 26 Hz), 38.6 (1P, dd, $^1J_{RhP}$ = 116 Hz, $^2J_{PP}$ = 26 Hz).

^{1}H, ^{103}Rh-NMR (22.1 MHz, $CDCl_3$) δ = -7940 (dd, $^1J_{PRh}$ = 108 Hz, $^1J_{PRh}$ = 116 Hz).

ATR IR (ν in cm-1): 3207 w, 2030 br, 1977 br, 1601 w, 1492 w, 1475 w, 1435 m, 1382 w, 1328 w, 1262 s, 1223 m, 1149 br, 1099 w, 1030 s, 972 w, 815 br, 797 m, 782 w, 751 s, 696 m, 669 w 636 s.

[Rh(TPP)(trop$_2$NH)]OTf (**23**)



MF = $C_{53}H_{41}F_3NO_3PRhS$

MW = 962.16

MP = 165-170 °C (dec)
Air stable

To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (200 mg, 0.19 mmol, 1 eq.) in DCM (10 mL) TPP (129 mg, 0.41 mmol, 2.2 eq.) and AgOTf (106 mg, 0.41 mmol, 2.2 eq.) was added. The resulting mixture was stirred for 3 h and then filtered through a plug of celite. The volume of the filtrate was reduced to about 5 mL. Addition of *n*-hexane precipitated the orange-red product complex [Rh(TPP)(trop$_2$NH)]OTf which was isolated by filtration followed by drying under high vacuum. Yield: 96%, 350 mg, 0.36 mmol.
Crystals suitable for X-ray diffraction were obtained by layering a solution of [Rh(TPP)(trop$_2$NH)]OTf in acetone with *n*-hexane.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 5.02 (2H, d, $^4J_{PH}$ = 8.1 Hz, C*H*^{benzyl}), 5.27 (2H, d, $^3J_{HH}$ = 9.0 Hz, C*H*^{olefin}), 5.64 (2H, ddd, $^3J_{HH}$ = 9.0 Hz, $^2J_{RhH}$ = 3.0 Hz, $^3J_{PH}$ = 3.0 Hz, C*H*^{olefin}), 5.89 (1H, d, $^3J_{PH}$ = 5.1 Hz, N*H*), 6.51 (2H, d, *J* = 7.5 Hz, C*H*^{ar}), 6.71-6.77 (2H, m, C*H*^{ar}), 6.83-6.91 (6H, m, C*H*^{ar}), 7.14-7.22 (4H, m, C*H*^{ar}), 7.28-7.44 (9H, m, C*H*^{ar}), 7.51-7.61 (8H, m, C*H*^{ar}), 8.12 (2H, dd, *J* = 6.9 Hz, *J* = 9.9 Hz, C*H*^{ar}).

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$) δ = 72.5 (2C, s, *C*H^{benzyl}), 73.5 (2C, d, *J* = 6.8 Hz, *C*H^{olefin}), 76.1 (2C, d, *J* = 12.1 Hz, *C*H^{olefin}), 117.9 (1C, m, *C*F$_3$), 122.1 (2C, s, *C*^{quart}), 123.5 (2C, s, *C*^{quart}), 124.1 (2C, s, *C*^{quart}), 126.8 (2C, d, *J* = 3.0 Hz, *C*H^{ar}), 127.2 (2C, s, *C*H^{ar}), 127.7 (2C, s, *C*H^{ar}), 128.1 (2C, s, *C*H^{ar}), 128.5 (2C, s, *C*H^{ar}), 129.1 (2C, s, *C*H^{ar}), 129.4-129.6 (10C, m, *C*H^{ar}, *C*^{quart}), 132.0 (1C, d, *J* = 2.3 Hz, *C*H^{ar}), 134.0 (2C, d, *J* = 10.6 Hz, *C*H^{ar}), 134.5 (1C, s, *C*H^{ar}), 134.7 (1C, d, *J* = 0.8 Hz, *C*H^{ar}), 134.9-135.1 (3C, m, *C*H^{ar}), 135.5 (1C, d, *J* = 2.3 Hz, *C*H^{ar}), 136.6 (1C, s, *C*H^{ar}), 147.0 (1C, s, *C*-Ph^{phosphole}), 147.5 (1C, s, *C*-Ph^{phosphole}).

^{19}F-NMR (188.3 MHz, $CDCl_3$) δ = -78.4 (s).

^{31}P{^{1}H}-NMR (121.5 MHz, $CDCl_3$) δ = 46.0 (d, $^1J_{RhP}$ = 133 Hz).

^{1}H, ^{103}Rh-NMR (22.1 MHz, $CDCl_3$) δ = -6792 (d, $^1J_{PRh}$ = 133 Hz).

ATR IR (ν in cm-1): 3152 w, 3048 w, 2970 w, 1598 w, 1489 w, 1476 m, 1439 m, 1289 s, 1262 w, 1230 s, 1177 m, 1162 m, 1094 w, 1025 s, 977 w 948 w, 873 w, 852 m, 824 w, 801 br, 761 s, 750 s, 744 s, 693 s, 633 s.

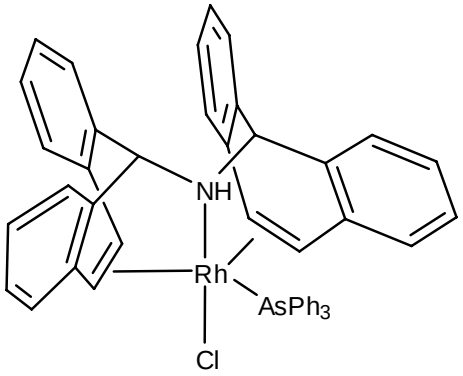
EA found% (calc%) for $C_{53}H_{41}F_3NO_3PRhS \cdot 2\ H_2O$: C: 63.19 (63.79), H: 4.32 (4.44), N: 1.39 (1.40);

[Rh(Cl)(trop$_2$NH)(AsPh$_3$)]

MF = $C_{48}H_{38}AsClNRh$

MW = 842.10 g/mol

MP > 220 °C (dec)
Air stable



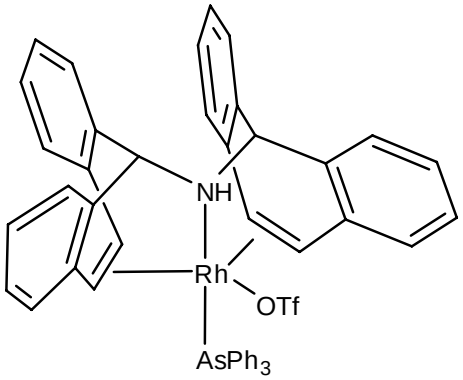
Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (170 mg, 0.16 mmol, 1 eq.) in DCM (3 mL) AsPh$_3$ (98 mg, 0.32 mmol, 2 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(AsPh$_3$)] which was isolated by filtration followed by drying under vacuum. Yield: 99%, 267 mg, 0.32 mmol.

^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.87 (s, 1H, N*H*), 3.96 (s, 2H, C*H*^{benzyl}), 5.36 (br s, 2H, C*H*^{ar}), 5.57 (d, $^3J_{HH}$ = 9.5 Hz, 2H, C*H*^{olefin}), 5.75 (d, $^3J_{HH}$ = 9.5 Hz, 2H, C*H*^{olefin}), 6.58 (d, *J* = 7.0 Hz, 2H, C*H*^{ar}), 6.71 (d, *J* = 7.3 Hz, 2H, C*H*^{ar}), 6.73 (d, *J* = 7.6 Hz, 2H, C*H*^{ar}), 6.88 (m, 11H, C*H*^{ar}), 7.23 (d, *J* = 7.6 Hz, 2H, C*H*^{ar}), 7.38 (br s, 6H, C*H*^{ar}), 8.01 (br s, 4H, C*H*^{ar});

^{13}C{^{1}H}-NMR (176 MHz, $CDCl_3$): δ = 65.5 (d, $^1J_{RhC}$ = 6.2 Hz, 2C, *C*H^{olefin}), 70.2 (d, $^1J_{RhC}$ = 9.1 Hz, 2C, *C*H^{olefin}), 72.6 (s, 2C, *C*H^{benzyl}), 124.0-141.1 (m, 42C, *C*H^{ar} and *C*^{quart});

ATR IR (ν in cm^{-1}): 3190 m, 3038 w, 1600 m, 1580 m, 1489 m, 1471 m, 1434 m, 1399 w, 1314 w, 1275 w, 1219 w, 1189 w, 1160 w, 1128 w, 1110 w, 1075 m, 1045 w, 1024 w, 1000 w, 971 m, 940 m, 888 w, 871 w, 828 w, 781 w, 767 m, 749 s, 733 s, 694 s, 671 m, 618 w;

[Rh(trop$_2$NH)(AsPh$_3$)]OTf (**24**)



MF = $C_{49}H_{38}AsF_3NO_3RhS$

MW = 955.72 g/mol

MP > 220 °C (dec)
Air stable

Preparation is analogous to **3**. [Rh(Cl)(trop$_2$NH)(AsPh$_3$)] (240 mg, 0.29 mmol, 1 eq.) and AgOTf (81 mg, 0.31 mmol, 1.1 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. DCM (5 mL) was added and the resulting suspension was stirred overnight. The solution was filtered over a plug of celite but some orange precipitate was observed. DCM was removed under reduced pressure and the resulting red solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 37%, 102 mg, 0.11 mmol, not optimized. Eventually better prepared from the direct reaction of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] and an xs. AsPh$_3$ in the presence of TlPF$_6$.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.85 (s, 2H, C*H*^{benzyl}), 5.27 (d, $^3J_{HH}$ = 9.1 Hz, 2H, C*H*^{olefin}), 5.78 (dd, $^3J_{HH}$ = 9.4 Hz, $^1J_{RhH}$ = 2.7 Hz, 2H, C*H*^{olefin}), 5.84 (s, 1H, N*H*), 6.75-6.95 (m, 8H, C*H*^{ar}),7.15-7.30 (m, 8H, C*H*^{ar}), 7.55-7.65 (m, 9H, C*H*^{ar}), 7.80-7.85 (m, 6H, C*H*^{ar});

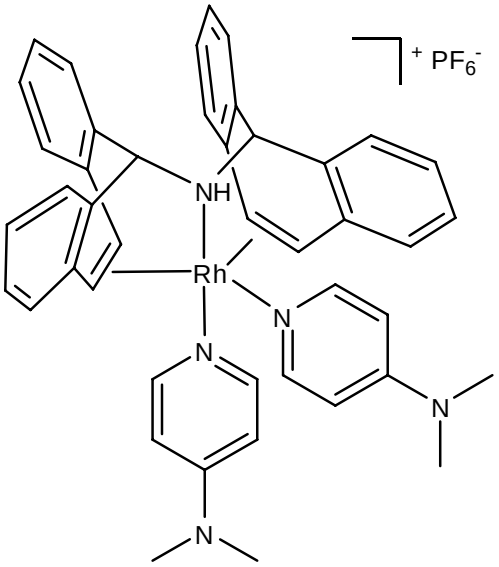
^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 70.9 (d, $^1J_{RhC}$ = 13.2 Hz, 2C, *C*H^{olefin}), 71.9 (d, $^1J_{RhC}$ = 7.3 Hz, 2C, *C*H^{olefin}), 73.3 (s, 2C, *C*H^{benzyl}), 126.5 (s, 2C, *C*H^{ar}), 126.6 (s, 2C, *C*H^{ar}), 127.2 (s, 2C, *C*H^{ar}), 127.8 (s, 2C, *C*H^{ar}), 128.9 (s, 2C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 129.7 (s, 6C, *C*H^{ar}), 129.8 (s, 2C, *C*H^{ar}), 130.1 (s, 2C, *C*H^{ar}), 130.5 (s, 3C 131.2 (s, 3 C, *C*H^{ar}), 134.4 (s, 6 C, *C*H^{ar}), 134.7 (s, 2C, *C*^{quart}), 134.9 (s, 2C, *C*^{quart}), 135.9 (s, 2C, *C*^{quart}), 137.7 (s, 2C, *C*^{quart});

^{19}F-NMR (188.3 MHz, $CDCl_3$): δ = -78.0 (s, C*F*$_3$);

^{1}H, ^{103}Rh-NMR (22.3 MHz, $CDCl_3$): δ = -6454 (s);

ATR IR (ν in cm^{-1}): 3138 w, 2988 m, 2901 w, 1602 w, 1579 w, 1490 w, 1479 w, 1437.36 m, 1405 m, 1299 m, 1276 m, 1257 w, 1226 s, 1215 s, 1171 s, 1158 s, 1132 w, 1067 m, 1023 s, 1005 m, 985 m, 943 w, 903 w, 860 w, 842 w, 826 w, 769 m, 759 s, 745 s, 702 m, 671 w, 633 w, 606 w;

$[Rh(trop_2NH)(DMAP)_2](PF_6)$ (**25**)



MF = $C_{44}H_{43}F_6N_5PRh$

MW = 889.72 g/mol

MP > 240 °C
Air stable

$[Rh_2(\mu_2\text{-}Cl)_2(trop_2NH)_2]$ (50 mg, 0.05 mmol, 1 eq.), DMAP (28 mg, 0.23 mmol, 5 eq) and $TlPF_6$ (33 mg, 0.09 mmol, 2 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. THF (5 mL) was added and the resulting suspension was stirred overnight. The THF was removed under reduced pressure, the complex dissolved in DCM and filtered over celite. The DCM was removed under reduced pressure and the yellow solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 70% 58 mg, 0.07 mmol.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 2.32 (br s,1H, N*H*), 2.95 (s, 6H, CH_3), 3.09 (s, 6H, CH_3), 4.68 (s, 2H, CH^{benzyl}), 4.77 (d, $^3J_{HH}$ = 9.1 Hz, 2H), 5.43 (dd, $^3J_{HH}$ = 9.4 Hz, $^2J_{RhH}$ = 2.1 Hz, 2H, CH^{olefin}), 6.27 (d, J = 7.0 Hz, 2H, CH^{ar}), 6.51 (d, J = 7.3 Hz, 2H, CH^{ar}), 6.87-6.97 (m, 6H, CH^{ar}), 7.13 (td, J = 7.46 Hz, J = 1.22 Hz, 2H, CH^{ar}), 7.17-7.23 (m, 4H, CH^{ar}), 7.27 (td, J = 7.5 Hz, J = 1.2 Hz, 2H, CH^{ar}), 7.41 (d, J = 6.4 Hz, 2H, CH^{ar}), 7.51 (d, J = 6.7 Hz, 2H, CH^{ar}), 7.55 (d, J = 7.0 Hz, 2H, CH^{ar});

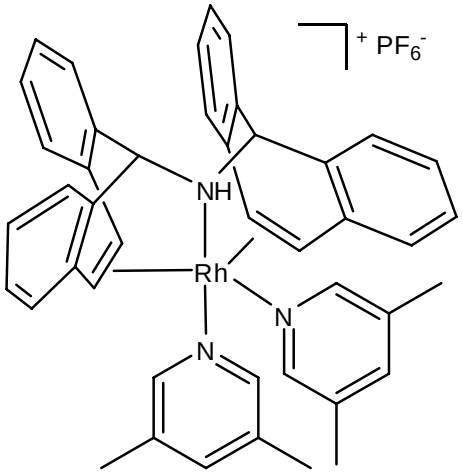
^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 39.2 (s, 2C, CH$_3$), 39.4 (s, 2C, CH$_3$), 70.2 (d, $^1J_{RhC}$ = 8.2 Hz, 2 C, CH^{olefin}), 70.8 (d, $^1J_{RhC}$ = 12.3 Hz, 2C, CH^{olefin}), 72.1 (s, 2C, CH^{benzyl}), 108.4 (s, 2C, CH^{ar}), 108.8 (s, 2C, CH^{ar}), 126.1 (s, 2C, CH^{ar}), 126.2 (s, 2C, CH^{ar}), 127.7 (s, 2C, CH^{ar}), 127.8 (s, 2C, CH^{ar}), 129.1 (s, 2C, CH^{ar}), 129.4 (s, 2C, CH^{ar}), 129.5 (s, 2C, CH^{ar}), 129.6 (s, 2C, CH^{ar}), 133.5 (s, 2C, C^{quart}), 135.1 (s, 2C, C^{quart}), 136.0 (d, J = 0.9 Hz, 2C, C^{quart}), 139.5 (s, 2C, C^{quart}), 150.5 (s, 2 C, CH^{ar}), 150.8 (s, 2C, CH^{ar}), 154.6 (s, 1C, C^{quart}), 154.8 (s, 1C, C^{quart});

^{31}P{^{1}H}-NMR (162 MHz, CD_2Cl_2): δ = -143.0 (m, $^1J_{PF}$ = 711.0 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -5733 (s);

ATR IR (ν in cm^{-1}): 3230 w, 2925 w, 1612 s, 1531 m, 1491 m, 1469 m, 1443 m 1390 s, 1347 w, 1316 w, 1275 w, 1258 w, 1224 s, 1189 m, 1126 w, 1086 w, 1062 m, 1021 m, 1003 s, 979 w, 968 w, 950 m, 833 s, 807 s, 751 s, 675 m;

$[Rh(trop_2NH)(3,5DMP)_2](PF_6)$ (**26**)



MF = $C_{44}H_{41}F_6N_3PRh$

MW = 859.69 g/mol

MP > 240 °C
Air stable

$[Rh_2(\mu_2\text{-}Cl)_2(trop_2NH)_2]$ (50 mg, 0.05 mmol, 1 eq.), 3,5-Dimethylpyridine (25 mg, 0.23 mmol, 5 eq.) and $TlPF_6$ (33 mg, 0.09 mmol, 2 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. THF (5 mL) was added and the resulting suspension was stirred overnight. The THF was removed under reduced pressure, the complex dissolved in DCM and filtered over celite. The DCM was removed under reduced pressure and the yellow solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 79%, 63 mg, 0.07 mmol.
Crystals suitable for X-ray diffraction were obtained from DCM/*n*-hexane.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 2.05 (s, 6H, CH_3), 2.35 (s, 6H, CH_3), 2.75 (s, 1H, N*H*), 4.76 (s, 2H, CH^{benzyl}), 4.86 (d, $^3J_{HH}$ = 8.8 Hz, 2H, CH^{olefin}), 5.65 (dd, J = 9.4 Hz, J = 2.4 Hz, 2H, CH^{olefin}), 6.95-7.05 (m, 6H, CH^{ar}), 7.17 (td, J = 7.46, 1.22 Hz, 2H, CH^{ar}), 7.25-7.35 (m, 7H, CH^{ar}), 7.46 (s, 2H, CH^{ar}), 7.52 (d, J = 6.7 Hz, 2H, CH^{ar}), 7.58 (s, 1H, CH^{ar}), 7.81 (s, 2H CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 18.4 (s, 2C, *C*H$_3$), 18.6 (s, 2C, *C*H$_3$), 71.7 (d, $^1J_{RhC}$ = 7.8 Hz, 2C, *C*H^{olefin}), 71.9 (s, 2C, *C*H^{benzyl}), 73.6 (d, $^1J_{RhC}$ = 12.3 Hz, 2C, *C*H^{olefin}), 126.7 (s, 2C, *C*H^{ar}), 126.8 (s, 2C, *C*H^{ar}), 127.7 (s, 2C, *C*H^{ar}), 128.3 (s, 2C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 129.4 (s, 2C, *C*H^{ar}), 129.5 (s, 2C, *C*H^{ar}), 129.8 (s, 2C, *C*H^{ar}), 133.5 (s, 2C, *C*^{quart}), 135.2 (s, 2C, *C*^{quart}), 135.5 (s, 2C, *C*^{quart}), 135.9 (s, 2C, *C*^{quart}), 136.7 (s, 2C, *C*^{quart}), 138.8 (s, 2C, *C*^{quart}), 139.6 (s, 1C, *C*H^{ar}), 140.4 (s, 1C, *C*H^{ar}), 149.5 (s, 2C, *C*H^{ar}), 149.9 (s, 2C, *C*H^{ar});

^{31}P{^{1}H}-NMR (162 MHz, CD_2Cl_2): δ = -143.1 (m, $^1J_{PF}$ = 711.0 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -5690 (s);

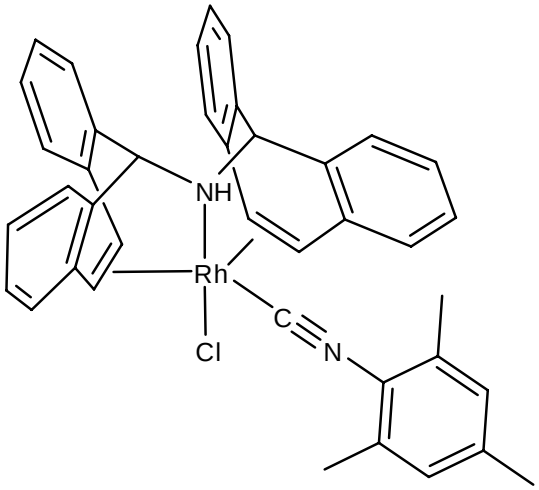
ATR IR (ν in cm^{-1}): 3230 w, 3026 w, 1599 m, 1491 m, 1472 m, 1385 w, 1318 w, 1275 w, 1258 w, 1224 w, 1189 w, 1149 m, 1128 w, 1112 w, 1092 w, 1045 w, 983 w, 968 w, 952 w, 831 s, 782 m, 770 m, 751 m, 741 m, 730 w, 688 w, 675 w, 645 w, 619 w, 606 w;

[Rh(Cl)(trop$_2$NH)(CNMes)]

MF = $C_{40}H_{34}ClN_2Rh$

MW = 681.07 g/mol

MP > 220 °C (dec)
Air stable



Preparation is analogous to **2**. To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (200 mg, 0.16 mmol, 1 eq.) in DCM (3 mL) mesityl isonitrile (69 mg, 0.47 mmol, 2.5 eq.) was added and an orange solution formed immediately. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(trop$_2$NH)(CNMes)] which was isolated by filtration followed by drying under vacuum. Yield: 83%, 210 mg, 0.31 mmol.

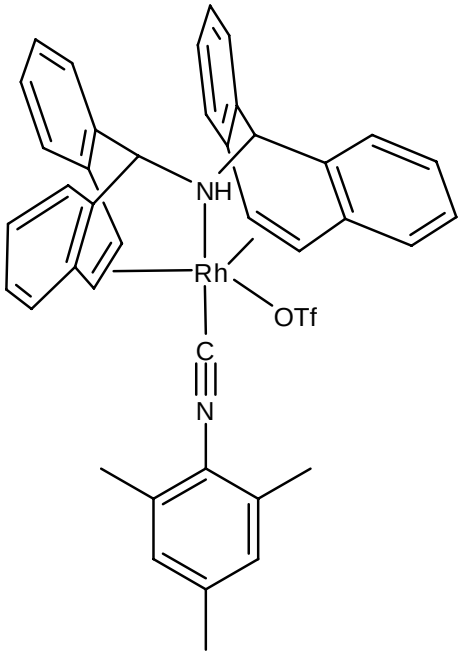
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.06 (s, 6H, C*H*$_3$), 2.25 (s, 3H, C*H*$_3$), 3.25 (s, 1H, N*H*), 4.41 (s, 2H, C*H*^{benzyl}), 5.34 (d, $^3J_{HH}$ = 9.1 Hz, 2H, C*H*^{olefin}), 5.59 (d, $^3J_{HH}$ = 9.1 Hz, 2H, C*H*^{olefin}), 6.70-6.75 (m, 2H, C*H*^{ar}), 6.80 (s, 2H, C*H*^{ar}), 6.83-6.93 (m, 4H, C*H*^{ar}), 7.00-7.07 (m, 4H, C*H*^{ar}), 7.10-7.15 (m, 2H, C*H*^{ar}), 7.18-7.25 (m, 2H, C*H*^{ar}), 7.67 (d, *J* = 7.31 Hz, 2H, C*H*^{ar});

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 19.1 (s, 2C, *C*H$_3$), 21.6 (s, 1C, *C*H$_3$), 66.9 (d, $^1J_{RhC}$ = 7.8 Hz, 2C, *C*H^{olefin}), 68.4 (d, $^1J_{RhC}$ = 9.1 Hz, 2C, *C*H^{olefin}), 73.2 (s, 2C, *C*H^{benzyl}), 124.6 (s, 2C, *C*H^{ar}), 125.2 (s, 1C, *C*^{quart}), 125.4 (s, 2C, *C*H^{ar}), 127.0 (s, 2C, *C*H^{ar}), 128.2 (s, 2C, *C*H^{ar}), 128.6 (s, 2C, *C*H^{ar}), 128.7 (s, 2C, *C*H^{ar}), 129.2 (s, 2C, *C*H^{ar}), 129.4 (s, 2C, *C*H^{ar}), 129.6 (s, 2C, *C*H^{ar}), 132.0 (s, 2C, *C*^{quart}), 135.3 (s, 2C, *C*^{quart}), 135.7 (s, 2C, *C*^{quart}), 136.2 (s, 2C, *C*^{quart}), 139.4 (s, 1C, *C*^{quart}), 142.3 (s, 2C, *C*^{quart}), 158.9 (d, $^1J_{RhC}$ = 64.0 Hz, 1C, *C*^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6409 (s);

ATR IR (ν in cm^{-1}): 3231 w, 3008 m, 1598 m, 1488 m, 1471 s, 1414 m, 1375 w, 1312 w, 1270 w, 1252 w, 1215 m, 1193 m, 1161 w, 1124 m, 1103 w, 1088 m, 1043 w, 970 m, 960 m, 933 w, 894 w, 865 w, 851 m, 826 w, 778.24 m, 760 m, 744 s, 739 s, 729 m, 718 m, 688 w, 672 w, 620 w;

[Rh(trop$_2$NH)(CNMes)]OTf (**27**)



MF = $C_{41}H_{34}F_3N_2O_3RhS$

MW = 794.69 g/mol

MP = 190-210 (dec) °C
Slightly air sensitive

[Rh(Cl)(trop$_2$NH)(CNMes)] (108 mg, 0.16 mmol, 1 eq.) and AgOTf (43 mg, 0.17 mmol, 1.05 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. THF (5 mL) was added and the resulting suspension was stirred overnight. The THF was removed under reduced pressure, the complex dissolved in DCM and filtered over celite. The DCM was removed under reduced pressure and the red solid recrystallized from THF/*n*-hexane and dried under vacuum. Yield: 76%, 232 mg, 0.27 mmol.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 2.40 (s, 3H, C*H*$_3$), 2.59 (s, 6H, C*H*$_3$), 4.14 (s, 1H, N*H*), 5.03 (s, 2H, C*H*^{benzyl}), 5.69 (d, $^3J_{HH}$ = 9.4 Hz, 2H, C*H*^{olefin}), 6.33 (dd, $^3J_{HH}$ = 9.1 Hz, $^2J_{RhH}$ = 3.1 Hz, 2H, C*H*^{olefin}), 6.90-6.95 (m, 2H, C*H*^{ar}), 7.01 (d, *J* = 3.96 Hz, 4H, C*H*^{ar}), 7.08 (s, 2H, C*H*^{ar}), 7.14 (d, *J* = 7.31 Hz, 2H, C*H*^{ar}), 7.25-7.37 (m, 6H, C*H*^{ar}), 7.50-7.55 (m, 2H, C*H*^{ar});

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 18.9 (s, 2C, *C*H$_3$), 21.4 (s, 1C, *C*H$_3$), 72.9 (s, 2C, *C*H^{benzyl}), 73.5 (d, $^1J_{RhC}$ = 6.9 Hz, 2C, *C*H^{olefin}), 73.9 (d, $^1J_{RhC}$ = 12.3 Hz, 2C, *C*H^{olefin}), 120.6 (q, $^1J_{CF}$ = 320.7 Hz, 1C, *C*F$_3$), 125.3 (s, 1C, *C*^{quart}), 127.3 (s, 2C, *C*H^{ar}), 127.4 (s, 2C, *C*H^{ar}), 127.7 (s, 2C, *C*H^{ar}), 127.7 (s, 2C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 129.1 (s, 2C, *C*H^{ar}), 129.2 (s, 2C, *C*H^{ar}), 130.2 (s, 2C, *C*H^{ar}), 130.3 (s, 2C, *C*H^{ar}), 135.0 (s, 2C, *C*^{quart}), 135.2 (s, 2C, *C*^{quart}), 135.2 (s, 2C, *C*^{quart}), 135.3 (d, *J* = 1.8 Hz, 2C, *C*^{quart}), 137.2 (s, 2C, *C*^{quart}), 140.2 (s, 1C, *C*^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6978 (s);

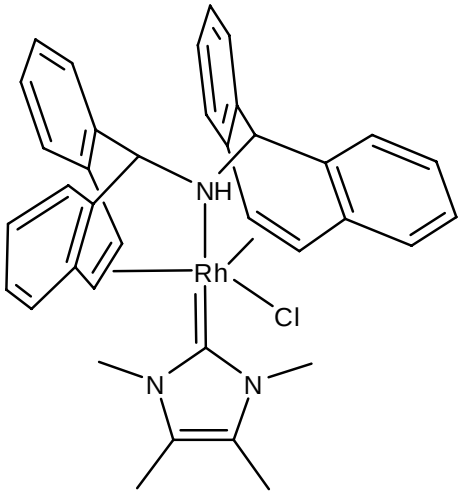
ATR IR (ν in cm^{-1}): 3218 w, 3047 w, 1736 w, 1602 w, 1491 m, 1476 m, 1422 m, 1377 w, 1295 m, 1277 m, 1260 m, 1230 s, 1219 s, 1170 m, 1144 s, 1081 m, 1047 m, 1024 w, 986 m, 973 m, 940 m, 891 m, 855 m, 826 m, 779 m, 743 s, 729 m, 712 m, 700 w, 686 w, 672 m, 631 s;

[Rh(Cl)(trop$_2$NH)(TMIY)]

MF = $C_{37}H_{35}ClN_3Rh$

MW = 660.05 g/mol

MP > 220 °C
Air stable



To a suspension of [Rh$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] (50 mg, 0.05 mmol, 1 eq.) in THF (3 mL) 1,2,4,5-tetramethylimidazole-2-ylidene (TMIY) (58 mg, 0.47 mmol, 10 eq.) was added. The dimer dissolves slowly and after 2 h a precipitate forms, but the precipitate is not pure. The suspension was stirred overnight and the solvent was removed under reduced pressure. Then the mixture of complexes was chromatographed on silica gel with DCM/Ethanol 10:1 to 7:3 starting with 10:1. The mixture should be dissolved when it is put on the column, a 1:1 mixture of DCM/Ethanol was found to work well. The product is in the last fraction. The [Rh(Cl)(trop$_2$NH)(TMIY)] was recrystallized from DCM/*n*-hexane (to remove eventual dissolved silica gel) followed by drying under vacuum. Yield: 62%, 38 mg, 0.06 mmol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 4.10 (s, 3H, CH_3), 4.25 (s, 3H, CH_3), 4.66 (s, 1H, N*H*), 4.69 (s, 2H, CH^{benzyl}), 4.89 (d, $^3J_{HH}$ = 9.4 Hz, 2H, CH^{olefin}), 5.08 (dd, $^3J_{HH}$ = 9.3 Hz, $^2J_{RhH}$ = 2.6 Hz, 2H, CH^{olefin}), 6.80-6.85 (m, 2H, CH^{ar}), 6.90 (d, *J* = 4.3 Hz, 4H, CH^{ar}), 7.02 (d, *J* = 7.3 Hz, 2H, CH^{ar}), 7.06 (dt, *J* = 7.3 Hz, *J* = 1.2 Hz, 2H, CH^{ar}), 7.15 (d, *J* = 7.3 Hz, 2H, CH^{ar}), 7.17 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 2H, CH^{ar}), 7.36 (d, *J* = 7.61 Hz, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 10.0 (s, 1C, *C*H_3), 10.4 (s, 1C, *C*H_3), 37.3 (s, 1C, *C*H_3), 37.9 (s, 1C, *C*H_3), 70.0 (d, $^1J_{RhC}$ = 13.7 Hz, 2C, *C*H^{olefin}), 71.4 (d, $^1J_{RhC}$ = 6.9 Hz, 2C, *C*H^{olefin}), 73.2 (s, 2C, *C*H^{benzyl}), 125.1 (s, 2C, *C*H^{ar}), 125.9 (s, 2C, *C*H^{ar}), 126.0 (s, 1C, *C*^{quart}), 126.1 (s, 2C, *C*H^{ar}), 126.9 (s, 1C, *C*^{quart}), 127.5 (s, 2C, *C*H^{ar}), 128.3 (s, 2C, *C*H^{ar}), 128.7 (s, 2C, *C*H^{ar}), 129.2 (s, 2C, *C*H^{ar}), 130.3 (s, 2C, *C*H^{ar}), 134.7 (s, 2C, *C*^{quart}), 135.1 (d, *J* = 1.4 Hz, 2C, *C*^{quart}), 137.5 (d, *J* = 1.8 Hz, 2C, *C*^{quart}), 140.6 (s, 2C, *C*^{quart}), 165.1 (d, $^1J_{RhC}$ = 48.8 Hz, 2C, *C*^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6612 (s);

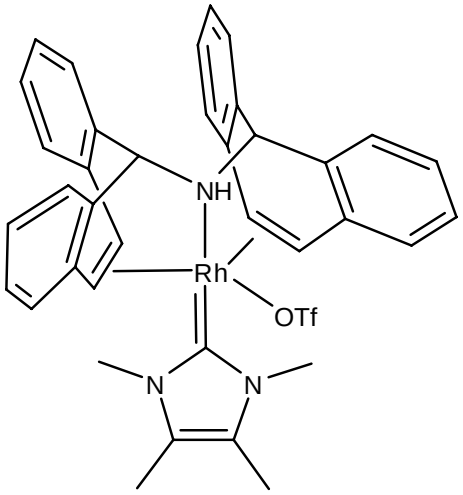
ATR IR (ν in cm^{-1}): 3623 w, 3412 w, 3026 w, 2025 br, 1673 w, 1627 w, 1600 w, 1490 m, 1475 m, 1435 w, 1381 w, 1355 w, 1307 w, 1262 w, 1225 w, 1188 w, 1159 w, 1086 w, 1060 m, 1045 w, 994 w, 976 m, 947 w, 871 w, 854 w, 824 m, 782 w, 749 s, 731 m, 688 m, 671 w.

[Rh(trop$_2$NH)(TMIY)]OTf (**28**)

MF = $C_{38}H_{35}F_3N_3O_3RhS$

MW = 773.67 g/mol

MP > 220 °C
Air stable



Preparation is analogous to **3**. [Rh(Cl)(trop$_2$NH)(TMIY)] (21 mg, 0.03 mmol, 1 eq.) and AgOTf (9 mg, 0.03 mmol, 1.1 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. DCM (5 mL) was added and the resulting suspension was stirred overnight. The solution was filtered over a plug of celite. DCM was removed under reduced pressure and the resulting red solid recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 91%, 22 mg, 0.03 mmol.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 2.24 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.42 (s, 1H, N*H*), 3.71 (s, 3H, CH_3), 4.07 (s, 3H, CH_3), 5.13 (d, $^3J_{HH}$ = 9.1 Hz, 2H, CH^{olefin}), 5.41 (s, 2H, CH^{benzyl}), 6.60 (dd, $^3J_{HH}$ = 9.1 Hz, $^2J_{RhH}$ = 3.4 Hz, 2H, CH^{olefin}), 7.01 (td, *J* = 7.5 Hz, *J* = 1.2 Hz, 2H, CH^{ar}), 7.12 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 2H, CH^{ar}), 7.21 (d, *J* = 7.3 Hz, 2H, CH^{ar}), 7.27-7.40 (m, 8H, CH^{ar}), 7.50-7.57 (m, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 9.0 (s, 1C, *C*H$_3$), 9.6 (s, 1C, *C*H$_3$), 35.2 (s, 1C, *C*H$_3$), 35.5 (s, 1C, *C*H$_3$), 72.4 (s, 2C, *C*H^{benzyl}), 81.0 (d, $^1J_{RhC}$ = 6.9 Hz, 2C, *C*H^{olefin}), 87.1 (d, $^1J_{RhC}$ = 14.2 Hz, 2 C, *C*H^{olefin}), 121.5 (q, $^1J_{CF}$ = 321.6 Hz, 1C, *C*F$_3$), 126.5 (d, *J* = 1.4 Hz, 2C, *C*H^{ar}), 127.0 (s, 1C, *C*^{quart}), 127.1 (s, 1C, *C*^{quart}), 128.4 (s, 2C, *C*H^{ar}), 128.6 (s, 2C, *C*H^{ar}), 128.7 (s, 2C, *C*H^{ar}), 128.9 (s, 2C, *C*H^{ar}), 129.3 (s, 2C, *C*H^{ar}), 129.5 (s, 2C, *C*H^{ar}), 131.3 (s, 2C, *C*H^{ar}), 134.6 (d, *J* = 1.8 Hz, 2C, *C*^{quart}), 135.2 (s, 2C, *C*^{quart}), 137.2 (s, 2C, *C*^{quart}), 137.3 (d, *J* = 2.7 Hz, 2C, *C*^{quart}), 164.2 (d, *J* = 48.4 Hz, 1C, *C*^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6868 (s);

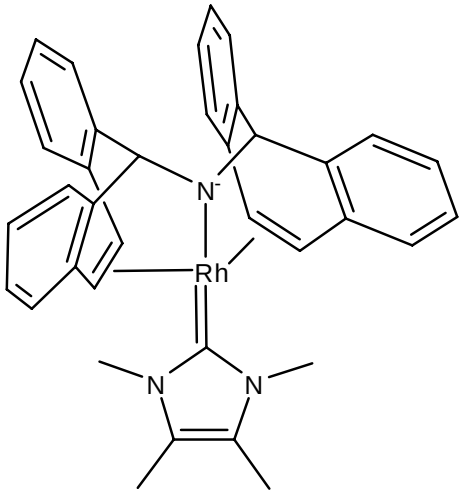
ATR IR (ν in cm^{-1}): 3705 w, 3046 w, 2950 w, 2032 br, 1662 w, 1600 w, 1491 br, 1429 w, 1385 w, 1366 w, 1270 w, 1258 s, 1223 m, 1154 w, 1145 s, 1070 w, 1027 s, 998 w, 977 w, 948 w, 847 w, 816 w, 786 w, 768 w, 757 s, 727 w, 691 w, 663 w, 635 s, 619 w.

[Rh(trop$_2$N)(TMIY)] (**29**)

MF = $C_{37}H_{34}N_3Rh$

MW = 623.59 g/mol

Air sensitive



The highly air-sensitive amide was prepared *in situ* in a young-NMR tube in [D_8] THF. [Rh(trop$_2$NH)(TMIY)]OTf **28** (10 mg, 0.03 mmol, 1 eq.) dissolved in [D_8] THF were deprotonated by addition of LiHDMS (4.7 mg, 0.03 mmol, 1.1 eq.) to give a dark green solution. However, the product precipitated from THF, the coupling constant of the carbene carbon could not be resolved due to very low intensity of the signal.

^{1}H-NMR (400 MHz, [D_8] THF, 200 K): δ = 2.21 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.52 (s, 3H, CH_3), 3.95 (s, 3H, CH_3), 4.77 (s, 2H, CH^{benzyl}), 4.78 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH^{olefin}), 6.02 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH^{olefin}), 6.60 (t, $^3J_{HH}$ = 7.2 Hz, 2H, CH^{ar}), 6.68 (t, $^3J_{HH}$ = 7.0 Hz, 2H, CH^{ar}), 6.89 (d, $^3J_{HH}$ = 7.3 Hz, 2H, CH^{ar}), 6.92-7.03 (m, 6H, CH^{ar}), 7.16 (br s, 4H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, [D_8] THF, 200 K): δ = 8.3 (s, 1C, CH$_3$), 8.6 (s, 1C, CH$_3$), 34.2 (s, 1C, CH$_3$), 34.9 (s, 1C, CH$_3$), 75.7 (br s, 2C, CH^{olefin}), 81.3 (br s, 2C, CH^{benzyl}), 81.3 (br s, 2C, CH^{olefin}), 124.4 (s, 2C, CH^{ar}), 124.8 (s, 2C, CH^{ar}), 124.9 (s, 2C, CH^{ar}), 125.2 (s, 2C, C^{quart}), 125.5 (s, 2C, CH^{ar}), 125.7 (s, 2C, CH^{ar}), 126.8 (s, 2C, CH^{ar}), 127.0 (s, 2C, CH^{ar}), 128.3 (s, 2C, CH^{ar}), 138.0 (s, 2C, C^{quart}), 138.7 (s, 2C, C^{quart}), 144.6 (s, 2C, C^{quart}), 147.2 (s, 2C, C^{quart}), 179.3 (d, *J* not resolved, C^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, [D_8] THF, 200 K): δ = -6969 (s);

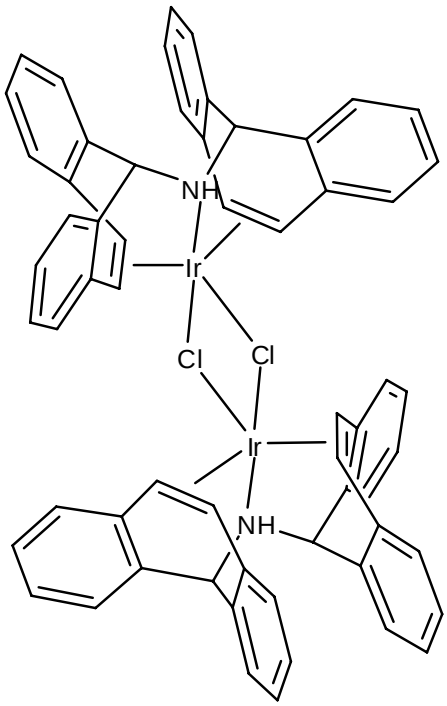
$[Ir_2(\mu_2\text{-}Cl)_2(trop_2NH)_2]$ (**30**)

MF = $C_{60}H_{46}Cl_2Ir_2N_2$

MW = 1250.36 g/mol

MP = > 250 °C

Air stable



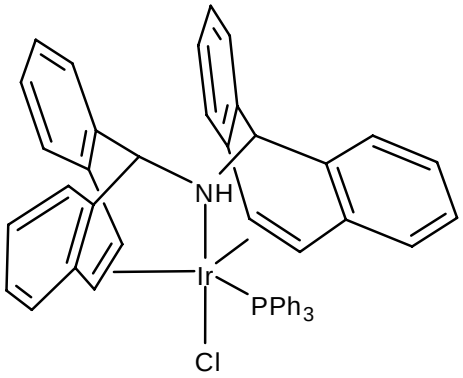
In a 250 mL three neck round bottom flask fitted with two stoppers, a reflux condenser and a stir bar $[Ir_2(\mu_2\text{-}Cl)_2(COE)_4]$ (1.00 g, 1.11 mmol, 1 eq.) are suspended under argon in 100 mL toluene/THF 1:1. After addition of $trop_2NH$ (950 mg, 2.39 mmol, 2.15 eq.) the reaction mixture is heated to 80 °C during 48 h. A yellow suspension forms and the air stable product is isolated by filtration, then washed with a small amount of toluene as well as pentane and dried under high vacuum. From the filtrate a second fraction can be obtained if the solvent is removed in vacuo, the resulting solid dissolved in a small amount of toluene/THF 1:1 and heated again for 48 h. Yield: 76%, 1056 mg, 0.84 mmol as yellow solid.

^{1}H-NMR (300.1 MHz, [D$_6$] DMSO): δ = 4.40 (d, $^3J_{HH}$ = 9.0 Hz, 4H, C*H*^{olefin}), 4.66 (s, 2H, N*H*), 4.93 (d, $^3J_{HH}$ = 9.0 Hz, 4H, C*H*^{olefin}), 4.95 (s, 4H, C*H*^{benzyl}), 6.70-6.85 (m, 12H, C*H*^{ar}), 7.04 (d, $^3J_{HH}$ = 5.1 Hz, 8H, C*H*^{ar}), 7.15-7.30 (m, 8H, C*H*^{ar}), 7.58 (d, $^3J_{HH}$ = 7.3 Hz, 4H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, [D$_6$] DMSO) δ = 51.1 (s, 4C, *C*H^{olefin}), 52.6 (s, 4C, *C*H^{olefin}), 69.9 (s, 4C, *C*H^{benzyl}), 124.3 (s, 4C, *C*H^{ar}), 125.0 (s, 4C, *C*H^{ar}), 127.6 (s, 4C, *C*H^{ar}), 128.2 (s, 4C, *C*H^{ar}), 128.3 (s, 4C, *C*H^{ar}), 128.8 (s, 4C, *C*H^{ar}), 128.9 (s, 4C, *C*H^{ar}), 129.6 (s, 4C, *C*H^{ar}), 134.2 (s, 4C, *C*^{quart}), 136.2 (s, 4C, *C*^{quart}), 137.0 (s, 4C, *C*^{quart}), 140.3 (s, 4C, *C*^{quart});

ATR IR (ν in cm^{-1}): 3199w (N-H st); 3023w (=C-Hs t); 2901w (-C-H st); 1600m; 1389s; 1464s; 1382w; 1311w; 1253m; 1216m; 1194w; 1106m; 1011w; 937m.

[Ir(Cl)(trop$_2$NH)(PPh$_3$)] (**31**)



MF = $C_{48}H_{38}ClIrNP$

MW = 887.47 g/mol

MP = > 220 °C

Air stable

Under aerobic conditions [Ir$_2$(μ_2-Cl)$_2$(trop$_2$NH)$_2$] **30** (600 mg, 0.48 mmol, 1 eq.) was suspended in 10 mL DCM and PPh$_3$ (375 mg, 1.43 mmol, 3 eq.) was added. After 30 min a pale yellow solution formed which was layered with *n*-hexane. Standing overnight yielded the product as pale yellow crystals. The mother liquor was decanted off, the crystals washed with *n*-hexane and dried under high vacuum. Yield: 89%, 756 mg, 0.85 mmol.

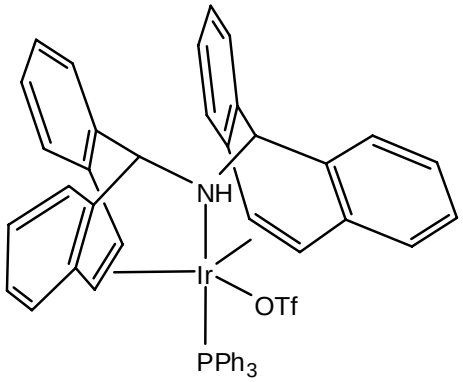
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 1H, N*H*), 4.02 (br s, 2H, C*H*^{benzyl}), 4.84 (dd, $^3J_{HH}$ = 9.4 Hz, $^3J_{PH}$ = 7.0 Hz, 2H, C*H*^{olefin}), 5.06 (dd, $^3J_{HH}$ = 9.4 Hz, $^3J_{PH}$ = 5.5 Hz, 2H, C*H*^{olefin}), 5.25-5.35 (m, 2H, C*H*^{ar}), 6.50-6.60 (m, 4H, C*H*^{ar}), 6.65-6.75 (m, 4H, C*H*^{ar}), 6.75-6.90 (m, 8H, C*H*^{ar}), 7.07-7.17 (m, 3H, C*H*^{ar}), 7.32-7.47 (m, 6H C*H*^{ar}), 8.12 (ddd, *J* = 9.9, *J* = 7.8, *J* = 1.8 Hz, 4H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$) δ = 49.6 (d, $^3J_{PC}$ = 6.4 Hz, 2C, *C*H^{olefin}), 53.1 (d, $^3J_{PC}$ = 18.3 Hz, 2C, *C*H^{olefin}), 72.8 (s, 2C, *C*H^{benzyl}), 123.6 – 141.6 (42C, CH^{ar} and C^{quart});

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$) δ = -19.7 (s);

ATR IR (ν in cm^{-1}): 3184 m, 3061 m, 1914 m, 1600 m, 1489 s, 1463 s, 1434 s, 1409 w, 1380 w, 1314 w, 1272 m, 1256 m, 1218 m, 1188 m, 1159 m, 1123 m, 1088 m, 1066 m, 1045 w, 1027 w, 998 w, 969 m, 936 m, 910 w, 896 w, 873 w, 829 w, 782 m, 751 m, 711 m, 697 s, 622 w;

[Ir(OTf)(trop$_2$NH)(PPh$_3$)] (**32**)



MF = $C_{49}H_{38}F_3IrNO_3PS$

MW = 1001.08 g/mol

MP > 220 °C (dec)

Air stable

[Ir(Cl)(trop$_2$NH)(PPh$_3$)] **31** (1078 mg, 1.21 mmol, 1 eq.) was suspended together with AgOTf (936 mg, 3.64 mmol, 3 eq.) in 20 mL DCM under argon. The suspension was stirred at RT for 96 h. The solution was filtered over celite (excessive losses should be avoided, parts of the product may be only sparingly soluble in DCM depending on how crystalline they are), washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure and the product crystallized from DCM. Yield 91%, 1105 mg, 1.10 mmol as off-yellow powder.
NMR for characterization was measured in [D$_6$] acetone due to the minimal solubility of the product in $CDCl_3$, however the values obtained in $CDCl_3$ are used for comparison to other compounds.
Crystals suitable for X-ray diffraction were obtained from DCM/*n*-hexane. Contamination with DCM should be avoided by recrystallization from hot THF/*n*-hexane for subsequent experiments, especially deprotonation.

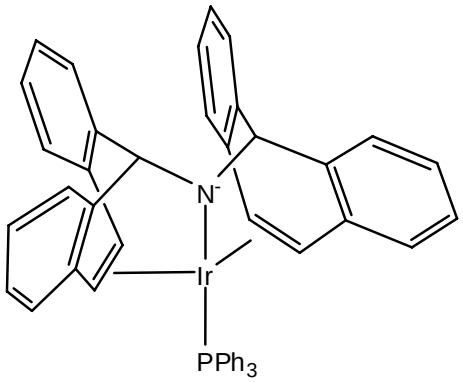
^{1}H-NMR (300 MHz, [D$_6$] acetone): δ = 2.91 (s, 1H, N*H*) 4.42 (dd, $^3J_{HH}$ = 9.4 Hz, $^3J_{PH}$ = 3.2 Hz, 2H, C*H*^{olefin}), 5.53 (dd, $^3J_{HH}$ = 9.4 Hz, $^3J_{PH}$ = 3.7 Hz, 2H, C*H*^{olefin}), 5.63 (d, $^3J_{PH}$ = 7.8 Hz, 2H, C*H*^{benzyl}), 6.76 (td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, C*H*^{ar}), 6.85-6.95 (m, 4H, C*H*^{ar}), 7.04 (d, $^3J_{HH}$ = 7.8 Hz, 2H C*H*^{ar}), 7.08 (td, $^3J_{HH}$ = 7.28, $^4J_{HH}$ = 1.6 Hz, 2H, C*H*^{ar}), 7.21 (m, 4H, C*H*^{ar}), 7.38 (d, $^3J_{HH}$ = 7.34 Hz, 2H, C*H*^{ar}), 7.69 (m, 9H, C*H*^{ar}), 7.86 (m, 6H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, [D$_6$] acetone): δ = 52.2 (s, 2C, *C*H^{olefin}), 58.1 (s, 2C, *C*H^{olefin}), 71.0 (s, 2C, *C*H^{benzyl}), 120.8 (q, $^1J_{FC}$ = 319.4 Hz, 1C, CF_3), 125.6 (s, 2C, *C*H^{ar}), 125.7 (s, 2C, *C*H^{ar}), 126.6 (s, 2C, *C*H^{ar}), 127.0 (s, 2C, *C*H^{quart}), 127.7 (s, 2C, *C*H^{quart}), 127.8 (s, 2C, *C*H^{ar}), 128.3 (s, 2C, *C*H^{ar}), 128.8 (d, $^2J_{PC}$ = 10.1 Hz, 6C, *C*H^{ar}), 128.8 (s, 2C, *C*H^{ar}), 129.2 (s, 2C, *C*H^{ar}), 129.9 (s, 2C, *C*H^{ar}), 131.4 (d, $^4J_{PC}$ = 2.4 Hz, 3C, *C*H^{ar}), 134.3 (s, 2C, *C*H^{quart}), 134.7 (d, $^3J_{PC}$ = 9.1 Hz, 6C, *C*H^{ar}), 135.8 (d, $^1J_{PC}$ = 31.4 Hz, 3C, *C*H^{quart}), 138.0 (s, 2C, *C*H^{quart});

^{31}P{^{1}H}-NMR (121 MHz, [D$_6$] acetone): δ = -0.1 (s);

ATR IR (ν in cm^{-1}): 3187 m, 3143 w, 3059 m, 1913 w, 1600 m, 1490 s, 1465 m, 1435 s, 1383 w, 1300 m, 1266 m, 1256 m, 1226 s, 1210 s, 1174 s, 1157 s, 1124 s, 1093 s, 1070 m, 1017 s, 980 m, 938 s, 910 w, 892 m, 871 w, 827 m, 781 w, 762 s, 744 s, 697 s, 629 s;

[Ir(trop$_2$N)(PPh$_3$)] (**33**)



MF = $C_{48}H_{37}IrNP$

MW = 851.00 g/mol

Air sensitive

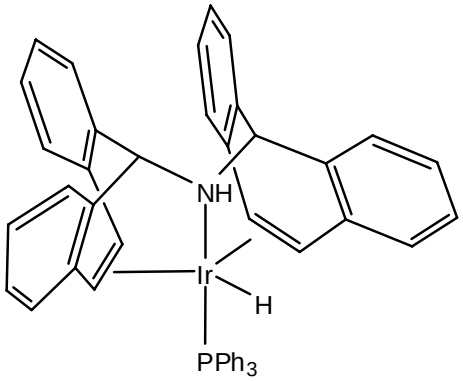
The amide complex [Ir(trop$_2$N)(PPh$_3$)] could not be isolated because it decomposed to several products when a THF solution was layered with *n*-hexane. It was only characterized in situ by NMR. [Ir(OTf)(trop$_2$NH)(PPh$_3$)] **32** (20 mg, 0.02 mmol, 1 eq.) was added to a young NMR tube, dissolved in 0.5 mL [D$_8$] THF and deprotonated by addition of LiHDMS (3.7 mg, 0.02 mmol 1.1 eq.). A dark green solution was obtained.

^{1}H-NMR (400 MHz, [D$_8$] THF): δ = 4.28 (dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{PH}$ = 8.1 Hz, 2H, C*H*^{olefin}), 5.59 (dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{PH}$ = 2.20 Hz, 2H, C*H*^{olefin}), 5.78 (d, $^3J_{PH}$ = 10.4 Hz, 2 H, C*H*^{benzyl}), 6.54 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}) 6.67 (t, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*^{ar}) 6.83 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 6.90-7.00 (m, 6 H, C*H*^{ar}) 7.05 (t, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*^{ar}), 7.27 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 7.50-7.70 (m, 15H, C*H*^{ar});

^{13}C{^{1}H}-NMR (101 MHz, [D$_8$] THF): δ = 64.6 (s, 2C, *C*H^{olefin}), 64.8 (s, 2C, *C*H^{olefin}), 81.2 (s, 2C, *C*H^{benzyl}), 124.5 (s, 2C, *C*H^{ar}), 125.1 (s, 2C, *C*H^{ar}), 125.6 (s, 2C, *C*H^{ar}), 126.2 (s, 2 C, *C*H^{ar}), 126.4 (s, 2 C, *C*H^{ar}), 126.6 (s, 2C, *C*H^{ar}), 127.7 (s, 2C, *C*H^{ar}), 128.3 (s, 2C, *C*H^{ar}), 128.9 (d, $^2J_{PC}$ = 8.9 Hz, 6C, *C*H^{ar}), 130.7 (s, 3C, *C*H^{ar}), 131.3 (d, *J* = 45.7 Hz, 3 C, *C*H^{quart}), 135.6 (d, $^3J_{PC}$ = 10.7 Hz, 6C, *C*H^{ar}), 137.1 (s, 2C, *C*H^{quart}), 137.3 (s, 2C, *C*H^{quart}), 143.9 (s, 2C, *C*H^{quart}), 146.0 (s, 2C, *C*H^{quart});

^{31}P{^{1}H}-NMR (162 MHz, [D$_8$] THF): δ = 14.6 (s);

[Ir(eq-H)(trop$_2$NH)(PPh$_3$)] (**34**)



MF = $C_{48}H_{39}IrNP$

MW = 853.02 g/mol

MP = 165 - 175 °C (dec)

Air sensitive

[Ir(OTf)(trop$_2$NH)(PPh$_3$)] **32** (50 mg, 0.05 mmol, 1 eq.) and NaOEt (4 mg, 0.05 mmol, 1 eq.) were dissolved in 2 mL THF and 1 mL ethanol. The THF was evaporated almost completely and the wet solid washed twice with 5 mL water. Residual water was removed under vacuum and the solid recrystallized from THF/*n*-hexane. The product was obtained as light yellow needles. Yield 89%, 38 mg, 0.04 mmol.

^{1}H-NMR (400 MHz, [D$_8$] THF): -11.92 (d, $^2J_{PH}$ = 21.05 Hz, 1H, Ir*H*), 3.30 – 3.35 (m, 4H, C*H*^{olefin}), 4.71 (d, $^4J_{PH}$ = 7.6 Hz, 2H, C*H*^{benzyl}), 5.80 (d, $^3J_{HH}$ = 5.9 Hz, 1H, N*H*), 6.45-6.50 (m, 2H, C*H*^{ar}), 6.57-6.67 (m, 6H, C*H*^{ar}), 6.84 (td, $^3J_{HH}$ = 7.30 Hz, $^4J_{HH}$ = 1.60 Hz, 2H, C*H*^{ar}), 7.00-7.10 (m, 6H, C*H*^{ar}), 7.45-7.50 (m, 9H, C*H*^{ar}), 7.77-7.85 (m, 6H, C*H*^{ar});

^{13}C{^{1}H}-NMR (101 MHz, [D$_8$] THF): δ = 39.0 (s, 2C, *C*H^{olefin}) 41.6 (d, $^2J_{PC}$ = 0.9 Hz, 2C, *C*H^{olefin}), 72.4 (d, $^3J_{PC}$ = 1.4 Hz, 2C, *C*H^{benzyl}), 121.3 (s, 2C, *C*H^{ar}), 123.1 (s, 2C, *C*H^{ar}), 127.2 (s, 2C, *C*H^{ar}), 127.3 (s, 2C, *C*H^{ar}), 127.7 (s, 2C, *C*H^{ar}), 127.9 (d, $^2J_{PC}$ = 10.1 Hz, 6C, *C*H^{ar}), 127.9 (s, 2C, *C*H^{ar}), 128.4 (s, 2C, *C*H^{ar}), 129.4 (s, 2C, *C*H^{ar}), 130.0 (d, $^4J_{PC}$ = 2.3 Hz, 3C, *C*H^{ar}), 132.0 (d, $^1J_{PC}$ = 55.3 Hz, 3C, *C*H^{quart}), 132.6 (s, 2C, *C*H^{quart}), 135.0 (d, $^3J_{PC}$ = 9.1 Hz, 6C, *C*H^{ar}), 137.6 (s, 2C, *C*H^{quart}), 138.2 (s, 2C, *C*H^{quart}), 144.9 (s, 2C, *C*H^{quart});

^{31}P{^{1}H}-NMR (162 MHz, [D$_8$] THF): δ = 18.1 (s);

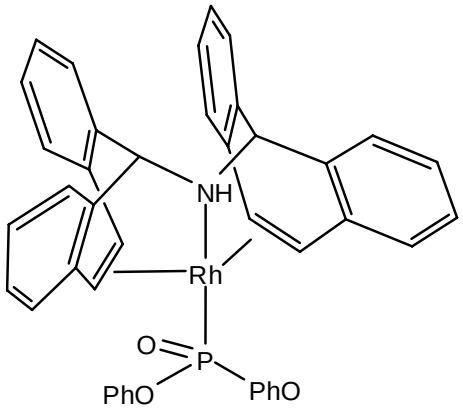
ATR IR (ν in cm^{-1}): 3264 w, 3047 w, 3019 w, 2890 w, 1881 m, 1598 m, 1489 m, 1462 m, 1434 m, 1411 w, 1384 w, 1316 w, 1253 w, 1235 w, 1221 w, 1185. w, 1160 w 1119 w, 1093 m, 1063 w, 1047 w, 1024 w, 997 w, 963 m, 930 w, 901 w, 858 w, 823 w, 782 w, 739 s, 713 m, 697 s, 685 s, 666 m, 626 m, 620 m, 610 m;

[Rh(trop$_2$NH)(PO(OPh)$_2$] (**35**)

MF = $C_{42}H_{33}NO_3PRh$

MW = 733.60 g/mol

MP > 220 (dec.)
Air stable



[Rh(trop$_2$NH)(P(OPh)$_3$]OTf **7** (50 mg, 0.05 mmol, 1 eq.) were dissolved in 2 mL THF under argon. KO*t*Bu (6.1 mg, 0.05 mmol, 1 eq.) was added. The color of the solution changed rapidly from orange to green to brownish yellow over 2 h. The THF was removed and the solid washed three times with 2 mL degassed water. The product was recrystallized from hot THF/diethylether. Yield: 81%, 31 mg, 0.04 mmol.

When the experiment was performed in [D_8] THF iso-butene and phenol were observed as byproducts.

^{1}H-NMR (300 MHz, [D_6] DMSO): δ = 4.16 (d, $^3J_{PH}$ = 8.3 Hz, 1H, N*H*), 5.01 (d, $^4J_{PH}$ = 12.0 Hz, 2H, C*H*^{benzyl}), 5.42 (d, $^3J_{HH}$ = 9.3 Hz, 2H, C*H*^{olefin}), 5.71 (d, $^3J_{HH}$ = 9.3 Hz, 2H, C*H*^{olefin}), 6.68-6.90 (m, 8H, C*H*^{ar}), 7.03-7.18 (m, 4H, C*H*^{ar}), 7.18-7.41 (m, 12H, C*H*^{ar}), 7.60 (d, $^3J_{HH}$ = 7.6 Hz, 2H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75 MHz, [D_6] DMSO): δ = 67.4 (d, $^1J_{RhC}$ = 11.9 Hz, 2C, *C*H^{olefin}), 68.3 (d, $^1J_{RhC}$ = 3.1 Hz, 2C, *C*H^{olefin}), 69.5 (s, 2C, *C*H^{benzyl}), 121.4 (d, $^2J_{PC}$ = 3.7 Hz, 4C, *C*H^{ar}), 123.6 (s, 2C, *C*H^{ar}), 125.7 (s, 2C, *C*H^{ar}), 126.6 (s, 2C, *C*H^{ar}), 128.4 (s, 4C, *C*H^{ar}), 128.5 (s, 4C, *C*H^{ar}), 129.2 (s, 2C, *C*H^{ar}), 129.7 (s, 4C, *C*H^{ar}), 129.9 (s, 2C, *C*H^{ar}), 135.2 (s, 2C, *C*^{quart}), 135.7 (s, 2C, *C*^{quart}), 137.8 (s, 2C, *C*^{quart}), 138.4 (s, 2C, *C*^{quart}), 153.2 (d, $^1J_{PC}$ = 13.7 Hz, 2C, *C*^{quart});

^{31}P{^{1}H}-NMR (121 MHz, [D_6] DMSO): δ = 74.1 (d, $^1J_{PC}$ = 171.1 Hz);

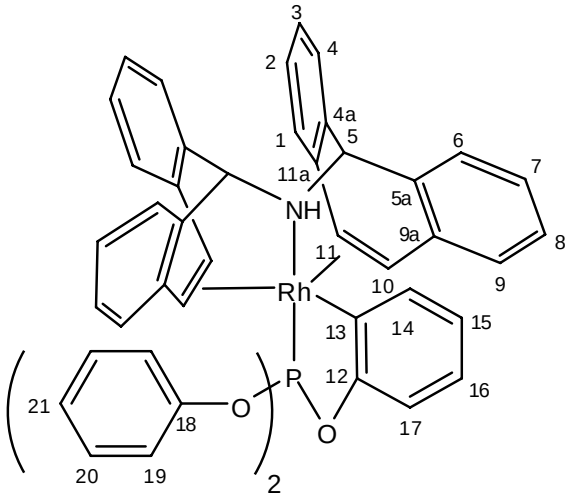
^{1}H, ^{103}Rh-NMR (12.6 MHz, [D_6] DMSO): δ = -7702 (d, $^1J_{RhP}$ = 171.1 Hz);

[Rh(trop$_2$NH)(P(OC$_6$H$_4$)(OPh)$_2$] (**36**)

MF = $C_{48}H_{37}NO_3PRh$

MW = 809.69 g/mol

MP = 180-185 (dec)
Slightly air sensitive



[Rh(trop$_2$NH)(P(OPh)$_3$]OTf **7** (50 mg, 0.05 mmol, 1 eq.) was dissolved in 2 mL THF under argon. LiHDMS (9.6 mg, 0.05 mmol, 1.05 eq.) was added. A deep green solution was obtained. The solution was heated for 6 h at 80 °C and the reaction followed by ^{31}P-NMR. THF was removed and the yellow solid washed three times with 2 mL degassed water to remove salts and excess base. The highly soluble product was recrystallized from a small amount of diethyl ether/*n*-hexane. Yield: 52%, 22 mg, 0.03 mmol.

^{1}H-NMR (500 MHz, [D$_6$] DMSO): δ = 3.29 (d, $^3J_{PH}$ = 7.0 Hz, 1H, N*H*), 4.47 (d, $^3J_{HH}$ = 9.2 Hz, 2H, C*H*^{olefin}), 4.61 (d, $^3J_{HH}$ = 9.2 Hz, 2H, C*H*^{olefin}), 4.82 (d, $^4J_{PH}$ = 11.7 Hz, 2H, C*H*^{5}), 5.76 (d, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*^{14}), 6.28 (t, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*^{15}), 6.58 (d, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*^{ar}), 6.70-6.80 (m, 8H, C*H*$^{ar\ 16,\ 17}$), 6.86 (d, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*^{ar}), 6.90-7.00 (m, 4H, C*H*^{ar}), 7.18 (d, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*^{ar}), 7.31 (d, *J* = 8.1 Hz, 6H, C*H*^{19} and C*H*^{21}), 7.49 (t, $^3J_{HH}$ = 7.3 Hz, 4H, C*H*^{20});

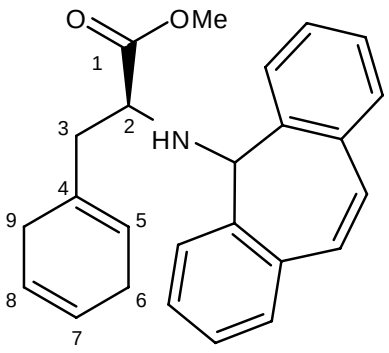
^{13}C{^{1}H}-NMR (126 MHz, [D$_6$] DMSO): δ = 55.8 (d, $^1J_{RhC}$ = 7.2 Hz, 2C, C*H*^{olefin}), 60.5 (d, $^1J_{RhC}$ = 8.2 Hz, 2C, C*H*^{olefin}), 71.3 (s, 2C, *C*H^5), 110.2 (d, $^3J_{PC}$ = 16.8 Hz, 1C, *C*H^{17}), 120.6 (d, $^3J_{PC}$ = 4.3 Hz, 4C, *C*H^{19}), 122.5 (s, 1C, *C*H^{15}), 123.6 (s, 2C, *C*H^{ar}), 124.6 (s, 1C, *C*H^{16}), 125.3 (s, 2C, *C*H^{ar}), 125.9 (s, 2C, *C*H^{21}), 128.5 (s, 6C, *C*H^{ar}), 128.9 (s, 2C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 130.3 (s, 2C, *C*H^{ar}), 131.0 (s, 4C, *C*H^{20}), 133.6 (s, 2C, *C*^{quart}), 134.9 (s, 1C, *C*H^{14}), 136.5 (s, 2C, *C*^{quart}), 137.1 (s, 2C, *C*^{quart}), 140.3 (s, 2C, *C*^{quart}), 150.0 (dd, $^1J_{RhC}$ = 34.5 Hz, $^3J_{PC}$ = 11.0 Hz, 1C, C^{13}) 152.1 (d, $^2J_{PC}$ = 11.0 Hz, 2C, C^{18}), 159.7 (d, $^2J_{PC}$ = 18.2 Hz, 1C, C^{12});
^{31}P{^{1}H}-NMR (121 MHz, [D$_6$] DMSO): δ = 139.0 (d, $^1J_{PC}$ = 223.5 Hz);

^{1}H, ^{103}Rh-NMR (15.8 MHz, [D$_6$] DMSO): δ = -8336 (d, $^1J_{RhP}$ = 223.5 Hz);

ATR IR (ν in cm^{-1}): 3249 w (NH), 3045 w (CH), 2886 w (CH), 1870 w, 1590 m, 1488 m, 1473 m, 1426 m, 1317 w, 1274 w, 1253 m, 1206 m, 1185 m, 1159 m, 1122 m, 1095 m, 1068 m, 1045 m, 1024 m, 1012 m, 967 m, 910 s, 882 s, 804 s, 742 s, 727 s, 706 s, 689 s, 667 m, 635 m, 615 m;

Compounds of section V

(2H-Phe)tropNH ((2*S*)-3-(Cyclohexa-1,4-dienyl)-2-(5*H*-dibenzo[*a,d*]cyclohepten-5-ylamino)-propionic acid methylester) (**37**) [99]



MF = $C_{25}H_{25}NO_2$

MW = 371.47 g/mol

MP = 68-71 °C
Air stable

(2*S*)-2-amino-3-cyclohexa-1,4-dien-1-ylpropanoate[99] (7.0 g, 32 mmol, 1 eq.) was suspended in 100 mL methylene chloride and triethyl amine (9 mL, 64 mmol, 2 eq.) was added. After stirring for 30 min, tropCl (7.3 g, 32 mmol, 1 eq.) was added. Stirring was continued for 2 h and the reaction mixture was washed with water (3x100 mL) and dried with $MgSO_4$. The solvent was removed *in vacuo* yielding a yellow oil. The product was purified by flash chromatography (ethyl acetate/*n*-hexane 1:4). Yield: 93%, 11 g, 30 mmol as off-white solid.

$[\alpha]_D^{22}$= -45.3° (*c*=0.1, CH_2Cl_2);

endo - conformer (85%):

^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.87 (dt, $^2J_{HH}$ = 22.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, CH_2^6), 2.15 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, CH_2^3), 2.23 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 3.6 Hz, 1H, CH_2^3), 2.25 (m, 1H, CH_2^6), 2.59 (br, 1H, N*H*), 2.71 (m, 2H, CH_2^9), 2.99 (dd, $^3J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, CH^2), 3.73 (s, 3H, OCH_3), 4.88 (s, 1H, CH^{benzyl}), 5.39 (br s, 1H, CH^5), 5.61 (m, 1H, CH^8), 5.73 (m, 1H, CH^7), 6.95 (d, $^3J_{HH}$ = 11.9 Hz, 1H, CH^{olefin}), 6.99 (d, $^3J_{HH}$ = 11.9 Hz, 1H, CH^{olefin}), 7.27-7.40 (m, 7H, CH^{ar}), 7.46 (d, $^3J_{HH}$ = 7.6 Hz, 1H, CH^{ar});

^{13}C{1H}-NMR (176 MHz, $CDCl_3$): δ = 26.9 (s, 1C, CH_2^9), 27.7 (s, 1C, CH_2^6), 41.1 (s, 1C, CH_2^3), 51.8 (s, 1C, OCH_3), 55.2 (s, 1C, CH^2), 67.5 (s, 1C, CH^{benzyl}), 123.3 (s, 1C, CH^5), 123.6 (s, 1C, CH^7), 124.1 (s, 1C, CH^8), 127.1 (s, 1C, CH^{ar}), 127.2 (s, 1C, CH^{ar}), 128.2 (s, 1C, CH^{ar}), 129.0 (s, 1C, CH^{ar}), 129.4 (s, 1C, CH^{ar}), 129.8 (s, 1C, CH^{ar}), 129.9 (s, 1C, CH^{ar}), 130.1 (s, 1C, CH^{ar}), 130.2 (s, 1C, CH^{olefin}), 130.4 (s, 1C, C^4), 130.5 (s, 1C, CH^{olefin}), 133.5 (s, 1C, C^{quart}), 133.5 (s, 1C, C^{quart}), 139.0 (s, 1C, C^{quart}), 139.4 (s, 1C, C^{quart}), 174.7 (s, 1C, C^1);

exo - conformer (15%):

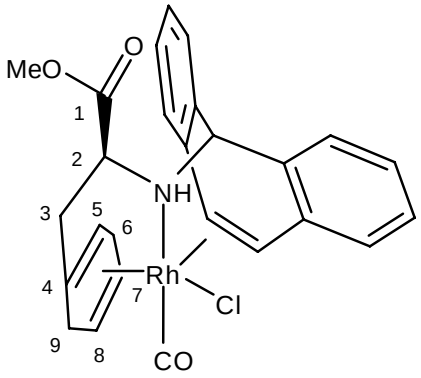
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.87 (m, 1H, CH_2^6), 2.27 (m, 1H, CH_2^6), 2.47 (m, 1H, CH_2^3), 2.52 (m, 1H, CH_2^3), 2.59 (s, 1H, N*H*), 2.71 (m, 1H, CH_2^9), 2.78 (m, 1H, CH_2^9), 3.58 (m, 1H, CH^2), 3.62 (s, 3H, OCH_3), 4.06 (s, 1H, CH^{benzyl}), 5.67 (br s, 1H, CH^5), 5.76 (m, 2H, CH^{7,8}), 7.21 (m, 2H, CH^{olefin}), 7.35 (m, 6H, CH^{ar}), 7.63 (d, $^3J_{HH}$ = 7.6 Hz, 1H, CH^{ar}), 7.69 (d, $^3J_{HH}$ = 7.9 Hz, 1H, CH^{ar});

$^{13}C\{1H\}$-NMR (176 MHz, $CDCl_3$): δ = 27.0 (s, 1C, CH_2^6), 29.4 (s, 1C, CH_2^9), 42.3 (s, 1C, CH_2^3), 51.6 (s, 1C, CH^2), 57.9 (s, 1C, OCH_3), 58.8 (s, 1C, CH^{benzyl}), 121.6 (s, 1C, CH^{ar}), 122.6 (s, 1C, CH^{ar}), 122.6 (s, 1C, CH^5), 124.0 (s, 1C, CH^7) 124.1 (s, 1C, CH^8), 125.6 (s, 1C, CH^{ar}), 125.6 (s, 1C, CH^{ar}), 127.6 (s, 1C, CH^{ar}), 127.7 (s, 1C, CH^{ar}), 128.5 (s, 1C, CH^{ar}), 128.6 (s, 1C, CH^{ar}), 131.0 (s, 1C, CH^{olefin}), 131.1 (s, 1C, CH^{olefin}), 131.2 (s, 1C, C^4), 133.5 (s, 1C, C^{quart}), 134.1 (s, 1C, C^{quart}), 139.3 (s, 1C, C^{quart}), 140.2 (s, 1C, C^{quart}), 175.6 (s, 1C, C^1);

ATR IR (ν in cm^{-1}): 3301 w (NH), 3027 w (CH), 2820 w (CH), 1736 s (CO), 1493 w, 1464 w, 1431 w, 1359 w, 1328 w, 1286 m, 1269 m, 1212 s, 1201 m, 1189 m, 1170 s, 1151 m, 1098 m, 1080 m, 1031 s, 984 m, 963 m, 878 m, 833 m, 803 s, 772 s, 763 m, 736 s, 722 m, 702 m, 684 m, 668 s;

EA found% (calc%) for $C_{25}H_{25}NO_2$: C: 80.67 (80.83), H: 6.84 (6.78), N: 3.79 (3.77);

[Rh(Cl)(CO)((2H-Phe)tropNH)] (**38**)



MF = $C_{26}H_{25}ClNO_3Rh$

MW = 537.84 g/mol

MP = 108-111 °C (dec)
Air stable

$[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (200 mg, 0.51 mmol, 1 eq.) were dissolved in 1 mL THF under argon and (2H-Phe)tropNH **37** (420 mg, 1.3 mmol, 2.2 eq.) added. The solution was stirred for 2 h and layered with *n*-hexane. A yellow crystalline material was obtained. Yield: 86%, 449 mg, 0.88 mmol.

$[\alpha]_D^{22}$= -108.0° (*c*=0.1, CH_2Cl_2);

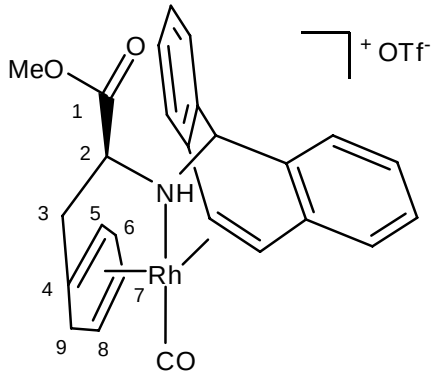
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 2.50 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, CH_2^3), 2.67 (m, 1H, CH_2^6), 2.70 (t, $^2J_{HH}$ = 14.5 Hz, 1H, CH_2^3), 2.80 (m, 1H, CH_2^9) 2.87 (m, 1H, CH_2^9), 2.93 (td, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 4.0 Hz, 1H, CH^2), 3.42 (m, 1H, CH_2^6), 3.87 (s, 3H, OCH_3), 3.92 (br s, 1H, CH^5), 4.45 (s, 1H, N*H*), 4.46 (s, 1H, CH^{benzyl}), 5.25 (dd, $^3J_{HH}$ = 9.2 Hz, $^2J_{RhH}$ = 2.1 Hz, 1H, CH^{olefin}), 5.28 (dd, $^3J_{HH}$ = 9.0 Hz, $^2J_{RhH}$ = 2.00 Hz, 1H, CH^{olefin}), 5.74 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 2.8 Hz, 1H, CH^7) 5.84 (dd, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 2.1 Hz, 1H, CH^8), 7.22 (t, $^3J_{HH}$ = 6.4 Hz, 2H, CH^{ar}), 7.28 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, CH^{ar}), 7.33 (td, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 1.2 Hz, 1H, CH^{ar}), 7.40 (dt, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 1.2 Hz, 1H, CH^{ar}), 7.45 (td, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.2 Hz, 1H, CH^{ar}), 7.64 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH^{ar});

^{13}C{1H}-NMR (176 MHz, $CDCl_3$): δ = 29.6 (s, 1C, CH_2^9), 30.9 (s, 1C, CH_2^6), 38.2 (s, 1C, CH_2^3), 53.1 (s, 1C, OCH_3), 56.6 (s, 1C, CH^2), 61.1 (d, $^1J_{RhC}$ = 11.3 Hz, 1C, CH^{olefin}), 63.7 (d, $^1J_{RhC}$ = 8.6 Hz, 1C, CH^{olefin}), 66.7 (s, 1C, CH^{benzyl}), 78.7 (d, $^1J_{RhC}$ = 8.6 Hz, 1C, CH^5), 98.0 (d, $^1J_{RhC}$ = 4.8 Hz, 1C, C^4), 123.4 (s, 1C, CH^7), 125.8 (s, 1C, CH^8), 126.6 (s, 1C, CH^{ar}), 126.8 (s, 1C, CH^{ar}), 127.8 (s, 1C, CH^{ar}), 128.7 (s, 1C, CH^{ar}), 129.2 (s, 1C, CH^{ar}), 129.3 (s, 1C, CH^{ar}), 129.6 (s, 1C, CH^{ar}), 129.8 (s, 1C, CH^{ar}), 133.4 (s, 1C, C^{quart}), 134.4 (s, 1C, C^{quart}), 137.6 (s, 1C, C^{quart}), 138.1 (d, $^2J_{RhC}$ = 1.3 Hz, 1C, C^{quart}), 171.1 (s, 1C, C^1), 186.2 (*d*, $^1J_{RhH}$ = 64.1 Hz, 1C, CO);

ATR IR (ν in cm^{-1}): 3170 w (NH), 3043 w (CH), 2899 w (CH), 2032 m (CO), 1738 s (CO), 1602 w, 1490 m, 1471 m, 1432 m, 1397 w, 1360 m, 1348 m; 1329 m, 1269 m, 1248 m, 1217 s, 1191 m, 1163 m, 1098 m, 1075 w, 1056 m, 1034.36 s, 1009 m, 978 m, 946 m, 922 m, 905 m, 894 m, 868 m, 843 m, 818 w, 773 s, 763 s, 747 m, 712 m, 660 m;

EA found% (calc%) for $C_{26}H_{25}ClNO_3Rh$: C: 57.92 (58.06), H: 4.72 (4.68), N: 2.61 (2.60);

[Rh(CO)((2H-Phe)tropNH)]OTf (**39**)



MF = $C_{27}H_{25}F_3NO_6RhS$

MW = 651.46 g/mol

MP = 162-165 °C (dec)
Slightly air sensitive

[Rh(Cl)(CO)((2H-Phe)tropNH)] (421 mg, 0.83 mmol, 1 eq.) and AgOTf (223 mg, 0.91 mmol, 1.1 eq.) were dissolved in DCM (20 mL). The reaction was stirred for 12 h and then filtered over celite. The yellow DCM solution was concentrated to 5 mL under reduced pressure. The solution was layered with hexane and the product was obtained as yellow powder. Yield: 89%, 478 mg, 0.73 mmol.

$[\alpha]_D^{22}$= -143.7° (*c*=0.1, CH_2Cl_2);

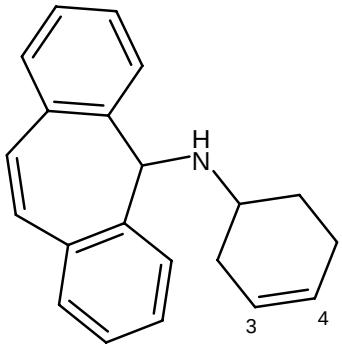
^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 2.53 (dd, $^2J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 13.4 Hz, 1H, CH_2^3), 2.67 (m, 1H, CH_2^3), 2.72 (m, 2H, CH_2^9), 2.73 (m, 1H, CH_2^6), 3.11 (dt, $^3J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 3.7 Hz, 1H, CH^2), 3.26 (m, 1H, CH_2^6), 3.90 (s, 3H, OCH_3), 4.47 (br, 1H, N*H*), 4.48 (br, 1H, 1H, CH^5), 4.65 (s, 1H, CH^{benzyl}), 5.47 (dd, $^3J_{HH}$ = 9.0 Hz, $^2J_{RhH}$= 1.0 Hz, 1H, CH^{olefin}), 5.76 (dd, $^3J_{HH}$ = 9.0 Hz, $^2J_{RhH}$= 2.8 Hz, 1H, CH^{olefin}), 5.80 (m, 1H, CH^7), 5.92 (m, 1H, CH^8), 7.29 (dt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, CH^{ar}), 7.36 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, CH^{ar}) 7.42-7.49 (m, 3H, CH^{ar}) 7.67 (d, $^3J_{HH}$ = 7.7 Hz, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (126 MHz, CD_2Cl_2): δ = 30.4 (s, 1C, CH_2^9), 31.0 (s, 1C, CH_2^6), 38.4 (s, 1C, CH_2^3), 53.7 (s, 1C, OCH_3), 57.3 (s, 1C, CH^2), 67.4 (s, 1C, CH^{benzyl}), 67.5 (m, 1C, CH^{olefin}), 67.5 (m, 1C, CH^{olefin}), 85.4 (m, 1C, CH^5), 102.3 (m, 1C, C^4), 120.4 (q, $^1J_{CF}$ = 320.1 Hz, 1C, CF_3), 123.8 (s, 1C, CH^7), 126.1 (s, 1C, CH^8), 127.9 (s, 1C, CH^{ar}), 128.1 (s, 1C, CH^{ar}), 128.4 (s, 1C, CH^{ar}), 129.2 (s, 1C, CH^{ar}), 129.7 (s, 1C, CH^{ar}), 130.5 (s, 1C, CH^{ar}), 130.6 (s, 1C, CH^{ar}), 130.7 (s, 1C, CH^{ar}), 134.7 (s, 1C, C^{quart}) 134.7 (d, $^2J_{RhC}$ = 1.4 Hz, 1C, C^{quart}) 136.1 (s, 1C, C^{quart}), 137.0 (d, $^2J_{RhC}$=1.9 Hz, 1C, C^{quart}), 170.9 (s, 1C, C^1), 185.8 (d, $^1J_{RhC}$ = 65.7 Hz, 1C, CO);

^{1}H, ^{103}Rh-NMR (15.8 MHz, CD_2Cl_2): δ = -7201;

ATR IR (ν in cm^{-1}): 3170 w (NH), 2899 w (CH), 2032 m (CO), 1737 s (CO), 1602 w, 1491 w, 1471 w, 1432 m, 1397 w, 1361 w, 1329 m, 1309 m, 1275 m, 1248 m, 1207 s, 1159 m, 1098 m, 1057m, 1034 s, 978 m, 946 w, 921 m, 905 m, 867 m, 844 w, 818 w, 773 s, 761 s, 711 m, 660 m;

cyhtropNH (N-cyclohex-3'-en-1'-yl-5*H*-dibenzo[*a,d*]cycloheptene-5-amine) (**40**)



MF = $C_{21}H_{21}N$

MW = 287.40 g/mol

MP = 88 °C
Air stable

Cyclohex-3-en-1-amine hydrochloride[102, 103] (1 g, 7.48 mmol, 1 eq.) was suspended in dry DCM (20 mL). Triethylamine (8 mL, 57 mmol, 7 eq.) was added and the mixture cooled to 0 °C. TropCl (1.86 g, 8.23 mmol, 1.1 eq.) was added and the mixture stirred overnight. A white solid (triethylamine hydrochloride) precipitated. The organic phase was washed with a saturated sodium hydrogen carbonate solution and dried over sodium sulfate. The product was purified by flash chromatography on silica gel with DCM. Yield: 69%, 1.48 g, 5.15 mmol.

Separation of enantiomers was successful on a Agilent 1100 series HPLC with a Chiralcel OJ column, *n*-hexane/isopropanol 80:20 1 mL/min. Retention time: enantiomer A: 18.3 min, enantiomer B: 26.7 min. 50 mg of the product were separated on a preparative HPLC from *Gilson* (306 pump, 156 UV-VIS detector, automatic sample collector) with a *Diacel Chiralcel* OJ column, *n*-hexane/isopropanol 85: 15, 15 mL/min Retention time: Enantiomer A: 18.3 min, Enantiomer B: 29.7 min. Enantiomeric purity was checked using a *Agilent 1100 Series* HPLC and the same column as above. It was >99% for both enantiomers. Yield: Enantiomer A: 44%, 22 mg; Enantiomer B: 32%, 17 mg as colorless oils. The separation was repeated several times without problems.

Enantiomer A: $[\alpha]_D^{22}$= +37.8° (*c*=0.1, CH_2Cl_2); Enantiomer B: $[\alpha]_D^{22}$= -38.0° (*c*=0.1, CH_2Cl_2);

endo - conformer (90%):
^{1}H-NMR (400 MHz, $CDCl_3$, 223K): δ = 1.2-1.5 (m, 1H, CH_2), 1.7-2.2 (m, 4H, CH_2), 2.3-2.5 (m, 1 H, CH_2), 2.83 (br s, 1H, N*H*), 4.36 (s, 1H, C*H*NH), 5.03 (s, 1H, CH^{benzyl}), 5.56 (m, 2H, C^3 and C^4), 7.09 (s, 2H, CH^{olefin}), 7.2-7.7 (m, 8H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$, 223K): δ = 25.1 (s, 1C, *C*H_2), 29.3 (s, 1C, *C*H_2), 32.4 (s, 1C, *C*H_2), 49.5 (s, 1C, *C*HNH), 65.4 (s, 1C, *C*H^{benzyl}), 125.5 (s, 1C, *C*H^3), 127.5 (s, 1C, *C*H^4), 127.6 (s, 1C, *C*H^{ar}), 127.6 (s, 1C, *C*H^{ar}), 129.4 (s, 1C, *C*H^{ar}), 129.5 (s, 1 C, *C*H^{ar}), 130.0 (s, 1C, *C*H^{ar}), 130.0 (s, 1C, *C*H^{ar}), 130.5 (s, 1C, *C*H^{ar}) 130.5 (s, 1C, *C*H^{ar}), 131.0 (s, 2C, *C*H^{olefin}), 133.3 (s, 1C, C^{quart}), 133.4 (s, 1C, C^{quart}), 139.7 (s, 1C, C^{quart}), 139.9 (s, 1C, C^{quart});

exo – conformer (10%):
^{1}H-NMR (400 MHz, $CDCl_3$, 223K): δ = 1.2-1.5 (m, 1H, CH_2), 1.7-2.2 (m, 4H, CH_2), 2.3-2.5 (m, 1 H, CH_2), 2.83 (br s, 1H, N*H*), 4.36 (s, 1H, C*H*NH), 5.06 (s, 1H, CH^{benzyl}), 5.63 (m, 2H, CH^{olefin}), 7.19 (s, 2H, CH^{olefin}), 7.2-7.7 (m, 8H, CH^{ar});

MS (EI, m/z, (%)):54.1 (40%), 79.1 (15%), 81.1 (15%), 165.0 (20%) 191.1 ($trop^+$, 100%), 287.2 (8%, M^+);

EA found% (calc%) for $C_{21}H_{21}N$: C: 87.48 (87.48), H: 7.41 (7.36), N: 4.84 (4.87);

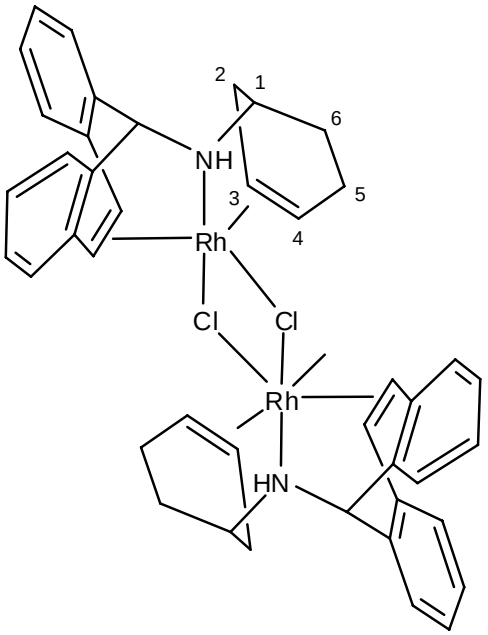
ATR IR (ν in cm^{-1}): 3022 w, 2914 w, 2817 w, 1653 w, 1483 w, 1449 w, 1432 w, 1389 w, 1355 w, 1265 w, 1199 w, 1155 w, 1127 w, 1101 m, 1038 m, 953 w, 931 w, 873 m, 853 w, 835 m, 797 s, 768 m, 748 s, 733 s, 696 m, 654 m, 636 m, 606 m;

$[Rh_2(\mu_2\text{-}Cl)_2(cyhtropNH)_2]$ (**41**)

MF = $C_{42}H_{42}Cl_2N_2Rh_2$

MW = 851.51 g/mol

MP > 230 °C (dec.)
Air stable

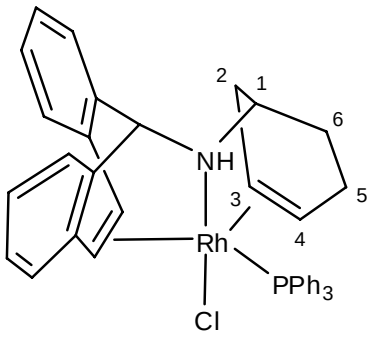


$[Rh_2(\mu_2\text{-}Cl)_2(COD)_2]$ (760 mg, 1.54 mmol, 1 eq.) and cyhtropNH **40** (893 mg, 3.11 mmol, 2.02 eq.) were dissolved in DCM under argon. Over the course of 72 h a red solid precipitates. The mother liquor is decanted off and the solid dried in high vacuum. Yield: 92%, 1210 mg, 1.42 mmol.

Since the product is very insoluble even in DMSO it was not characterized further by NMR.

ATR IR (ν in cm^{-1}): 3179 m, 3013 m, 2897 m, 2836 m, 2118 w, 1898 w, 1599 m, 1487 m, 1469 m, 1447 m, 1426 m, 1400 m, 1346 m, 1330 m, 1314 m, 1262 m, 1239 m, 1220 m, 1188 m, 1161 m, 1120 m, 1105 m, 1090 m, 1069 m, 1052 m, 1002 m, 975 m, 955 m, 908 m, 872 m, 852 m, 835 m, 805 m, 778 m, 750 s, 734 m, 728 s, 686 m, 641 m, 618 s;

[Rh(Cl)(cyhtropNH)(PPh_3)] (**42**)



MF = $C_{39}H_{36}ClNPRh$

MW = 688.04 g/mol

MP > 230 °C (dec.)
Air stable

To a suspension of [$Rh_2(\mu_2\text{-}Cl)_2$(cyhtropNH)$_2$] **41** (600 mg, 0.7 mmol, 1 eq.) in DCM (4 mL) PPh_3 (390 mg, 1.48 mmol, 2.1 eq.) and an orange solution formed after 10 min. Addition of *n*-hexane precipitated the orange-red product complex [Rh(Cl)(cyhtropNH)(PPh_3)] which was isolated by filtration followed by drying under vacuum. Yield: 92%, 893 mg, 1.3 mmol.

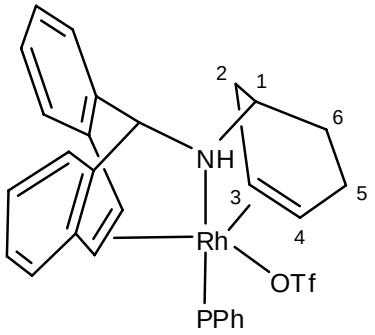
^{1}H-NMR (300 MHz, $CDCl_3$): δ = -0.38 (m, 1H, C*H*^{6}), 0.46 (m, 1H, C*H*^{2}), 0.90 (m, 1H, C*H*^{2}), 1.00 (m, 1H, N*H*), 1.19 (m, 1H, C*H*^{6}), 2.16 (m, 1H, C*H*^{1}), 2.2 (m, 1H, C*H*^{5}), 2.3 (m, 1 H, C*H*^{5}), 4.06 (m, 1H, C*H*^{benzyl}), 4.70 (t, *J* = 8.5 Hz, 1H, C*H*^{olefin}), 4.75 (m, 1H, CH_4), 4.95 (m, 1H, CH_3), 5.50 (m, 1H, C*H*^{olefin}), 6.10-6.20 (m, 3 H, C*H*^{ar}), 6.86-7.38 (m, 15 H, C*H*^{ar}), 7.60-8.04 (m, 5H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 20.1 (d, *J* = 8.3 Hz, 1C, *C*H^5), 28.1 (s, 1C, *C*H^6), 29.4 (d, *J* = 3.6 Hz 1C, *C*H^2), 60.0 (d, *J* = 2.7 Hz, 1 C, *C*H^1), 65.8 (dd, *J* = 8.2 Hz, *J* = 5.9 Hz, 1C, *C*H^{olefin}), 67.3 (dd, *J* = 8.7 Hz, *J* = 6.9 Hz, 1C, *C*H^4), 69.5 (dd, *J* = 20.8 Hz, *J* = 9.4 Hz, 1C, *C*H^{olefin}), 71.1 (dd, *J* = 16.0 Hz, *J* = 9.1 Hz,1C, *C*H^3), 71.6 (s, 1 C, CH^{benzyl}), 123.9-140.2 (m, 30 C, *C*H^{ar} and *C*^{quart});

^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 10.6 (d, $^1J_{RhP}$ = 112.6 Hz);

ATR IR (ν in cm^{-1}): 3220 (w), 3045 (w), 2837 (w), 2360 (w), 2160 (w), 1977 (w), 1597 (w), 1470 (w), 1433 (m), 1090 (m), 977 (w), 876 (w), 750 (s), 696 (s), 621 (m)

[Rh(OTf)(cyhtropNH)(PPh_3)] (**43**)



MF = $C_{40}H_{36}F_3NO_3PRhS$

MW = 801.66 g/mol

MP = 218 - 224 °C (dec.)
Air stable

[Rh(Cl)(cyhtropNH)(PPh_3)] **42** (315 mg, 0.46 mmol, 1 eq.) and AgOTf (124 mg, 0.48 mmol, 1.05 eq.) were placed in a Schlenk-tube with a stir-bar and put under argon. DCM (5 mL) was added and the resulting suspension was stirred 12 h. The solution was filtered over celite. Some of the DCM was removed under reduced pressure and the product complex precipitated by addition of *n*-hexane. Yield: 90%, 112 mg, 0.13 mmol as orange solid.

Enantiomer A: $[\alpha]_D^{22}$= -49.8° (*c*=0.1, CH_2Cl_2); Enantiomer B: $[\alpha]_D^{22}$= 52.0° (*c*=0.1, CH_2Cl_2);

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 0.61 (d, *J* = 13.9 Hz, 1H, C*H*^{2}), 0.74 (d, *J* = 15.7 Hz, 1H, C*H*^{2}), 1.68-1.75 (m, 1H, C*H*^{5}), 2.12 (t, *J* = 12.5 Hz, 1H, C*H*^{5}), 2.38 (t, *J* = 13.9 Hz, 1H, C*H*^{6}), 2.87-3.00 (m, 1H, C*H*^{6}), 3.08 (s, 1H, C*H*^{1}), 4.23 (br s, 1H, C*H*^{4}), 4.64 (d, $^3J_{PH}$ = 4.0 Hz, 1H, N*H*), 4.89 (d, *J* = 8.8 Hz, 1H, C*H*^{olefin}), 4.96 (d, *J* = 7.3 Hz, 1H, C*H*^{3}), 5.03 (d, *J* = 8.8 Hz, 1H, C*H*^{benzyl}), 5.82 (dt, $^3J_{HH}$ = 9.2 Hz, $^2J_{RhH}$ = 3.5 Hz, 1H, C*H*^{olefin}), 7.42-7.62 (m, 8H, C*H*^{ar}), 7.47-7.62 (m, 9H, C*H*^{ar}), 7.63-7.76 (m, 6H, C*H*^{ar});

^{13}C{^{1}H}-NMR (126 MHz, CD_2Cl_2): δ = 19.0 (s, 1C, *C*H^6), 27.6 (s, 1C, *C*H^5), 34.4 (s, 1C, *C*H^2), 57.3 (d, $^3J_{PC}$ = 2.7 Hz, 1C, CH^1), 71.1 (s, 1C, *C*H^{benzyl}), 73.9 (d, $^1J_{RhC}$ = 7.6 Hz, 1C, *C*H^{olefin}), 74.1 (d, $^1J_{RhC}$ = 14.0 Hz, 1C, *C*H^{olefin}), 77.1 (d, $^1J_{RhC}$ = 7.3Hz, 1C, CH^4), 92.8 (d, $^1J_{RhC}$ = 12.2 Hz, 1C, CH^3), 120.4 (q, $^1J_{CF}$ = 320.7 Hz, 1C, *C*F$_3$), 126.7 (s, 1C, *C*H^{ar}), 126.9 (s, 1C, *C*H^{ar}), 127.2 (s, 1C, *C*H^{ar}), 127.6 (s, 1C, *C*H^{ar}), 128.7 (d, *J* = 9.7 Hz, 6C, *C*H^{ar}), 128.6 (s, 1C, *C*H^{ar}), 129.1 (s, 1C, *C*H^{ar}), 129.5 (d, *J* = 46.3 Hz, 3C, *C*^{quart}), 129.3 (s, 1C, *C*H^{ar}), 129.6 (s, 1C, *C*H^{ar}), 130.8 (d, *J* = 2.4 Hz, 3C, *C*H^{ar}), 134.0 (d, *J* = 9.7 Hz, 6C, *C*H^{ar}), 134.3 (s, 1C, *C*^{quart}), 135.9 (d, *J* = 1.5 Hz, 1C, *C*^{quart}), 137.1 (s, 1C, *C*^{quart}), 137.5 (d, *J* = 2.4 Hz, 1C, *C*^{quart});

^{19}F NMR (183 MHz, CD_2Cl_2) δ = –78.1 (s);

^{31}P{^{1}H}-NMR (203 MHz, CD_2Cl_2): δ = 39.7 (d, $^1J_{RhP}$ = 140.9 Hz);

^{1}H, ^{103}Rh-NMR (15.8 MHz, CD_2Cl_2): δ = -6898 (d, $^1J_{RhP}$ = 140.9 Hz);

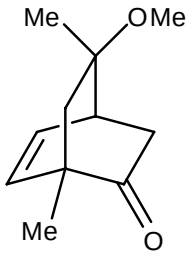
ATR IR (ν in cm-1): 3220 w, 3045 w, 2929 w, 2837 w, 1597 w, 1482 m, 1470 m, 1433 m, 1416 w, 1349 w, 1314 w, 1261 w, 1223 w, 1191 w, 1158 w, 1120 w, 1090 m,

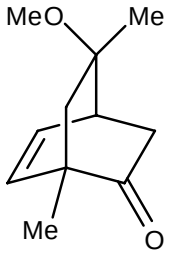
1070 w, 1058 w, 1026 w, 996 w, 976 w, 910 w, 875 w, 857 w, 778 w, 749 s, 695 s,6 46 w, 621 m, 579 w, 556 w;

(l*S*,4*S*,8*R*)- and (lS,4S,8S)-8-Methoxy-l ,8 dimethylbicyclo-[2.2.2]oct-5-en-2-one (**44** and **45**) [105]

MF = $C_{11}H_{16}O_2$

MW = 180.24 g/mol



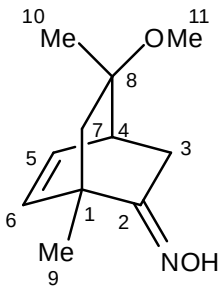


Air stable

The two diastereoisomers were synthesized as described in the literature [105] but were separated by FC with ethyl acetate/*n*-hexane (1: 4) on silica gel and a longer column. **44** R_f = 0.4; **45** R_f = 0.3; Separation on a later stage proved not to work well.

The compounds do not absorb well in UV light and should be made visible by staining, a standard p-anisaldehyde stain proved to work very well. Analytical data was in agreement with the literature.

(l*S*,4*S*,8*R*)-8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-one oxime (**46**)
MF = $C_{11}H_{17}NO_2$



MW = 195.26 g/mol

MP = 104 °C
Air stable

(l*S*,4*S*,8*R*)-8-Methoxy-l,8 dimethylbicyclo-[2.2.2]oct-5-en-2-one **44** (1.63 g, 9.0 mmol, 1 eq.), sodium acetate (1.48 g, 18 mmol, 2 eq.) and hydroxylamine hydrochloride (1.57 g, 22.6 mmol, 2.5 eq.) were added to a round bottom flask. Methanol (50 mL) was added and the mixture heated 6 h at reflux. The methanol was removed under reduced pressure and the residue dissolved in diethyl ether, which was washed with a saturated hydrogen carbonate solution and dried over sodium sulfate. The solvent was removed under reduced pressure and the product optionally recrystallized from *n*-hexane. Yield: 95%, 1.668 g, 8.6 mmol.

$[\alpha]_D^{22}$= -454.8° (*c*=0.1, CH_2Cl_2);

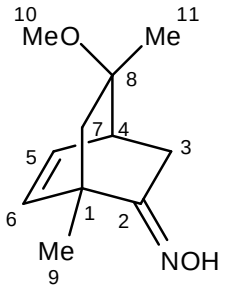
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 3H, CH_3^{10}), 1.31 (s, 3H, CH_3^9), 1.37 (d, $^2J_{HH}$ = 13.2 Hz, 1H, CH_2^7), 1.73 (d, $^2J_{HH}$ = 13.2 Hz, 1H, CH_2^7), 2.05 (dd, $^2J_{HH}$ = 18.3 Hz, $^3J_{HH}$ = 3.4 Hz, 1H, CH_2^3), 2.83 (dd, $^2J_{HH}$ = 18.3 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, CH_2^3), 2.86 (m, 1H, CH^4), 3.19 (s, 3H, OCH_3^{11}), 5.92 (d, $^3J_{HH}$ = 8.1 Hz, 1H, CH^6), 6.35 (t, $^3J_{HH}$ = 7.6 Hz, 1H, CH^5), 9.14 (s, 1H, O*H*);

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 19.2 (s, 1C, *C*H$_3^9$), 24.8 (s, 1C, *C*H$_3^{10}$), 25.9 (s, 1C, CH$_2^3$), 40.3 (s, 1C, *C*H^4), 41.6 (s, 1C, *C*^{1}), 47.8 (s, 1C, CH$_2^7$), 49.6 (s, 1C, O*C*H$_3^{11}$), 78.6 (s, 1C, *C*^{8}), 134.7 (s, 1C, *C*H^5), 136.2 (s, 1C, *C*H^6), 163.8 (s, 1C, *C*^{2});

EA found% (calc%) for $C_{11}H_{17}NO_2$: C:67.52 (67.66), H: 8.80 (8.78), N: 7.19 (7.17);

ATR IR (ν in cm^{-1}): 3257 w, 3140 w, 3038 w, 2965 m, 2928 m, 2827 w, 2161 w, 1682 w, 1614 w, 1435 m, 1372 m, 1338 w, 1321 w, 1284 m, 1252 m, 1188 m, 1164 m, 1152 m, 1129 w, 1096 w, 1072 m, 1059 m, 1020 w, 992 w, 931 s, 913 s, 888 m, 848 m, 812 m, 758 m, 722 s, 675 m, 646 m;

(l*S*,4*S*,8*S*)-8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-one oxime (**47**)
MF = $C_{11}H_{17}NO_2$



MW = 195.26 g/mol

MP = 74 °C
Air stable

(l*S*,4*S*,8*S*)-8-Methoxy-l,8 dimethylbicyclo-[2.2.2]oct-5-en-2-one **45** (1.89 g, 10.5 mmol, 1 eq.), sodium acetate (1.72 g, 21 mmol, 2 eq.) and hydroxylamine hydrochloride (1.82 g, 26.2 mmol, 2.5 eq.) were added to a round bottom flask. Methanol (50 mL) was added and the mixture heated 6 h under reflux. The methanol was removed under reduced pressure and the residue dissolved in diethyl ether, which was washed with a saturated hydrogen carbonate solution and dried over sodium sulfate. The solvent was removed under reduced pressure and the product optionally recrystallized from *n*-hexane. Yield: 93%, 1.89 g, 9.7 mmol.

$[\alpha]_D^{22}$= -387.3° (*c*=0.1, CH_2Cl_2);

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3H, CH_3^9) 1.33 (s, 3H, CH_3^{11}), 1.51 (d, $^2J_{HH}$ = 13.5 Hz, 1H, CH_2^7), 1.65 (d, $^2J_{HH}$ = 13.5 Hz, 1H, CH_2^7), 2.20 (dd, $^2J_{HH}$ = 18.8 Hz, $^3J_{HH}$ = 3.4 Hz, 1H, CH_2^3), 2.50 (dd, $^2J_{HH}$ = 18.8 Hz, $^3J_{HH}$ = 2.4 Hz, 1H, CH_2^3), 2.94 (m, 1H, CH^4), 3.17 (s, 3H, OCH_3^{10}), 6.00 (d, $^3J_{HH}$ = 8.1 Hz, 1H, CH^6), 6.39 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, CH^5), 8.98 (s, 1H, O*H*);

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 19.2 (s, 1C, *C*H$_3^9$), 22.5 (s, 1C, *C*H$_3^{11}$), 27.8 (s, 1C, *C*H$_2^3$), 39.9 (s, 1C, *C*H^4), 41.6 (s, 1C, *C*^{1}), 48.8 (s, 1C, *C*H$_2^7$), 49.3 (s, 1C, O*C*H$_3^{10}$), 79.0 (s, 1C, C^8), 134.4 (s, 1C, *C*H^6), 134.6 (s, 1C, *C*H^5), 163.7 (s, 1C, *C*^{2});

EA found% (calc%) for $C_{11}H_{17}NO_2$: C:67.52 (67.66), H: 8.71 (8.78), N: 7.19 (7.17);

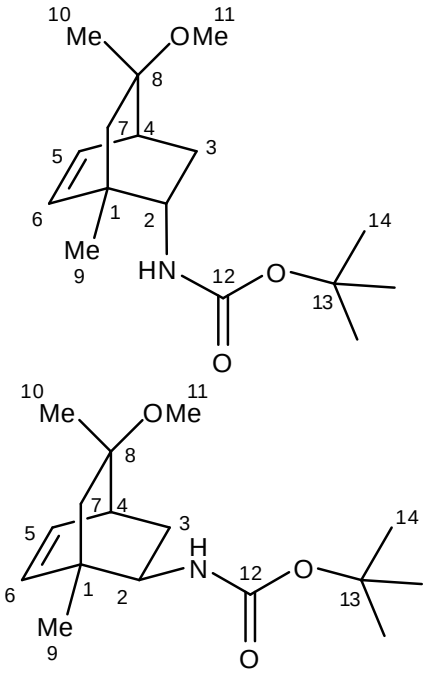
ATR IR (ν in cm^{-1}): 3261 w, 2969 w, 2824 w, 1676 w, 1465 w, 1422 w, 1376 w, 1322 w, 1284 w, 1249 w, 1229 w, 1196 w, 1176 w, 1143 m, 1133 m, 1078 s, 1062 m, 1017 w, 992 w, 931 s, 893 m, 850 w, 814 m, 771 m, 748 m, 727 m, 718 s, 674 m, 661 m;

(l*S*,2*S*,4*S*,8*R*)- *tert*-butyl (8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate (**48**) and (l*S*,2*R*,4*S*,8*R*)-*tert*-butyl (8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate (**49**):
MF = $C_{16}H_{27}NO_3$

MW = 281.39 g/mol

MP = 73 °C (**48)**

Air stable



Sodium (2.4 g, 103 mmol, 20 eq.) was suspended in 100 mL dry toluene in a three neck round bottom flask equipped with a large stir bar, an efficient reflux condenser with an argon inlet and a dropping funnel. The dropping funnel was charged with a solution of (l*S*,4*S*,8*R*)-8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-one oxime **46** (1 g, 5.15 mmol, 1 eq.) in 50 mL toluene (only diastereoisomer **46** was used, but **47** should work also). The toluene was refluxed until a fine suspension of sodium was obtained. Then the solution of the oxime was added dropwise over 15 min. The reaction was refluxed for another 15 min and 20 mL dry ethanol added carefully to the hot solution until all the sodium was reacted. The solution was cooled in an ice bath and acidified with 8 mL 37% HCl. A little more 4 M HCl was added to acidify the solution. All volatiles were removed under reduced pressure and the solid dissolved in as little water as possible, extracted with *n*-hexane and made basic with sodium hydroxide. The crude free amine was extracted five times with small portions of diethyl ether and the organic phase dried over pulverized potassium hydroxide. The diethyl ether was removed under reduced pressure. The amine is quite volatile and should not be dried under high vacuum. It can be purified by column chromatography on silica gel with DCM/ethanol 5:1 but the yields obtained were very poor. The obtained crude (l*S*,2*RS*,4*S*,8*R*) (8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)amine (790 mg, 4.36 mmol, 85%) was dissolved in 8 mL dry DCM, triethylamine (0.8 mL, 5.7 mmol, 1.3 eq.) and Di-*tert*-butyl dicarbonate (1050 mg, 4.8 mmol, 1.1 eq.) were added. The mixture was stirred overnight. The organic phase was washed with an aqueous solution of sodium carbonate and dried over sodium sulfate. The diastereoisomers were separated by chromatography over silica gel with *n*-hexane/ethyl acetate 10:1 and dried under high vacuum. They do not absorb well in UV and should be made visible by staining, a standard anisaldehyde stain or a ninhydrin stain proved to work well. (l*S*,2*S*,4*S*,8*S*)- tert-butyl (8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate **48**: R_f = 0.32. Yield: 61%, 748 mg, 2.66 mmol as white solid. (l*S*,2*R*,4*S*,8*S*)- tert-butyl (8-methoxy-1,8-

dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate **49**: R_f = 0.43. Yield: 29%, 355 mg, 1.26 mmol as colorless oil. Yield combined: 90%, 1103 mg, 3.92 mmol.

(l*S*,2*S*,4*S*,8*S*)- tert-butyl (8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate **48**:

$[\alpha]_D^{22}$= -76.3° (*c*=0.1, CH_2Cl_2);

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.77 (dt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 2.90 Hz, 1H, CH_2^7), 1.11 (s, 3H, CH_3^{10}), 1.14 (s, 3H, CH_3^9), 1.17 (d, $^2J_{HH}$ = 13.6 Hz, 1H, CH^7), 1.45 (s, 9H, CH_3^{14}), 1.52 (d, $^2J_{HH}$ = 13.6 Hz, 1H, CH^7), 2.54 (dt, $^3J_{HH}$ = 6.0, $^3J_{HH}$ = 2.9 Hz, 1H, CH^4), 2.65 (ddd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH_2^3), 3.18 (s, 3H, OCH_3^{11}), 3.75 (ddd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH^2), 4.20 (d, $^3J_{HH}$ = 9.5 Hz, 1H, N*H*), 5.82 (d, $^3J_{HH}$ = 8.1 Hz, 1H, CH^6), 6.35 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, CH^5);

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 21.8 (s, 1C, *C*H_3^9), 25.0 (s, 1C, *C*H_3^{10}), 28.9 (s, 3C, *C*H_3^{14}), 33.0 (s, 1C, *C*H_2^3), 40.5 (s, 1C, *C*^{1}), 40.5 (s, 1C, *C*H^4), 47.8 (s, 1C, *C*H_2^7), 50.0 (s, 1C, O*C*H_3^{11}), 53.2 (s, 1C, *C*H^2), 79.1 (s, 1C, *C*^{1}), 79.2 (s, 1C, *C*^{8}), 135.6 (s, 1C, *C*H^5), 136.1 (s, 1C, *C*H^6), 156.1 (s, 1C, *C*^{12});

EA found% (calc%) for $C_{16}H_{27}NO_3$: C: 68.26 (68.29), H: 9.61 (9.67), N: 4.91 (4.98);

ATR IR (ν in cm^{-1}): 3315 m (NH), 3044 w (CH), 2964 m (CH), 2933 m (CH), 2826 w, 1682 s (C=O), 1529 s (C=C), 1454 m, 1390 m, 1377 m, 1365 m, 1330 m, 1287 m, 1270 m, 1248 m, 1214 m, 1171 s, 1129 m, 1103 m, 1076 m, 1060 s, 1051 s, 1030 m, 1003 m, 975 m, 955 w, 926 w, 901 m, 879 m, 836 m, 786 m, 755 m, 744 s, 722 s, 674 m, 644 m, 613 m;

(l*S*,2*R*,4*S*,8*S*)- tert-butyl (8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate **49**:

$[\alpha]_D^{22}$= -96.9° (*c*=0.1, CH_2Cl_2);

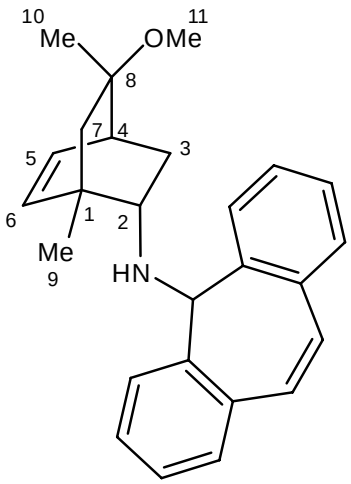
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.04 (dd, $^2J_{HH}$ = 13.6 Hz, *J* = 1.8 Hz, 1H, CH_2^7), 1.08 (s, 3H, CH_3^9), 1.14 (s, 3H, CH_3^{10}), 1.47 (s, 9H, CH_3^{14}), 1.52 (dt, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH_2^3), 1.69 (d, $^2J_{HH}$ = 13.6 Hz, 1H, CH_2^7), 1.76 (ddd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH_2^3), 2.57 (dt, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH^4), 3.22 (s, 3H, OCH_3^{11}), 3.56 (ddd, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH^2), 4.92 (d, $^3J_{HH}$ = 9.5 Hz, 1H, N*H*), 5.98 (d, $^3J_{HH}$ = 8.1 Hz, 1H, CH^6), 6.24 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, CH^5);

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 21.9 (s, 1C, *C*H_3^9), 25.1 (s, 1C, *C*H_3^{10}), 28.9 (s, 3 C, *C*H_3^{14}), 31.3 (s, 1C, *C*H_2^3), 39.4 (s, 1C, *C*H^4), 40.1 (s, 1C, *C*^{1}), 44.5 (s, 1C, *C*H_2^7), 49.9 (s, 1C, O*C*H_3^{11}), 50.3 (s, 1C, *C*H^2), 79.1 (s, 1C, *C*^{8}), 79.2 (s, 1C, *C*^{13}), 134.1 (s, 1C, *C*H^5), 139.7 (s, 1C, *C*H^6), 156.5 (s, 1C, *C*^{13});

ATR IR (ν in cm^{-1}): 3438 w (NH), 2966 w (CH), 2932 w (CH), 2870 w, 2826 w, 1715 s (C=O), 1497 s (C=C), 1453 m, 1390 m, 1364 m, 1322 m, 1298 m, 1284 m, 1248 m,

1209 m, 1166 s, 1124 m, 1097 m, 1065 m, 1044 m, 1029 m, 992 w, 968 w, 931 w, 889 m, 844 m, 776 w, 760 w, 699 s, 677 m;

222tropNH ((l'*S*,2'*S*,4'*S*,8'*S*)- 8'-methoxy-1',8'-dimethylbicyclo [2.2.2]oct-5'-en-2'-yl -5*H*-dibenzo[*a,d*]cycloheptene-5-amine) (**50**)
MF = $C_{26}H_{29}NO$



MW = 371.51 g/mol

MP = 58 °C
Air stable

(l*S*,2*S*,4*S*,8*S*)- tert-butyl (8-methoxy-1,8-dimethylbicyclo[2.2.2]oct-5-en-2-yl)carbamate **48** (300 mg, 1.07 mmol, 1 eq.) was dissolved in DCM and the solution cooled to 0 °C. Trifluoroacetic acid (0.25 mL, 3.2 mmol, 3 eq.) was added dropwise and the reaction stirred at room temperature for 4 h. The reaction was monitored by TLC. 5 mL water were added and the reaction neutralized with potassium carbonate until no further CO_2 was evolved. The aqueous phase was extracted five times with 5 mL DCM and the organic phase dried over potassium carbonate. The solvent was removed under reduced pressure to yield the deprotected amine. The amine (170 mg, 0.94 mmol, 87%) was dissolved in 5 mL dry DCM and triethylamine (0.65 mL, 4.7 mmol, 5 eq.) added. The solution was cooled with an ice bath and tropCl (319 mg, 1.41 mmol, 1.5 eq.) was added. The reaction was stirred for 6 h. The organic phase was washed with aqueous sodium carbonate and the organic phase dried over sodium sulfate. The product was chromatographed on silica gel with DCM containing 1% to 5% ethanol, starting with 1%. Yield: 87%, 302 mg, 0.81 mmol.

$[\alpha]_D^{22}$= +0.4° (*c*=0.1, CH_2Cl_2);

endo – conformer (50%):
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.91 (dt, $^2J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH_2^3), 0.95 (s, 3H, CH_3^9), 0.99 (d, $^2J_{HH}$ = 13.1 Hz, 1H, CH_2^7), 1.05 (s, 3H, CH_3^{10}), 1.14 (d, $^2J_{HH}$ = 13.1 Hz, 1H, CH_2^7), 2.12 (ddd, $^3J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 2.0 Hz, 1H, CH_2^2), 2.15 (ddd, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH^3), 2.50 (dt, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH^4), 3.10 (s, 3H, OCH_3^{11}), 4.83 (s, 1H, CH^{benzyl}), 5.73 (d, $^3J_{HH}$ = 7.9 Hz, 1H, CH^6), 6.18 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, CH^5), 7.03 (s, 2H, CH^{olefin}), 7.15-7.45 (m, 7H, CH^{ar}), 7.54 (d, $^3J_{HH}$ = 7.9 Hz, 1H, CH^{ar});

^{13}C{^{1}H}-NMR (176 MHz, $CDCl_3$): δ = 21.7 (s, 1C, CH_3^9), 24.6 (s, 1C, CH_3^{10}), 31.7 (s, 1C, CH_2^3), 39.6 (s, 1C, CH^4), 39.7 (s, 1C, C^1), 48.7 (s, 1C, CH_2^7), 49.4 (s, 1C, OCH_3), 57.7 (s, 1C, CH^2), 66.9 (s, 1C, CH^{benzyl}), 79.0 (s, 1C, C^8), 121.8 (s, 1C, CH^{ar}), 130.4 (s, 1C, CH^{olefin}), 130.6 (s, 1C, CH^{olefin}), 132.6 (s, 1C, CH^5), 136.6 (s, 1C, CH^6), 125-134 (11C, CH^{ar} and C^{quart});

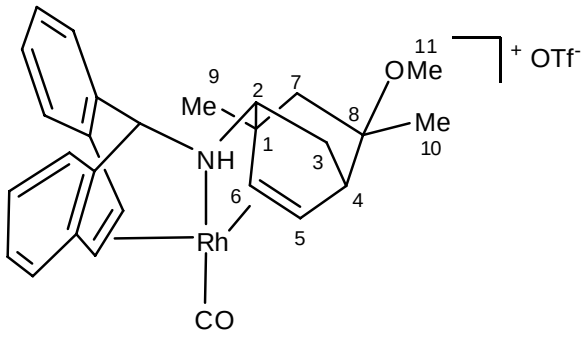
exo – conformer (50%):
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.87 (dt, $^{2}J_{HH}$ = 12.8 Hz, $^{3}J_{HH}$ = 2.9 Hz, 1H, CH_2^3), 1.12 (s, 3H, CH_3^{10}), 1.24 (d, $^{2}J_{HH}$ = 13.4 Hz, 1H, CH_2^7), 1.39 (d, $^{2}J_{HH}$ = 13.4 Hz, 1H, CH_2^7), 1.60 (s, 3H, CH_3^9), 2.26 (ddd, $^{2}J_{HH}$ = 12.7 Hz, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 2.1 Hz, 1H, CH_2^3), 2.54 (dt, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HH}$ = 2.9 Hz, 1H, CH^4), 2.78 (dt, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 2.9 Hz, 1H, CH^2), 3.11 (s, 3H, OCH_3^{11}), 4.18 (s, 1H, CH^{benzyl}), 6.04 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, CH^6), 6.31 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H, CH^5), 7.15 (d, $^{3}J_{HH}$ = 11.6 Hz, 1H, CH^{olefin}) 7.19 (d, $^{3}J_{HH}$ = 11.6 Hz, 1H, CH^{olefin}), 7.2-7.45 (m, 7H, CH^{ar}), 7.85 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, CH^{ar});

^{13}C{^{1}H}-NMR (176 MHz, $CDCl_3$): δ = 22.7 (s, 1C, CH_3^9), 24.5 (s, 1C, CH_3^{10}), 31.4 (s, 1C, CH_2^3), 39.7 (s, 1C, CH^4), 40.4 (s, 1C, C^1), 48.8 (s, 1C, CH_2^7), 49.4 (s, 1C, OCH_3^{11}), 56.2 (s, 1C, CH^{benzyl}), 57.4 (s, 1C, CH^2), 79.0 (s, 1C, C^8), 123.7 (s, 1, CH^{ar}), 130.6 (s, 1C, CH^{olefin}), 131.3 (s, 1C, CH^{olefin}), 134.3 (s, 1C, CH^5), 136.5 (s, 1C, CH^6), 125-134 (11C, CH^{ar} and C^{quart});

ATR IR (ν in cm^{-1}): 3017 w, 2924 m, 2823 w, 1671 w, 1597 w, 1484 w, 1440 m, 1366 m, 1334 w, 1243 w, 1199 w, 1157 m, 1143. m, 1102 m, 1070 m, 1038 m, 995 w, 945 w, 892 w, 876 w, 861 w, 845 m, 795 s, 764 s, 736 m, 724 s, 678 m, 641 m;

HiRes MS (MALDI, 3-HPA) m/z found (calc) for $C_{26}H_{29}NO + H^+$: 370.2161 (370.2165);

[Rh(222tropNH)(CO)]OTf (**51**)



MF = $C_{28}H_{29}F_3NO_5RhS$

MW = 651.50 g/mol

MP = 198 °C (dec.)
Slightly air sensitive

$[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (21 mg, 0.05 mmol, 1 eq.) was dissolved in 1 mL THF under argon and 222tropNH **50** (40 mg, 0.11 mmol, 2 eq.) added. After 1 h AgOTf (31 mg, 0.12 mmol, 2 eq.) was added. The THF was removed under reduced pressure and the residue dissolved in 2 mL DCM, filtered over celite and the DCM removed under reduced pressure. The complex was recrystallized from THF/*n*-hexane. Yield: 68%, 48 mg, 0.07 mmol, not optimized.

$[\alpha]_D^{22}$= -20.4° (*c*=0.1, CH_2Cl_2);

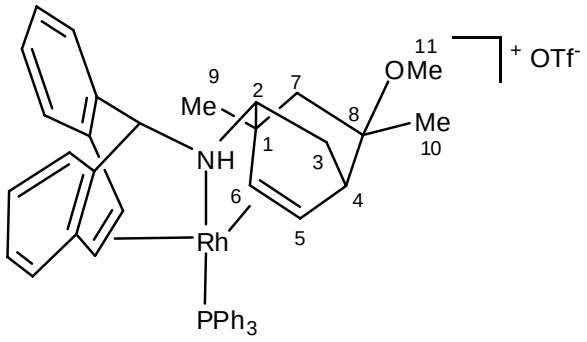
^{1}H-NMR (400 MHz, CD_2Cl_2): δ = -0.06 (dd, $^2J_{HH}$ = 14.9 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, CH_2^3), 1.24 (s, 3H, CH_3^{10}), 1.29 (s, 3H, CH_3^9), 1.30 (d, $^2J_{HH}$ = 14.0 Hz, 1H, CH_2^7), 1.61 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, CH_2^3), 1.67 (d, $^2J_{HH}$ = 14.0 Hz, 1H, CH_2^7), 2.20 (t, $^3J_{HH}$ = 5.3 Hz, 1H, CH^4), 3.02 (d, $^3J_{HH}$ = 7.9 Hz, 1H, CH^2), 3.06 (s, 3H, OCH_3^{11}), 3.49 (s, 1H, N*H*), 4.96 (s, 1H, CH^{benzyl}), 5.47 (d, $^3J_{HH}$ = 6.7 Hz, 1H, CH^6), 6.24 (d, $^3J_{HH}$ = 8.83 Hz, 1H, CH^{olefin}), 6.43 (ddd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 5.3 Hz, $^1J_{RhH}$ = 3.2 Hz, 1H, CH^5), 6.64 (dd, $^3J_{HH}$ = 9.1, $^1J_{RhH}$ = 3.3 Hz, 1H, CH^{olefin}), 7.34 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 1.5 Hz, 1H, CH^{ar}), 7.40-7.50 (m, 5H, CH^{ar}), 7.67 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 22.1 (s, 1C, *C*H_3^9), 23.9 (s, 1C, *C*H_3^{10}), 24.4 (d, $^3J_{RhC}$ = 1.8 Hz, 1C, *C*H_2^3), 39.0 (s, 1C, *C*H^4), 43.5 (s, 1C, *C*H_2^7), 43.6 (s, 1C, *C*^{1}), 50.0 (s, 1C, O*C*H_3^{11}), 68.9 (s, 1C, *C*H^{benzyl}), 69.4 (s, 1C, *C*H^2), 79.4 (d, $^1J_{RhC}$ = 6.4 Hz, 1C, *C*H^{olefin}), 79.8 (d, $^1J_{RhC}$ = 7.8 Hz, 1C, *C*H^{olefin}), 79.9 (s, 1C, *C*^{8}), 98.7 (d, $^1J_{RhC}$ = 11.4 Hz, 1C, *C*H^5), 100.7 (d, $^1J_{RhC}$ = 6.4 Hz, 1C, *C*H^6), 120.8 (q, $^1J_{CF}$ = 320.3 Hz, 1C, *C*F_3), 127.7 (s, 1C, *C*H^{ar}), 128.6 (s, 1C, *C*H^{ar}), 128.6 (s, 1C, *C*H^{ar}), 128.9 (s, 1C, *C*H^{ar}), 129.0 (s, 1C, *C*H^{ar}), 129.7 (s, 1C, *C*H^{ar}), 129.8 (s, 1C, *C*H^{ar}), 131.3 (s, 1C, *C*H^{ar}), 135.3 (d, $^2J_{RhC}$ = 2.3 Hz, 1C, *C*^{quart}), 135.4 (s, 1C, *C*^{quart}), 136.2 (s, 1C, *C*^{quart}), 138.0 (d, $^2J_{RhC}$ = 1.8 Hz, 1C, *C*^{quart}), 185.5 (d, $^1J_{RhC}$ = 63.5 Hz, 1C, *C*O);

^{1}H, ^{103}Rh-NMR (12.6 MHz, CD_2Cl_2): δ = -7569 (s);

ATR IR (ν in cm^{-1}): 3234 w (NH), 2961 w (CH), 2882 w (CH), 2036 m (CO), 1465 w, 1389 w, 1371 w, 1326 w, 1294 m, 1283 s, 1231 s, 1218 s, 1156 s, 1103 m, 1059 m, 1023 s, 992 m, 953 w, 895 w, 880 w, 864 w, 847 w, 817 w, 778 w, 752 m, 743 w, 706 w, 689 w, 666 w, 633 s, 609 w;

[Rh(222tropNH)(PPh_3)]OTf (**52**)



MF = $C_{45}H_{44}F_3NO_4PRhS$

MW = 885.77 g/mol

MP = 220-222 °C (dec.)
Air stable

[$Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4$] (26.2 mg, 0.07 mmol, 1 eq.) was dissolved in 1 mL THF under argon and 222tropNH **50** (50 mg, 0.13 mmol, 2 eq.) added. After 1 h PPh_3 (35.3 mg, 0.13 mmol, 2 eq.) was added. After another 1 h AgOTf (38 mg, 0.15 mmol, 2.2 eq.) was added. The THF was removed under reduced pressure and the residue dissolved in 2 mL DCM, filtered over celite and the DCM removed under reduced pressure. The complex was recrystallized from DCM/*n*-hexane. Yield: 60%, 71 mg, 0.08 mmol not optimized.

$[\alpha]_D^{22}$= 76.6° (*c*=0.1, CH_2Cl_2);

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 0.04 (dd, *J* = 14.7, 4.4 Hz, 1H, CH_2^3), 0.77 (s, 3H, CH_3^{10}) 1.01 (d, *J* = 13.6 Hz, 1H, CH_2^7), 1.25 (s, 3H, CH_3^9), 1.62 (d, *J* = 13.9 Hz, 1H, CH_2^7), 1.70 (dd, *J* = 14.5, 7.9 Hz, 1H, CH_2^3), 2.22 (t, *J* = 4.8 Hz, 1H, CH^4), 3.02 (s, 3H, OCH_3^{11}), 3.18 (t, *J* = 7.2 Hz, 1H, CH^2), 3.44 (d, *J* = 3.7 Hz, 1H, N*H*), 4.58 (d, *J* = 6.2 Hz, 1H, CH^6), 5.09 (d, *J* = 8.5 Hz, 1H, CH^{olefin}), 5.16 (d, *J* = 8.1 Hz, 1H, CH^{benzyl}), 5.80 (d, *J* = 8.8 Hz, 1H, CH^{olefin}), 5.96 (s, 1H, CH^5), 7.13 (d, *J* = 7.7 Hz, 1H, CH^{ar}), 7.35-7.45 (m, 5H, CH^{ar}), 7.52 (t, *J* = 7.89 Hz, 2H, CH^{ar}), 7.60-7.90 (m, 9H, CH^{ar}), 7.71-7.91 (m, 6H, CH^{ar}),

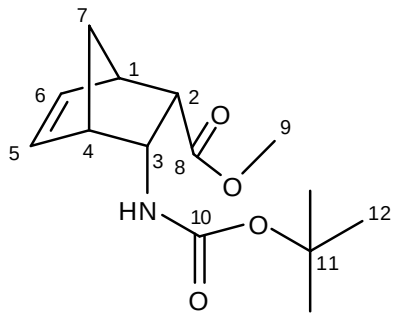
^{13}C{^{1}H}-NMR (126 MHz, CD_2Cl_2): δ = 22.5 (s, 1C, *C*H_3^9), 23.8 (s, 1C, *C*H_3^{10}), 26.1 (s, 1C, *C*H_2^3), 40.5 (s, 1C, *C*H^4), 43.2 (s, 1C, *C*H_2^7), 50.0 (s, 1C, O*C*H_3^{11}), 68.8 (s, 1C, *C*H^{benzyl}), 70.3 (s, 1C, *C*H^2), 79.4 (d, 4Hz, *C*^{1}), 82.5 (d, *J* = 7.08 Hz, 1C, CH^{olefin}), 87.2 (d, *J* = 11.7 Hz, 1C, CH^{olefin}), 103.3 (d, *J* = 7.1 Hz, 1C, *C*H^6), 107.6 (d, *J* = 12.6 Hz, 1C, *C*H^5), 128.1 (s, 1C, *C*H^{ar}), 128.5 (s, 1C, *C*H^{ar}), 129.0 (s, 1C, *C*H^{ar}), 129.1 (s, 1C, *C*H^{ar}), 129.4 (s, 1 C, *C*H^{ar}), 129.4 (s, 1C, *C*H^{ar}), 129.5 (d, *J* = 9.8 Hz, 6C, *C*H^{ar}), 129.6 (s, 1C, *C*H^{ar}), 130.0 (d, *J* = 19.4 Hz, 3C, *C*^{quart}), 131.9 (d, *J* = 2.2 Hz, 3C, *C*H^{ar}), 131.9 (s, 1C, *C*H^{ar}), 134.5 (d, *J* = 10.2 Hz, 6C, *C*H^{ar}), 135.7 (s, 1C, *C*^{quart}), 136.3 (s, 1C, *C*^{quart}), 136.4 (s, 1C, *C*^{quart}), 137.4 (s, 1C, *C*^{quart});

^{31}P{^{1}H}-NMR (203 MHz, CD_2Cl_2): δ = 42.7 (d, $^1J_{RhP}$ = 140.5 Hz);

^{1}H, ^{103}Rh-NMR (15.8 MHz, CD_2Cl_2): δ = 789 (d, $^1J_{RhP}$ = 140.5 Hz);

ATR IR (ν in cm^{-1}): 3514 w, 3220 w, 2949 w, 1630 w, 1479 w, 1455 w, 1439 m, 1374 w, 1281 w, 1248 m 1227 m, 1156 m, 1103 m, 1093 m, 1071 m, 1060 m, 1032 s, 1013 m, 988 m, 950 m, 892 w, 880 w, 863 w, 846 w, 814 w, 781 m, 756 s, 746 s, 704 s, 697 s, 638 s;

(2*S*3*R*) - methyl 3-[(tert-butoxycarbonyl) amino]bicyclo[2.2.1]hept-5-ene-2-carboxylate (**53**)
MF = $C_{14}H_{21}NO_4$



MW = 267.32 g/mol

MP = 44 °C
Air stable

The compound was obtained as a gift from the group of Prof. C. Bolm of RWTH Aachen. The compound was synthesized by the procedure described for the stereo selective anhydride opening [106, 107], but Boc was used instead of Cbz as protecting group.

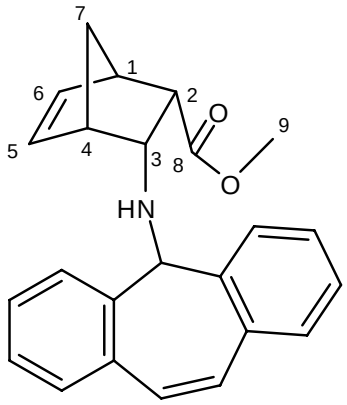
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.38 (d, $^2J_{HH}$ = 8.9 Hz, 1H, CH_2^7), 1.44 (s, 9H, CH_3), 1.51 (d, $^2J_{HH}$ = 9.2 Hz, 1H, CH_2^7), 3.08 (m, 1H, CH^4), 3.11 (m, 1H, CH^1), 3.24 (dd, $^3J_{HH}$ = 9.0, $^3J_{HH}$ = 2.3 Hz, 1H, CH^2), 3.64 (s, 3H, OCH_3^9), 4.61 (td, $^3J_{HH}$ = 10 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, CH^3), 4.88 (d, $^3J_{HH}$ = 9.2 Hz, 1H, N*H*), 6.20 (dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 3.0 Hz, 1H, CH^5), 6.46 (dd, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 3.1 Hz, 1H, CH^6);

^{13}C{^{1}H}-NMR (176 MHz, $CDCl_3$): δ = 28.4 (s, 3C, *C*H$_3^{12}$), 46.4 (s, 1C, *C*H^1), 47.2 (s, 1C, *C*H^4), 47.6 (s, 1C, *C*H$_2^7$), 48.9 (s, 1C, *C*H^2), 51.5 (s, 1C, O*C*H$_3^9$), 53.8 (s, 1C, *C*H^3), 79.1 (s, 1C, *C*^{11}), 133.0 (s, 1C, *C*H^5), 138.5 (s, 1C, *C*H^6), 155.5 (s, 1C, *C*^{10}), 173.2 (s, 1C, *C*^{8});

ATR IR (ν in cm^{-1}): 3409 w (NH), 2978 w, 2954 w, 2878 w, 1709 s (C=O), 1501 s (C=C) 1449 m, 1437 m, 1390 m, 1356 s, 1338 m, 1300 m, 1259 m, 1240 m, 1220 m, 1207 m, 1160 s, 1120 m, 1090 m, 1072 m, 1056 s, 1031 s, 1015 m, 984 m, 963 m, 945 m, 916 m, 879 m, 858 m, 844 m, 825 m, 789 m, 776 m, 721 m, 679 m;

EA found% (calc%) for $C_{25}H_{25}NO_2$: C: 62.63 (62.90), H: 8.06 (7.92), N: 5.24 (5.24);

221tropNH ((2*S*3*R*) - methyl 3-(5*H*-dibenzo[*a,d*]cycloheptene-5 – amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate) (**54**)
MF = $C_{24}H_{23}NO_2$



MW = 357.44 g/mol

MP = 127 °C
Air stable

Methyl 3-[(tert-butoxycarbonyl)amino]bicyclo[2.2.1]hept-5-ene-2-carboxylate **53** (270 mg, 1.01 mmol, 1 eq.) was dissolved in dry DCM and the solution cooled to 0 °C. Trifluoroacetic acid (0.23 mL, 3.0 mmol, 3 eq.) was added dropwise and the reaction stirred at room temperature for 4 h. The reaction was monitored by TLC. 5 mL water were added and the reaction neutralized with potassium carbonate until no further CO_2 was evolved. The aqueous phase was extracted five times with 5 mL DCM and the organic phase dried over potassium carbonate. The solvent was removed under reduced pressure to yield the deprotected amine. The amine (110 mg, 0.66 mmol, 65%) was dissolved in 5 mL dry DCM and triethylamine (0.45 mL, 3.3 mmol, 5 eq.) added. The solution was cooled with an ice bath and tropCl (223 mg, 0.99 mmol, 1.5 eq.) was added. The reaction was stirred for 6 h. The organic phase was washed with aqueous sodium carbonate and the organic phase dried over sodium sulfate. The product was chromatographed on silica gel with DCM containing 1% ethanol. Yield: 85%, 202 mg, 0.56 mmol as white solid.

$[\alpha]_D^{22}$= -25.3° (*c*=0.1, CH_2Cl_2);

exo - conformer (66%):
^{1}H-NMR (700 MHz, C_6D_6): δ= 0.77 (d, $^2J_{HH}$ = 8.5 Hz, 1H, CH_2^7), 1.29 (d, $^2J_{HH}$ = 8.5 Hz, 1H, CH_2^7), 2.57 (d, $^3J_{HH}$ = 11.9 Hz, 1H, N*H*), 2.84 (m, 1H, CH^1), 2.89 (m, 1H, CH^4), 3.07 (dd, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 3.4 Hz, 1H, CH^2), 3.50 (s, 3H, OCH_3^9), 3.82 (ddd, $^3J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 3.5 Hz, 1H, CH^3), 4.45 (s, 1H, CH^{benzyl}), 6.07 (dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 3.1 Hz, 1H, CH^5), 6.64 (dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 3.1 Hz, 1H, CH^6), 7.14 (m, 2H, CH^{olefin}), 7.10-7.45 (m, 6, CH^{ar}), 7.97 (d, $^3J_{HH}$ = 7.9 Hz, 1H, CH^{ar}), 8.07 (d, $^3J_{HH}$ = 7.9 Hz, 1H, CH^{ar});

^{13}C{^{1}H}-NMR (176 MHz, C_6D_6): δ= 46.0 (s, 1C, CH^4), 46.2 (s, 1C, CH^1) 47.5 (s, 1C, CH_2^7), 49.5 (s, 1C, CH^2), 50.7 (s, 1C, OCH_3^9), 58.8 (s, 1C, CH^{benzyl}), 60.4 (s, 1C, CH^3), 122.5 (s, 1C, CH^{ar}), 123.1 (s, 1C, CH^{ar}), 125.6 (s, 1C, CH^{olefin}), 125.7 (s, 1C, CH^{ar}), 127.7 (s, 1C, CH^{ar}), 128.1 (s, 1C, CH^{ar}), 128.8 (s, 1C, CH^{ar}), 128.9 (s, 1C, CH^{ar}), 131.1 (s, 1C, CH^{olefin}), 131.2 (s, 1C, CH^{ar}), 132.4 (s, 1C, CH^5), 134.1 (s, 1C, C^{quart}), 134.1 (s, 1C, C^{quart}), 138.5 (s, 1C, CH^6), 140.4 (s, 1C, C^{quart}), 141.1 (s, 1C, C^{quart}), 173.1 (s, 1C, C^8);

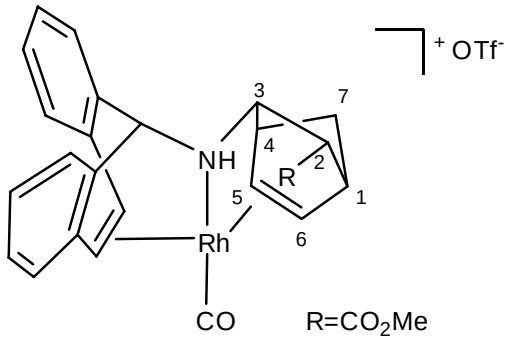
endo - conformer (33%):
^{1}H-NMR (700 MHz, C_6D_6): δ = 0.80 (d, $^{2}J_{HH}$ = 8.9 Hz, 1H, CH_2^7), 1.31 (d, $^{2}J_{HH}$ = 8.9 Hz, 1H, CH_2^7), 2.42 (s, 1H, N*H*), 2.66 (m, 1H, CH_1), 2.84 (s, 1H, CH_4), 2.87 (dd, $^{3}J_{HH}$ = 9.5 Hz, $^{3}J_{HH}$ = 3.4 Hz, 1H, CH^2), 3.37 (s, 3H, OCH_3^9), 3.37 (m, 1H, CH^3), 4.95 (s, 1H, CH^{benzyl}), 6.05 (dd, $^{3}J_{HH}$ = 5.7 Hz, $^{3}J_{HH}$ = 2.9 Hz, 1H, CH^5), 6.61 (dd, $^{3}J_{HH}$ = 5.5 Hz, $^{3}J_{HH}$ = 2.8 Hz, 1H, CH^6), 6.94 (m, 2H, CH^{olefin}), 7.15-7.45 (m, 8H, CH^{ar});

^{13}C{^{1}H}-NMR (176 MHz, C_6D_6): δ = 45.4 (s, 1C, *C*H^4), 46.4 (s, 1C, *C*H^1), 46.8 (s, 1C, *C*H_2^7) 50.0 (s, 1C, *C*H^2), 50.5 (s, 1C, O*C*H_3^9), 60.1 (s, 1C, *C*H^4), 68.99 (s, 1C, *C*H^{benzyl}), 126.7 (s, 1C, *C*H^{ar}), 126.9 (s, 1C, *C*H^{ar}), 128.3 (s, 1C, *C*H^{ar}), 128.4 (s, 1C, *C*H^{ar}), 129.4 (s, 1C, *C*H^{ar}), 129.4 (s, 1C, *C*H^{ar}), 130.0 (s, 1C, *C*H^{ar}), 130.1 (s, 1C, *C*H^{ar}), 130.3 (s, 1C, *C*H^{ar}), 130.8 (s, 1C, *C*H^{ar}), 132.7 (s, 1C, *C*H^5), 134.0 (s, 1C, *C*^{quart}), 134.1 (s, 1C, *C*^{quart}), 137.4 (s, 1C, *C*H^6), 140.4 (s, 1C, *C*^{quart}), 141.1 (s, 1C, *C*^{quart}), 172.4 (s, 1C, *C*^{8});

ATR IR (ν in cm-1): 2967 w, 2945 w, 1723 s, 1597 w, 1562 w, 1482 w, 1467 w, 1450 m, 1433 m, 1364 m, 1340 m, 1298 w, 1248 m, 1192 m, 1172 m, 1155 m, 1130 w, 1113 m, 1067 w, 1037 w, 963 m, 935 w, 913 w, 897 w, 887 w, 862 w, 846 w, 835 w, 816 w, 794 m, 777 m, 762 s, 749 s, 734 s, 714 m, 702 s, 674 m, 635 m, 610 m;

HiRes MS (MALDI, 3-HPA) m/z found (calc) for $C_{24}H_{23}O_2N + H^+$: 358.1798 (358.1802);

[Rh(221tropNH)(CO)]OTf (**55**)



MF = $C_{26}H_{23}F_3NO_6RhS$

MW = 637.43 g/mol

MP = 218 - 224 °C(dec.)
Slightly air sensitive

$[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (16.8 mg, 0.04 mmol, 1 eq.) was dissolved in 1 mL THF under argon and 221tropNH **54** (31 mg, 0.09 mmol, 2 eq.) added. After 1 h AgOTf (22.3 mg, 0.09 mmol, 2 eq.) was added. The THF was removed under reduced pressure and the residue dissolved in 2 mL DCM, filtered over celite and the DCM removed under reduced pressure. The complex was recrystallized from THF/*n*-hexane. Yield: 64%, 36 mg, 0.06 mmol, not optimized.

$[\alpha]_D^{22}$= -50.1° (*c*=0.1, CH_2Cl_2);

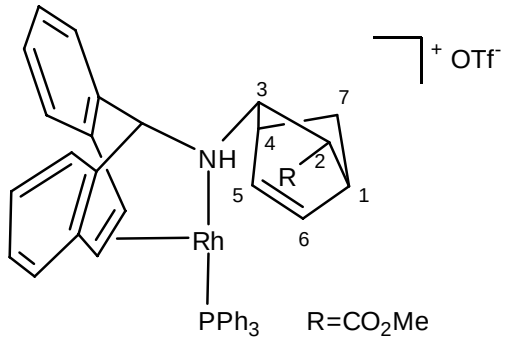
^{1}H-NMR (700 MHz, CD_2Cl_2): δ = 1.76 (d, $^3J_{HH}$ = 9.8 Hz, 1H, CH_2^7), 1.94 (d, $^3J_{HH}$ = 9.8 Hz, 1H, CH_2^7), 2.32 (s, 1H, CH^4), 3.13 (s, 1H, CH^1), 3.70 (dd, $^3J_{HH}$ = 8.5, $^3J_{HH}$ 3.05 Hz, 1H, CH^2), 3.92 (s, 3H, OCH_3), 4.03 (ddd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 1.2 Hz, 1H, CH^3), 4.94 (dd, $^3J_{HH}$ = 8.5 Hz, $^2J_{RhH}$ = 2.1 Hz, 1H, CH^{olefin}), 4.99 (s, 1H, N*H*), 5.07 (s, 1H, CH^{benzyl}), 5.27 (dd, $^3J_{HH}$ = 8.7 Hz, $^2J_{RhH}$ = 2.6 Hz, 1H, CH^{olefin}), 6.34 (t, $^3J_{HH}$ = 4.4 Hz, 1H, CH^6), 7.39 (td, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, CH^{ar}), 7.42 (td, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, CH^{ar}), 7.35-7.50 (m, 4H, CH^{ar}), 7.67 (m, 1H, CH^{ar}), 7.69 (dd, $^3J_{HH}$ = 7.5 Hz, 1.07 Hz, 1H, CH^{ar}), 7.76 (m, 1H, CH^5);

^{13}C{^{1}H}-NMR (176 MHz, CD_2Cl_2): δ = 46.2 (s, 1C, CH^1) 46.3 (s, 1C, CH^4), 51.0 (s, 1C, CH^2), 53.2 (s, 1C, CH^7), 54.0 (d, $^1J_{RhC}$ = 14.2 Hz, 1H, CH^{olefin}), 54.9 (s, 1C, OCH_3), 58.5 (d, $^1J_{RhC}$ = 15.4 Hz, 1C, CH^{olefin}), 67.8 (s, 1C, CH^{benzyl}), 69.0 (s, 1C, CH^3), 122.3 (s, 1C, CH^6), 124.9 (s, 1C, CH^5), 127.3 (s, 1C, CH^{ar}), 128.2 (s, 1C, CH^{ar}), 128.7 (s, 1C, CH^{ar}), 128.9 (s, 1C, CH^{ar}), 129.1 (s, 1C, CH^{ar}), 129.3 (s, 1C, CH^{ar}), 129.4 (s, 1C, CH^{ar}), 129.5 (s, 1C, CH^{ar}), 134.9 (d, *J* = 1.8 Hz, 1C, C^{quart}), 136.3 (s, 1C, C^{quart}), 136.8 (d, *J* = 1.8 Hz, 1C, C^{quart}), 136.9 (d, *J* = 1.8 Hz, 1C, C^{quart}), 181.0 (s, 1C, C^{quart}), 184.0 (d, $^1J_{RhC}$ = 64.8 Hz, 1C, CO);

^{1}H, ^{103}Rh-NMR (22.1 MHz, CD_2Cl_2): δ = -7348 (s);

ATR IR (ν in cm^{-1}): 3125 w (NH), 2957 w (CH), 2052 m (CO), 2038 m (CO), 1645 m (C=O), 1492 w, 1448 m, 1385 m, 1373 m, 1327 w, 1264 s, 1222 s, 1190 m, 1151 s, 1092 m, 1077 m, 1047 m, 1028 s, 960 w, 927 m, 910 m, 893 m, 868 w, 841 w, 831 w, 814 w, 778 w, 770 m, 759 s, 751 w, 733 m, 721 m, 683 w, 635 s, 617 m, 605 m;

[Rh(221tropNH)(PPh_3)]OTf (**56**)



MF = $C_{43}H_{38}F_3NO_5PRhS$

MW = 871.71 g/mol

MP > 230 °C (dec.)
Air stable

$[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (27.2 mg, 0.07 mmol, 1 eq.) was dissolved in 1 mL THF under argon and 221tropNH **54** (50 mg, 0.14 mmol, 2 eq.) added. After 1 h PPh_3 (36.7 mg, 0.14 mmol, 2 eq.) was added. The reaction was stirred for an additional 1 h and AgOTf (40 mg, 0.15, 2.2 eq.) was added. The THF was removed under reduced pressure and the residue dissolved in 2 mL DCM, filtered over celite and the DCM removed under reduced pressure. The complex was recrystallized from DCM/*n*-hexane. Yield: 52%, 64 mg, 0.07 mmol not optimized.

$[\alpha]_D^{22}$= -2.1° (*c*=0.1, CH_2Cl_2);

^{1}H-NMR (400 MHz, CD_2Cl_2): δ= 1.35 (d, *J* = 9.4 Hz, 1H, CH_2^7), 1.69 (d, *J* = 9.8 Hz, 1H, CH_2^7), 2.79 (m, 1H, N*H*), 3.15 (s, 3H, OCH_3), 3.24 (dd, *J* = 8.5 Hz, 3.5 Hz, 1H, CH^2), 3.26 (s, 1H, CH^1), 3.44 (ddd, *J* = 12.5 Hz, 9.0 Hz, 3.2 Hz, 1H, CH^3), 3.59 (s, 1H, CH^4), 3.67 (ddd, *J* = 8.4 Hz, 4.0 Hz, 1.7 Hz, 1H, CH^{olefin}), 4.09 (ddd, *J* = 8.3 Hz, 4.0 Hz, 2.0 Hz, 1 H) 5.06 (d, *J* = 6.70 Hz, 1H, CH^{olefin}), 6.37 (dd, *J* = 5.48, 2.74 Hz, 1H, CH^5), 6.43 (dd, *J* = 5.78, 2.43 Hz, 1H, CH^6), 7.35-7.65 (m, 17H, CH^{ar}), 7.70-7.80 (m, 6H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 45.2 (d, *J* = 1.8 Hz, 1C, *C*H^4), 45.5 (s, 1C, *C*H^1), 46.3 (s, 1C, CH_2^7), 50.0 (s, 1C, *C*H^2), 55.6 (s, 1C, O*C*H$_3$), 58.3 (d, *J* = 16.9 Hz, 1C, *C*H^{olefin}), 60.4 (d, *J* = 18.0 Hz, 1C, *C*H^{olefin}), 60.3 (s, 1C, *C*H^3), 66.0 (s, 1C, *C*H^{benzyl}), 127.9 (s, 1C, *C*H^{ar}), 128.1 (s, 1C, *C*H^{ar}), 129.3 (d, $^2J_{PC}$ = 10.1 Hz, 6C, *C*H^{ar}), 129.5 (s, 1C, *C*H^{ar}), 129.7 (d, $^1J_{PC}$ = 29.2 Hz, 3C, *C*^{quart}), 129.7 (s, 1C, *C*H^{ar}), 130.0 (s, 1C, *C*H^{ar}), 130.1 (s, 2C, *C*H^{ar}), 130.1 (s, 1C, *C*H^{ar}), 131.6 (d, $^4J_{PC}$ = 2.3 Hz, 3C, *C*H^{ar}), 133.0 (s, 1C, *C*H^5), 133.6 (s, 1C, *C*^{quart}), 134.4 (d, $^3J_{PC}$ = 11.4 Hz, 6C, *C*H^{ar}), 136.2 (s, 1C, *C*^{quart}), 138.4 (d, *J* = 1.8 Hz, 1C, *C*^{quart}), 139.7 (d, *J* = 2.3 Hz, 1C, *C*^{quart}), 141.0 (s, 1C, C*H*^{6}), 182.1 (s, 1C, *C*^{quart});

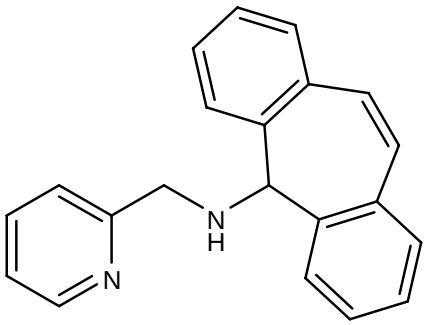
^{31}P{^{1}H}-NMR (162 MHz, CD_2Cl_2): δ= 45.5 (d, $^1J_{RhP}$ = 162.5 Hz);

^{1}H, ^{103}Rh-NMR (12.6 MHz, CD_2Cl_2): δ= -7472 (d, $^1J_{RhP}$ = 162.5 Hz);

ATR IR (ν in cm^{-1}): 3125 m, 1977 w, 1629 m, 1573 w, 1473 w, 1453 w, 1436 m, 1356 m, 1301 m, 1282 m, 1249 m, 1224 m, 1183 w, 1142 m, 1094 m, 1058 m, 1028 m, 999 m, 935 w, 915 m, 897 w, 867 w, 842 w, 827 w, 810 w, 776 w, 769 m, 761 m, 747 m, 726 m, 707 m, 697 m, 635 s, 607 m;

Compounds of section VI

pyCH$_2$tropNH (N-(pyridin-2-ylmethyl)-5*H*-dibenzo [*a,d*]cycloheptene-5-amine) (**57**)
MF = $C_{21}H_{18}N_2$



MW = 298.38 g/mol

MP = 95 °C
Air stable

Pyridine-2-carbaldehyde (0.23 mL, 2.41 mmol, 1.0 eq.) was added to a solution of trop-amine (0.50 g, 2.41 mmol, 1.0 eq.) in DCM (8 mL) containing 4 Å mole sieve at RT in a dry 25 mL round bottomed flask under argon. After 72 h the reaction solution was filtrated and concentrated under reduced pressure to give crude N-[(1E)-pyridin-2-ylmethylene]- 5*H*-dibenzo [*a,d*]cycloheptene-5-amine (0.65 g, 2.16 mmol, 91%). Attempts to purify this product by FC or crystallization were unsuccessful and it was directly used in the reduction step. The crude product was dissolved in DCM/methanol 3:2 (30 mL) at RT in a dry 50 mL round bottomed flask under argon. Sodium borohydride (0.164 g, 4.235 mmol, 2.0 eq.) was added and the reaction followed by TLC. After 2 h the reaction was quenched by addition of water under vigorous stirring. The aqueous phase was extracted 3 x with small amounts of DCM. The combined organic phases were dried with magnesium sulfate and concentrated under reduced pressure. The product was purified by flash chromatography on silica gel with DCM and later DCM/ethanol 40:1. Yield: 83%, 0.6 g, 2.01 mmol over 2 steps.

Old method: To a solution of 2-Methylaminepyridine (2.4 mL, 23 mmol, 1 eq.) in DCM triethylamine (8mL, 57 mmol, 2.5 eq.) was added. The solution was cooled in an ice bath and tropCl (6.5 g, 29 mmol, 1.25 eq.) was added. The solution was stirred overnight and the organic phase washed with a saturated sodium carbonate solution, dried over sodium sulfate and flash chromatographed on silica gel with DCM and later DCM/ethanol 40:1. The product was dried in high vacuum. Yield: 22%, 1.48 g, 49 mmol not optimized.

endo - conformer: (66%)
^{1}H-NMR (400 MHz, $CDCl_3$, 220K): δ = 2.83 (s, 1H, N*H*), 3.56 (s, 2H, CH_2N), 4.96 (s, 1H, CH^{benzyl}), 7.12 (m, 2H, CH^{olefin}), 7.1-7.8 (m, 13H, CH^{olefin} and CH^{ar}), 8.53 (d, $^3J_{HH}$ = 4.4 Hz, 1H, CH^{ar});

^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 220K): δ = 53.1 (s, 1C, *C*H_2N), 69.2 (s, 1C, *C*H^{benzyl}), 122.5(s, 1C, *C*H^{ar}), 122.8 (s, 2C, *C*H^{ar}), 127.8 (s, 2C, *C*H^{ar}), 129.3 (s, 1C, *C*H^{ar}), 130.3 (s, 2C, *C*H^{ar}), 130.6 (s, 2C, *C*H^{ar}), 131.1(s, 1C, *C*H^{ar}), 133.7 (s, 2C, C^{quart}), 137.2 (s, 1C, *C*H^{ar}), 139.5 (s, 2C, *C*^{quart}), 149.8 (s, 1C, *C*H^{ar}), 159.3 (s, 1C, *C*^{quart});

exo - conformer: (33%)
^{1}H-NMR (400 MHz, $CDCl_3$, 220K): δ = 3.18 (s, 1H, N*H*), 4.02 (d, J_{HH} = 6.0Hz, 2H, CH_2), 4.25 (s, 1H, CH^{benzyl}), 7.1-7.8 (m, 13H, CH^{olefin} and C*H*ar), 8.64 (d, $^{3}J_{HH}$ = 4.0Hz, 1H, CH^{ar});

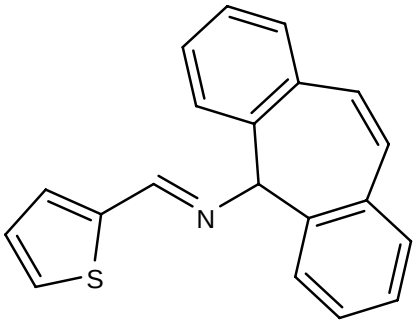
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 220K): δ = 53.8 (s, 1C, CH_2N), 61.1 (s, 1C, CH^{benzyl}), 122.9(s, 2C, CH^{ar}), 122.9 (s, 1C, CH^{ar}), 123.2 (s, 1C, CH^{ar}), 126.4 (s, 2C, CH^{ar}), 128.3(s, 2C, CH^{ar}), 129.3 (s, 2C, CH^{ar}), 131.7 (s, 2C, CH^{ar}), 134.2 (s, 2C, C^{quart}), 137.4 (s, 1C, CH^{ar}), 140.0 (s, 2C, C^{quart}), 150.0(s, 1C, CH^{ar}), 159.8 (s, 1C, C^{quart})

ATR IR (ν in cm^{-1}): 3328(w), 3044(w), 2936(w), 2819(w), 1952(w), 1590(m), 1568(m), 1494(m), 1476(m), 1449(m), 1434(m), 1371(w), 1298(m), 1091(m), 953(w), 806(s), 755(s), 568(s).

EA found% (calc%) for $C_{21}H_{18}N_2$: C: C 84.29 (84.53), H: 6.17 (6.08), N: 9.21 (9.93);

MS (EI, m/z, (%)): 206 (tropNH, 100%); 93 (pyCH_2, 90%); 191 (trop, 40%) 298(M^+, 10);

N-((1E)-2-thienylmethylene)-5*H*-dibenzo[*a,d*]cycloheptene-5-amine



MF = $C_{20}H_{15}NS$

MW = 301.42 g/mol

MP = 160 °C
Air stable

Thiophene-2-carbaldehyde was vacuum distilled prior to use. $TropNH_2$ (1.375 g, 6.63 mmol, 1 eq.) was added to a solution of thiophene-2-carbaldehyde (0.61 mL, 6.63 mmol, 1 eq.), in DCM containing sodium sulfate (0.5 g) at 0 °C in a 25 mL round bottomed flask under argon. After 5 min the reaction mixture was warmed to RT and stirred for 48 h before it was filtered, the DCM removed under reduced pressure and the solid washed 3 x with 10 mL pentane and dried *in vacuo*. Yield: 75%, 1.506 g, 4.99 mmol as yellowish solid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.97 (s, 1 H, C*H*^{benzyl}), 7.11 - 7.52 (m, 11H, C*H*^{ar}), 7.78 (d, *J* = 7.8 Hz, 2H, C*H*^{ar}), 8.43 (s, 1H, C*H*N);

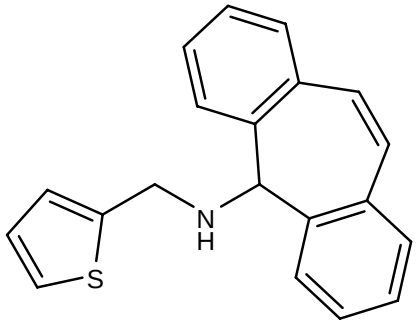
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$) δ = 54.6 (s, 1 C, *C*HN), 72.1 (b, 1C, *C*H^{benzyl}), 124.8 (s, 2C, *C*H^{ar}), 126.1 (s, 2C, *C*H^{ar}), 127.5 (s, 1C, *C*H^{ar}), 127.9 (s, 2C, *C*H^{ar}), 128.6 (s, 2C, *C*H^{ar}), 129.3 (s, 1C, *C*H^{ar}), 130.8 (s, 1C, *C*H^{ar}), 131.3 (s, 2C, *C*H^{ar}), 133.3 (s, 2C, C_q), 141.2 (s, 2C, C_q), 142.9 (s, 1C, C_q);

EA found% (calc%) for $C_{20}H_{15}NS$: C: 79.60 (79.70), H: 5.14 (5.02), N: 4.59 (4.65);

MS (EI, m/z, (%)): 191 (tropNH$^+$, 100%), 301 (M$^+$, 18%);

ATR IR (ν in cm^{-1}): 3058 - 3017 (m, CH), 799 - 690 (s, CH_δ);

thioCH_2tropNH (N-(2-thienylmethyl)-5*H*-dibenzo[*a,d*]cycloheptene-5-amine) (**58**)
MF = $C_{20}H_{17}NS$



MW = 303.44 g/mol

MP = 105 °C
Air stable

Sodium borohydride (0.68 g, 16.6 mmol, 2 eq.) was added to a solution of (N-((1E)-2-thienylmethylene)-5*H*-dibenzo[*a,d*]cycloheptene-5-amine (2.5 g, 8.3 mmol, 1 eq.) in DCM/methanol 3:2 (120 mL) at RT in a dry 250 mL round bottomed flask under argon. The reaction solution was cooled to 0 °C upon intense bubbling. The reaction progress was monitored by TLC (*n*-hexane/ethyl acetate 3:1). After 1 h the reaction was quenched by addition of water (ca. 150 mL). The aqueous phase was extracted 3 times with 40 mL DCM. Combined organic phases were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude oil was recrystallized from hot *n*-hexane. Yield: 97%, 2.45 g, 8.07 mmol.

endo - conformer (75%):
^{1}H-NMR (500 MHz, $CDCl_3$, 250 K): δ = 2.67 (dt, J_1 = 11.5 Hz, J_2 = 6.0 Hz, 1H, N*H*), 3.64 (d, J = 4.0 Hz, 2H, CH_2), 4.94 (d, J = 11.5 Hz, 1H, CH^{benzyl}), 6.89 (d, J = 3.0 Hz, 1H, CH^{ar}), 7.00 - 7.07 (m, 1H, CH^{ar}), 7.11 (s, 2H, CH^{olefin}), 7.28 - 7.51 (m, 9H, CH^{ar});

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$, 250 K): δ = 45.8 (s, 1C, CH_2), 66.8 (s, 1C, CH^{benzyl}), 125.4 (s, 1C, CH^{ar}), 125.9(s, 1C, CH^{ar}), 127.2 (s, 1C, CH^{ar}), 127.8 (s, 2C, CH^{ar}) 129.3 (s, 2C, CH^{ar}), 130.4 (s, 2C, CH^{ar}), 130.6 (s, 2C, CH^{ar}), 131.0 (s, 2C, CH^{olefin}), 133.7 (s, 2C, C_q), 139.4 (s, 2C, C_q), 144.7 (s, 1C, C_q);

exo - conformer (25%):
^{1}H-NMR (500 MHz, $CDCl_3$, 250 K): δ = 2.43 (t, J = 7.5 Hz, 1H, N*H*), 4.09 (d, J = 7.5 Hz, 2H, CH_2), 4.26 (s, 1H, CH^{benzyl}), 7.00 - 7.07 (m, 2H, CH^{ar}), 7.23 (s, 2H, CH^{olefin}), 7.28 - 7.51 (m, 7H, CH^{ar}), 7.76 (d, J = 8.0 Hz, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$, 250 K): δ = 47.2 (s, 1C, CH_2), 60.5 (s, 1C, CH^{benzyl}), 122.7 (s, 2C, CH^{ar}), 125.4 (s, 1C, CH^{ar}), 125.5 (s, 1C, CH^{ar}), 126.4 (s, 2C, CH^{ar}), 127.5 (s, 1C, CH^{ar}), 128.3 (s, 2C, CH^{ar}), 129.4 (s, 2C, CH^{ar}), 131.6 (s, 2C, CH^{olefin}), 134.2 (s, 2C, C_q), 139.8 (s, 2C, C_q), 144.3 (s, 1C, C_q);

EA found% (calc%) for $C_{20}H_{17}NS$: C: 78.90 (79.17), H: 5.65% (5.65), N: 4.52 (4.62);

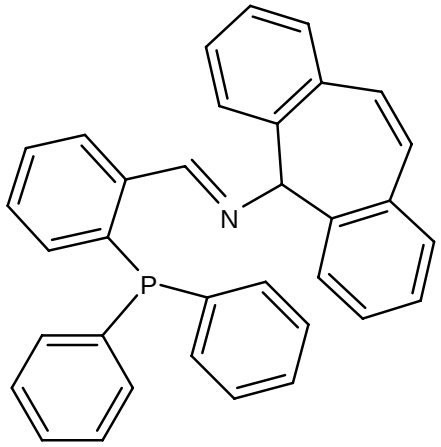
MS (EI, m/z, (%)): 191 (tropNH$^+$, 100%), 303 (M^+, 20%);

ATR IR (ν in cm^{-1}): 3329 (m, NH), 3105 - 2848 (m, CH), 1597 (w, CCar), 806 - 700 (s, CH_δ);

N-(1E)-(2-(diphenylphosphino)phenyl) methylene)-5*H*-dibenzo[*a,d*] cycloheptene-5-amine
MF = $C_{34}H_{26}NP$

MW = 479.58 g/mol

Slightly air sensitive



$TropNH_2$ (0.714 g, 3.44 mmol, 1.0 eq.) was added to a solution of 2-diphenylphosphine benzaldehyde (1.0 g, 3.44 mmol, 1.0 eq.) in DCM (6 mL) containing sodium sulfate (1 g) at RT in a 25 mL round bottomed flask under argon. The reaction was stirred for 72 h, afterwards the solution was filtrated off and the solvent removed under reduced pressure. The obtained oil was stirred vigorously with pentane for 10 min to get a solid. Then the pentane was poured off and the product dried *in vacuo* to give a powdery solid. Yield: 91%, 1.5 g, 3.1 mmol.

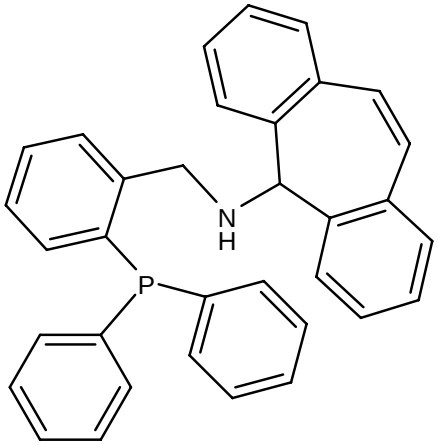
^{1}H-NMR (300 MHz, $CDCl_3$) δ = 4.95 (b, 1H, C*H*^{benzyl}), 6.99 - 8.12 (m, 24H, C*H*^{ar}), 8.83 (b, 1H, C*H*N);

$^{31}P\{^{1}H\}$-NMR (121.5 MHz, $CDCl_3$) δ = -12.84 (s);

Ph_2PPhCH_2tropNH (N-(2-(diphenylphosphino)benzyl)-5*H*-dibenzo[*a,d*]cycloheptene-5-amine) (**59**)
MF = $C_{34}H_{28}NP$

MW = 481.60 g/mol

MP = 66 - 72 °C
Slightly air sensitive



Sodium borohydride (0.234 g, 6.18 mmol, 2.0 eq.) was added to a solution of N-(1E)-(2-(diphenylphosphino)phenyl)methylene)-5*H*-dibenzo[*a,d*]cycloheptene-5-amine (1.48 g, 3.09 mmol, 1.0 eq.) in DCM/methanol 3:2 (50 mL) at RT in a 100 mL Schlenk under argon. After 1 h the reaction was quenched by addition of water under vigorous stirring. The aqueous phase was extracted 3 x with small portions of DCM and the combined organic phases dried over sodium sulfate. The solvent was removed under reduced pressure and the oil purified by flash chromatography (SiO_2, *n*-hexane/ethyl acetate 3:2). The chromatographed product solidifies under high vacuum overnight. Yield: 90%, 1.34 g, 2.78 mmol.

endo – conformer (50%):
^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 2.06 (s, 1H, N*H*), 4.07 (s, 2H, CH_2), 4.82 (s, 1H, CH^{benzyl}), 6.80 (dd, *J* = 6.7 Hz, *J* = 4.6 Hz, 1H, CH^{ar}) 6.92 (s, 2H, CH^{olefin}), 6.96 (dd, *J* = 7.2 Hz, *J* = 4.7 Hz, 1H. CH^{ar}) 7.1-7.5 (m, 20H, CH^{ar})

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2) δ = 51.9 (d, *J* = 19.2 Hz, 1C, *C*H_2), 69.2 (s, 1C, *C*H^{benzyl}), 130.8 (s, 2C, *C*H^{olefin}), 122-146 (m, 30C, *C*H^{ar} and *C*^{quart});

^{31}P{^{1}H}-NMR (166 MHz, CD_2Cl_2) δ = -16.3 (s);

exo – conformer (50%):
^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 2.28 (s, 1H, N*H*), 3.54 (s, 2H, CH_2), 4.07 (s, 1H, CH^{benzyl}), 7.17 (m, 2H, CH^{olefin}), 7.1-7.5 (m, 20H, CH^{ar}), 7.56 (dd, *J* = 6.9 Hz, *J* = 5.0 Hz, 2H);

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2) δ = 50.1 (d, *J* = 21.9 Hz, 1C, *C*H_2), 61.4 (s, 1C, *C*H^{benzyl}), 131.4 (s, 2C, *C*H^{olefin}), 122-146 (m, 30C, *C*H^{ar} and *C*^{quart});

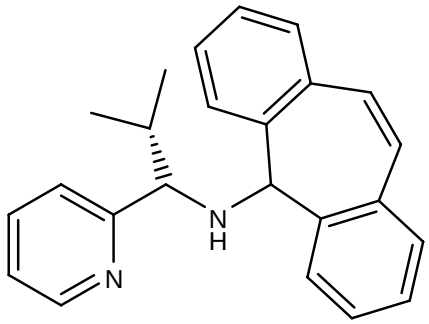
^{31}P{^{1}H}-NMR (166 MHz, CD_2Cl_2) δ = - 15.8 (s);

EA found% (calc%) for $C_{34}H_{28}NP$: C: 82.57 (84.80), H: 5.76 (5.86), N: 2.72 (2.91);

MS (EI, m/z, (%)): 191 (trop+, 100%), 481 (M+, <1%);

ATR IR (ν in cm^{-1}): 3052 (m, CH), 1971 (w, CCar), 1434 (m, CCar), 740 - 694 (s, CHδ).

py(*i*Pr)CHtropNH (N-[(1*S*)-2-methyl-1-pyridin-2-ylpropyl]-5*H*-dibenzo[*a,d*]cycloheptene-5-amine) (**60**)
MF = $C_{21}H_{18}N_2$



MW = 298.38 g/mol

Air stable

To a solution of (1*S*)-2-methyl-1-pyridin-2-ylpropylamine[110] (0.8 g, 5.3 mmol, 1 eq.) in 5 mL DCM triethylamine (2.7 mL, 14 mmol, 2.7 eq.) was added. The solution was cooled with an ice bath and tropCl (1.5 g, 6.6 mmol, 1.25 eq.) was added and the reaction stirred overnight. The organic phase was washed with a saturated sodium carbonate solution and the organic phase dried over sodium sulfate. All volatiles were removed and the obtained oil purified by flash chromatography on silica gel with *n*-hexane/ethyl acetate 10:1 to 5:1 starting with 10:1. Yield: 39%, 0.7 g, 2.3 mmol as slightly yellow oil.

endo - conformer (70%):
^{1}H-NMR (400 MHz, $CDCl_3$, 298K): δ = 0.58 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 0.75 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.80 (8, $^3J_{HH}$ = 6.8 Hz, 1 H, CH(CH_3)$_2$), 2.70 (s, 1 H, NH), 3.06 (d, $^3J_{HH}$ = 7.2 Hz, 1H, CHN), 4.55 (s, 1H, CH^{benzyl}), 6.6-7.0 (m, 13H, CH^{ar}), 8.59 (d, $^3J_{HH}$ = 4.0 Hz, 1H, CH^{ar});

^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 289K): δ = 19.0 (s, 1C, CH$_3$), 20.3 (s, 1C, CH$_3$), 34.8 (s, 1C, CH(CH_3)$_2$), 67.6 (s, 1C, CH^{benzyl}), 67.6 (s, 1C, CHNH), 121-142 (m, 17C, CH^{olefin}, CH^{ar} and C^{quart}), 149.3 (s, 1C, CH^{ar}), 163.9 (s, 1C, C^{quart});

exo - conformer (30%):
^{1}H-NMR (400 MHz, $CDCl_3$, 298K): δ = 0.87 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH_3), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 2.23 (8, $^3J_{HH}$ = 6.8 Hz, 1H, CH(CH_3)$_2$), 2.56 (s, 1H, NH), 3.57 (d, $^3J_{HH}$ = 7.2 Hz, 1H, CH), 3.74 (s, 1H, CH^{benzyl}), 6.6-7.0 (m, 13H, CH^{ar}), 8.49 (d, $^3J_{HH}$ = 4.0 Hz, 1H, CH^{ar});

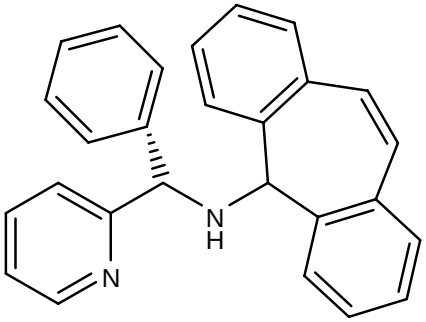
^{13}C{^{1}H}-NMR (100.6 MHz, $CDCl_3$, 289K): δ = 19.5 (s, 1C, CH$_3$), 20.4 (s, 1C, CH$_3$), 34.5 (s, 1C, CH(CH3)2), 58.2 (s,1 C, CH^{benzyl}), 66.9 (s, 1 C, CHNH), 121-142 (m, 17 C, CH^{olefin}, CH^{ar} and C^{quart}), 150.0 (s, 1 C, CH^{ar}), 163.0 (s, 1C, C^{quart});

MS (EI, m/z, (%)): 191 (trop$^+$, 100%), 206 (tropNH$_2^+$, 26%), 340 (M$^+$, 3%), 341 (M+1, 4%);

ATR IR (ν in cm^{-1}): 3058 w, 3015 w, 2957 w, 2869 w, 1637 w, 1588 w, 1569 w, 1469 m, 1431 m, 1383 w, 1363 w, 1304 w, 1269 w, 1201 w, 1147 w, 1120 w, 1079 m, 1047 m, 995 m, 946 m, 887 m, 835 m, 796 s, 749 s, 739 s, 645 m, 624 m, 610 m;

py(Ph)CHtropNH (N-[(1*S*)-2-methyl-1-pyridin-2-ylpropyl]-5*H*-dibenzo[*a,d*]cycloheptene-5-amine) (**61**)
MF = $C_{27}H_{22}N_2$

MW = 374.48 g/mol



Air stable

To a solution of (*S*)-1-phenyl-1-pyridin-2-ylmethanamine[110] (0.5 g, 2.72 mmol, 1 eq.) in 5 mL DCM triethylamine (1.8 mL, 13.5 mmol, 5 eq.) was added. The solution was cooled with an ice bath and tropCl (0.73 g, 3.26 mmol, 1.2 eq.) was added and the reaction stirred overnight. The organic phase was washed with a saturated sodium carbonate solution and the organic phase dried over sodium sulfate. All volatiles were removed and the obtained oil purified by flash chromatography on silica gel with *n*-hexane/ethyl acetate 10:1 to 5:1 starting with 10:1. Yield: 50%, 0.5 g, 1.4 mmol as slightly yellow oil.

endo - conformer (80%):
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 3.15 (s, 1H, N*H*), 4.52 (s, 1H, C*H*^{benzyl}), 4.82 (s, 1H, C*H*), 7.0-8.5 (m, 19H, CH^{ar} and CH^{olefin});

^{13}C{^{1}H}-NMR (176 MHz, $CDCl_3$): δ = 65.3 (s, 1C, *C*H^{benzyl}), 66.5 (s, 1C, C*H*), 121.6 (s, 1C, *C*H^{ar}), 121.7 (s, 1C, *C*H^{ar}), 127.0 (s, 1C, *C*H^{ar}), 127.1 (s, 1C, *C*H^{ar}), 127.3 (s, 1C, *C*H^{ar}), 128.1 (s, 2C, *C*H^{ar}), 128.3 (s, 1C, *C*H^{ar}), 128.5 (s, 2C, *C*H^{ar}), 128.7 (s, 1C, *C*H^{ar}), 129.7 (s, 1C, *C*H^{ar})129.7 (s, 1C, *C*H^{ar}) 130.0 (s, 1C, *C*H^{ar}), 130.1 (s, 1C, *C*H^{ar}), 130.6 (s, 1C, *C*H^{ar}), 130.6 (s, 1C, *C*H^{ar}), 133.6 (s, 1C, C^{quart}), 133.6 (s, 1C, C^{quart}), 136.4 (s, 1C, *C*H^{ar}) 139.7 (s, 1C, C^{quart}), 139.8 (s, 1C, C^{quart}), 142.4 (s, 1 C^{quart}), 149.0 (s, 1C, *C*H^{ar}), 162.8 (s, 1C, C^{quart});

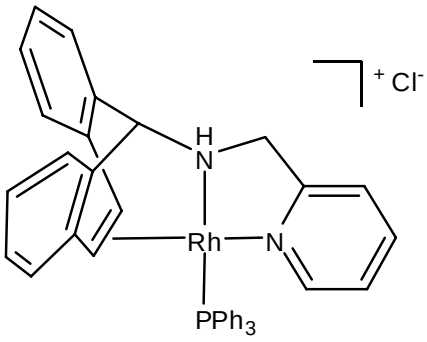
exo - conformer (20%):
^{1}H-NMR (700 MHz, $CDCl_3$): δ = 3.76 (s, 1H, N*H*), 4.11 (s, 1H, CH^{benzyl}), 5.10 (s, 1H, C*H*), 7.0-8.5 (m, 19H, CH^{ar} and CH^{olefin});

^{13}C{^{1}H}-NMR (176 MHz, $CDCl_3$): δ = 57.8 (s, 1C, C*H*^{benzyl}), 64.6 (s, 1C, C*H*), 121 - 162 (m, 25C, *C*Har, *C*H^{olefin} and C^{quart});

MS (EI, m/z, (%)):191.1 (trop$^+$, 75%), 206.1 (tropNH$_2^+$, 100%), 374.1 (M$^+$, 52%);

ATR IR (ν in cm^{-1}): 3055 w (CH), 3018 w (CH), 1663 w, 1587 m, 1560 m, 1492 w, 1453 m, 1432 m, 1303 w, 1282 w, 1243 w, 1198 w, 1157 w, 1072 w, 1047 w, 1029 w, 995 w, 941 w, 927 w, 894 w, 877 w, 844 w, 826 w, 798 s, 742 s, 698 s, 666 m, 650 m, 631 m, 618 m;

[$Rh(PPh_3)(PyCH_2tropNH)$]Cl (**62**)



MF = $C_{39}H_{33}ClN_2PRh$

MW = 698.11 g/mol

MP = 164 °C (dec)
Slightly air sensitive

[$Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4$] (93 mg, 0.24 mmol, 1 eq.) was dissolved together with $pyCH_2tropNH$ **57** (150 mg, 0.50 mmol, 2.1 eq.) in 10 mL DCM under argon. The solution turned orange-red immediately and ethylene was liberated. The reaction was stirred overnight and PPh_3 (132 mg, 0.50 mmol, 2.1 eq.) was added as solid. The reaction was stirred for another hour and the DCM removed under reduced pressure. The residue was recrystallized from DCM/*n*-hexane and dried under vacuum. Yield: 82%, 278 mg, 0.36 mmol.

^{1}H-NMR (700.1 MHz, CD_2Cl_2): δ = 3.54 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{RhH}$ = 3.5 Hz, 1H, C*H*^{olefin}), 3.60 (dd, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 4.2 Hz, 1H, CH_2N), 3.80 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{RhH}$ = 4.8 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, C*H*^{olefin}), 4.66 (dt, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, CH_2N), 5.08 (d, $^4J_{PH}$ = 7.7 Hz, 1H, C*H*^{benzyl}), 6.15 (t, *J* = 4.6 Hz, 1H, N*H*), 6.64 (t, *J* = 6.7 Hz, 1H, C*H*^{ar}), 7.16 (td, *J* = 7.4 Hz, *J* = 1.4 Hz, 1H, C*H*^{ar}), 7.20-7.23 (m, 3H, C*H*^{ar}), 7.24 (dd, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H, C*H*^{ar}), 7.29 (m, 1H, C*H*^{ar}), 7.35 (d, *J* = 7.7 Hz, 1H, C*H*^{ar}), 7.38 (d, J = 7.7 Hz, 1H, C*H*^{ar}), 7.45-7.53 (m, 12H, C*H*^{ar}), 7.86-7.89 (m, 6H, C*H*^{ar});

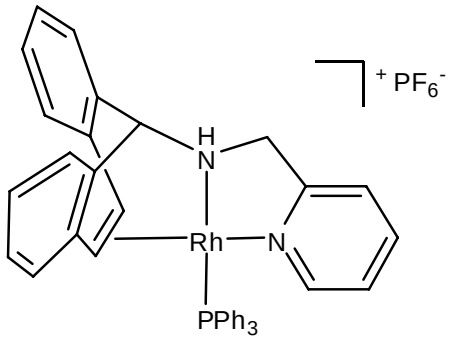
^{13}C{^{1}H}-NMR (176.1 MHz, CD_2Cl_2): δ = 53.7 (br m, 1C, *C*H^{olefin}), 55.5 (d, *J* = 2.5 Hz, 1C, *C*H_2N), 60.4 (br m, 1C, *C*H^{olefin}), 67.2 (s, 1C, *C*H^{benzyl}), 122.5 (s, 2C, *C*H^{ar}), 126.1 (s, 1C, *C*H^{ar}), 126.3 (s, 1C, *C*H^{ar}), 128.6 (d, $^2J_{PC}$ = 9.9 Hz, 6C, *C*H^{ar}), 128.6 (s, 1C, *C*H^{ar}), 128.6 (s, 1C, *C*H^{ar}), 128.7 (s, 1C, *C*H^{ar}), 128.9 (s, 1C, *C*H^{ar}), 129.4 (s, 1C, *C*H^{ar}), 129.7 (s, 1C, *C*H^{ar}), 130.7 (d, $^4J_{PC}$ = 1.3 Hz, 3C, *C*^{quart}), 131.1 (d, $^1J_{PC}$ = 43.8 Hz, 3C, *C*H^{ar}), 134.9 (d, $^3J_{PC}$ = 11.3 Hz, 6C, *C*H^{ar}), 135.2 (s, 1C, *C*^{quart}), 136.5 (s, 1C, *C*^{quart}), 137.8 (s, 1C, *C*H^{ar}), 139.8 (s, 1C, *C*^{quart}), 140.0 (s, 1C, *C*^{quart}), 150.9 (d, *J* = 1.9 Hz, 1C, *C*H^{ar}), 163.9 (s, 1C, *C*^{quart});

^{31}P{^{1}H}-NMR (283.4 MHz, CD_2Cl_2): δ = 51.0 (d, $^1J_{RhP}$ = 161.6 Hz);

^{1}H, ^{103}Rh-NMR (22.1 MHz, CD_2Cl_2): δ = -7345 (d, $^1J_{RhP}$ = 161.6 Hz);

ATR IR (ν in cm^{-1}): 3221 (w), 3045 (w), 2936 (w), 1612 (w), 1569 (w), 1487 (m), 1459 (w), 1433 (m), 1376 (w), 1260 (w), 1217 (w), 1185 (w), 1154 (w), 1094 (m), 990 (m), 751 (s), 694 (s);

[$Rh(PPh_3)(PyCH_2tropNH)]PF_6$ (**63**)



MF = $C_{39}H_{33}F_6N_2P_2Rh$

MW = 808.57 g/mol

MP = 155 °C
Slightly air sensitive

[$Rh(PyCH_2tropNH)(PPh_3)]Cl$ **62** (250 mg, 0.36 mmol, 1 eq.) and $TlPF_6$ (125 mg, 0.36 mmol, 1 eq.) were dissolved in 3 mL THF and stirred overnight. THF was removed under reduced pressure and the residue dissolved in 5 mL DCM. The solution was filtered over celite and the DCM removed under reduced pressure. The solid was recrystallized from THF/*n*-hexane. Yield: 90%, 261 mg, 0.32 mmol.

^{1}H-NMR (300.1 MHz, CD_2Cl_2): δ = 3.72 (m, 1H, C*H*^{olefin}), 3.75 (m, 1H, C*H*$_2$N), 4.30 (br s, 1H, N*H*), 4.31 (m, 1H, C*H*^{olefin}), 4.30, 4.52 (dt, $^2J_{HH}$ = 15.3 Hz, $^3J_{PH}$ = 3.8 Hz, 1H, C*H*$_2$N), 5.16 (d, $^3J_{PH}$ = 7.8 Hz, 1H, C*H*^{benzyl}), 6.69 (t, *J* = 6.6 Hz, 1H, C*H*^{ar}), 7.1-7.85 (m, 27H, C*H*^{ar});

^{13}C{^{1}H}-NMR (75.5 MHz, CD_2Cl_2): δ = 55.0 (s, 1C, *C*H$_2$N), 60.8 (d, $^1J_{RhC}$ = 12.9 Hz, 1C, *C*H^{olefin}), 67.0 (s, 1C, *C*H^{benzyl}), 68.2 (d, $^1J_{RhC}$ = 15.5 Hz, 1C, *C*H^{olefin}), 123.6 (s, 1C, *C*H^{ar}), 123.9 (s, 1C, *C*H^{ar}), 127.7 (s, 1C, *C*H^{ar}), 128.2 (s, 1C, *C*H^{ar}), 129.3 (s, 1C, *C*H^{ar}), 129.3 (s, 1C, *C*H^{ar}), 129.3 (d, $^2J_{PC}$ = 10.2 Hz, 6C, *C*H^{ar}), 129.5 (s, 1C, *C*H^{ar}), 129.9 (s, 1C, *C*H^{ar}), 130.0 (s, 1C, *C*H^{ar}), 130.7 (d, $^1J_{PC}$ = 44.3 Hz, 3C, *C*^{quart}), 131.0 (s, 1C, *C*H^{ar}), 131.7 (d, $^4J_{PC}$ = 2.1 Hz, 3C, *C*H^{ar}), 135.1 (d, $^3J_{PC}$ = 11.7 Hz, 6C, *C*H^{ar}), 135.5 (s, 1C, *C*^{quart}), 137.0 (s, 1C, *C*^{quart}), 138.0 (s, 1C, *C*^{quart}), 138.9 (s, 1C, *C*^{quart}), 139.8 (s, 1C, *C*H^{ar}), 151.7 (s, 1 C, *C*H^{ar}), 164.2 (s, 1 C, *C*^{quart});

^{19}F-NMR (188.3 MHz, CD_2Cl_2): δ = -73.0 (d, $^1J_{PF}$ = 713.7 Hz);

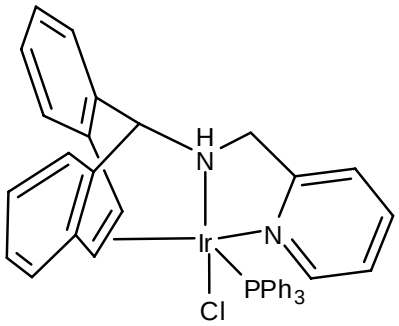
^{31}P{^{1}H}-NMR (162.0 MHz, CD_2Cl_2): δ = -143 (7, $^1J_{FP}$ = 713.7 Hz), 52 (d, $^1J_{RhP}$ = 166.2 Hz);

^{1}H, ^{103}Rh-NMR (12.7 MHz, CD_2Cl_2): δ = -7612 (d, $^1J_{RhP}$ = 166.2 Hz);

ATR IR (ν in cm^{-1}): 3177 (w), 3066 (w), 2939 (w), 2349 (w), 2160 (w), 1612 (w), 1480 (w), 1434 (w), 1311 (w), 1093 (w), 1054 (w), 830 (s), 758 (m), 698 (m), 556 (s).

EA found% (calc%) for $C_{39}H_{33}F_6N_2P_2Rh$: C: 57.90 (57.93), H: 4.21 (4.11), N: 3.46 (3.46);

[Ir(Cl)(PPh_3)($PyCH_2$tropNH)] (**64**)



MF = $C_{39}H_{33}ClIrN_2P$

MW = 788.33 g/mol

MP = 160 °C (dec)
Air sensitive

$[Ir_2(\mu_2\text{-}Cl)_2(COE)_4]$ (202 mg, 0.23 mmol, 1 eq.) was dissolved together with $pyCH_2$tropNH **57** (141 mg, 0.47 mmol, 2.1 eq.) in 10 mL THF under argon. The reaction was stirred overnight and a yellow solution was obtained. A solution of PPh_3 (142 mg, 0.54 mmol, 2.4 eq.) in THF was added. The solution turned orange and a yellow precipitate was observed. The precipitation was completed by standing at -18 °C overnight and the precipitate collected by filtration and dried under vacuum. Yield: 70%, 251 mg, 0.31 mmol.

The product is quite sensitive to air in solution but the crystalline material is stable on air for a few hours before decomposition is visible.

^{1}H-NMR (300.1 MHz, CD_2Cl_2): δ = 3.21 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, CH_2N), 3.48 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 7 Hz, 1H, CH_2N), 3.51 (s, 1H, N*H*), 3.99 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, CH^{olefin}), 4.16 (d, J = 1.8 Hz, 1H, CH^{benzyl}), 4.50 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{PH}$ = 2.4 Hz, 1H, CH^{olefin}), 6.7-7.5 (m, 26 H, CH^{ar}), 8.91 (d, $^3J_{HH}$ = 5.5 Hz, 1H, CH^{ar});

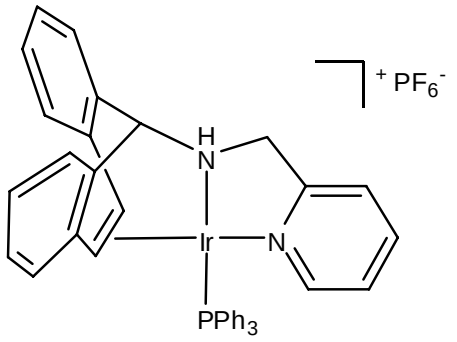
^{13}C{^{1}H}-NMR (75.5 MHz, CD_2Cl_2): δ = 29.1 (d, $^2J_{CP}$ = 5.1 Hz, 1C, CH^{olefin}), 40.9 (d, $^2J_{CP}$ = 47.4 Hz, 1C, CH^{olefin}), 57.6 (s, 1C, CH_2N), 70.4 (s, 1C, CH^{benzyl}), 119.0 (s, 1C, CH^{ar}) 121.7 (s, 1C, CH^{ar}) 121.7 (s, 1C, CH^{ar}) 123.5 (s, 1C, CH^{ar}) 126.0 (s, 1C, CH^{ar}) 128.1 (d, $^1J_{PC}$ = 30.5 Hz, 3C), 128.0 (s, 1C, CH^{ar}), 128.1 (d, $^2J_{PC}$ = 8.8 Hz, 6C, CH^{ar}) 128.9 (d, $^4J_{PC}$ = 1.8 Hz, 3C, CH^{ar}), 129.1 (s, 1C, CH^{ar}), 131.1 (d, J = 3.0 Hz, 1C, C^{quart}), 133.2 (d, $^3J_{PC}$ = 11.0 Hz, 6C, CH^{ar}) 133.8 (s, 1C, C^{quart}), 134.1 (s, 1C, CH^{ar}), 134.3 (s, 1C, CH^{ar}), 134.8 (s, 1C, C^{quart}) 146.0 (d, J = 5.8 Hz, 1C, C^{quart}) 147.2 (d, J = 2.4 Hz, 1C, C^{quart}) 149.5 (s, 1C, CH^{ar}) 160.5 (s, 1C, C^{quart});

^{31}P{^{1}H}-NMR (121.5 MHz, CD_2Cl_2): δ = 0.1 (s);

ATR IR (ν in cm^{-1}): 3209 (w), 3069 (w), 2955 (w), 1972 (w), 1593 (m), 1482 (m), 1432 (m), 1351(w), 1268 (w), 1090 (m), 1002 (w), 859 (w), 762 (m), 748 (m), 695 (s), 558 (m);

EA found% (calc%) for $C_{39}H_{33}ClIrN_2P$: C: 59.61 (59.42), H: 4.41 (4.22), N: 3.57 (3.55);

[Ir(PPh$_3$)(PyCH$_2$tropNH)]PF$_6$ (**65**)



MF = $C_{39}H_{33}F_6N_2P_2Ir$

MW = 897.85 g/mol

MP = 169 °C (dec)
Air sensitive

[Ir(Cl)(PyCH$_2$tropNH)(PPh$_3$)] **64** (250 mg, 0.32 mmol, 1 eq.) and TlPF$_6$ (110 mg, 0.32 mmol, 1 eq.) were dissolved in 3 mL THF and stirred overnight. THF was removed under reduced pressure and the residue dissolved in 5 mL DCM. The solution was filtered over celite and the DCM removed under reduced pressure. The solid was recrystallized from THF/*n*-hexane. Yield: 97%, 277 mg, 0.31 mmol.

^{1}H-NMR (300.1 MHz, CD_2Cl_2): δ = 3.62 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{PH}$ = 3.3 Hz, 1H, C*H*^{olefin}), 3.92 (m, 1H, C*H*$_2$N), 3.95 (m, 1H, C*H*^{olefin}), 4.72 (br s, 1H, N*H*), 4.81 (m, 1H, C*H*$_2$N), 5.36 (d, $^4J_{PH}$ = 6.9 Hz, 1H, C*H*^{benzyl}), 6.82 (t, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*^{ar}), 7.2-7.9 (m, 26H, C*H*^{ar});

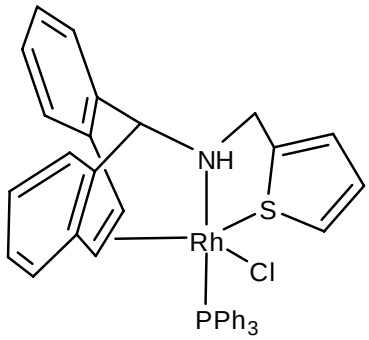
^{13}C{^{1}H}-NMR (75.5 MHz, CD_2Cl_2): δ = 44.1 (s, 1C, C*H*^{olefin}), 53.7 (s, 1C, C*H*^{olefin}), 55.3 (d, $^3J_{PC}$ = 2.8 Hz, 1C, *C*H$_2$N), 67.3 (d, $^3J_{PC}$ = 1.6 Hz, 1C, *C*H^{benzyl}), 123.0 (s, 1C, *C*H^{ar}), 124.1 (s, 1C, *C*H^{ar}), 126.3 (s, 1C, *C*H^{ar}), 127.0 (s, 1 C, *C*H^{ar}), 128.5 (s, 1 C, *C*H^{ar}), 128.7 (d, $^2J_{PC}$ = 10.2 Hz, 6C, *C*H^{ar}), 128.8 (s, 1C, *C*H^{ar}), 129.1 (s, 1C, *C*H^{ar}), 129.1 (s, 1C, *C*H^{ar}), 129.8 (d, $^1J_{PC}$ = 53.8 Hz, 3C, *C*^{quart}), 129.9 (s, 1C, *C*H^{ar}), 130.5 (s, 1C, *C*H^{ar}), 131.2 (d, $^4J_{PC}$ = 2.4 Hz, 3C, *C*H^{ar}), 133.9 (s, 1 C, *C*^{quart}), 135.0 (d, $^3J_{PC}$ = 10.8 Hz, 6C, *C*H^{ar}), 136.1 (s, 1 C, *C*^{quart}), 138.3 (s, 1 C, *C*^{quart}), 139.6 (s, 1C, *C*^{quart}), 140.4 (s, 1C, *C*H^{ar}), 152.8 (d, *J* = 2.6 Hz, 1C, *C*H^{ar}), 165.3 (d, $^3J_{PC}$ = 1.1Hz, 1C, *C*^{quart});

^{31}P{^{1}H}-NMR (121.5 MHz, CD_2Cl_2): δ = -144 (7, $^1J_{PF}$ = 712.0 Hz, PF_6), 19 (s);

ATR IR (ν in cm^{-1}): 3156 (w), 2938 (w), 2161 (w), 1978 (w), 1615 (w), 1481 (w), 1434 (w), 1311 (w), 1093 (w), 1054 (w), 829 (s), 758 (m), 698 (m), 556 (s).

EA found% (calc%) for $C_{39}H_{33}F_6N_2P_2Ir$: C: 51.98 (52.17), H: 3.97 (3.70), N: 3.00 (3.12);

[Rh(Cl)(thiotropNH)(PPh_3)] (**66**)



MF = $C_{38}H_{32}NSPClRh$

MW = 704.10 g/mol

MP = 110 °C (dec)
Slightly air sensitive

THF (ca. 20 mL) was added to a mixture of thioCH_2tropNH **58 (**492 mg, 1.62 mmol, 2.1 eq.) and [$Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4$] (300 mg, 0.77 mmol, 1.0 eq.) in a Schlenk flask under argon. 5 min later PPh_3 (425 mg, 1.62 mmol, 2.1 eq.) was added to the solution which turned dark red-brown. Probably the [$Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4$] was not clean enough so after 72 h a black precipitate and some orange crystals were observed. The crystals were dissolved again and the suspension was filtered over celite. The solvent was then partially removed until the solution turned cloudy. It was layered with *n*-hexane. The obtained crystals were separated from the mother liquor and dried under vacuum. From the mother liquor a second fraction was obtained. Yield (overall): 84%, 955 mg, 1.35 mmol.

^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 3.17 (t, J = 8.0 Hz, 1H, CH^{olefin}), 3.23 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 10.3 Hz, 1H, CH_2), 3.59 (m, 1H, CH^{olefin}), 4.79 (d, J = 14.0 Hz, 1H, CH_2), 4.87 (d, J = 7.3 Hz, 1H, CH^{benzyl}), 5.20 (d, J = 10.3 Hz, 1H, NH), 7.02 (d, J = 3.2 Hz, 1H, CH^{ar}), 7.09 - 7.13 (m, 2H, CH^{ar}), 7.24 - 7.41 (m, 8H, CH^{ar}), 7.45 - 7.52 (m, 9H, CH^{ar}), 7.91 - 7.86 (m, 6H, CH^{ar});

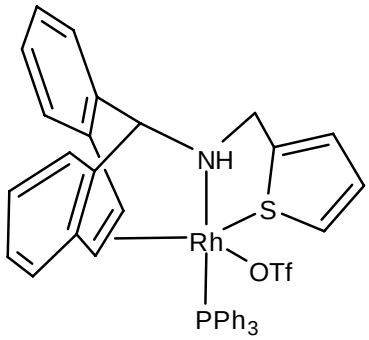
^{13}C{^{1}H}-NMR (100 MHz, CD_2Cl_2) δ = 46.7 (s, 1C, CH_2), 54.6 (d, $^1J_{Rh,C}$ = 14.4 Hz, 1C, CH^{olefin}), 58.0 (d, $^1J_{Rh,C}$ = 15.4 Hz, 1C, CH^{olefin}), 64.3 (s, 1C, CH^{benzyl}), 126.0 (s, 1C, CH^{ar}), 126.2 (s, 1C, CH^{ar}), 126.6 (s, 1C, CH^{ar}), 127.6 (s, 1C, CH^{ar}), 128.3 (s, 1C, CH^{ar}), 128.3 (d, $^2J_{C,P}$ = 9.8 Hz, 6C, CH^{ar}(meta-PPh_3)), 128.8 (s, 1C, CH^{ar}), 129.0 (s, 1C, CH^{ar}), 129.3 (s, 1C, CH^{ar}), 129.5 (d, $^1J_{C,P}$ = 7.1 Hz, 3C, C_q(ipso-PPh_3)), 130.3 (s, 1C, CH^{ar}), 130.5 (d, $^4J_{C,P}$ = 2.3 Hz, 3C, CH^{ar}(para-PPh_3)), 132.2 (s, 1C, CH^{ar}), 132.7 (s, 1C, CH^{ar}), 133.9 (s, 1C, C_q), 135.4 (d, $^2J_{C,P}$ = 10.6 Hz, 6C, CH^{ar}(ortho-PPh_3)), 136.9 (s, 1C, C_q), 140.0 (d, J = 3.5 Hz, 1C, C_q), 140.7 (s, 1C, C_q), 141.1 (d, J = 2.4 Hz, 1C, C_q);

^{31}P{^{1}H}-NMR (161.98 MHz, CD_2Cl_2) δ = 50.4 (d, $^1J_{Rh,P}$ = 163.3 Hz);

^{1}H, ^{103}Rh-NMR (15.7 MHz, CD_2Cl_2): δ = -7462 (d, $^1J_{Rh,P}$ = 163.3 Hz);

ATR IR (ν in cm^{-1}): 3243 (w, NH), 3049 (m, CH), 1434 (w, CCar), 754 - 651 (s, CHδ).

[Rh(thiotropNH)(PPh_3)]OTf (**67**)



MF = $C_{39}H_{32}NO_3S_2PF_3Rh$

MW = 817.72 g/mol

MP = 220 °C (dec)
Slightly air sensitive

THF (ca. 10 mL) was added to a mixture of [Rh(Cl)(thiotropNH)(PPh_3)] **66** (60 mg, 0.085 mmol, 1 eq.) and AgOTf (22 mg, 0.085 mmol, 1 eq.) under argon. It was stirred for 19 h protected from light before the solvent was removed under reduced pressure. The solid was dissolved in dichloromethane and filtrated over celite. The solvent was removed and the product recrystallized from THF/*n*-hexane and dried under high vacuum. Yield: 92%, 64 mg, 0.08 mmol.

^{1}H-NMR (400.13 MHz, CD_2Cl_2): δ = 3.31 (dd, $^2J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 10.6 Hz, 1H, CH_2), 3.82 (m, 1H, CH^{olefin}), 3.99 (m, 1 H, CH^{olefin}), 4.15 (dt, $^2J_{HH}$ = 13.0 Hz, J = 4.8 Hz,1H, CH_2), 4.98 (d, J = 7.5 Hz, 1H, CH^{benzyl}), 5.08 (b, 1H, NH), 5.85 (d, J = 5.0 Hz, 1H, CH^{ar}), 6.74 (s, 1H, CH^{ar}), 6.89 (t, J = 5.0 Hz, 1H, CH^{ar}), 7.18 (d, J = 7.5 Hz, 1H, CH^{ar}), 7.27 - 7.24 (m, 1H, CH^{ar}), 7.42 - 7.34 (m, 6H, CH^{ar}), 7.77 (t, J = 9.0 Hz, 6H, CH^{ar}), 7.62 - 7.54 (m, 10H, CH^{ar});

^{13}C{^{1}H}-NMR (100.61 MHz, CD_2Cl_2): δ = 47.5 (s, 1C, CH$_2$), 56.7 (t, J = 15.5 Hz, 2C, CH^{olefin}), 68.0 (s, 1C, CH^{benzyl}), 126.7 (s, 1C, CH^{ar}), 126.9 (s, 1C, CH^{ar}), 127.0 (s, 1C, CH^{ar}), 127.2 (s, 1C, CH^{ar}), 129.1 (d, $^2J_{C,P}$ = 10.2 Hz, 7C, CH^{ar}(ortho-PPh_3), CH^{ar}), 129.3 (d, $^1J_{C,P}$ = 3.5 Hz, 3C, C_q(ipso-PPh_3)), 129.4 (s, 1C, CH^{ar}), 129.6 (s, 2C, CH^{ar}), 130.3 (s, 1C, CH^{ar}), 130.9 (s, 1C, CH^{ar}), 131.3 (s, 3C, CH^{ar}(para-PPh_3)), 131.9 (s, 1C, CH^{ar}), 134.8 (d, $^3J_{C,P}$ = 10.6 Hz, 6C, CH^{ar}(meta-PPh_3)), 135.2 (s, 1C, C_q), 135.4 (s, 1C, C_q), 138.7 (s, 1C, C_q), 139.1 (s, 1C, C_q), 142.2 (s, 1C, C_q);

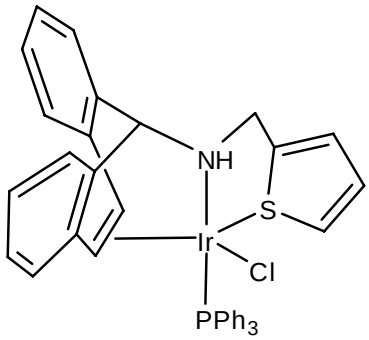
^{31}P{^{1}H}-NMR (202.5 MHz, CD_2Cl_2) δ = 42.93 (d, $^1J_{Rh,P}$ = 150.0 Hz);

^{1}H, ^{103}Rh-NMR (15.7 MHz, CD_2Cl_2): δ = -7091 (d, $^1J_{Rh,P}$ = 150.0 Hz);

EA found% (calc%) for $C_{39}H_{32}NO_3S_2PF_3Rh$: C: 57.01 (57.29), H: 4.24 (3.94), N: 1.69 (1.71);

ATR IR (ν in cm^{-1}): 3172 (w, NH), 3000 (m, CH), 1435 (w, CCar), 1223 (m, S=O), 743 - 630 (s, CH_δ);

[Ir(Cl)(thiotropNH)(PPh_3)] (**68**)



MF = $C_{38}H_{32}NSPClIr$

MW = 793.41 g/mol

MP >230 °C
Air sensitive

THF (ca. 20 mL) was added to a mixture of [$Ir_2(\mu_2\text{-}Cl)_2(COE)_4$] (747 mg, 0.83 mmol, 1.0 eq.) and thioCH_2tropNH **58** (531 mg, 1.75 mmol, 2.1 eq.) under argon until everything was dissolved. After 18 h triphenylphosphine (437 mg, 1.67 mmol, 2 eq.) was added to the solution. THF was removed under reduced pressure to a final volume of ca. 3 mL and the solution layered with *n*-hexane. Four days later, crystals were obtained; they were separated from the mother liquor and dried under vacuum. Yield: 95%, 17 mg, 0.021 mmol.

^{1}H-NMR (300.13 MHz, $CDCl_3$) δ = 2.86 (br s, 1H, C*H*^{olefin}), 2.99 (br s, 1H, C*H*^{olefin}), 3.25 (m, 1H, CH_2), 4.96 (d, $^2J_{HH}$ = 14.2 Hz, 1H, CH_2), 5.04 (d, J = 6.6 Hz, 1H, C*H*^{benzyl}), 5.99 (br s, 1H, N*H*), 7.02 - 7.18 (m, 10H, C*H*^{ar}), 7.41 - 7.50 (m, 10H, C*H*^{ar}), 7.76 (m, 6H, C*H*^{ar});

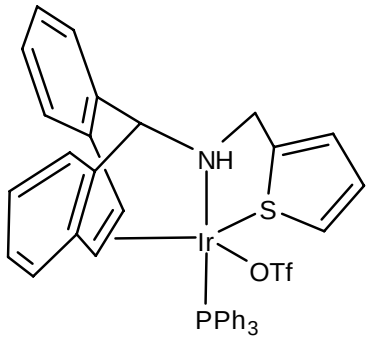
^{13}C{^{1}H}-NMR (75.47 MHz, $CDCl_3$) δ = 34.7 (s, 1C, *C*H^{olefin}), 37.6 (s, 1C, *C*H^{olefin}), 47.6 (s, 1C, *C*H_2), 63.6 (s, 1C, *C*H^{benzyl}), 124.9 (s, 1C, *C*H^{ar}), 125.1 (s, 1C, *C*H^{ar}), 126.5 (s, 1C, *C*H^{ar}), 127.8 (s, 2C, *C*H^{ar}), 128.3 (d, $^2J_{C,P}$ = 9.7 Hz, 6C, *C*H^{ar}(ortho-PPh_3)), 128.5 (s, 2C, *C*H^{ar}), 129.1 (s, 2C, *C*H^{ar}), 129.7 (s, 1C, *C*H^{ar}), 130.4 (s, 1C, *C*H^{ar}), 130.6 (s, 3C, *C*H^{ar}(para-PPh_3)), 131.2 (d, $^1J_{C,P}$ = 31.2 Hz, 3C, C_q(ipso-PPh_3)), 134.0 (s, 1C, C_q), 135.3 (d, $^3J_{C,P}$ = 9.7 Hz, 6C, *C*H^{ar}(meta-PPh_3)), 136.6 (s, 1 C, *C*H^{ar}), 139.3 (s, 1C, C_q), 140.7 (s, 1C, C_q), 141.6 (s, 1C, C_q);

^{31}P{^{1}H}-NMR (121.49 MHz, $CDCl_3$) δ = 10.40 (s);

EA found% (calc%) for $C_{38}H_{32}NSPClIr$: C: 57.60 (57.53), H: 4.19 (4.07), N 1.77 (1.77);

ATR IR (ν in cm^{-1}): 3048 (m, CH), 1572 (w, CCar), 754 - 687 (s, CH_δ).

[Ir(thiotropNH)(PPh_3)]OTf (**69**)



MF = $C_{39}H_{32}NS_2PO_3F_3Ir$

MW = 907.03 g/mol

MP = 110 °C (dec)
Air sensitive

THF (15 mL) was added to a mixture of [Ir(Cl)(thiotropNH)(PPh_3)] **68** (483 mg, 0.609 mmol, 1.0 eq.) and silver triflate (156 mg, 0.609 mmol, 1.0 eq.) in a Schlenk flask under argon. The solution was protected form light and stirred for 1 h. The solvent was removed under reduced pressure. The residue was dissolved in DCM and filtered over celite and the DCM removed again under reduced pressure. The residue was recrystallized from DME/diethylether. Yield: 90%, 474 mg, 0.52 mmol.

The complex shows broad NMR signals in non coordinating solvents like CD_2Cl_2.

^{1}H-NMR (500 MHz, d_6-DMSO) δ = 3.06 (m, 1H, C*H*$_2$), 3.44 (m, 1H, C*H*^{olefin}), 3.54 (m, 1H, C*H*^{olefin}), 4.07 (m, 1H, C*H*$_2$), 5.28 (d, *J* = 7.0 Hz, 1H, C*H*^{benzyl}), 6.10 (b, 1H, N*H*), 6.94 (s, 1H, C*H*^{ar}), 7.17 (m, 1H, C*H*^{ar}), 7.23 - 7.33 (m, 5H, C*H*^{ar}), 7.39 - 7.43 (m, 2H, C*H*^{ar}), 7.51 (m, 2H, C*H*^{ar}), 7.69 (br, 15H, C*H*^{ar});

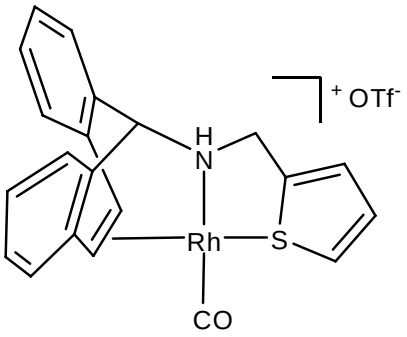
^{13}C{^{1}H}-NMR (125 MHz, d_6-DMSO) δ = 32.7 (s, 1C, *C*H^{olefin}), 42.5 (s, 1C, *C*H^{olefin}), 47.7 (s, 1C, *C*H$_2$), 66.7 (s, 1C, *C*H^{benzyl}), 126.0 (s, 1C, *C*H^{ar}), 127.0 (s, 1C, *C*H^{ar}), 128.23 (s, 1C, *C*H^{ar}), 128.7 (s, 1C, *C*H^{ar}), 129.0 (s, 1C, *C*H^{ar}), 129.3 (s, 1C, *C*H^{ar}), 129.5 (s, 1C, *C*H^{ar}), 130.0 (d, $^2J_{C,P}$ = 9.6 Hz, 6C, *C*H^{ar}(ortho-PPh_3)), 130.3 (d, $^1J_{C,P}$ = 50.4 Hz, 3C, C_q(ipso-PPh_3)), 130.9 (s, 1C, C*H*^{ar}), 131.5 (s, 1C, C_q), 132.58 (s, 3C, *C*H^{ar}(para-PPh_3)), 133.1 (s, 1C, C_q), 134.7 (s, 1C, C_q), 135.3 (b, 6C, *C*H^{ar}(meta-PPh_3)), 135.6 (s, 1C, *C*H^{ar}), 139.5 (s, 1C, C_q), 139.6 (s, 1C, C_q), 145.4 (s, 1C, C_q);

^{31}P{^{1}H}-NMR (202.5 MHz, d_6-DMSO) δ = 3.70 (s);

EA found% (calc%) for $C_{39}H_{32}NS_2PO_3F_3Ir$: C: 51.37 (51.65), H: 3.82 (3.56), N: 1.48 (1.54);

ATR IR (ν in cm^{-1}): 3059 (m, CH), 2962 (w, CH), 1602 (w, CCar), 1260 (m, S=O), 1029 (m, CF), 754 - 635 (s, CH_δ).

[Rh(CO)(thiotropNH)]OTf (**70**)



MF = $C_{22}H_{17}NS_2O_4F_3Rh$

MW = 583.44 g/mol

MP = 175-180 °C (dec)
Air sensitive

$[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (10 mg, 0.03 mmol, 1.0 eq.) was added to a solution of thioCH_2tropNH **58** (15.5 mg, 0.05 mmol, 2 eq.) in THF (ca. 5 mL) in a small vial in a glovebox. After 1 h AgOTf (13 mg, 0.05 mmol, 1 eq.) was added. The solution was stirred protected from light overnight. The solvent was removed under reduced pressure. The solid was dissolved in DCM and filtered over celite to get an orange solution and the solvent was removed under reduced pressure. The product was recrystallized from THF/*n*-hexane and dried under high vacuum. Yield: 72%, 21.5 mg, 0.04 mmol.

^{1}H-NMR (400.13 MHz, CD_2Cl_2) δ = 3.70 - 3.84 (m, 1H, CH_2), 3.86- 3.87 (m, 2H, N*H*, CH_2), 4.97 - 4.97 (m, 2H, CH^{olefin}, CH^{benzyl}), 5.22 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, CH^{olefin}), 6.86 (d, J = 3.2 Hz, 1 H, CH^{ar}), 7.12 (dd, J_1 = 5.2 Hz, J_2 = 3.2 Hz, 1H, CH^{ar}), 7.27 - 7.30 (m, 1H, CH^{ar}), 7.38 - 7.50 (m, 6H, CH^{ar}), 7.71 - 7.78 (m, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (100.61 MHz, CD_2Cl_2) δ = 46.5 (s, 1C, *C*H_2), 57.1 (d, J = 15 Hz, 1C, *C*H^{olefin}), 61.4 (d, J = 15 Hz, 1C, *C*H^{olefin}), 65.6 (s, 1C, *C*H^{benzyl}), 120.0 (q, $^2J_{C,F}$ = 319 Hz, 1C, *C*F_3), 127. 3 (s, 1C, *C*H^{ar}), 128.7 (s, 1C, *C*H^{ar}), 129. 0 (s, 2C, *C*H^{ar}), 129. 3 (s, 1 C, *C*H^{ar}), 129.9 (s, 1 C, *C*H^{ar}), 130.1 (s, 1 C, *C*H^{ar}), 130.3 (s, 1 C, *C*H^{ar}), 130.4 (s, 1 C, *C*H^{ar}), 130.7 (s, 1 C, *C*H^{ar}), 130.9 (s, 1 C, *C*H^{ar}), 135.1 (s, 1 C, C_q), 136.3 (s, 1 C, C_q), 136.4 (s, 1 C, C_q), 136.7 (s, 1 C, C_q), 137.2 (s, 1 C, C_q), 182.7 (d, $^1J_{C,Rh}$ = 69 Hz, 1 C, *C*O);

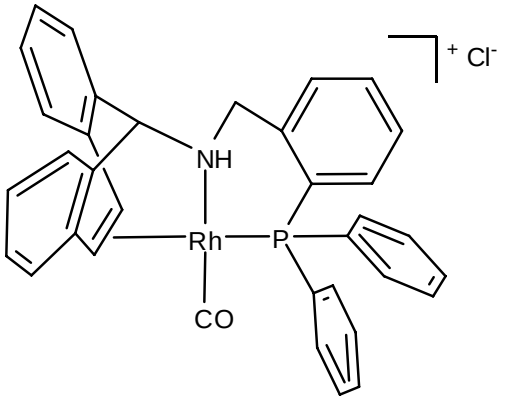
ATR IR (ν in cm^{-1}): 3146 w (NH), 3109 w (NH), 2948 w (CH), 2856 w (CH),2036 m (CO), 2025 m (CO), 1603 w, 1492 m, 1468 w, 1451 w, 1435 w, 1398 w, 1372 w, 1358 w, 1332 w, 1287 s, 1272 s, 1259 m, 1227 s, 1216 s, 1178 s, 1160 s, 1126 m, 1110 w, 1084 w, 1022 s, 995 m, 953 m, 908 m, 874 w, 850 m, 838 m, 817 m, 779 w, 761 s, 746 m, 732 m, 716 m, 693 m, 677 w, 624 s;

[Rh(Cl)(CO)(Ph_2PPhtropNH)]

MF = $C_{35}H_{28}NPOClRh$

MW = 648.70 g/mol

MP = 200 °C (dec)
Air sensitive



Ph_2PPhCH_2tropNH **59** (248 mg, 0.541 mmol, 2 eq.) was added to a solution of $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ (100 mg, 0.257 mmol, 1 eq.) in 5 mL THF under argon. After vigorous stirring a big amount of yellow solid precipitated. *n*-Hexane was added to precipitate the remainder of the product, which was isolated by filtration and dried under high vacuum. Yield: 90%, 301 mg, 0.46 mmol.

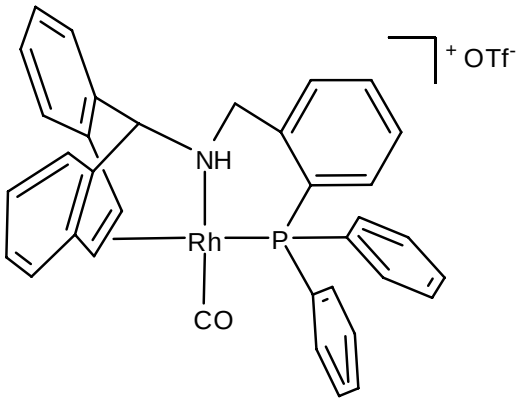
^{1}H-NMR (550.2 MHz, CD_2Cl_2) δ = 3.00 (b, 1 H, N*H*), 3.71 (m, 1 H, CH_2), 4.79 (m, 2 H, CH^{olefin}, CH_2), 5.07 (s, 1 H, CH^{benzyl}), 5.47 (s, 1 H, CH_2), 6.71 (s, 1 H, CH^{ar}), 7.26 - 7.65 (m, 21 H, CH^{ar});

^{13}C{^{1}H}-NMR (125.8 MHz, CD_2Cl_2) δ = 55.6 (m, 1C, *C*H^{olefin}), 57.0 (d, *J* = 15.3 Hz, 1C, *C*H_2), 58.0 (s, 1C, *C*H^{olefin}), 71.1 (s, 1C, *C*H^{benzyl}), 125.8 (s, 1C, *C*H^{ar}), 126.5 (s, 1C, *C*H^{ar}), 129.0 (s, 1C, *C*H^{ar}), 129.4 - 129.9 (m, 8C, *C*H^{ar}), 131.1 (s, 1C, *C*H^{ar}), 131.4 (s, 1 C, *C*H^{ar}), 131.6 (d, *J* = 5.7 Hz, 2C, *C*H^{ar}), 132.1 (m, 2C, *C*H^{ar}), 133.7 (d, *J* = 8.3 Hz, 1C, *C*H^{ar}), 134.3 (m, 1C, C_q), 135.8 (s, 2C, C_q), 136.0 (s, 2C, C_q), 137.8 (s, 1C, C_q), 139.7 (s, 1 C, C_q), 140.0 (s, 1 C, C_q), 140.1 (s, 1C, C_q), 191.4 (dd, $^1J_{C,Rh}$ = 61.0 Hz, $^2J_{C,P}$ = 16.5 Hz, 1C, *C*O);

^{31}P{^{1}H}-NMR (202.5 MHz, CD_2Cl_2) δ = 16.2 (d, $^1J_{Rh,P}$ = 135.3 Hz);

ATR IR (ν in cm^{-1}): 3194 (m, NH), 3056 (m, CH), 2956 (m, CH), 2000 (s, CO), 1600 (w, CCar), 1437 (m), 1096 (s, S=O), 752 - 680 (s, CH_δ);

[Rh(CO)(Ph_2PPhtropNH)]OTf (**71**)



MF = $C_{36}H_{28}NPSO_4F_3Rh$

MW = 761.59 g/mol

MP = 150 °C (dec)
Air sensitive

THF (5 mL) was added to a mixture of [Rh(Cl)(CO)(Ph_2PPhtropNH)] (100 mg, 0.154 mmol, 1 eq.) and AgOTf (40 mg, 0.154 mmol, 1 eq.) under argon. The solution was stirred protected from light overnight. The solvent was removed under reduced pressure; the solid dissolved in DCM and filtrated over celite. The DCM was removed and the solid recrystallized from THF/*n*-hexane and dried under high vacuum. Yield: 73%, 76 mg, 0.1 mmol.

^{1}H-NMR (500.2 MHz, CD_2Cl_2) δ = 2.95 (t, J = 10.5 Hz, 1H, CH_2), 3.81 (t, J = 10.5 Hz, 1H, CH_2), 5.24 (s, 1H, CH^{benzyl}), 5.29 (d, J = 9.5 Hz, 1H, NH), 5.55 (t, J = 8.0 Hz, 1H, CH^{olefin}), 6.28 (d, J = 9.0 Hz, 1H, CH^{olefin}), 6.75 (t, J = 8.5 Hz, 1H, CH^{ar}), 7.17 (t, J = 7.5 Hz, 1H, CH^{ar}), 7.25 (t, J = 7.5 Hz, 1H, CH^{ar}), 7.31 - 7.66 (m, 17H, CH^{ar}), 7.80 (dd, J_1 = 7.8 Hz, J_2 = 14.3 Hz, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (125.8 MHz, CD_2Cl_2) δ = 56.5 (d, J = 14.7 Hz, 1C, CH$_2$), 64.5 (m, 1C, CH^{olefin}), 70.5 (m, 1C, CH^{olefin}), 71.4 (s, 1C, CH^{benzyl}), 127.72 (s, 1C, CH^{ar}), 128.2 (s, 1C, CH^{ar}), 129.1 (s, 1C, C_q), 129.5 (s, 1C, C_q), 129.5 (s, 1C, CH^{ar}), 129.7 (s, 1C, CH^{ar}), 129.8 (d, J = 3.8 Hz, 1C, CH^{ar}), 129.9 (s, 1C, CH^{ar}), 130.0 (s, 1 C, CH^{ar}), 130.1 (s, 1 C, CH^{ar}), 130.2 (s, 1 C, CH^{ar}), 130.2 (s, 1 C, CH^{ar}), 130.3 (s, 1 C, CH^{ar}), 130.4 (s, 1 C, CH^{ar}), 130.5 (s, 1 C, CH^{ar}), 130.7 (d, J = 6.5 Hz, 1C, CH^{ar}), 131.3 (s, 1C, CH^{ar}), 132.2 (s, 1C, CH^{ar}), 132.3 (s, 1C, CH^{ar}), 132.6 (s, 1C, CH^{ar}), 134.2 (s, 1C, CH^{ar}), 134.3 (d, J = 12.6 Hz, 3C, CH^{ar}), 135.6 (s, 1C, C_q), 136.5 (s, 1C, C_q), 136.6 (s, 1C, C_q), 137.3 (d, J = 4.9 Hz, 1C, C_q), 140.4 (s, 1C, C_q), 140.5 (s, 1 C, C_q), 187.7 (dd, $^1J_{C,Rh}$ = 60.9 Hz, $^2J_{C,P}$ = 17.2 Hz, 1 C, CO);

^{31}P{^{1}H}-NMR (202.5 MHz, CD_2Cl_2) δ = 16.7 (d, $^1J_{Rh,P}$ = 140.1 Hz);

^{1}H, ^{103}Rh-NMR (15.7 MHz, CD_2Cl_2): δ = -7952 (d, $^1J_{Rh,P}$ = 140.1 Hz);

EA found% (calc%) for $C_{36}H_{28}NPSO_4F_3Rh$: C 56.76 (56.78), H 3.99 (3.71), N 1.72 (1.84);

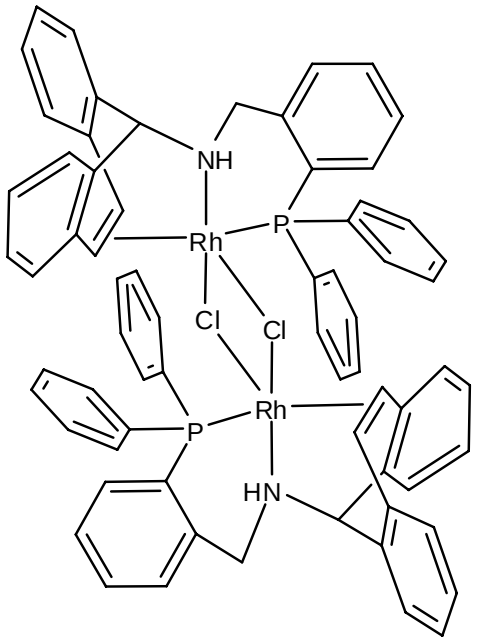
ATR IR (ν in cm^{-1}): 3063 (m, CH), 2002 (w, CO), 1435 (w, CCar), 1263 (s, C-O), 1029 (s, S=O), 753 - 635 (s, CH$_\delta$);

$[Rh_2(\mu\text{-}Cl)_2(Ph_2PPhtropNH)_2]$ (**72**)

MF = $C_{68}H_{56}N_2P_2Cl_2Rh_2$

MW = 1239.88 g/mol

MP >230 °C
Air sensitive



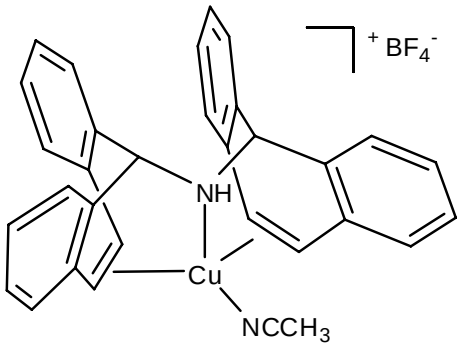
$[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (30 mg, 0.077 mmol, 1 eq.) was added to a solution of $Ph_2PPhCH_2tropNH$ **59** (74 mg, 0.154 mmol, 2 eq.) in toluene to get a dark red solution. After standing overnight most of the product precipitated. The solid was filtered off, washed with *n*-hexane and dried under vacuum. Yield: 84%, 81 mg, 0.065 mmol. The product is not very soluble.

^{1}H-NMR (300 MHz, d^6-DMSO) δ = 3.40 (b, 1 H, N*H*), 3.57 (d, *J* = 9.9 Hz, 1 H, CH_2), 4.34 (t, *J* = 8.4 Hz, 1 H, CH^{olefin}), 4.46 (b, 1 H, CH_2), 4.69 (s, 1 H, CH^{benzyl}), 4.83 (d, *J* = 8.4 Hz, 1 H, CH^{olefin}), 6.38 (t, *J* = 7.5 Hz, 1 H, CH^{ar}), 6.72 (t, *J* = 7.2 Hz, 1 H, CH^{ar}), 6.81 - 6.92 (m, 2 H, CH^{ar}), 7.04 - 7.43 (m, 17 H, CH^{ar}), 7.58 (d, *J* = 7.5 Hz, 1 H, CH^{ar});

^{31}P{^{1}H}-NMR (202.5 MHz, CD_2Cl_2) δ = 12.06 (d, $^1J_{Rh,P}$ = 146.1 Hz);

Compounds of section VII

$[Cu(CH_3CN)(trop_2NH)]BF_4$ (**73**)



MF = $C_{32}H_{26}BCuF_4N_2$

MW = 588.91 g/mol

MP = 110-115 (dec.)
Air stable

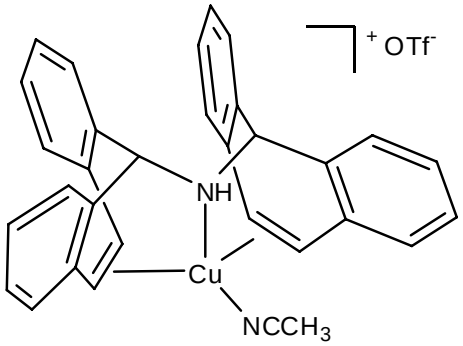
$[Cu(CH_3CN)_4]BF_4$ (474 mg, 1.51 mmol, 1 eq.) was dissolved in 10 mL DCM under argon and $trop_2NH$ **1** (463 mg, 1.51 mmol, 1 eq.) was added. The crude product was obtained as oil after addition of *n*-hexane. The product was recrystallized from DCM/*n*-hexane. Yield: 85%, 751 mg, 1.27 mmol.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 2.19 (s, 3H, C*H*$_3$), 2.61 (s, 1H, N*H*), 5.34 (s, 2H, C*H*^{benzyl}), 6.74-6.80 (m, 4H, C*H*^{olefin}), 7.00-7.10 (m, 4H, C*H*^{ar}), 7.10-7.20 (m, 4H, C*H*^{ar}), 7.35-7.40 (m, 2H, C*H*^{ar}), 7.42-7.55 (m, 6H, C*H*^{ar});

^{13}C{^{1}H}-NMR (126 MHz, CD_2Cl_2): δ = 2.6 (s, 1C, *C*H$_3$), 70.1 (s, 2C, *C*H^{benzyl}), 110.6 (s, 2C, *C*H^{olefin}), 112.1 (s, 2C, *C*H^{olefin}), 118.2 (s, 1C, *C*^{quart}), 128.6 (s, 2C, *C*H^{ar}), 128.9 (s, 2C, *C*H^{ar}), 129.3 (s, 2C, *C*H^{ar}), 129.8 (s, 2C, *C*H^{ar}), 130.0 (s, 2C, *C*H^{ar}), 130.4 (s, 2C, *C*H^{ar}), 130.5 (s, 2C, *C*H^{ar}), 131.0 (s, 2C, *C*H^{ar}), 132.4 (s, 2C, *C*^{quart}), 133.01 (s, 2C, *C*^{quart}), 134.81 (s, 2C, *C*^{quart}), 138.28 (s, 2C, *C*^{quart});

ATR IR (ν in cm^{-1}): 3265 w (NH), 2938 w (CH), 1600 w (C=C), 1494 w (C=C), 1437 w, 1315 w, 1282 w, 1189 w, 1052 s, 1024 s, 950 m, 886 w, 815 m, 773 m, 743 s, 721 m, 706 w, 654 w, 639 w;

[$Cu(CH_3CN)(trop_2NH)$]OTf (**74**)



MF = $C_{33}H_{26}CuF_3N_2O_3S$

MW = 651.18 g/mol

MP = 221 °C (dec.)
Air stable

[$Cu(CH_3CN)_4$]OTf (201 mg, 0.53 mmol, 1 eq.) was dissolved in 3 mL THF under argon and $trop_2NH$ **1** (164 mg, 0.53 mmol, 1 eq.) dissolved in 2 mL THF added. Precipitation of the product starts after addition of the ligand and is completed by addition of *n*-hexane. Yield: 76%, 265 mg, 0.41 mmol.

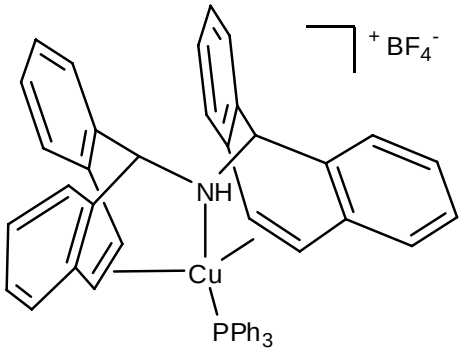
Crystals suitable for X-ray diffraction were obtained from THF/*n*-hexane but also from DCM/*n*-hexane.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 2.06 (s, 3H, C*H*$_3$), 2.79 (s, 1H, N*H*), 5.27 (s, 2H, C*H*^{benzyl}), 6.78-6.84 (m, 4H, C*H*^{olefin}), 7.01 (t, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*^{ar}), 7.05-7.12 (m, 4H, C*H*^{ar}), 7.15 (t, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*^{ar}), 7.32-7.40 (m, 2H, C*H*^{ar}), 7.44 (d, *J* = 4.0 Hz, 4H, C*H*^{ar}), 7.51 (d, $^3J_{HH}$ = 7.7 Hz, 2H, C*H*^{ar});

^{13}C{^{1}H}-NMR (126 MHz, CD_2Cl_2): δ = 2.4 (s, 1C, *C*H$_3$), 70.7 (s, 2C, *C*H^{benzyl}), 109.4 (s, 2C, *C*H^{olefin}), 112.3 (s, 2C, *C*H^{olefin}), 117.6 (s, 1C, *C*^{quart}), 120.7 (q, $^1J_{CF}$ = 320.1 Hz, 1C, *C*F$_3$), 128.4 (s, 2C, *C*H^{ar}), 128.6 (s, 2C, *C*H^{ar}), 128.8 (s, 2C, *C*H^{ar}), 129.7 (s, 2C, *C*H^{ar}), 129.8 (s, 2C, *C*H^{ar}), 130.3 (s, 2C, *C*H^{ar}), 130.9 (s, 2C, *C*H^{ar}), 131.0 (s, 2C, *C*H^{ar}), 132.7 (s, 2C, *C*^{quart}), 133.1 (s, 2C, *C*^{quart}), 135.0 (s, 2C, *C*^{quart}), 138.0 (s, 2C, *C*^{quart});

ATR IR (ν in cm^{-1}): 3205 m (NH), 2927 w (CH), 1600 w (C=C), 1489 w, 1453 w, 1436 m, 1411 w, 1366 m, 1306 w, 1273 s, 1247 s, 1224 s, 1197 m, 1161 s, 1148 s, 1077 w, 1051 w, 1027 s, 992.20 m, 985 m, 978 m, 951 m, 909 w, 878 w, 863 w, 815 m, 780 s, 766 s, 742 s, 721 m, 706 w, 658 w, 636 s;

$[Cu(trop_2NH)(PPh_3)]BF_4$ (**75**)



MF = $C_{48}H_{38}BCuF_4NP$

MW = 810.15 g/mol

MP = 120 °C (dec.)
Air stable

$[Cu(CH_3CN)(trop_2NH)]BF_4$ **73** (52 mg, 0.09 mmol, 1 eq.) was dissolved in 2 mL DCM and PPh_3 (23 mg, 0.09 mmol, 1 eq.) added. The solution was carefully layered with *n*-hexane to precipitate the product, which is often obtained as oil. Yield: 82%, 59 mg, 0.07 mmol.

Crystals suitable for X-ray diffraction were obtained from $CDCl_3$/*n*-hexane.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 2.96 (s, 1H, N*H*), 5.08 (d, *J* = 3.7 Hz, 2H, C*H*^{benzyl}), 6.76 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 6.85-6.95 (m, 4H, C*H*^{olefin}), 6.95-7.05 (d, *J* = 6.1 Hz, 8H, C*H*^{ar}), 7.10-7.20 (m, 8H, C*H*^{ar}), 7.28 (d, *J* = 7.6 Hz, 3H, C*H*^{ar}), 7.42 (d, *J* = 7.31 Hz, 7H, C*H*^{ar}), 7.53 (br s, 3H, C*H*^{ar});

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 69.5 (s, 2C, *C*H^{benzyl}), 117.9 (s, 2C, *C*H^{olefin}), 119.3 (s, 2C, *C*H^{olefin}), 128.5-138.0 (m, 42C, *C*H^{ar} and *C*^{quart});

^{31}P{^{1}H}-NMR (121.5 MHz, CD_2Cl_2) δ = 7.6 (s);

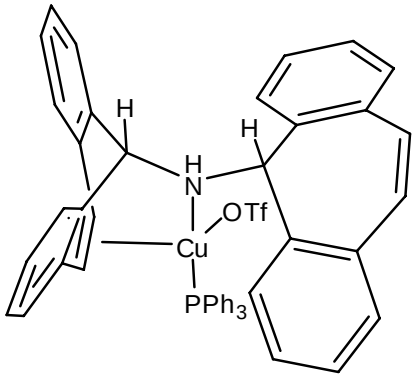
ATR IR (ν in cm^{-1}): 3055 w, 2931 w, 1600 w, 1481 w, 1435 m, 1371 w, 1313 w, 1282 w, 1188 w, 1161 w, 1052 s, 997 m, 947 m, 885 w, 849 w, 808 m, 779 m, 764 m, 743 m, 694 s, 653 m, 639 m, 618 m;

[Cu(trop$_2$NH)(PPh$_3$)]OTf (**76**)

MF = $C_{49}H_{38}CuF_3NO_3PS$

MW = 872.41 g/mol

MP = 217-219 °C (dec)
Air stable



[Cu(CH_3CN)(trop$_2$NH)]OTf **74** (100 mg, 0.15 mmol, 1 eq.) was dissolved in 2 mL DCM and PPh_3 (41 mg, 0.15 mmol, 1 eq.) added. The solution was carefully layered with *n*-hexane to precipitate the product. Yield: 73%, 98 mg, 0.11 mmol.

Crystals suitable for X-ray diffraction were obtained from DCM/*n*-hexane.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 3.89 (s, 1H, N*H*), 4.79 (d, *J* = 5.5 Hz, 2H, C*H*^{benzyl}), 6.54 (d, $^3J_{HH}$ = 10.6 Hz, 2H, C*H*^{olefin}), 6.69 (br s, 4H, C*H*^{ar}), 6.75 (d, $^3J_{HH}$ = 11.3 Hz, 2H, C*H*^{olefin}), 7.00-7.55 (m, 27H, C*H*^{ar});

^{13}C{^{1}H}-NMR (126 MHz, CD_2Cl_2): δ = 67.6 (s, 2C, *C*H^{benzyl}), 120.8 (q, $^1J_{CF}$ = 320.5 Hz, 1C, *C*F_3), 123.6 (br s, 2C, *C*H^{olefin}), 125.1 (s, 2C, *C*H^{olefin}), 128.0-137.0 (m, 42C, *C*H^{ar} and *C*^{quart});

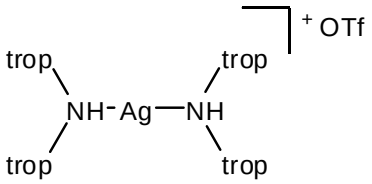
^{31}P{^{1}H}-NMR (203 MHz, CD_2Cl_2) δ = 2.5 (s);

ATR IR (ν in cm^{-1}): 3054 w, 1491 w, 1433 w, 1301 m, 1231 m, 1212 w, 1165 m, 1093 m, 1020 s, 950 m, 940 m, 881 w, 814 w, 800 m, 778 m, 762 s, 742 s, 693 s, 652, w, 633 m;

[Ag(trop$_2$NH)$_2$]OTf (**77**)

MF = $C_{61}H_{46}AgF_3N_2O_3S$

MW = 1051.96 g/mol



MP = 222 °C (dec.)
Air stable

AgOTf (50 mg, 0.19 mmol, 1 eq.) was dissolved in 1 mL CH_3CN and a solution of trop$_2$NH **1** (155 mg, 0.39 mmol, 2 eq.) in 3 mL DCM was added. The product was precipitated by adding diethylether/*n*-hexane 1:1. Yield 64%, 132 mg, 0.12 mmol.

Crystals suitable for X-Ray crystallography were obtained from $CDCl_3$/*n*-hexane.

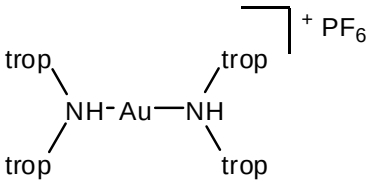
^{1}H-NMR(500 MHz, CD_2Cl_2, 200K): δ = 3.61 (br d, J = 6.5 Hz, 2H, N*H*), 4.36 (d, $^3J_{HH}$ = 8.1 Hz, 2H, C*H*^{benzyl}), 4.69 (d, $^3J_{HH}$ = 9.2 Hz, 2H, C*H*^{benzyl}), 6.32 (d, $^3J_{HH}$ = 11.7 Hz, 2H, C*H*^{olefin}), 6.64 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 6.70 (d, $^3J_{HH}$ = 11.7 Hz, 2H, C*H*^{olefin}), 6.82 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 6.90-7.00 (m, 4H, C*H*^{olefin}), 7.02 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 7.08 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 7.15-7.45 (m, 18H, C*H*^{ar}), 7.55-7.70 (m, 6H, C*H*^{ar});

^{13}C{^{1}H}-NMR (125 MHz, CD_2Cl_2, 200K): δ = 69.0 (d, $^2J_{AgC}$ = 2.4 Hz, 2C, *C*H^{benzyl}), 69.6 (d, $^2J_{AgC}$ = 2.4 Hz, 2C, *C*H^{benzyl}), 121.2 (q, $^1J_{CF}$ = 320.5 Hz, 1C, *C*F$_3$), 127.9 (s, 2C, *C*H^{olefin}), 128.2 (s, 2C, *C*H^{ar}), 128.5 (s, 2C, *C*H^{ar}), 128.5 (s, 2C, CH^{ar}), 128.7 (s, 2C, *C*H^{olefin}), 129.2 (s, 2C, CH^{ar}), 129.4 (s, 2C, *C*H^{olefin}), 129.4 (s, 2C, CH^{ar}), 129.7 (s, 4C, CH^{ar}), 130.0 (s, 2C, CH^{ar}), 130.2 (s, 4C, CH^{ar}), 130.3 (s, 2C, CH^{ar}), 130.4 (s, 4C, CH^{ar}), 130.4 (s, 2C, CH^{ar}), 130.8 (s, 2C, *C*H^{olefin}), 131.1 (s, 2C, C^{quart}), 131.8 (s, 2C, C^{quart}), 131.9 (s, 2C, C^{quart}), 132.6 (s, 2C, C^{quart}), 132.6 (s, 2C, C^{quart}), 133.2 (s, 2C, C^{quart}), 135.4 (d, J = 3.8 Hz, 2C, C^{quart}), 135.8 (d, J = 3.8 Hz, 2C, C^{quart}), 136.6 (s, 2C, C^{quart}), 137.3 (s, 2C, C^{quart});

ATR IR (ν in cm^{-1}): 3246 m, 3018 w, 1597 w, 1493 w, 1430 m, 1376 w, 1320 w, 1260 s, 1227 s, 1147 m, 1112 m, 1070 w, 1029 s, 1004 m, 947 w, 913 w, 887 w, 849 w, 803 s, 775 s, 760 s, 727 s, 712 m, 652 m, 636 s, 619 m;

$[Au(trop_2NH)_2]PF_6$ (**78**)

MF = $C_{60}H_{46}AuF_6N_2P$



MW = 1136.95 g/mol

MP = 175-190 °C (dec.)
Slightly air sensitive

$Trop_2NH$ **1** (150 mg, 0.38 mmol, xs) was suspended in 1 mL CH_3CN under argon and a solution of $AuPF_6$ in CH_3CN of unknown concentration was added drop wise until the $trop_2NH$ was dissolved. Additional $trop_2NH$ (50 mg, 0.13 mmol, xs) was added and the solution filtered over celite. The product was precipitated by addition of diethyl ether as white micro crystals. Yield: 38% from $trop_2NH$, 110 mg, 0.10 mmol.

Crystals suitable for X-ray crystallography were obtained from CH_3CN/diethyl ether.

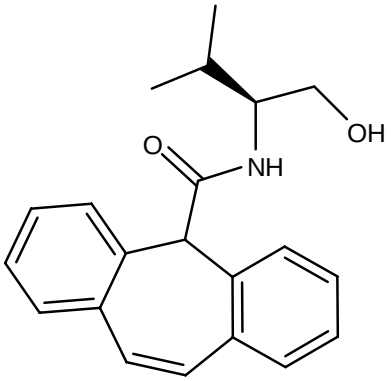
^{1}H-NMR(400 MHz, CD_2Cl_2): δ = 4.42 (d, $^3J_{HH}$ = 10.0 Hz, 2H, C*H*^{benzyl}), 4.67 (d, $^3J_{HH}$ = 10.1 Hz, 2H, C*H*^{benzyl}), 5.20 (t, $^3J_{HH}$ = 10.2 Hz, 2H, N*H*), 6.49 (d, $^3J_{HH}$ = 11.9 Hz, 2H, C*H*^{olefin}), 6.60-6.82 (m, 8H, C*H*^{olefin} and C*H*^{ar}), 6.87-7.15 (m, 16H, C*H*^{ar}), 7.34-7.40 (m, 2H, C*H*^{ar}), 7.48-7.58 (m, 6H, C*H*^{ar}), 7.65-7.71 (m, 2H, C*H*^{ar}), 7.79-7.91 (m, 4H, C*H*^{ar});

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 74.3 (s, 2C, *C*H^{benzyl}), 74.9 (s, 2C, *C*H^{benzyl}), 128.1 (s, 2C, *C*H^{ar}), 128.3 (s, 2C, *C*H^{ar}), 128.6 (s, 2C, *C*H^{olefin}), 129.0 (s, 2C, *C*H^{ar}), 129.1 (s, 2C, *C*H^{ar}), 129.2 (s, 2C, *C*H^{ar}), 129.4 (s, 2C, *C*H^{ar}), 129.4 (s, 2C, *C*H^{ar}), 129.6 (s, 2C, *C*H^{ar}), 129.8 (s, 6C, *C*H^{ar}), 129.9 (s, 4C, *C*H^{ar}), 129.9 (s, 2C, *C*H^{ar}), 130.0 (s, 2C, *C*H^{ar}), 130.2 (s, 2C, *C*H^{olefin}), 130.7 (s, 2C, *C*H^{ar}), 130.7 (s, 2C, *C*H^{olefin}), 131.2 (s, 2C, *C*H^{olefin}), 132.0 (s, 2C, *C*^{quart}), 132.3 (s, 2C, *C*^{quart}), 132.8 (s, 2C, *C*^{quart}), 133.1 (s, 2C, *C*^{quart}), 133.9 (s, 2C, *C*^{quart}), 134.3 (s, 2C, *C*^{quart}), 137.6 (s, 2C, *C*^{quart}), 137.7 (s, 2C, *C*^{quart});

ATR IR (ν in cm^{-1}):3220 w, 1686 w, 1560 w, 1495 w, 1439 w, 1408 m, 1397 w, 1374 w, 1304 w, 1284 w, 1230 w, 1199 w, 1162 w, 1146 w, 1117 w, 1040 w, 973 w, 951 w, 914 w, 876 m, 836 s, 802 s, 775 m, 761 m, 727 m, 715 m, 675 w, 666 w, 645 w, 620 w;

Compounds of section VIII

5*H*-dibenzo[*a,d*]cycloheptene-5-carboxylic acid ((*S)*-1-hydroxymethyl-2-methyl-propyl)-amide (**79**)
MF = $C_{21}H_{23}NO_2$



MW = 321.41 g/mol

MP = 125-128 °C
Air stable

To a 100 mL three neck round bottom flask equipped with an Ar inlet and a dropping funnel L-Valinol (2.091 g, 0.018 mol, 1 eq.) was added and dissolved in 35 mL DCM. Dry triethylamine (12 mL, 0.085 mol, 5 eq.) was added and the solution cooled to 0 °C. To this solution 5*H*-dibenzo[*a,d*]cycloheptene-5-carbonyl chloride[139, 140] (4.33 g, 0.018 mol, 1 eq.) dissolved in 15 mL DCM was added dropwise over 15 min. The solution was stirred another 30 min at RT, then washed with 1 M HCl and brine. The organic phase was dried over sodium sulfate and the solvent removed under reduced pressure. The residue was recrystallized from ethyl acetate and dried under high vacuum. Yield: 83%, 4.8 g, 14.93 mmol.

$[\alpha]_D^{22}$= -9.3° (*c*=0.1, CH_2Cl_2);

^{1}H-NMR (300.1 MHz, $CDCl_3$): δ = 0.65 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 0.78 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.67 (7, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*CH_3), 2.94 (s, 1H, O*H*), 3.50 (m, 2H, CH_2OH), 3.54 (m, 1H, C*H*NH), 4.91 (s, 1H, NH_2), 5.19 (d, $^3J_{HH}$ = 5.4 Hz, 1H, N*H*), 7.00 (m, 2H, CH^{olefin}), 7.39 (m, 8H, CH^{ar});

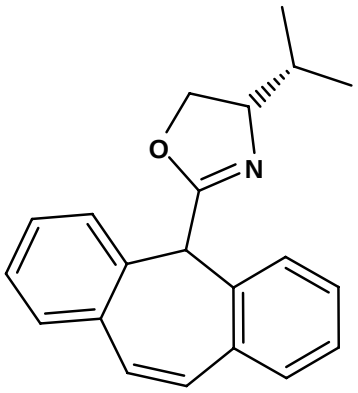
^{13}C{^{1}H}-NMR (75.5 MHz, $CDCl_3$): δ = 18.0 (s, 1C, *C*H_3), 19.5 (s, 1C, *C*H_3), 28.7 (s, 1 C, *C*H), 58.1 (s, 1C, *C*HNH), 59.8 (s, 1C, *C*H^{benzyl}), 64.7 (s, 1C, *C*H_2O), 127.5 (s, 1C, *C*H^{ar}), 127.6 (s, 1C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 129.4 (s, 2C, *C*H^{ar}), 130.3 (s, 1C, *C*H^{ar}), 130.3 (s, 1C, *C*H^{ar}), 130.7 (s, 1C, *C*H^{olefin}), 131.1 (s, 1C, *C*H^{olefin}), 134.4 (s, 1C, *C*^{quart}), 134.5 (s, 1C, *C*^{quart}), 136.6 (s, 2C, *C*^{quart}), 172.4 (s, 1C, *C*^{quart});

ATR IR (ν in cm^{-1}): 3458 m (OH), 3416 m (NH), 3014 w (CH), 2964 w (CH), 2936.33 w (CH), 2875 w (CH), 1736 w, 1670 s (C=O), 1595 w, 1516 s, 1491 m, 1457 m, 1436 m, 1392 m, 1369 m, 1336 m, 1289 m, 1260 m, 1247 m, 1230 m, 1204 m, 1157 m, 1139 m, 1106 m, 1082 m, 1060 s, 1022 m, 969 m, 960 m, 942 m, 922 m, 905 886 m, 878 m, 836 m, 815 m, 798 s, 775 s, 767 s, 733 s, 711 m, 698 m, 646 m, 635 m, 614.35 m;

tropOxaz$^{i\text{-Pr}}$
(5*H*-dibenzo[*a,d*]cycloheptene-4-(S)-isopropyl-4,5-dihydro-oxazole) (**80**)
MF = $C_{21}H_{21}NO$

MW = 303.40 g/mol

MP = 103-108 °C
Air stable



The reaction was adapted from a procedure published by Evans[141]. 5*H*-dibenzo[*a,d*]cycloheptene-5-carboxylic acid ((*S)*-1-hydroxymethyl-2-methyl-propyl)-amide **79** (1 g, 3.1 mmol, 1 eq.) and DMAP (19 mg, 0.15 mmol, 0.05 eq.) were dissolved in 15 mL dry DCM. Dry triethylamine (1 mL, 7.2 mmol, 2.3 eq.) was added and the solution cooled with an ice bath. A solution of p-toluenesulfonyl chloride (0.57 g, 3.1 mmol, 1 eq.) dissolved in 20 mL DCM was added dropwise over 15 min. The solution was refluxed for 24 h and washed with a saturated ammonium chloride solution, a saturated solution of sodium hydrogen-carbonate and dried over sodium sulfate. All volatiles were removed under reduced pressure and the residue chromatographed over a short column with *n*-hexane/ethyl acetate 1:1 on silica gel and dried under high vacuum. Note: the product may hydrolyze on the silica gel if a longer column in employed. Yield: 66%, 620 mg, 2.04 mmol.

$[\alpha]_D^{22}$= -81.8° (*c*=0.1, CH_2Cl_2);

^{1}H-NMR (300.1 MHz, C_6D_6): δ = 0.78 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 0.90 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3), 1.60 (7, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*), 3.59 (t, $^3J_{HH}$ = 6.85 Hz, 1H, CH_2O), 3.71 (m, 1H, C*H*N), 3.79 (m, 1H, CH_2O), 4.98 (s, 1H, CH^{benzyl}), 6.98 (m, 2H, CH^{olefin}), 7.1-7.2 (m, 2H, CH^{ar}), 7.2-7.3 (m, 4H, CH^{ar}), 7.45-7.6 (br, 2H, C*H*ar);

^{13}C{^{1}H}-NMR (75.5 MHz, C_6D_6): δ = 18.4 (s, 1C, *C*H_3), 18.8 (s, 1C, *C*H_3), 32.8 (s, 1C, *C*H), 51.9 (br s, 1C, *C*H^{benzyl}), 69.7 (s, 1C, *C*H_2O), 72.8 (s, 1C, *C*HN), 126.7 (s, 2C, *C*H^{ar}), 128.4 (s, 2C, *C*H^{ar}), 128.9 (br s, 2C, *C*H^{ar}), 129.0 (s, 2C, *C*H^{ar}), 130.77 (s, 1C, *C*H^{olefin}), 131.44 (s, 1C, *C*H^{olefin}), 135.09 (s, 1C, *C*^{quart}), 135.27 (s, 1C, *C*^{quart}) 137.18 (s, 1C, *C*^{quart}) 137.39 (s, 1C, *C*^{quart}) 164.74 (s, 1C, *C*^{quart});

ATR IR (ν in cm^{-1}): 2914-3064 w (C-H), 1655 s (C=N), 1493 w, 1456 w, 1433 w, 1202 m, 1176 m, 986 m, 950 m;

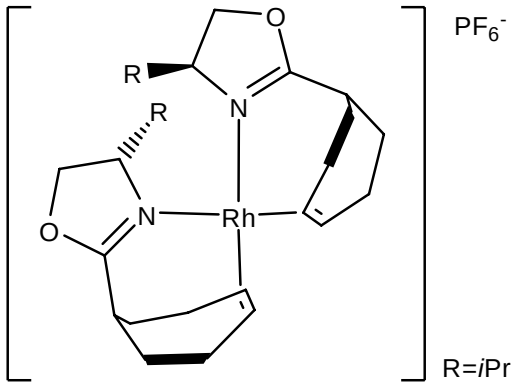
EA found% (calc%) for $C_{21}H_{21}NO$: C: 82.87 (83.15), H: 7.12 (6.98), N: 4.57 (4.62);

[Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]PF$_6$ (**81**)

MF = $C_{42}H_{42}F_6N_2O_2PRh$

MW = 854.664 g/mol

MP = 205- 210 °C
Air stable



Under argon [$Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4$] (150 mg, 0.4 mmol, 1 eq.) was dissolved in 2 mL THF and tropOxaz$^{i\text{-Pr}}$ **80** (468 mg, 1.54 mmol, 4 eq.) added. Evolution of ethylene was observed. The solution was stirred for 1 h and turned dark red. Then $AgPF_6$ (252 mg, 0.77 mmol, 2 eq.) was added. The mixture was left standing protected from light for 36 h, the product crystallized out of the solution. The mother liquor was removed, the solid dissolved in DCM and the AgCl filtered off over celite. The solution was layered with *n*-hexane and the product isolated as dark red needles after standing overnight and dried under high vacuum. Yield: 85%, 560 mg, 0.65 mmol.

Crystals suitable for X-Ray diffraction were obtained from DCM/*n*-hexane.

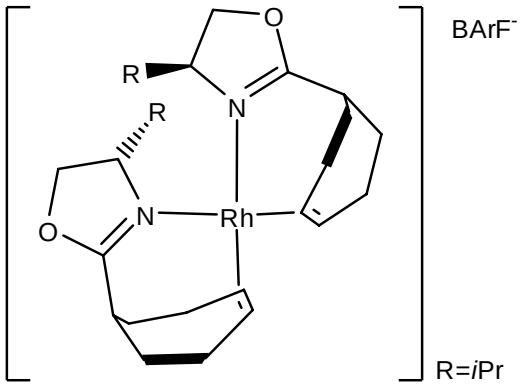
^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 0.09 (d, $^3J_{HH}$ = 6.6 Hz, 6H, C*H*$_3$), 0.24 (d, $^3J_{HH}$ = 7.3 Hz, 6H, C*H*$_3$), 1.38 (m, 2H, C*H*), 3.10 (d, $^3J_{HH}$ = 9.5 Hz, 2H, C*H*^{olefin}), 3.23 (m, 2H, C*H*N), 4.16 (dd, $^3J_{HH}$ = 9.7Hz, $^3J_{HH}$ = 4.9 Hz, 2H, C*H*$_2$O), 4.31 (t, $^3J_{HH}$ = 9.7 Hz, 2H, C*H*$_2$O), 4.98 (s, 2H, C*H*^{benzyl}), 5.55 (dd, $^3J_{HH}$ = 9.7 Hz, $^2J_{RhH}$ = 2.0 Hz, 2H, C*H*^{olefin}), 7.37 (t, $^3J_{HH}$ = 7.3 Hz, 4H, C*H*^{ar}), 7.4-7.5 (m, 4H, C*H*^{ar}), 7.5-7.6 (m, 4H, C*H*^{ar}), 7.76 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*^{ar}), 8.03 (d, $^3J_{HH}$ = 7.5 Hz, 2H, C*H*^{ar});

^{13}C{^{1}H}-NMR (125 MHz, CD_2Cl_2): δ = 12.7 (s, 2C, *C*H$_3$), 18.9 (s, 2C, *C*H$_3$), 31.4 (s, 2C, *C*H), 53.9 (s, 2C, *C*H^{benzyl}), 65.4 (d, $^1J_{RhC}$ = 10.6 Hz, 2C, *C*H^{olefin}), 69.6 (s, 2C, *C*H$_2$O), 71.7 (s, 2C, *C*HN), 82.8 (d, $^1J_{RhC}$ = 13.4 Hz, 2C, *C*H^{olefin}), 128.3 (s, 2C, *C*H^{ar}), 130.2 (s, 2C, *C*H^{ar}), 130.4 (s, 2C *C*H^{ar}), 131.2 (s, 2C, *C*H^{ar}), 131.7 (s, 2C, *C*H^{ar}), 132.1 (s, 2C, *C*H^{ar}), 132.3 (s, 2C, C^{quart}), 132.8 (s, 2C, *C*H^{ar}), 133.8 (s, 2C, C^{quart}), 134.8 (s, 2C, *C*H^{ar}) 137.2 (d, $^2J_{RhC}$ = 1.9 Hz, 2C, C^{quart}), 138.2 (s, 2C, C^{quart}), 169.5 (s, 2C, C^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ =-6407;

ATR IR (ν in cm^{-1}): 2961 w, 1728 w, 1641 m, 1597 w, 1492 w, 1458 w, 1388 m, 1319 w, 1200 m, 1174 m, 1117 w, 1021 w, 998 w, 950 m, 835 s, 756 s, 729 m, 650 s, 614 m;

[Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]BArF (**82**)



MF = $C_{74}H_{54}BF_{24}N_2O_2Rh$

MW = 1572.91 g/mol

MP = 165 °C
Air stable

[Rh(tropOxaz$^{i\text{-Pr}}$)$_2$]PF_6 **81** (454 mg, 0.53 mmol, 1 eq.) and NaBArF (470 mg, 0.53 mmol, 1 eq.) was dissolved in 5 mL DCM and stirred for 30 min. The solution was filtered over celite and the DCM removed under reduced pressure. The residue was recrystallized from THF/*n*-hexane and dried under high vacuum. Yield: 95%, 794 mg, 0.50 mmol.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.05 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH_3), 0.14 (d, $^3J_{HH}$ = 7.3 Hz, 6H, CH_3), 1.38 (m, 2H, C*H*), 3.03 (d, $^3J_{HH}$ = 9.5 Hz, 2H, CH^{olefin}), 3.06(m, 2H, C*H*N), 3.96-4.10 (m, 4H, CH_2O), 4.89 (s, 2H, CH^{benzyl}), 5.50 (dd, $^3J_{HH}$ = 9.4 Hz, $^2J_{RhH}$ = 1.8 Hz, 2H, CH^{olefin}), 7.30 (m, 4H, CH^{ar}), 7.36-7.50 (m, 12H, CH^{ar}), 7.6-7.75 (m, 10H, CH^{ar}), 7.98 (dd, $^3J_{HH}$ = 7.16 Hz, $^4J_{HH}$ = 1.68 Hz, 2H, CH^{ar});

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 12.6 (s, 2C, *C*H_3), 19.1 (s, 2C, *C*H_3), 31.4 (s, 2C, *C*H), 53.9 (s, 2C, *C*H^{benzyl}), 65.6 (d, $^1J_{RhC}$ = 11.0 Hz, 2C, *C*H^{olefin}), 69.1 (s, 2C, *C*H_2O), 71.8 (s, 2C, *C*HN), 83.0 (d, $^1J_{RhC}$ = 13.3 Hz, 2C, *C*H^{olefin}), 117.86 (m, 4C, *C*H^{ar}), 125.0 (q, $^1J_{FC}$ = 272.7 Hz, 8C, *C*F_3) 128.7 (s, 2C, *C*H^{ar}), 129.3 (m, 8C, C^{quart}), 130.5 (s, 2C, *C*H^{ar}), 130.5 (s, 2C, *C*H^{ar}), 131.4 (s, 2C, *C*H^{ar}), 131.9 (s, 2C, C^{quart}), 131.9 (s, 2C, *C*H^{ar}), 132.0 (s, 2C, *C*H^{ar}), 132.7 (s, 2C, *C*H^{ar}), 133.5 (s, 2C, C^{quart}), 134.8 (s, 2C, *C*H^{ar}), 135.2 (br m, 8C, *C*H^{ar}), 137.0 (d, $^2J_{RhC}$ = 1.4 Hz, 2C, C^{quart}), 137.7 (s, 2C, C^{quart}), 162.1 (q, $^1J_{BC}$ = 49.8 Hz, 1C, C^{quart}), 169.8 (s, 1C, C^{quart});

^{1}H, ^{103}Rh-NMR (12.6 MHz, $CDCl_3$): δ = -6416;

ATR IR (ν in cm^{-1}): 2970 w, 1646 m, 1611 w, 1494 w, 1485 w, 1459 w, 1426 w, 1389 m, 1354 s, 1320 w, 1273 s, 1160 s, 1116 s, 1048 m, 1022 m, 998 m, 953 m, 887 m, 839 m, 823 m, 785 m, 766 m, 754 s, 745 m, 728 m, 714 s, 682 s, 668 s, 650 m, 615 m;

X. Appendix

1 List of Abbreviations

ATR	attenuated total reflectance
$BArF^-$	$[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$
BOC	tert-butyl carbamate
COE	cyclooctene
COD	1,5-cyclooctadiene
DCM	dichloromethane
DHC	dehydrogenative coupling
DMSO	dimethyl sulfoxide
DMPP	3,4-dimethyl-1-phenylphosphole
EA	elemental analysis
ESI	electron spray ionization
FC	flash chromatography
GC	gas chromatography
IR	infra red
Me	methyl
MF	molecular formula
MP	melting point
MW	molecular weight
NMR	nuclear magnetic resonance
OTf	$CF_3SO_3^-$ / triflate
Ph	Phenyl
RT	room temperature
THF	tetrahydrofuran
TMIY	1,3,4,5 tetramethylimidazol-2-ylidene
TPP	1,2,5-Triphenylphosphole
trop	dibenzotropylidene
UV/vis	ultraviolet/visible

2 Crystallographic Data

Crystal data and structure refinement for [Rh(trop$_2$NH)(PPh$_3$)]BArF (**6**)

Identification code	[Rh(trop$_2$NH)(PPh$_3$)]BArF	
Empirical formula	$C_{80}H_{50}BF_{24}NPRh$	
Formula weight	1625.91	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.0678(14) Å	α = 78.540(16) °.
	b = 15.480(3) Å	β = 77.412(12) °.
	c = 18.761(4) Å	γ = 82.493(12) °.
Volume	3614.9(10) Å^3	
Z	2	
Absorption coefficient	0.366 mm^{-1}	
F(000)	1636	
Crystal size	0.32 x 0.28 x 0.14 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.50 to 28.28 °.	
Limiting indices	-17<=h<=17, -20<=k<=20, -25<=l<=24	
Reflections collected / unique	59376 / 17903 [R(int) = 0.0296]	
Completeness to theta = 28.28°	99.8%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17903 / 0 / 973	
Goodness-of-fit on F^2	0.989	
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.1534	
R indices (all data)	R1 = 0.0829, wR2 = 0.1619	
Largest diff. peak and hole	1.061 and -0.664 e.Å^{-3}	
Operator	Timo Ott	

Crystal data and structure refinement for [Rh(trop$_2$NH)(P(OPh)$_3$]OTf (**7**)

Identification code	[Rh(trop$_2$NH)(P(OPh)$_3$]OTf
Empirical formula	$C_{55}H_{50}F_3NO_8PRhS$
Formula weight	1075.927
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
space group	P-1
Unit cell dimensions	a = 11.0060(15) Å α = 79.873(15) °.
	b = 11.9617(15) Å β = 73.504(18) °.
	c = 20.130(5) Å γ = 64.311(13) °.
Volume	2285.6(7) Å^3
Z	2
Absorption coefficient	0.521 mm^{-1}
F(000)	1044
Crystal size	0.42 x 0.32 x 0.20 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	2.92 to 31.81 °.
Limiting indices	-16<=h<=16, -17<=k<=17, -29<=l<=28
Reflections collected / unique	33805 / 14050 [R(int) = 0.0242]
Completeness to theta = 31.81°	89.9%
Absorption correction	None
Max. and min. transmission	0.9029 and 0.8107
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14050 / 0 / 595
Goodness-of-fit on F^2	0.995
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0755
R indices (all data)	R1 = 0.0498, wR2 = 0.0790
Largest diff. peak and hole	0.409 and -0.478 e.Å^{-3}
Operator	Timo Ott

Crystal data for $[Rh(trop_2NH)(P(OCH_2)_3CCH_3)_2]PF_6$ (**15**)

Identification code	$[Rh(trop_2NH)(P(OCH_2)_3CCH_3)_2]PF_6$
Empirical formula	$C_{57}H_{73}F_3NO_{13}P_2RhS$
Formula weight	1234.10
Temperature	200 K
Wavelength	0.71073 Å
Crystal system	$P2_1/n$
Space group	monoclinic
Unit cell dimensions	a = 11.3093(15) Å α = 90.000(0) °.
	b = 26.7737(35) Å β = 103.232(3) °.
	c = 19.1193(26) Å γ = 90.000(0) °.
Volume	5635 $Å^3$
Z	4
F(000)	2560.0
Crystal size	0.1 x 0.08 x 0.05 mm
Data collection	Bruker SMART Apex with CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	1.63 to 24.71°.
Limiting indices	-9 =< h =< 13, -31 =< k =< 31, -22 =< l =< 22
Reflections collected / unique	32015 / 9617 [R(int)= 0.0412]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9617/ 0 / 694
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1238
R indices (all data)	R1 = 0.0613, wR2 = 0.1238
Largest diff. peak and hole	0.73 and -0.45 $e.Å^{-3}$
Operator	Daniel Stein

Crystal data for $[Rh(trop_2NH)(NC_5H_3(CH_3)_2)_2]PF_6$ (**26**)

Identification code	$[Rh(trop_2NH)(NC_5H_3(CH_3)_2)_2]PF_6$
Empirical formula	$C_{46}H_{45}Cl_4F_6N_3PRh$
Formula weight	1029.55
Temperature	200 K
Wavelength	0.71073 Å
Crystal system	P-1
Space group	triclinic
	Unit cell dimensions
	a = 12.2108(16) Å α = 92.098(2) °.
	b = 12.2821(16) Å β = 106.322(2) °.
	c = 16.1500(20) Å γ = 97.659(9) °.
Volume	2296 $Å^3$
Z	2
F(000)	1048.0
Crystal size	0.1 x 0.08 x 0.05 mm
Data collection	Bruker SMART Apex with CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	2.50 to 26.4 °.
Limiting indices	-15 =< h =< 15, -15 =< k =< 15, -20 =< l =< 20
Reflections collected / unique	21046 / 9333 [R(int)= 0.0219]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9333/ 0 / 550
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1546
R indices (all data)	R1 = 0.0634, wR2 = 0.1546
Largest diff. peak and hole	1.09 and -0.75 e.$Å^{-3}$
Operator	Daniel Stein

Crystal data and structure refinement for [Rh(trop$_2$NH)(TMIY)]OTf (**28**)

Identification code	[Rh(trop$_2$NH)(TMIY)]OTf	
Empirical formula	$C_{38}H_{35}F_3N_3O_3RhS$	
Formula weight	773.67	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.8138(5) Å	α = 90 °.
	b = 22.6610(9) Å	β = 107.022(4) °.
	c = 15.8130(4) Å	γ = 90 °.
Volume	3362.6(2) Å^3	
Z	4	
Absorption coefficient	0.629 mm^{-1}	
F(000)	1584	
Crystal size	0.1 x 0.08 x 0.05 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.69 to 28.85 °.	
Limiting indices	-12<=h<=12, -28<=k<=25, -19<=l<=20	
Reflections collected / unique	32008 / 8039 [R(int) = 0.1665]	
Completeness to theta = 28.85°	91.1%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8039 / 0 / 449	
Goodness-of-fit on F^2	0.565	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.0644	
R indices (all data)	R1 = 0.2176, wR2 = 0.0750	
Largest diff. peak and hole	0.717 and -0.523 e.Å^{-3}	
Operator	Timo Ott	

Crystal data and structure refinement for [Ir(trop$_2$NH)(PPh$_3$)]OTf (**32**)

Identification code	[Ir(trop$_2$NH)(PPh$_3$)]OTf
Empirical formula	$C_{50}H_{40}Cl_2F_3IrNO_3PS$
Formula weight	1086.01
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	$P2_1/n$
Space group	monoclinic
Unit cell dimensions	a = 14.2350(15) Å α = 90 °.
	b = 16.2139(17) Å β = 109.864(2) °.
	c = 20.024(2) Å γ = 90 °.
Volume	4346.7(8) Å^3
Z	4
Absorption coefficient	3.338 mm^{-1}
F(000)	2160
Crystal size	0.1 x 0.08 x 0.05 mm
Data collection	Bruker CCD1k diffractometer
	Mo K_α, graphite monochromator
Theta range for data collection	1.66 to 28.43 °.
Limiting indices	-18<=h<=19, -21<=k<=21, -26<=l<=26
Reflections collected / unique	45235 / 10904 [R(int) = 0.0870]
Completeness to theta = 28.43°	99.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10904 / 0 / 559
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0608, wR2 = 0.1491
R indices (all data)	R1 = 0.0927, wR2 = 0.1706
Largest diff. peak and hole	5.862 and -2.833 e.Å^{-3}
Operator	Karin Häbe

Crystal data and structure refinement for [Rh(OTf)(cyhtropNH)(PPh_3)] (**43**)

Identification code	[Rh(OTf)(cyhtropNH)(PPh_3)]	
Empirical formula	$C_{41}H_{38}Cl_2F_3NO_3PRhS$	
Formula weight	886.56	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
space group	$P2_1/n$	
Unit cell dimensions	a = 10.5178(9) Å	α = 64.3720(10) °.
	b = 14.1050(12) Å	β = 82.892(2) °.
	c = 14.5010(12) Å	γ = 78.926(2) °.
Volume	1901.5(3) $Å^3$	
Z	2	
Absorption coefficient	0.742 mm^{-1}	
F(000)	904	
Crystal size	0.48 x 0.23 x 0.07 mm	
Data collection	Bruker SMART Apex with CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	1.62 to 26.38 °.	
Limiting indices	-13<=h<=13, -17<=k<=17, -18<=l<=18	
Reflections collected / unique	17067 / 7744 [R(int) = 0.0459]	
Completeness to theta = 26.38°	99.6%	
Max. and min. transmission	0.9499 and 0.7171	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7744 / 0 / 478	
Goodness-of-fit on F^2	1.185	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1019	
R indices (all data)	R1 = 0.0616, wR2 = 0.1067	
Largest diff. peak and hole	0.836 and -0.793 e.$Å^{-3}$	
Operator	Timo Ott	

Crystal data and structure refinement for [Rh(222tropNH)(PPh_3)]OTf (**52**)

Identification code	[Rh(222tropNH)(PPh_3)]OTf	
Empirical formula	$C_{45}H_{44}F_3NO_4PRhS$	
Formula weight	885.77	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.5792(5) Å	α = 90 °.
	b = 18.372(4) Å	β = 90 °.
	c = 24.793(8) Å	γ = 90 °.
Volume	4363.3(16) $Å^3$	
Z	4	
Absorption coefficient	1.130 mm^{-1}	
F(000)	2709	
Crystal size	0.5 x 0.2 x 0.2 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.53 to 34.42 °.	
Limiting indices	-14<=h<=14, -27<=k<=28, -39<=l<=38	
Reflections collected / unique	43321 / 17012 [R(int) = 0.0846]	
Completeness to theta = 34.42°	94.7%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17012 / 15 / 578	
Goodness-of-fit on F^2	0.793	
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1425	
R indices (all data)	R1 = 0.1535, wR2 = 0.1496	
Absolute structure parameter	-0.04(3)	
Largest diff. peak and hole	1.431 and -0.369 e.$Å^{-3}$	
Operator	Timo Ott	

Crystal data and structure refinement for $[Rh(PPh_3)(PyCH_2tropNH)]PF_6$ (**63**)

Identification code	$[Rh(PPh_3)(PyCH_2tropNH)]PF_6$	
Empirical formula	$C_{47}H_{49}F_6N_2O_2P_2Rh$	
Formula weight	952.74	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.6365(5) Å	α = 89.897(4) °.
	b = 16.2297(9) Å	β = 90.984(4) °.
	c = 24.9982(13) Å	γ = 89.970(4) °.
Volume	4314 $Å^3$	
Z	4	
F(000)	1276.0	
Crystal size	0.5 x 0.2 x 0.2 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.53 to 34.40 °.	
Limiting indices	-15 =< h =< 16, -25 =< k =< 23, -38 =< l =< 38,	
Reflections collected / unique	34971 / 15533 [R(int) = 0.0734]	
Completeness to theta = 34.42°	94.7%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15533 / 5 / 517	
Goodness-of-fit on F^2	2.004	
Final R indices [I>2sigma(I)]	R1 = 0.1193, wR2 = 0.3444	
R indices (all data)	R1 = 0.1474, wR2 = 0.3444	
Largest diff. peak and hole	4.56 and -2.47 e.$Å^{-3}$	
Operator	Timo Ott	

Crystal data and structure refinement for $[Ir(PPh_3)(PyCH_2tropNH)]PF_6$ (**65**)

Identification code	$[Ir(PPh_3)(PyCH_2tropNH)]PF_6$	
Empirical formula	$C_{47}H_{49}F_6IrN_2O_2P_2$	
Formula weight	1042.08	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system		
Space group		
Unit cell dimensions	a = 10.495(3) Å	α = 90.007(12) °.
	b = 16.037(4) Å	β = 89.182(13) °.
	c = 25.219(2) Å	γ = 89.97(2) °.
Volume	4244.1(18) $Å^3$	
Z	4	
Absorption coefficient	0.329 mm^{-1}	
F(000)	2088	
Crystal size	0.5 x 0.2 x 0.2 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.54 to 34.34 °.	
Limiting indices	-16<=h<=16, -16<=k<=24, -40<=l<=39	
Reflections collected / unique	41816 / 15141 [R(int) = 0.0520]	
Completeness to theta = 34.34°	85.1%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15141 / 0 / 681	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0585, wR2 = 0.1380	
R indices (all data)	R1 = 0.0966, wR2 = 0.1470	
Largest diff. peak and hole	9.308 and -5.648 e.$Å^{-3}$	
Operator	Timo Ott	

Crystal data and structure refinement for [Rh(thiotropNH)(PPh_3)]OTf (**67**)

Identification code	[Rh(thiotropNH)(PPh_3)]OTf	
Empirical formula	$C_{39}H_{32}F_3NO_3PRhS_2$	
Formula weight	817.66	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.648(3) Å	α = 72.722(13) °.
	b = 12.8007(11) Å	β = 72.348(19) °.
	c = 13.864(3) Å	γ = 69.080(13) °.
Volume	1798.2(6) $Å^3$	
Z	2	
Absorption coefficient	0.690 mm^{-1}	
F(000)	832	
Crystal size	0.5 x 0.2 x 0.2 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.59 to 25.96 °.	
Limiting indices	-13<=h<=11, -15<=k<=14, -16<=l<=14	
Reflections collected / unique	14240 / 5795 [R(int) = 0.0148]	
Completeness to theta = 25.96°	82.2%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5795 / 0 / 455	
Goodness-of-fit on F^2	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0750	
R indices (all data)	R1 = 0.0352, wR2 = 0.0768	
Extinction coefficient	0.0037(6)	
Largest diff. peak and hole	0.486 and -0.493 e.$Å^{-3}$	
Operator	Timo Ott	

Crystal data and structure refinement for [Ir(thiotropNH)(PPh_3)]OTf (**69**)

Identification code	[Ir(thiotropNH)(PPh_3)]OTf	
Empirical formula	$C_{42}H_{38}NS_2PO_4F_3Ir$	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 14.7549(8) Å	α= 90°.
	b = 15.6998(9) Å	β= 91.8470(10)°.
	c = 16.0628(9) Å	γ = 90°.
Volume	3719.0(4) $Å^3$	
Z	24	
Density (calculated)	1.724 Mg/m^3	
Absorption coefficient	3.806 mm^{-1}	
F(000)	1920	
Crystal size	0.30 x 0.18 x 0.17 mm^3	
Data collection	Bruker SMART Apex with CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	1.81 to 28.36°.	
Index ranges	-19<=h<=19, -20<=k<=20, -21<=l<=21	
Reflections collected	38161	
Independent reflections	9271 [R(int) = 0.0794]	
Completeness to theta = 28.36°	99.6 %	
Absorption correction	None	
Max. and min. transmission	0.5639 and 0.3948	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9271 / 0 / 491	
Goodness-of-fit on F^2	0.926	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0820	
R indices (all data)	R1 = 0.0620, wR2 = 0.0877	
Largest diff. peak and hole	2.904 and -1.140 $e.Å^{-3}$	
Operator	Mathias Vogt	

Crystal data and structure refinement for [Rh(CO)(Ph_2PPhtropNH)]OTf (**71**)

Identification code	[Rh(CO)(Ph_2PPhtropNH)]OTf
Empirical formula	$C_{40}H_{36}F_3NO_5PRhS$
Formula weight	833.66
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 10.9755(17) Å α = 94.928(26) °.
	b = 11.3582(29) Å β = 96.327(21) °.
	c = 15.2244(63) Å γ = 94.651(16) °.
Volume	1871 $Å^3$
Z	2
Absorption coefficient	3.680 mm^{-1}
F(000)	1012
Crystal size	0.5 x 0.2 x 0.2 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	2.73 to 34.39 °.
Limiting indices	-16 =< h =< 17, -18 =< k =< 17, -23 =< l =< 24,
Reflections collected / unique	39046 / 14563 [R(int) = 0.1013]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14563/ 0 / 472
Goodness-of-fit on F^2	0.678
Final R indices [I>2sigma(I)]	R1 = 0.0546, wR2 = 0.1234
R indices (all data)	R1 = 0.2528, wR2 = 0.2336
Largest diff. peak and hole	0.87 and -0.54 e.$Å^{-3}$
Operator	Timo Ott

Crystal data and structure refinement for [Cu(CH_3CN)($trop_2NH$)]OTf (**74**)

Identification code	[Cu(CH_3CN)($trop_2NH$)]OTf	
Empirical formula	$C_{33}H_{26}CuF_3N_2O_3S$	
Formula weight	651.18	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.9526(26 Å	α = 89.961(14) °.
	b = 10.9347(18) Å	β = 95.601(18) °.
	c = 29.1636(50) Å	γ = 90.163(18) °.
Volume	2841 $Å^3$	
Z	4	
F(000)	2040	
Crystal size	0.5 x 0.2 x 0.2 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.73 to 34.39 °.	
Limiting indices	-13 =< h =< 13, -17 =< k =< 16, -45 =< l =< 44	
Reflections collected / unique	40295 / 11051 [R(int) = 0.0554]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11051/ 0 / 383	
Goodness-of-fit on F^2	0.655	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1079	
R indices (all data)	R1 = 0.1412, wR2 = 0.1536	
Largest diff. peak and hole	0.87 and -0.54 e.$Å^{-3}$	
Operator	Timo Ott	

Crystal data and structure refinement for $[Cu(trop_2NH)(PPh_3)]BF_4$ (**75**)

Identification code	$[Cu(trop_2NH)(PPh_3)]BF_4$
Empirical formula	$C_{49}H_{40}BCl_2CuF_4NP$
Formula weight	895.08
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.6313(10) Å α = 90 °.
	b = 12.6369(12) Å β = 92.336(2) °.
	c = 31.339(3) Å γ = 90 °.
Volume	4206.8(7) $Å^3$
Z	4
Absorption coefficient	0.738 mm^{-1}
F(000)	1840
Crystal size	0.5 x 0.2 x 0.2 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	1.74 to 26.37 °.
Limiting indices	-13<=h<=13, -15<=k<=15, -38<=l<=39
Reflections collected / unique	30840 / 8549 [R(int) = 0.0513]
Completeness to theta = 26.37°	99.2%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8549 / 0 / 535
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0771, wR2 = 0.2034
R indices (all data)	R1 = 0.0984, wR2 = 0.2180
Largest diff. peak and hole	1.872 and -1.378 e.$Å^{-3}$
Operator	Hartmut Schönberg

Crystal data and structure refinement for [Cu(trop$_2$NH)(PPh$_3$)]OTf (**76**)

Identification code	[Cu(trop$_2$NH)(PPh$_3$)]OTf	
Empirical formula	$C_{49}H_{37}CuF_3NO_3PS$	
Formula weight	871.37	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.066(5) Å	α= 90°.
	b = 17.688(4) Å	β= 101.77(4)°.
	c = 21.523(10) Å	γ = 90°.
Volume	4124(3) Å^3	
Z	4	
Absorption coefficient	0.677 mm^{-1}	
F(000)	1796	
Crystal size	0.5 x 0.2 x 0.2 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.67 to 34.38°.	
Index ranges	-16<=h<=17, -27<=k<=26, -31<=l<=33	
Reflections collected / unique	45744 / 15910 [R(int) = 0.0669]	
Completeness to theta = 34.38°	91.9%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15910 / 0 / 532	
Goodness-of-fit on F^2	0.631	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.0980	
R indices (all data)	R1 = 0.1998, wR2 = 0.1098	
Largest diff. peak and hole	1.003 and -0.441 e.Å^{-3}	
Operator	Timo Ott	

Crystal data and structure refinement for $[Ag(trop_2NH)_2]OTf$ (**77**)

Identification code	$[Ag(trop_2NH)_2]OTf$	
Empirical formula	$C_{63}H_{48}AgCl_6F_3N_2O_3S$	
Formula weight	1290.71	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7965(16) Å	α = 102.44(2) °.
	b = 16.160(5) Å	β = 94.346(16) °.
	c = 17.660(5) Å	γ = 90.188(17) °.
Volume	2999.5(13) $Å^3$	
Z	2	
Absorption coefficient	0.687 mm^{-1}	
F(000)	1485	
Crystal size	0.5 x 0.2 x 0.2 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.60 to 34.38 °.	
Limiting indices	-17<=h<=16, -24<=k<=25, -27<=l<=27	
Reflections collected / unique	59288 / 23392 [R(int) = 0.0878]	
Completeness to theta = 34.38°	92.8%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23392 / 0 / 713	
Goodness-of-fit on F^2	0.601	
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1561	
R indices (all data)	R1 = 0.2442, wR2 = 0.1681	
Largest diff. peak and hole	0.934 and -0.709 e.$Å^{-3}$	
Operator	Timo Ott	

Crystal data and structure refinement for $[Au(trop_2NH)_2]PF_6$ (**78**)

Identification code	$[Au(trop_2NH)_2]PF_6$
Empirical formula	$C_{62}H_{49}AuF_6N_3P$
Formula weight	1178.00
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P1
Unit cell dimensions	a = 11.1858(14) Å α = 83.981(10) °.
	b = 12.3823(12) Å β = 76.358(12) °.
	c = 21.7298(31) Å γ = 63.180(6) °.
Volume	2610 $Å^3$
Z	2
F(000)	1800
Crystal size	0.5 x 0.2 x 0.2 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	2.60 to 32.00 °.
Limiting indices	-16 =< h =< 12, -17 =< k =< 18, -31 =< l =< 31
Reflections collected / unique	41135 / 21656 [R(int) = 0.0179]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21656 / 3 / 1318
Goodness-of-fit on F^2	0.923
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0570
R indices (all data)	R1 = 0.0407, wR2 = 0.0760
Largest diff. peak and hole	0.86 and -0.48 $e.Å^{-3}$
Operator	Timo Ott

Crystal data and structure refinement for $[Rh(tropOxaz^{i\text{-}Pr})_2]PF_6$ (**81**)

Identification code	$[Rh(tropOxaz^{i\text{-}Pr})_2]PF_6$	
Empirical formula	$C_{42}H_{42}F_6N_2O_2PR$	
Formula weight	854.66	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2	
Unit cell dimensions	a = 42.233(10) Å	α= 90°.
	b = 10.3295(9) Å	β= 116.33(3)°.
	c = 19.829(5) Å	γ = 90°.
Volume	7753(3) $Å^3$	
Z	8	
Absorption coefficient	0.549 mm^{-1}	
F(000)	3508	
Crystal size	0.5 x 0.2 x 0.2 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	2.85 to 32.00°.	
Index ranges	-55<=h<=62, -15<=k<=15, -27<=l<=27	
Reflections collected	37225	
Independent reflections	21346 [R(int) = 0.0435]	
Completeness to theta = 32.00°	91.6%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21346 / 1 / 974	
Goodness-of-fit on F^2	0.680	
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0681	
R indices (all data)	R1 = 0.0958, wR2 = 0.0734	
Largest diff. peak and hole	0.458 and -0.441 e.$Å^{-3}$	
Operator	Timo Ott	

Curriculum vitae (removed)

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