Heterobinuclear Organometallic Complexes

A Study of the Structure, Electronic Behaviour and Reactivity of New Low-Valent Compounds

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Abstract

Six new heterobimetallic Rh(I)Pt(II) complexes supported by a novel type of chelating tropPPh₂ ligand were synthesised, characterised (figure 1) and tested in nitrous oxide activation. Heterobinuclear complex 13 proved to be the most efficient homogeneous catalyst for the hydrogenation of the greenhouse gas N₂O up to date (TON = 430), producing benign water and nitrogen under mild reaction conditions. Ligand alteration at the rhodium centre led to fundamental insight into the nature of the bimetallic core: NMR and XRD studies revealed that cationic compounds contained a shorter metal-metal bond and stronger ¹⁰³Rh-¹⁹⁵Pt coupling in NMR, while neutral complexes demonstrated a longer intermetallic distance and weaker ¹J_RhPt coupling. Furthermore, a correlation between ¹⁹⁵Pt satellites in ³¹P{¹H} NMR and the intermetallic bond length was found. In these heterobimetallic systems, the platinum centre appeared to serve as a supporting ligand, donating electron density to the rhodium, which is suggested to be essential in the rhodium platinum bond.

Figure 1. Novel type of chelating tropPPh₂ ligand that enables the coordination of rhodium(I) and platinum(II). Ligand variation of the rhodium centre gave fundamental insight in the intermetallic bond.

10: L = Cl⁻  
11: L = ACN, X = PF₆⁻  
12: L = ACN, X = BArF⁻  
13: L = OTf⁻  
14: L = μ-Cl, X = BArF⁻  
15: L = μ-CITICl, X = BArF⁻
1. Introduction

Nature is a great source of inspiration for the rational design of new catalysts. Since the presence of multimetallic centres in biomolecules are recognised to be of vital importance in enzymatic processes, bimetallic complexes are considered highly interesting for the activation of different inorganic and organic substrates.\(^1\) A prominent example is a group of metalloenzymes that are involved in hydrogen reduction/water oxidation. These so-called hydrogenases can be categorised depending on their metal active sites in monometallic [Fe], homobimetallic [FeFe] and heterobimetallic [NiFe] hydrogenases (figure 2). These metalloenzymes, found in various microorganisms, are responsible for providing energy and balancing the redox potential of a cell. In particular, the homobimetallic and heterobimetallic hydrogenases are more active in the oxidation of hydrogen and generation of dihydrogen.\(^2\)

![Figure 2](image-url)

**Figure 2.** Active site of a) monometallic [Fe] hydrogenase model b) homobimetallic [FeFe] hydrogenase and c) heterobimetallic [NiFe] hydrogenase.

Also, in synthetic chemistry there are well-known bimetallic catalysts that show the importance of catalytic systems containing metal-metal bonds. The study of intermetallic bonds has been of great interest for many researchers over half a century,\(^3\) with the description of the first multiple metal-metal bonds by Prof. F. Albert Cotton in 1964.\(^4\) His work contributed a great deal to the understanding of intermetallic interactions.\(^5,6\) Although numerous binuclear compounds are described in literature, the catalytic application of these complexes is not well documented.\(^7-14\) A renowned example of a bimetallic catalyst is the rhodium(II) acetate dimer discovered in the 70’s that is utilised as a carbene and nitrene transfer catalyst and is superior to mononuclear analogues in terms of functional group tolerance and catalyst loading (figure 3).\(^3\) Lately, a renewed interest in
bimetallic systems resulted in the use of metal-metal bonded compounds in various catalytic applications\textsuperscript{[15]} such as hydrogenation reactions\textsuperscript{[16]}, small molecule activation\textsuperscript{[17,18]}, coupling reactions\textsuperscript{[19]} and diazo-free cyclopropanation.\textsuperscript{[20]}

![Figure 3. Schematic representation of rhodium(II) acetate dimer. This dimer is known for carbene and nitrene transfer reaction and is thought to be one of the most potent catalysts containing a metal-metal bond.](image)

The synthesis and application of homobimetallic complexes are more established than the preparation of heterobinuclear species, as these compounds, where two different metal centres are combined within the molecule, are often more challenging to prepare.\textsuperscript{[21]} Nevertheless the study to heterobimetallic catalysts remains interesting, since the combination of two different metal centres has proven to lead to unprecedented catalytic transformations and activities.\textsuperscript{[8]} Most of these heteronuclear transition metal complexes incorporate an early and a late transition metal, bridged by a ligand framework. The intermetallic bond in these heterobimetallic complexes can be described as a dative interaction between a hard, Lewis acidic early transition metal or main group element and a soft Lewis basic late transition metal.\textsuperscript{[22]} The group of Lu recently described a series of early transition metal-cobalt heterobimetallic complexes capable of nitrogen activation at the cobalt centre. The early-late metal set is supported by a heptadentate ligand with chelating phosphorus and nitrogen donor atoms (figure 4).\textsuperscript{[23]}
Figure 4. Structure of early-late heterobimetallic complex where a heptadentate ligand, containing phosphorus and nitrogen donor atoms, enforces the dinuclear M-M’ axis.

The intermetallic interaction and the catalytic application of heterobinuclear complexes bearing two late transition metals remain rather underexplored. Still, this field has been a subject of significant research interest. For example, the group of Chen synthesises late-late heterobimetallic Pd/M (M: Cu, Ag, Au) and Pd(II)/Zn(II) model systems to gain detailed mechanistic information on transmetalation reactions in Sonogashira and Negishi coupling reactions, respectively.\(^{[24,25]}\) Furthermore, Nocera and co-workers described a heterobimetallic complex with a Rh(II)Pt(I) core which is readily oxidised to a Pt(III)Rh(II) core. Irradiation of the oxidised product promotes the photoelimination of halogen and regenerates the reduced Rh(II)Pt(I) core. Halogen oxidation and halogen photoelimination chemistry is considered promising for the production of dihydrogen from HX substrates to store solar energy.\(^{[26]}\) Additionally, Mankad et al. recently studied a heterobimetallic ruthenium-silver compound for hydrogen activation and the catalytic semi-hydrogenation of alkynes (figure 5).\(^{[27]}\)

Figure 5. A ruthenium-silver heterobimetallic complex for the catalytic semi-hydrogenation of alkynes.
During this catalysis the metal-metal bond is cleaved, leading to two monometallic species. To close the catalytic cycle the silver ruthenium bond must be restored, which likely caused the high catalyst loading (20%). However, bimetallic cooperation led to the observed cis selectivity, which only was observed in very few monometallic systems before.\cite{28,29} This phenomenon of fragmentation during catalysis is common in bimetallic catalysis, since metal-metal bonds are often more labile than organic bonds.\cite{30} Ligand design can be a tool to avoid breaking the intermetallic bond by creating a system that allows the coordination of two different metal centres in close proximity, assisting a metal-metal interaction that remains intact throughout a complete catalytic cycle.

In this current study, a new type of ligand was designed which enables the coordination of two different late transition metals. The newly designed chelating ligand features a trop (trop = 5-dibenzosuberene) unit, which contains a seven-membered ring, providing the preparation of robust complexes. A chelating concavely shaped tropPPh$_2$ ligand can be prepared binding a σ-donor diphenylphosphine to the trop unit, which itself bears a sterically encumbered double bond that functions as a π-accepting coordination site.\cite{31} Previous work of the Grützmacher group showed that this ligand allows strong coordination to different late transition metals, such as rhodium, palladium and iridium, and is especially valuable for stabilizing low-valent oxidation states.\cite{32-35} Further studies on this tropPPh$_2$ ligand resulted in the development of a ligand, $^{\text{TMS} \equiv \text{C} \text{TropPPh}_2}$, that is able to coordinate to two electron rich group 9 and 10 d$^8$-metals, while leaving open coordination sites at the metal centres. Whereas the first metal is bound to the trop moiety via interaction with the phosphine and alkene, the second metal is coordinated to the alkyne moieties (figure 6).\cite{36}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Previous work of the Grützmacher group, where the specially designed $^{\text{TMS} \equiv \text{C} \text{TropPPh}_2}$ ligand allows the coordination of two different late transition metals in a chelating fashion.}
\end{figure}
In the synthesis of this novel type of chelating ligand the alkyne groups were introduced by a cross-coupling Sonogashira reaction. This product required purification by column chromatography, which involved the use of large amounts of solvents and could not be scaled up successfully. The last step in this synthesis, the substitution of a chloride by the diphenylphosphine, was rather tedious, since deprotection of the trimethylsilyl (TMS) group can occur by strongly basic or protic reactants or solvents. From ligand 1 a synthetic route to heterobimetallic Rh(I)Pt(II) complexes was developed (figure 7). The synthesis of 2 posed problems, as the isolation and purification required a fine tuned, non-trivial reaction protocol and purification step.

Figure 7. Previous work of the Grützmacher group: synthesis of heterobimetallic Rh(I)Pt(II) complexes 3 and 4 based on the TMSCH₂C₆H₄C₆H₄CH₂PPh₂ ligand 1.

Heterogeneous rhodium-platinum carbonyl catalysts have proven to be active in hydrogenation reactions of aromatic compounds and CO. In toluene hydrogenation to methylcyclohexane the presence of platinum appeared to improve the activity of the catalyst. However both catalysts decomposed after a few runs. The hydrogenation of CO yielded ethylene glycol and methanol that suggested that mixed metal clusters, which could not be determined, were involved in the catalytic reactions.
The goal of this study was to synthesise a similar chelating trop ligand, allowing the coordination of two different late transition metals, while avoiding the previously described problems. Furthermore, the preparation of different heterobimetallic complexes, based on the new ligand, were studied, using $d^8$ metals rhodium(I) at the $M_1$ position and platinum(II) as $M_2$ (figure 6). Additionally, the coordination of other group 9 metals, iridium(I) and cobalt(I), to the chelating trop ligand was investigated. Also, the influence of various ligands coordinated to the $M_1$ metal centre on the metal-metal bond was explored. Studying the structure and electronic properties of these different heterobinuclear complexes could give fundamental insight in this underdeveloped late metal-metal bond. Finally, the reactivity of this class of compounds towards the activation of the greenhouse gas nitrous oxide ($N_2O$) with hydrogen was studied.
2. Results and Discussion

2.1 Synthesis and Characterisation of the Trop Ligand: \( \text{PhC≡C}_\text{TropPPh}_2 \)

Based upon the synthesis of ligand 1 that was described in unpublished results of the Grützmacher group, an experimental procedure for the preparation of a new chelating trop ligand 8 was developed (figure 8).\[^{36}\] In this new ligand, the TMS groups on the alkyne moiety were replaced by phenyl groups. First, a Sonogashira coupling was performed to introduce phenylacetylene in the trop moiety and by nucleophilic substitution using thionyl chloride the OH group is replaced by a chloride, forming compound 7. For the last step of the ligand synthesis, the substitution of the chloride by the phosphine, a different procedure was applied and optimised to obtain the final product. Diphenylphospine was added to compound 7 and the reaction mixture was stirred at 50°C while forming a precipitate of chlorodiphenylphosphonium salt. Upon addition of Na\(_2\)CO\(_3\) as a base, HCl was eliminated, leading to product 8 with a 63 % yield. This step deviates from the ligand synthesis of the TMS analogue, where n-butyllithium was used as reagent to deprotonate diphenylphospine. The \textit{in situ} formed lithium diphenylphospine then replaced the chloride. However, deprotonation of the TMS groups could occur during this step. The yield of the synthesis of the \( \text{PhC≡C}_\text{TropPPh}_2 \) ligand 8 was comparable to the TMS analogue and upscale of the reaction was possible. Therefore, the preparation of the \( \text{PhC≡C}_\text{TropPPh}_2 \) ligand was shown to be more reliable and scalable compared to the \( \text{TMS}_\text{C≡C}_\text{TropPPh}_2 \) ligand. In figure 9 the crystal structure of the chelating ligand 8 is depicted. This ligand design enables the anchoring of two metals using a set of different chelating ligands: phosphine, alkene and alkynes.
Figure 8. Three-step synthesis of ligand 8, including a Sonogashira coupling to introduce the alkyne moieties in the molecule, yielding 6. This is followed by substitution of the alcohol by the chloride and the final product 8 is obtained by the reaction of 7 with diphenylphosphine.

2.2 Synthesis and Characterisation of the Rhodium PhC≡C-TropPPh₂ Dimer

Complex 9 was synthesised by reacting ligand 8 with [Rh(C₂H₄)₂Cl]₂ in benzene at room temperature (figure 10). Clean 9 precipitated from the reaction mixture as a red powder in good yield. The synthesis of 9 is considerably more convenient compared to the TMSC≡CTropPPh₂ trop dimer, where isolation and purification of the product is tedious and non-scalable. Single crystals of complex 9 were obtained by slow diffusion of n-hexane into solution of 9 in dichloromethane and analysed by X-ray diffraction. The structure of this complex is shown in figure 11. Back donation from the metal into the π* orbital of the olefins leads to weakening and elongation of the double bond (1.470(3) Å in 9, compared to 1.373(5) Å in free ligand 8).

\[ \text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_2 + \text{ligand 8} \rightarrow \text{complex 9} \]

**Figure 10.** Synthesis of complex 9 from ligand 8 with [Rh(C₂H₄)₂Cl]₂.

**Figure 11.** Molecular structure of 9. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°], centroid of C2=C3 is indicated as ct1 and ct1' is centroid of C2'=C3': Rh1/1'-ct1/1': 2.009(2), Rh1/1'-P1/1': 2.169(6), C2/2'=C3/3': 1.470(3), Rh1-Cl1: 2.375(6), Rh1-Cl1': 2.507(6), ct1-Rh1-P1: 92.013(6), ct1-Rh1-Cl1': 100.008(6) Cl1'-Rh1-Cl1: 80.76(2) Cl1-Rh1-P1: 87.94(2).
In $^1$H NMR and $^{31}$P NMR spectra of complex 9 broad signals were observed at room temperature. Line broadening in NMR can be caused by several factors, such as fast relaxation of the molecule, the presence of a paramagnetic species and chemical exchange. Cooling and heating experiments of the NMR sample indicated that there is indeed a dynamic process, which causes the line broadening in the NMR spectra. When there is an equilibrium between two species cooling the sample can slow down the exchange and at the low-temperature limit a static spectrum can be observed. Heating the sample increases the rate of exchange, which at the high-temperature limit leads to the fully averaged spectrum. Between these two extremes broad signals are observed$^{[39]}$. Variable temperature $^1$H NMR and $^{31}$P NMR spectra from 248 K to 378 K in 1,1,2,2-tetrachloroethane-d$_2$ were recorded (figure 12). $^1$H NMR is zoomed in on the signal of the benzylic proton.

Figure 12 revealed that compound 9 was present as two species in equilibrium in solution, with different Rh-P couplings of 260 Hz and 194 Hz. NMR studies in a coordinating solvent, ACN-d$_3$, resulted in cleavage of the dimer and coordination of the acetonitrile to the rhodium. Sharp signals were recorded, indicating that there was no chemical exchange. Based on these results it is proposed that there is an equilibrium between the cis- and trans-isomer (figure 13).
Figure 12. a) Variable temperature $^1$H NMR and b) $^{31}$P NMR of 9 in 1,1,2,2-tetrachloroethane-d$_2$ reveals an equilibrium in chlorinated solvents. Shimming was not carried out before every experiment, which resulted in broadening of the signals in some of the experiments. The $^1$H NMR spectra are zoomed in on signal of the benzylic proton.
Figure 13. Equilibrium between trans-isomer 9 and cis-isomer 9a in chlorinated solvents led to broad signals in NMR at room temperature.

2.3 Heterobimetallic Rh(I)Pt(II) Complexes

Complex 9 was used as building block for the synthesis of the heterobimetallic species studied in this thesis. Here we describe the preparation and analysis of these dinuclear Rh(I)Pt(II) compounds will be described.

2.3.1 Synthesis and XRD Studies of Heterobimetallic Rh(I)Pt(II) Complexes

The second metal, platinum(II), was introduced by reacting complex 9 with [Me₂Pt(μ-SMe)]₂ in dichloromethane to produce complex 10. In a one-pot synthesis, complexes 11 and 12 were prepared from 9 by abstracting the chloride with TIPF₆ or NaBARF, respectively (figure 14). This salt metathesis reaction was carried out in the presence of acetonitrile, leading to the coordination of acetonitrile to the rhodium centre, with non coordinating anions PF₆ and BARF as counterions.
Figure 14. Synthesis of $^{\text{PhC}}\text{TropPPh}_2$ heterobimetallic Rh(I)Pt(II) complexes 10, 11 and 12 from $^{\text{PhC}}\text{TropPPh}_2$ dimer 9 and [Me$_2$Pt(SMe)$_2$]$_2$.

Figure 15. a) Molecular structure of 10. b) Molecular structure of 11 and 12. Hydrogen atoms, counterions and solvent molecules are omitted for clarity.
Table 1. Selected bond distances [Å] and angles [°] for 10, 11 and 12, where the centroid of C2=C3 is indicated as ct1, ct2 for C4≡C5 and ct3 for C6≡C7.

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<th>Compound</th>
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<th>11</th>
<th>12</th>
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<td>1.979(3)</td>
<td>1.978(5)</td>
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<td>2.2055(9)</td>
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<tr>
<td>C2=C3</td>
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<td>1.467(5)</td>
<td>1.454(6)</td>
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<td>98.41(11)</td>
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</table>

The geometry of 10-12 can be described as a square planar geometry around the rhodium centre, while the geometry around the platinum metal centre can be defined as square pyramidal, where the rhodium centre occupies the axial position of the square pyramidal structure (figure 15 and table 1). The significantly elongated olefin bond for 10 (1.471(4) Å), 11 (1.467(5) Å) and 12 (1.454(6) Å) indicates strong back donation from the metal into the anti-bonding orbitals $\pi^*$ of the C=C double bond. The Rh-Pt bond is considerably longer in complex 10 (2.7657(2) Å) than in complexes 11 (2.6784(3) Å) and 12 (2.6979(4) Å).
Furthermore, the Rh-Cl (2.3294(7) Å) bond is substantially longer than the Rh-N (2.059(3) Å and 2.02(3) Å) bond. Although the differences in the olefin bond length are rather small between complexes 10-12, it is observed that the stronger π-donor chloride results in more back donation to C=C olefin trop anti-bonding orbitals, which indicates a more electron rich rhodium centre. This interaction can be described as a “push-pull” interaction, where the olefin accepts electron density into the π^* anti-orbital to reduce the electron density on the metal (“pull”). This reduces the destabilisation generated by the π donation of the chloride to the metal (“push”). This push-pull mechanism is known for square planar d^8 complexes.[40] Since compounds 11 and 12 are cationic, while 10 is neutral, it is expected that all bond lengths are shortened in the cationic complexes. This is because the positive charge will decrease all orbital energies resulting in better overlap between the ligand and the metal orbitals. Remarkably, this is not observed for the Rh-ct1, which may be explained by the push-pull effect of the chloride compared to the acetonitrile that is solely a σ-donor. However, the influence of the positive charge is strongly reflected in the Rh-Pt bond that indeed becomes much shorter in cations 11 and 12 compared to neutral 10.

Furthermore, NMR and crystallography data of the acetonitrile bound complexes 11 and 12 were very similar to one another, which indicates that the counterion does not influence the electronic behaviour and geometrical features of the complexes. However, BAr^+ considerably increases the solubility of the complex in non-coordinating solvents compared to compound 11. Furthermore, the use of toxic thallium(I) is avoided in the synthesis of complex 12. Therefore the synthesis and use of complex 12 is more preferred compared to 11.

Consequently, silver triflate was used to abstract the chloride from 10 to bind a weakly coordinating anionic triflate, to the rhodium centre, leading to complex 13 (figure 16). XRD studies revealed that the geometry of complex 13 can be described as square planar around the rhodium centre and square pyramidal around the platinum (figure 17 and table 2). The C=C olefin trop bond is elongated in a similar fashion as in chloride complex 10 due to π back donation (1.473(7) Å in 13, 1.471(4) Å in 10). Also, the measured metal-metal bond of 13 (2.7427(4) Å) is rather comparable to the Rh-Pt bond of 10 (2.7657(2) Å). This demonstrates the similar electronic properties for both neutral complexes. Moreover, the metal-metal bond length of 13 is longer than the acetonitrile coordinated complexes 11 (2.6784(3) Å) and
12 (2.6979(4) Å), indicating as well that a neutral complex results in an elongated Rh-Pt bond.

![Figure 16. Synthesis of complex 13 from 10 with AgOTf.](image)

Figure 16. Synthesis of complex 13 from 10 with AgOTf.

![Figure 17. Molecular structure of 13. Hydrogen atoms and solvent molecules are omitted for clarity.](image)

Figure 17. Molecular structure of 13. Hydrogen atoms and solvent molecules are omitted for clarity.
Table 2. Selected bond distances [Å] and bond angles [°] of 10 and 13, where the centroid of C2=C3 is indicated as ct1, ct2 for C4≡C5 and ct3 for C6≡C7.

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<td>Pt1-Rh1-Cl1/O1</td>
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<td>89.87(10)</td>
</tr>
<tr>
<td>Cl1/N1-Rh1-P1</td>
<td>94.86(3)</td>
<td>100.04(11)</td>
</tr>
<tr>
<td>ct2-Pt1-C8</td>
<td>92.556(12)</td>
<td>94.085(2)</td>
</tr>
<tr>
<td>ct3-Pt1-C9</td>
<td>94.427(11)</td>
<td>91.781(2)</td>
</tr>
<tr>
<td>ct2-Pt1-ct3</td>
<td>93.889(10)</td>
<td>91.040(18)</td>
</tr>
<tr>
<td>C8-Pt1-C9</td>
<td>86.87(13)</td>
<td>85.1(2)</td>
</tr>
<tr>
<td>Rh1-Pt-ct2</td>
<td>79.832(10)</td>
<td>77.785(13)</td>
</tr>
<tr>
<td>Rh1-Pt1-ct3</td>
<td>78.966(10)</td>
<td>78.050(14)</td>
</tr>
<tr>
<td>Rh1-Pt1-C8</td>
<td>99.80(9)</td>
<td>100.50(16)</td>
</tr>
<tr>
<td>Rh1-Pt1-C9</td>
<td>97.14(9)</td>
<td>100.16(15)</td>
</tr>
</tbody>
</table>

Then, the preparation of a T-shaped rhodium complex, with a non-coordinating anion, leading to open coordination site cis to the M-M’ bond was attempted (figure 18). Such a T-shaped bimetallic complexes is expected to show enhanced reactivity due to the readily available open coordination site, as is described for monometallic Rh(I) analogues.\[41\]
Attempted preparation of T-shaped rhodium complex with an open coordination site cis to the Rh-Pt axis. NaBAR\textsuperscript{F} and TlBAR\textsuperscript{F} were used as chloride scavengers.

The reaction of 10 with NaBAR\textsuperscript{F} in toluene did not result in a T-shaped rhodium, but only one chloride could be abstracted and dimerisation of the complex was observed, leading to 14. When using TIBAR\textsuperscript{F}, another chloride scavenger, to remove the chloride bridged chloride-thallium-chloride 15 complex was formed (figure 19). This indicated that the chloride is strongly coordinated to the rhodium centre. Single crystals of 14 and 15 were analysed by XRD (figure 20). These dimeric structures can be as well described as square planar d\textsuperscript{8} around rhodium and square pyramidal for the platinum centre (table 3).

Figure 19. Synthesis of dimeric complexes 14 and 15 from 10, using different BAR\textsuperscript{F} salts in attempt to abstract the chloride from the rhodium centre. For 15 no yield is reported, since the reaction was only performed at test reaction scale.
Figure 20. a) Molecular structure of 14. b) Molecular structure of 15. Hydrogen atoms, counterions and solvent molecules are omitted for clarity.
Table 3. Selected bond distances [Å] and bond angles [°] for terminal chloride 10, 14 and 15, where the centroid of C2=C3 is indicated as ct1, ct2 for C4≡C5 and ct3 for C6≡C7.

<table>
<thead>
<tr>
<th>Compound</th>
<th>10</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1-C2=C3</td>
<td>1.953(3)</td>
<td>1.958(5)</td>
<td>1.964(4)</td>
</tr>
<tr>
<td>Rh1-P1</td>
<td>2.1850(8)</td>
<td>2.178(13)</td>
<td>2.183(11)</td>
</tr>
<tr>
<td>C2=C3</td>
<td>1.471(4)</td>
<td>1.456(7)</td>
<td>1.460(4)</td>
</tr>
<tr>
<td>Rh1-Cl1</td>
<td>2.3294(7)</td>
<td>2.403(11)</td>
<td>2.340(10)</td>
</tr>
<tr>
<td>Rh1-Pt1</td>
<td>2.7657(2)</td>
<td>2.788(4)</td>
<td>2.750(3)</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.227(4)</td>
<td>1.233(8)</td>
<td>1.227(6)</td>
</tr>
<tr>
<td>C6-C7</td>
<td>1.228(4)</td>
<td>1.212(8)</td>
<td>1.225(6)</td>
</tr>
<tr>
<td>Pt1-C4-C5</td>
<td>2.233(3)</td>
<td>2.217(6)</td>
<td>2.241(4)</td>
</tr>
<tr>
<td>Pt1-C6-C7</td>
<td>2.215(3)</td>
<td>2.256(6)</td>
<td>2.245(4)</td>
</tr>
<tr>
<td>P1-Rh1-ct1</td>
<td>93.167(8)</td>
<td>92.933(14)</td>
<td>94.079(11)</td>
</tr>
<tr>
<td>ct1-Rh1-Pt1</td>
<td>75.701(8)</td>
<td>76.049(13)</td>
<td>76.140(11)</td>
</tr>
<tr>
<td>Pt1-Rh1-Cl1</td>
<td>96.34(2)</td>
<td>97.60(3)</td>
<td>97.60(3)</td>
</tr>
<tr>
<td>Cl1-Rh1-P1</td>
<td>94.86(3)</td>
<td>92.85(4)</td>
<td>92.15(4)</td>
</tr>
<tr>
<td>ct2-Pt1-C8</td>
<td>92.556(12)</td>
<td>92.847(2)</td>
<td>93.439(19)</td>
</tr>
<tr>
<td>ct3-Pt1-C9</td>
<td>94.427(11)</td>
<td>92.816(2)</td>
<td>93.459(18)</td>
</tr>
<tr>
<td>ct2-Pt1-ct3</td>
<td>93.889(10)</td>
<td>91.042(18)</td>
<td>92.685(15)</td>
</tr>
<tr>
<td>C8-Pt1-C9</td>
<td>86.87(13)</td>
<td>85.5(2)</td>
<td>85.8(2)</td>
</tr>
<tr>
<td>Rh1-Pt-C4C5</td>
<td>79.832(10)</td>
<td>76.798(13)</td>
<td>79.407(11)</td>
</tr>
<tr>
<td>Rh1-Pt1-C6C7</td>
<td>78.966(10)</td>
<td>79.123(14)</td>
<td>79.066(11)</td>
</tr>
<tr>
<td>Rh1-Pt1-C8</td>
<td>99.80(9)</td>
<td>97.816(13)</td>
<td>98.605(14)</td>
</tr>
<tr>
<td>Rh1-Pt1-C9</td>
<td>97.14(9)</td>
<td>104.653(16)</td>
<td>99.161(13)</td>
</tr>
</tbody>
</table>

Comparison of bridged compound 15 and terminal chloride complex 10 revealed that 15 matched the trend in the electronic behaviour established previously, in which a cationic compound led to a shorter intermetallic bond. However, 15 can be considered an intermediate case, since the cationic charge is divided over two bridged molecules. Therefore, the metal-metal bond is only slightly shorter in 15 (2.750(3) Å) compared to 10 (2.7657(2) Å). Since the same chloride orbital is responsible for π donation to the rhodium centre and σ donation to the thallium centre in 15, there is less electron density present on
the rhodium centre, resulting in less back donation and a shorter olefin bond (1.460(4) Å in 15 compared to 1.471(4) in 10). In 14 the π donation of the chloride is divided onto two metal centres, which was demonstrated in a comparable olefin bond length as 15 (1.456(7) Å). However, the Rh-Pt bond was considerably longer in cationic complex 14 (2.788(4) Å), which did not fit the electronic trend. Therefore, this elongated intermetallic interaction was explained as a steric effect up to formation of the dimer.

A survey of the CCDC crystallographic database\(^1\) concerning all reported Rh-Pt bond distances (214 rhodium-platinum bonds) reveals that the measured Rh-Pt bond lengths in this study (2.698 Å – 2.788 Å) are in range with described data in literature. Figure 22a displays an example of a similar rhodium-platinum heterobimetallic compound with an intermetallic bond distance of 2.750(1) Å.\(^{42}\) This reported value is comparable with the data found in this study. Another similar heterobimetallic Rh-Pt complex reported a longer metal-metal bond distance (2.949(2) Å) that is explained due to the bridging hydride (figure 22b).\(^{43}\)

![Figure 21. Plot of the survey result of the CCDC crystallography database regarding all reported Rh-Pt bond lengths in Å (X-axis). The Y-axis represents the number of structures for the given bond distances. The range of measured Rh-Pt bond distances in this study is indicated in red.]

\(^1\) CSD Conquest 2018 version 5.39, accessed 14 August 2018.
Figure 22. a) Heterobimetallic complex with a Rh-Pt bond distance of 2.750(1) Å b) heterobimetallic compound with a Rh-Pt bond length of 2.949(2) Å.

2.3.2 NMR Studies

Figure 23. Synthesised ligand 8, rhodium dimer 9 and heterobimetallic Rh(I)Pt(II) complexes 10-15.

Table 4 summarises selected $^1$H NMR data for the ligand 8, rhodium dimer precursor 9 and the heterobimetallic complexes 10-15, that are displayed in figure 23. The benzylic proton is a distinctive feature of this trop system. Up to coordination to a rhodium centre the $^2J_{PH}$ coupling gets stronger. Additionally, the protons of the methyl groups on the platinum are observed as a singlet around 1.29-1.46 ppm, showing the characteristic $^{195}$Pt satellites. NMR spectra of compound 14 and 15 showed broad signals. Since these are dimeric structures as well, this could indicate a chemical exchange. The samples were cooled down, which resulted in a static spectra where two species were observed, demonstrating indeed a dynamic process. Moreover, sharp signals were observed when NMR spectra of 14 were recorded in ACN-d$_3$, therefore it was assumed that an equilibrium between the cis- and
trans-isomer, as seen for 9 (vide supra, figure 13), is responsible for the observed broad signals in NMR in case of 14 and 15. Although the uncoupled signal from the protons of methyl groups on the platinum was sharp, broad signals for the $^{195}$Pt satellites were still observed. This can be explained by $^{195}$Pt relaxation effects on the methyl $^1$H line shapes.\cite{44} Therefore, accurate determination of the $^2J_{PH}$ of compound 14 and 15 was not possible. As the $^1$H NMR data was not conclusive about the electronic behaviour of these heterobimetallic compounds, further NMR studies including $^{31}$P, $^{103}$Rh and $^{195}$Pt NMR were performed to gain more insight in the electronic behaviour of this binuclear system.

Table 4. Selected $^1$H NMR spectroscopic data of compounds 8-15 in different deuterated solvents. All data were obtained at 298 K unless otherwise stated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta H_{benzylic}$ (ppm)</th>
<th>$^2J_{PH}$ (Hz) / $^2J_{RhH}$ (Hz)</th>
<th>$\delta Pt(CH_3)$_2 (ppm)</th>
<th>$^2J_{PPh}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>CDCl$_3$</td>
<td>4.70</td>
<td>5.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>ACN-d$_3$</td>
<td>5.10</td>
<td>14.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>THF-d$_8$</td>
<td>4.92</td>
<td>14.4</td>
<td>1.46</td>
<td>92.4</td>
</tr>
<tr>
<td>11</td>
<td>CD$_2$Cl$_2$</td>
<td>4.98</td>
<td>15.4 / 2.3</td>
<td>1.35</td>
<td>87.7</td>
</tr>
<tr>
<td>12</td>
<td>CD$_2$Cl$_2$</td>
<td>4.94</td>
<td>15.3 / 2.4</td>
<td>1.35</td>
<td>87.9</td>
</tr>
<tr>
<td>13</td>
<td>THF-d$_8$</td>
<td>5.19</td>
<td>14.8 / 2.8</td>
<td>1.46</td>
<td>90.1</td>
</tr>
<tr>
<td>14 $^{[a]}$</td>
<td>THF-d$_8$</td>
<td>4.69</td>
<td>14.3 / - $^{[b]}$</td>
<td>1.42</td>
<td>- $^{[b]}$</td>
</tr>
<tr>
<td>15</td>
<td>THF-d$_8$</td>
<td>5.29</td>
<td>14.4 / 2.4</td>
<td>1.29</td>
<td>- $^{[b]}$</td>
</tr>
</tbody>
</table>

$^{[a]}$ Measured at 193 K
$^{[b]}$ Broad signal

In $^{31}$P($^1$H) NMR data a large change in chemical shift was observed upon coordination of rhodium to diphenylphosphine (table 5). The chemical shift range (88-93 ppm) is characteristic for these rhodium tropPPh$_2$ complexes.\cite{34,45,46} Introduction of the platinum did only lead to minor changes of the chemical shift. Since $^{195}$Pt is also an NMR active nuclei platinum satellites with 33.7% intensity of the $^{31}$P($^1$H) signal could be detected.\cite{44} NMR data showed that complexes 11 and 12 have the weakest phosphorus-rhodium coupling (197.9 Hz for both compounds), while the $J_{PP}$ is stronger (537.4 Hz and 537.9 Hz, respectively). For the other complexes applied that if the $J_{PH}$ coupling is stronger, the $J_{PP}$ is weaker.
Table 5. Selected $^{31}$P($^1$H) NMR spectroscopic data of compounds 8-15. Chemical shifts ($\delta$) are given in ppm and couplings constants ($J$) in Hz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta$ (ppm)</th>
<th>$^1J_{\text{Prh}}$ (Hz)</th>
<th>$^2J_{\text{PPt}}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>CDCl$_3$</td>
<td>-12.95</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>ACN-d$_3$</td>
<td>93.70</td>
<td>186.5</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>THF-d$_8$</td>
<td>89.88</td>
<td>217.5</td>
<td>519.9</td>
</tr>
<tr>
<td>11</td>
<td>CD$_2$Cl$_2$</td>
<td>91.40</td>
<td>197.9</td>
<td>537.4</td>
</tr>
<tr>
<td>12</td>
<td>C$_6$D$_6$</td>
<td>91.26</td>
<td>197.9</td>
<td>537.9</td>
</tr>
<tr>
<td>13</td>
<td>THF-d$_8$</td>
<td>91.60</td>
<td>211.8</td>
<td>519.0</td>
</tr>
<tr>
<td>14</td>
<td>THF-d$_8$</td>
<td>88.76</td>
<td>215.6</td>
<td>505.7</td>
</tr>
<tr>
<td>15</td>
<td>THF-d$_8$</td>
<td>90.12</td>
<td>218.9</td>
<td>513.6</td>
</tr>
</tbody>
</table>

Additionally, other NMR active nuclei, $^{195}$Pt and $^{103}$Rh, were measured to study the electronic behaviour of the heterobimetallic complexes (table 6 and 7). Complex 15 was not studied by $^{195}$Pt and $^{103}$Rh NMR, since there was no sufficient amount of compound produced to measure $^{195}$Pt and $^{103}$Rh NMR spectra. Especially $^{195}$Pt NMR gives valuable information about the Rh(I)-Pt(II) bond, since the coupling between these two nuclei can be measured. The $^{195}$Pt spectra were acquired with $^1$H decoupling, as this leads to less crowded spectra. For compound 10 the weakest Pt-Rh coupling was measured (83.4 Hz), whereas for compounds 11 and 12 stronger metal-metal couplings were determined (104.1 Hz and 109.1 Hz). The $^1J_{\text{RhPt}}$ coupling for compound 14 could not be detected, because of fast relaxation of the $^{195}$Pt nuclei, which leads to line broadening. As described in the literature, a relevant contribution to the relaxation of heavy nuclei, such as $^{195}$Pt, is the chemical shift anisotropy (CSA) mechanism. Since $^{195}$Pt has a large chemical shift range, the CSA effect is larger as well. Potentially, this is why the $^1J_{\text{RhPt}}$ for 14 could not be observed. In literature, one reported $^1J_{\text{RhPt}}$ of 24 Hz for a [PtRh$_5$(CO)$_{15}$]$^-$ cluster was found, which is considerably weaker than the measured couplings here. However, the cluster is hardly comparable to the bimetallic complexes presented here, since oxidation state and ligand sphere are very different.
Table 6. $^{195}$Pt NMR spectroscopic data of complex 10-15, with exception of 14. Chemical shifts ($\delta$) are given in ppm and couplings constants ($J$) in Hz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta$ (ppm)</th>
<th>$^1J_{PtP}$ (Hz)</th>
<th>$^2J_{PtRh}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>THF-d$_8$</td>
<td>-3274</td>
<td>530.1</td>
<td>83.4</td>
</tr>
<tr>
<td>11</td>
<td>CD$_2$Cl$_2$</td>
<td>-3223</td>
<td>546.7</td>
<td>104.1</td>
</tr>
<tr>
<td>12</td>
<td>CD$_2$Cl$_2$</td>
<td>-3196</td>
<td>538.0</td>
<td>109.3</td>
</tr>
<tr>
<td>13</td>
<td>THF-d$_8$</td>
<td>-3263</td>
<td>519.4</td>
<td>94.5</td>
</tr>
<tr>
<td>14</td>
<td>THF-d$_8$</td>
<td>-3321</td>
<td>502.5</td>
<td>- [a]</td>
</tr>
</tbody>
</table>

[a] Broad signal

Although $^{103}$Rh has a natural abundance of 100%, direct measuring of $^{103}$Rh NMR is difficult, since it has a low (negative) gyromagnetic ratio, 31.8 times smaller than $^1$H. Therefore, $^{103}$Rh NMR is often detected indirectly by heteronuclear correlation, where $^1$H is correlated with $^{103}$Rh, which enhances the sensitivity of the rhodium nucleus[49]. Here, $^{103}$Rh was detected using heteronuclear multiple-quantum coherence (HMQC). As for the data from the $^{31}$P($^1$H) spectra, a weaker Rh-P coupling for the acetonitrile bound complexes 11 and 12, compared to complexes 10, 13 and 15, where an anionic ligand is bound to the rhodium centre, was observed.

Table 7. $^{103}$Rh NMR spectroscopic data of complex 9-15, with exception of 14. Chemical shifts ($\delta$) are given in ppm and couplings constants ($J$) in Hz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta$ (ppm)</th>
<th>$^1J_{RhP}$ (Hz)</th>
<th>$^2J_{RhRh}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>CDCl$_3$</td>
<td>-6926</td>
<td>237.2</td>
<td>13.5</td>
</tr>
<tr>
<td>10</td>
<td>THF-d$_8$</td>
<td>-7045</td>
<td>215.2</td>
<td>13.8</td>
</tr>
<tr>
<td>11</td>
<td>CD$_2$Cl$_2$</td>
<td>-7207</td>
<td>196.2</td>
<td>15.0</td>
</tr>
<tr>
<td>12</td>
<td>CD$_2$Cl$_2$</td>
<td>-7304</td>
<td>200.3</td>
<td>15.2</td>
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<td>210.6</td>
<td>14.6</td>
</tr>
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<td>14</td>
<td>THF-d$_8$</td>
<td>-7491</td>
<td>209.1</td>
<td>14.9</td>
</tr>
</tbody>
</table>

In table 8 NMR and XRD data of the heterobimetallic Rh(I)Pt(II) complexes 10-15 were compared. It was observed that a shorter metal-metal bond length corresponded to a
stronger $J_{\text{RhPt}}$ coupling. For example, complexes 11 and 12 included the shortest Rh-Pt bond length (2.678 Å and 2.698 Å, respectively) and the strongest Rh-Pt coupling (104.1 Hz and 109.3 Hz, respectively), whereas a longer M-M' bond length of 2.766 Å and a weaker $J_{\text{RhPt}}$ coupling (83.4 Hz) was measured for 10. Furthermore, the $2J_{\text{PPt}}$ measured in $^{31}\text{P}^{[\text{1}]}\text{H}$ NMR was related to the Rh-Pt bond lengths, where a shorter metal-metal bond correlated to a stronger $J_{\text{PPt}}$ coupling (graph 1). Thus, information about the intermetallic distance could already be retrieved from an accessible $^{31}\text{P}^{[\text{1}]}\text{H}$ spectrum.

**Table 8.** Selected XRD and NMR spectroscopic data of complexes 10-15.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$d_{\text{Rh-Pt}}$ (Å)</th>
<th>$J_{\text{PRh}}$ (Hz)</th>
<th>$2J_{\text{PPt}}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.766</td>
<td>83.4</td>
<td>519.9</td>
</tr>
<tr>
<td>11</td>
<td>2.678</td>
<td>104.1</td>
<td>537.4</td>
</tr>
<tr>
<td>12</td>
<td>2.698</td>
<td>109.3</td>
<td>537.9</td>
</tr>
<tr>
<td>13</td>
<td>2.743</td>
<td>94.5</td>
<td>519.0</td>
</tr>
<tr>
<td>14</td>
<td>2.788</td>
<td>-</td>
<td>505.7</td>
</tr>
<tr>
<td>15</td>
<td>2.750</td>
<td>-</td>
<td>513.6</td>
</tr>
</tbody>
</table>

**Graph 1.** Correlation between P-Pt coupling ($2J_{\text{PPt}}$ in Hz) and Rh-Pt bond length ($d_{\text{RhPt}}$ in Å).
2.3.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of compound 12 was conducted. The mass change was measured over a period of time, while changing the temperature. From these experiments more information about the formation of a T-shaped rhodium compound could be retrieved. At 171°C there was a mass loss of 41 g/mol detected, which corresponds to acetonitrile (figure 24). Afterwards, it was tested to remove the acetonitrile thermally by heating at this temperature. However, this led to decomposition of the compound.

![TGA of complex 12](image)

**Figure 24.** TGA of complex 12. Blue curve: thermogravimetry (%), green curve: differential scanning calorimetry, DSC, (µV/mg), pink curve: quasi multiple ion detection, QMID, (A). At 171°C a mass loss was detected through a decrease in the DSC, which correlated to the loss of acetonitrile determined with QMID.

2.3.3 Platinum Influence

The coordination environment of the platinum metal was altered to study the electronic effect of the platinum centre on the intermetallic bond. Methyl groups are strong σ donors.
Therefore donation of their electron density to the platinum centre results in an electron rich metal. Here, the methyl groups on the platinum were protonated with a strong acid, trifluoroacetic acid to remove the methyl groups and investigate the influence of these σ donors on the platinum centre (figure 25). In $^{31}$P{$^1$H} NMR loss of platinum was observed upon protonation, as the Pt satellites were lost, and ultimately complete decomposition of the compound was observed. This could indicate that electron density on the platinum, donated by the σ donor methyl groups, is essential for the rhodium-platinum bond, by electron donation from the platinum to the rhodium and suggests that the platinum acts as a ligand to the rhodium centre.

![Figure 25](image)

**Figure 25.** Protonation of the methyl groups on the platinum by trifluoroacetic acid led to loss of the platinum metal.

### 2.4 Reactivity of Heterobimetallic Rh(I)Pt(II) Complexes

Nitrous oxide is a greenhouse gas with a warming potential that is about 300 times bigger than CO$_2$.$^{[50]}$ Anthropogenic emissions of nitrous oxide, mainly due to large-scale application of fertilizers, are causing an increase of the level of N$_2$O in the atmosphere.$^{[51]}$ Although N$_2$O is thermodynamically unstable it is kinetically inert,$^{[52]}$ which necessitates the use of a catalyst to activate the molecule and convert it to harmless molecules. The conversion of N$_2$O into nitrogen and water could be considered highly interesting for reducing the nitrous oxide levels in atmosphere that are involved in climate change and ozone depletion (figure 26).
**Figure 26.** Schematic overview of nitrous oxide emissions in the atmosphere. Natural emissions are responsible for 64% of the nitrous oxide emissions. 30% is emitted due to denitrification of the soil, whereas 6% is released in the atmosphere due to industrial processes, such as the synthesis of adipic acid and nitric acid. Nitrous oxide is a greenhouse gas and related to climate change and ozone depletion. Catalytic conversion of N$_2$O to harmless nitrogen and water molecules could reduce the levels in atmosphere. – Figure reprinted with permission from Prof. Gianetti, University of Arizona.

N$_2$O is known to be a unreactive and poor ligand for transition metals.\(^{[53]}\) In nature N$_2$O is activated and reduced in a cooperative fashion to nitrogen by the enzyme nitrous oxide reductase at a tetranuclear copper site binding to adjacent copper centres (figure 27a).\(^{[54]}\) Also in a heterogeneous catalytic system, Cu-ZSM-5, N$_2$O is activated by metal-metal cooperation of two adjacent copper sites (figure 27b).\(^{[55,56]}\)

**Figure 27.** Activation of N$_2$O by a) tetranuclear copper site in nitrous oxide reductase and b) adjacent copper sites in Cu-ZSM-5.
The development of homogeneous catalytic systems for the hydrogenation of N₂O is of interest, since this could give mechanistic understanding in this reaction, which is valuable for rational catalytic design. Recently, Milstein reported a homogeneously catalysed reaction of N₂O with hydrogen by a PNP ruthenium complex (figure 28), using relatively high pressures of the gasses, 3 bar of N₂O and 4 bar of H₂, to produce water and nitrogen.\[57\] Furthermore, a rhodium(I) carbene complex featuring a trop system was described in previous work of the Grützmacher group to perform dehydrogenation of alcohols with nitrous oxide as a hydrogen acceptor.\[58\] To our knowledge, there is no bimetallic system identified for this reaction.

**Figure 28.** Hydrogenation of nitrous oxide homogeneously catalysed by a PNP ruthenium complex, generating water and nitrogen under 3 bar N₂O and 4 bar H₂ at 65°C for 48 hours. A TON of 417 was measured based upon the formation of water.

In this work the activity of the different Rh(I)Pt(II) complexes (10-14) was systematically tested for this reaction (figure 29). A solution of the catalyst in benzene or THF was pressurised with one bar N₂O and hydrogen. After stirring the reaction mixture for 22 hours at room temperature, the turnover number (TON) was determined by ²H NMR spectrum of the reaction solution using mesitylene as an internal standard (figure 30). The results of these experiments are listed in table 9. A control experiment without the presence of the catalyst was performed and showed no formation of H₂O.
**Figure 29.** The reactivity towards the hydrogenation of nitrous oxide is systematically tested for the synthesized heterobimetallic complexes 10-14 in different solvents at room temperature for 22 hours.

**Figure 30.** $^1$H NMR spectrum of reaction solution after the hydrogenation of nitrous oxide by 13. The amount of H$_2$O formed and the TON can be calculated, using mesitylene as an internal standard.
Table 9. Overview of the TONs based on the amount of H₂O formed after hydrogenation of nitrous oxide with complexes 10-14 in different solvents.

<table>
<thead>
<tr>
<th>Rh(I)Pt(II) catalyst</th>
<th>Solvent</th>
<th>TON based on H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>THF</td>
<td>11</td>
</tr>
<tr>
<td>11</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>12</td>
<td>THF</td>
<td>11</td>
</tr>
<tr>
<td>12</td>
<td>Benzene</td>
<td>47</td>
</tr>
<tr>
<td>13</td>
<td>THF</td>
<td>62</td>
</tr>
<tr>
<td>14</td>
<td>Benzene</td>
<td>6</td>
</tr>
</tbody>
</table>

Compound 11 was not able to perform the activation of N₂O with H₂, since the complex formed a highly reactive species under hydrogen atmosphere, which led to intramolecular follow-up reactions. Ultimately this resulted in decomposition of the compound. Since the non-coordinating counterion BAr⁷ increased the solubility in non-coordinating solvents considerably, the catalysis reactions using complexes 12 and 14 were performed in benzene. This enhanced the reactivity of the catalyst 12 and a TON of 54 was obtained. Furthermore, a side reaction was observed for 12 and 14 in benzene, which was the hydrogenation of benzene to cyclohexane. A TON of 9 was calculated for 12 and 14 for 14. This reaction seemed to compete with the hydrogenation of nitrous oxide and is quite remarkable, considering the fact that very mild reaction conditions were used.[59] As the other compounds were not soluble in benzene, the reactions were carried out in THF. Weakly coordinating triflate complex 13 was shown to be superior to all other complexes (TON: 62) 13. This could indicate that coordination of nitrous oxide to the complex is necessary. However, further studies are necessary to gain more insight in the activation of N₂O and H₂ on the complex. ³¹P{¹H} NMR of the reaction solution revealed that the complex was still intact after catalysis.

In an attempt to optimise the reaction conditions, the reaction time was prolonged while 13 was used as a catalyst (figure 31). This resulted in a TON of 430 based on the formation of H₂O, which is the best performing homogeneous catalyst for the activation of N₂O with H₂ at this moment to our knowledge, even under remarkably mild reaction conditions.
Figure 31. Homogeneously catalysed hydrogenation of nitrous oxide by complex 13 gave the highest TON for this reaction. This complex can be considered as the best performing homogeneous catalyst for this reaction at this moment.

Although no evidence is present yet, a catalytic cycle could be envisioned, as shown in figure 32. As in other similar studies on nitrous oxide activation, hydrogen activation is proposed to take place first to afford complex B. The bonding mode of hydrogen on the metal complex was not determined yet. This step is followed by an oxygen transfer from N₂O to give complex C, and the release of water and coordination of the ligand could regenerate A. However, thorough investigation on the catalytic mechanism is required to present a proposal of the genuine reaction sequence of the hydrogenation of nitrous oxide.

Figure 32. Envisioned catalytic mechanism for the hydrogenation of nitrous oxide by Rh(I)Pt(II) complexes investigated in this work.
2.5 Heterobimetallic Complexes – Other Group 9 Metals (Iridium & Cobalt)

Besides the synthesis and analysis of Rh(I)Pt(II) dinuclear compounds, the preparation of other group 9 metal bimetallic complexes was studied. First, the synthesis of iridium complexes using the $\text{TMS} \equiv \text{C} \text{TropPPh}_2$ ligand and different iridium dimer precursors were examined (figure 33). However, the synthesis of these complexes was not successful and $^{31}\text{P}(^1\text{H})$ NMR data showed multiple signals, which could not be explained, but indicated that iridium complexes were not formed.

Then, the preparation of cobalt (I) complexes was studied, but the hypothesized complexes were not obtained and NMR data gave no conclusion about the formed species (figure 34). It could be argued that formation of both complexes was not possible, since replacing the PPh$_3$ groups by the trop ligand is not favourable. The synthesis of homobimetallic iridium
PhC≡C-TropPPh₂ complexes was also investigated (figure 35). However, these complexes could not be synthesized successfully. A possible explanation for the unsuccessful preparation of the iridium TMS C≡C-TropPPh₂ and PhC≡C-TropPPh₂ complexes is that the insertion of iridium in this chelating ligand is sterically and electronically not feasible.

![Diagram](image1)

**Figure 34.** Attempted synthesis of homobimetallic cobalt(I) TMS C≡C-TropPPh₂ complexes.

![Diagram](image2)

**Figure 35.** Attempted synthesis of homobimetallic iridium(I) PhC≡C-TropPPh₂ complexes.
3. Conclusion & Outlook

In conclusion, six new heterobimetallic Rh(I)Pt(II) with a novel type of chelating ligand were synthesised and characterised. Several of these compounds were found to be active in the homogeneously catalysed hydrogenation of nitrous oxide under mild conditions, yielding water and nitrogen. The highest TON was achieved using catalyst 13, which is to our knowledge the best performing catalyst for this reaction at this moment. This reaction catalysed by a heterobimetallic Rh(I)Pt(II) complex offers a green, efficient and mild procedure for the removal of the greenhouse gas nitrous oxide.

Furthermore, NMR and XRD studies revealed that longer Rh-Pt bond lengths corresponded to a weaker Rh-Pt coupling in NMR, while a shorter metal-metal bond length is related to a stronger coupling. Additionally, a longer metal-metal bond was in agreement with a weaker $^2J_{PPt}$ measured in $^{31}P\{^1H\}$ NMR and vice versa, which implies that information about the Rh-Pt bond length could already be retrieved from an accessible $^{31}P\{^1H\}$ spectrum.

In general, a shorter rhodium-platinum bond was observed for the cationic bimetallic complexes compared to the neutral compounds. Exception from this effect was complex 14, where the longest Rh-Pt bond length was measured (2.788(4) Å), which could be explained by steric reasons upon formation of the dimer. Moreover, further studies on the metal-metal bond suggested that an electron rich Pt(II) is essential for the Rh-Pt bond, which indicated that the platinum most likely act as an electron donating supporting metalloligand.

Further research is required to find out whether a heterobimetallic system is superior to a homo(bi)metallic system in the activation of N$_2$O with H$_2$. This could then be the evidence that the presence of two different metal centres indeed enhances the catalytic activity. Moreover, additional studies are necessary to gain more insight in the catalytic mechanism of this reaction. Stoichiometric reactions of the complexes with N$_2$O, H$_2$, H$_2$O and N$_2$ could give insight into the activation of the substrates and the steps in the catalytic cycle. Additionally, the reaction set-up should be improved in order to determine the precise amount of gasses used and produced. Furthermore, the internal standard should be
calibrated. These actions should then lead to a more accurate determination of the TON based on the amount of H$_2$O, determined by $^1$H NMR and N$_2$, determined by GC. Besides, a homogeneity test is necessary in order to rule out the possibility that nanoparticles and not the heterobimetallic complex catalyse the hydrogenation of nitrous oxide. Scanning electron microscope (SEM) images of the reaction mixture after catalysis should give information about any nanoparticle formation.
4. Experimental Section

**General techniques:** All experiments were performed under an inert atmosphere of argon using standard Schlenk and glove-box (argon atmosphere) techniques unless otherwise specified. DCM, THF, toluene, diethyl ether, n-hexane and acetonitrile were purified using an Innovative Technologies PureSolv system. Deuterated solvents were purchased from Euriso-Top, degassed and distilled from the proper drying agent, and stored over molecular sieves.

**Chemicals:** Basic chemicals were ordered at ABCR, Acros, Aldrich, Fluka, Lancaster or STREM. The following organic compounds and metal precursors were prepared by literature methods: $^{\text{B}10}\text{TropOH}$,[60], $[\text{Rh}({\text{C}_2\text{H}_4}_2\text{Cl})_2]_2$,[61], $[\text{Me}_3\text{Pt}({\text{SMe}_2}_2)]_2$.[62]. $\text{PhC}≡\text{C-TropCl}$ 7 was synthesised according to earlier results of the host group.

**IR spectra** were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer. The absorption bands are described as follows: strong (s), very strong (vs), middle (m), weak (w), or broad (br).

**NMR** spectra were recorded on Bruker Avance 200, 300, 400 and 500 MHz spectrometers at 298 K (if not indicated differently). Chemical shifts (d) are reported in ppm. The absolute values of the coupling constants (J) are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q) and broad (br). Spectra were referenced with external standards: for $^1\text{H}$ and $^{13}\text{C}$ NMR with TMS, for $^{19}\text{F}$ NMR with CFCl₃, for $^{31}\text{P}$ NMR with $\text{H}_3\text{PO}_4$, for $^{103}\text{Rh}$ NMR with Rh(acac)₃ and for $^{195}\text{Pt}$ NMR with $\text{K}_2\text{PtCl}_6$. Quaternary carbons are indicated as $\text{C}_{\text{quat}}$, aromatic carbons as $\text{CH}_{\text{ar}}$ and protons as $\text{H}_{\text{ar}}$. The benzylic protons and carbon atoms in the central seven-membered ring are indicated as $\text{H}_{\text{benz}}$ and $\text{CH}_{\text{benz}}$, respectively.

**X-ray** Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil under inert atmosphere, transferred to a nylon loop and then transferred to the goniometer of a Bruker X8 APEX2 or D8-Venture diffractometer or on an Oxford Excalibur equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å). Preliminary data was collected to determine the crystal system. The space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) on OLEX2 completed by Fourier synthesis and refined by full-matrix least-squares procedures.
10,11-Di-(phenyl)acetylene-5H-dibenzo[a,d]cyclohepten-5-diphosphine. \( \text{PhC≡CTropPPh}_2 \) (8)

**MF:** \( \text{C}_{43}\text{H}_{29}\text{P} \)

**MW:** 576.66

\( \text{PhC≡CTropCl} \) (2.84 g, 6.64 mmol) was dissolved in toluene (30 mL) and \( \text{n-hexane} \) (15 mL) and diphenylphosine (1.2 mL, 1.2 g, 6.64 mmol) was added to the clear orange brown solution. The reaction mixture was stirred at 50°C over the weekend, while yellow precipitate was formed. The solution mixture was heated to reflux for 30 minutes and after it was cooled down degassed \( \text{Na}_2\text{CO}_3 \) (12 mL, 10% in \( \text{H}_2\text{O} \)) was added. The solution was heated at 50°C for 3 hours before it was heated under reflux for 30 minutes. After cooling down, the toluene phase was separated from the aqueous phase and this phase was extracted with toluene twice (2 x 10 mL). The solvent was evaporated and the brown/orange oil was treated with \( \text{n-hexane} \). The brown/orange powder was stirred vigorously in acetonitrile (24 mL) and a yellow powder was precipitated out of the solution. The product was filtrated, washed with hexane (12 mL) and dried under vacuum. The filtrate was placed in the freezer overnight and after filtration a second batch of the yellow product was obtained, which was dried under vacuum. Yield: 2.4 g (63%). Yellow crystals were obtained by slow diffusion of \( \text{n-hexane} \) in a solution of 8 in diethyl ether.

\(^1\text{H} \text{NMR (300 MHz, CDCl}_3\}): \delta \text{ (ppm) 4.70 (d, } J_{\text{PH}} = 5.7 \text{ Hz, 1 H, H}_{\text{benz}}, \) 6.89 (d, \( J_{\text{HH}} = 7.4 \text{ Hz, 2 H, H}_{\text{ar}}, \) 7.01 - 7.15 (m, 10 H, H_{ar}), 7.22 - 7.29 (m, 10 H, H_{ar}), 7.55 - 7.59 (m, 4H, H_{ar}), 7.82 (d, \( J_{\text{HH}} = 7.5 \text{ Hz, 2H, H}_{\text{ar}} \). – \(^{13}\text{C} \text{ NMR (75.5 MHz, CDCl}_3\)): 55.41 (d, \( J_{\text{CP}} = 21.32 \text{ Hz, 1 C, CH}_{\text{benz}}, \) 90.99 (s, 2 C, C≡CPh, \( \text{C}_{\text{quat}} \)), 96.73 (s, 2 C, C≡CPh, \( \text{C}_{\text{quat}} \)), 122.73 (s, 2 C, \( \text{C}_{\text{quat}} \)), 125.73 (d, \( J_{\text{CP}} = 1.4 \text{ Hz, 2 C, CH}_{\text{ar}}, \) 126.86 (d, \( J_{\text{CP}} = 6.5 \text{ Hz, 4 C, CH}_{\text{ar}}, \) 127.33 (s, 4 C, \( \text{CH}_{\text{ar}}, \) 127.43 (d, \( J_{\text{CP}} = 7.4 \text{ Hz, 2 C, } \text{CH}_{\text{ar}}, \) 128.10 (d, \( J_{\text{CP}} = 3.6 \text{ Hz, 2 C, CH}_{\text{ar}}, \) 128.15 (s, 4 C, \( \text{CH}_{\text{ar}}, \) 129.13 (d, \( J_{\text{CP}} = 1.7 \text{ Hz, 2 C, CH}_{\text{ar}}, \) 129.21 (d, \( J_{\text{CP}} = 6.3 \text{ Hz, 2 C, C}_{\text{olefintrrop}}, \) 130.74 (s, 4 C, \( \text{CH}_{\text{ar}}, \) 132.54 (d, \( J_{\text{CP}} = 19.7 \text{ Hz, 4 C, CH}_{\text{ar}}, \) 133.63 (d, \( J_{\text{CP}} = 4.4 \text{ Hz, 2 C, C}_{\text{quat}}, \) 137.05 (d, \( J_{\text{CP}} = 19.6 \text{ Hz, 2 C, } \text{C}_{\text{quat}}, \) 149.99 (d, \( J_{\text{CP}} = 8.9 \text{ Hz, 2 C, C}_{\text{quat}} \). – \(^{31}\text{P} \text{ NMR (121.5 MHz, CDCl}_3\)): \delta \text{ (ppm) -12.95 (s, 1 P, PPh}_2 \).
[**(PhC≡C-TropPPh₂)₂Rh₂(μ-Cl)₂**] (9)

MF: C₄₅H₅₆Cl₂P₂Rh₂

MW: 1430.04

[Rh₂(μ-Cl)₂(C₂H₄)₄] (344.9 mg, 0.89 mmol) and 8 (852.4 mg, 1.48 mmol) were combined in a flask and stirred in benzene (10 mL) for 3 hours at room temperature. The solution mixture was placed in a fridge overnight. The orange product was filtrated and washed with n-hexane (5 mL) and dried in vacuo. The filtrate was layered with n-hexane and a second batch of the product was obtained after recrystallization. Yield: 1000.6 mg (79%). Red crystals were attained by slow diffusion of n-hexane in a solution of 9 in dichloromethane.

¹H NMR (300 MHz, CD₃CN): δ (ppm) 5.10 (dd, ²Jₚₚ = 14.9 Hz, ²Jₕₘₜ = 1.7 Hz, 1 H, Hₜₚₑₙ), 7.03 (d, ³Jₕₜ = 7.4 Hz, 2 H, Hₜₚₑₙ), 7.23 – 7.30 (m, 10 H, Hₜₚₑₙ), 7.35 – 7.43 (m, 10 H, Hₜₚₑₙ), 7.63 – 7.71 (m, 4 H, Hₜₚₑₙ), 8.56 (d, ³Jₕₜ = 7.5 Hz, 2 H, Hₜₚₑₙ). – ¹³C NMR (75.5 MHz, CD₃CN): δ (ppm) 50.57 (d, ¹Jₚₚ = 26.1 Hz, 1 C, CHₜₚₑₙ), 54.13 (m, 2 C, Cₜₚₑₙ), 94.52 (s, 2 C, C≡CPh), 95.71 (s, 2 C, C≡CPh), 125.35 (s, 2 C, Cₜₚₑₙ), 128.27 (s, 2 C, CHₜₚₑₙ), 128.65 (d, ³Jₚₚ = 10.9 Hz, 4 C, CHₜₚₑₙ), 129.25 (s, 2 C, CHₜₚₑₙ), 129.78 (s, 4 C, CHₜₚₑₙ), 130.19 (s, 2 C, CHₜₚₑₙ), 130.31 (d, ⁴Jₚₚ = 6.4 Hz, 4 C, CHₜₚₑₙ), 131.10 (d, ¹Jₚₚ = 52.6 Hz, 2 C, Cₜₚₑₙ), 131.56 (d, ³Jₚₚ = 2.5 Hz, 2 C, CHₜₚₑₙ), 131.82 (s, 4 C, CHₜₚₑₙ), 135.20 (d, ²Jₚₚ = 9.7 Hz, 4 C, CHₜₚₑₙ), 136.91 (d, ³Jₚₚ = 4.5 Hz, 2 C, Cₜₚₑₙ), 137.80 (dd, ²Jₚₚ = 7.7 Hz, 2 C, Cₜₚₑₙ). – ³¹P NMR (121.5 MHz, CD₃CN): δ (ppm) -6926 (d, ¹Jₚₚₚ = 237.2 Hz). – IR (ATR): 3052 (w, vCH), 3017 (w, vCH), 2992 (w, vCH), 1479 (s), 1344(s), 1260 (m), 1097 (m), 1024 (m), 791 (m).

[[**(PhC≡C-TropPPh₂)₂Rh(Cl)Pt(CH₃)₂**]] (10)

MF: C₄₅H₅₅ClIPtRh

MW: 940.17

9 (500.0 mg, 0.35 mmol) and [[(Me)₂Pt(SMe₂)]₂] (241.1 mg, 0.42 mmol) were stirred in dichloromethane (20 mL) for 3 hours. After removal of the solvent the product was washed with n-hexane and dried in vacuo. Yield: 558.7 mg (85%). Red crystals were grown by slow diffusion of n-hexane in a solution of 10 in dichloromethane.

¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 1.46 (s, ²Jₚₚ = 92.4 Hz, 6 H, Pt(CH₃)₂), 4.92 (d, ²Jₚₚ = 14.4 Hz, 1 H, Hₜₚₑₙ), 7.04 (d, ³Jₕₜ = 7.1 Hz, 2 H, Hₜₚₑₙ), 7.19 – 7.42 (m, 10 H, Hₜₚₑₙ), 7.45 – 7.53 (m, 6 H,
H\textsubscript{ar}), 7.70 – 7.76 (m, 4 H, H\textsubscript{ar}), 7.90 – 7.93 (m, 4 H, H\textsubscript{ar}), 7.13 (d, \textsuperscript{3}J\textsubscript{HH} = 7.5 Hz, 2 H, H\textsubscript{ar}). \textsuperscript{13}C NMR (75.5 MHz, THF-d\textsubscript{8}): \(\delta\) (ppm) 12.08 (s, 2 C, Pt(CH\textsubscript{3})\textsubscript{2}), 40.13 (d, \textsuperscript{1}J\textsubscript{CRh} = 2.2 Hz, 1 C, Colefintrop), 40.31 (d, \textsuperscript{1}J\textsubscript{CRh} = 2.1 Hz, 1 C, Colefintrop), 49.52 (d, \textsuperscript{1}J\textsubscript{CP} = 27.2 Hz, 1 C, CH\textsubscript{benz}), 91.41 (s, 2 C, C\textequivCPh), 122.89 (s, 2 C, C\textsubscript{quat}), 126.73 (s, 2 C, C\textequivCPh), 126.96 (s, 2 C, CH\textsubscript{ar}), 127.15 (d, \textsuperscript{3}J\textsubscript{CP} = 10.4 Hz, 4 C, CH\textsubscript{ar}), 129.25 (s, 2 C, CH\textsubscript{ar}), 128.26 (s, 4 C, CH\textsubscript{ar}), 128.70 (s, 2 C, CH\textsubscript{ar}), 129.11 (d, \textsuperscript{4}J\textsubscript{CP} = 6.5 Hz, 2 C, CH\textsubscript{ar}), 129.79 (d, \textsuperscript{4}J\textsubscript{CP} = 2.4 Hz, 4 C, CH\textsubscript{ar}), 130.53 (d, \textsuperscript{1}J\textsubscript{CP} = 46.8 Hz, 2 C, C\textsubscript{quat}), 131.56 (d, \textsuperscript{3}J\textsubscript{CP} = 2.5 Hz, 2 C, CH\textsubscript{ar}), 131.52 (s, 4 C, CH\textsubscript{ar}), 133.58 (d, \textsuperscript{2}J\textsubscript{CP} = 10.2 Hz, 4 C, CH\textsubscript{ar}), 136.32 (d, \textsuperscript{3}J\textsubscript{CP} = 7.2 Hz, 2 C, C\textsubscript{quat}), 135.39 (m, 2 C, C\textsubscript{quat}). \textsuperscript{31}P NMR (121.5 MHz, THF-d\textsubscript{8}): \(\delta\) (ppm) -89.88 (d, \textsuperscript{1}J\textsubscript{PRh} = 217.5 Hz, \textsuperscript{2}J\textsubscript{PPt} = 519.9 Hz, 1 P, tropP). \textsuperscript{103}Rh NMR (15.8 MHz, THF-d\textsubscript{8}): \(\delta\) (ppm) -7045 (d, \textsuperscript{1}J\textsubscript{PRh} = 215.2 Hz). \textsuperscript{195}Pt NMR (64.4 MHz, THF-d\textsubscript{8}): \(\delta\) (ppm) -3274 (dd, \textsuperscript{2}J\textsubscript{PPt} = 530.1 Hz, \textsuperscript{1}J\textsubscript{PRh} = 83.4 Hz)

\[[\text{PhC\textsubscript{c}TropPh\textsubscript{2}}]\text{Rh(CH\textsubscript{3}CN)Pt(CH\textsubscript{3})\textsubscript{2}}]\text{PF\textsubscript{6}}\] (11):

MF: C\textsubscript{44}H\textsubscript{38}F\textsubscript{6}NP\textsubscript{2}PtRh

MW: 1090.73

9 (100 mg, 0.07 mmol) and [[(Me\textsubscript{2})\textsubscript{2}Pt(SMe\textsubscript{2})]\textsubscript{2}] (40.2 mg, 0.07 mmol) were combined in a flask and flushed with dichloromethane (5 mL). The reaction mixture was stirred for one hour at room temperature, before a solution of TiPF\textsubscript{6} (48.9 mg, 0.14 mmol) in acetonitrile (5 mL) was added. After one hour the mixture was filtered over Celite and washed with dichloromethane (5 mL). The solvent was evaporated and the red product was washed with n-hexane (10 mL) and dried in vacuo. Yield: 96.6 mg (63%). Red crystals were obtained by slow diffusion of n-hexane in a solution of 11 in dichloromethane.

\textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) (ppm) 1.35 (s, \textsuperscript{2}J\textsubscript{PHH} = 92.4 Hz, 6 H, Pt(CH\textsubscript{3})\textsubscript{2}), 2.14 (s, 3 H, CH\textsubscript{3}CN), 4.98 (dd, \textsuperscript{2}J\textsubscript{PH} = 15.4 Hz, \textsuperscript{2}J\textsubscript{HH} = 2.3 Hz, 1 H, H\textsubscript{benz}), 7.13 (d, \textsuperscript{3}J\textsubscript{HH} = 7.2 Hz, 2 H, H\textsubscript{ar}), 7.29 – 7.40 (m, 10 H, H\textsubscript{ar}), 7.46 – 7.62 (m, 10 H, H\textsubscript{ar}), 7.89 - 7.93 (m, 4 H, H\textsubscript{ar}), 8.14 (d, \textsuperscript{3}J\textsubscript{HH} = 7.3 Hz, 2 H, H\textsubscript{ar}). \textsuperscript{13}C NMR (75.5 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) (ppm) 3.40 (s, 1 C, CH\textsubscript{3}CN), 10.09 (s, 2 C, Pt(CH\textsubscript{3})\textsubscript{2}), 50.43 (d, \textsuperscript{1}J\textsubscript{CP} = 27.2 Hz, 1 C, CH\textsubscript{benz}), 71.79 (d, \textsuperscript{1}J\textsubscript{HH} = 4.0 Hz, 2 C, Colefintrop), 89.56 (s, 2 C, C\textequivCPh), 95.77 (s, 2 C, C\textequivCPh), 121.84 (s, 2 C, C\textsubscript{quat}), 128.38 (s, 2 C, CH\textsubscript{ar}), 128.88 (s, 1 C, CH\textsubscript{3}CN), 129.06 (d, \textsuperscript{1}J\textsubscript{CP} = 47.1 Hz, 2 C, C\textsubscript{quat}), 129.37 (d, \textsuperscript{3}J\textsubscript{CP} = 10.5 Hz, 4 C, CH\textsubscript{ar}), 129.54 (s, 4 C, CH\textsubscript{ar}), 129.91 (s, 2 C, CH\textsubscript{ar}), 130.15 (d, \textsuperscript{4}J\textsubscript{CP} = 6.7 Hz, 2 C, CH\textsubscript{ar}), 131.13 (s, 4 C, CH\textsubscript{ar}), 132.34 (d, \textsuperscript{3}J\textsubscript{CP} = 2.6 Hz, 2 C, CH\textsubscript{ar}), 132.82 (s, 4 C, CH\textsubscript{ar}), 132.97 (d, \textsuperscript{3}J\textsubscript{CP} = 7.2 Hz, 2 C, C\textsubscript{quat}), 133.35 (d,
$^2J_{CP} = 10.2$ Hz, 4 C, CH$_{ar}$), 135.70 (m, 2 C, C$_{quat}$). – $^{31}$P NMR (121.5 MHz, CD$_2$Cl$_2$): δ (ppm) 91.40 (d, $^1J_{PPH} = 197.9$ Hz, $^2J_{PPP} = 537.4$ Hz, 1 P, tropP). -144.45 (hept, $^1J_{PP} = 708.5$ Hz, 1 P, PF$_6$). – $^{19}$F NMR (188.3 MHz, CD$_2$Cl$_2$): δ (ppm) -72.92 (d, $^1J_{FP} = 710$ Hz, 1 P, PF$_6$). – $^{103}$Rh NMR (15.8 MHz, CD$_2$Cl$_2$): δ (ppm) -7207 (d, $^1J_{PRH} = 196.2$ Hz). – $^{195}$Pt NMR (64.4 MHz, CD$_2$Cl$_2$): δ (ppm) -3223 (dd, $^2J_{PP} = 546.7$ Hz, $^1J_{PP} = 104.1$ Hz). – IR (ATR): 3052 (w, ν$_{CH}$), 2959 (m, ν$_{CH}$), 2900 (w, ν$_{CH}$), 1480 (s), 1434(s), 1260 (m), 1095 (m), 1024 (m), 791 (m).

$$[(^9$$H$_{9}$$C$_{9}$$C$_{9}$$TROP$P$_{P}$)Rh(C$_{9}$H$_{10}$CN)Pt(CH$_{3}$)$_{2}$]BAr$_{F}$ (12)

MF: C$_{79}$H$_{50}$BF$_{24}$NPPtRh

MW: 1808.98

9 (100.0 mg, 0.07 mmol) and [(Me)$_2$Pt(SMe)$_2$)$_2$ (36.2 mg, 0.06 mmol) were combined in a flask and flushed with dichloromethane (5 mL). The reaction mixture was stirred for an hour at room temperature, before a solution of NaBAr$_F$ (123.9 mg, 0.14 mmol) in acetonitrile (5 mL) was added. After one hour the mixture was filtered over Celite and washed with dichloromethane (5 mL). The solvent was evaporated and the red product was washed with n-hexane (10 mL) and dried in vacuo. Yield: 145.9 mg (58%). Red crystals were obtained by slow diffusion of n-hexane in a solution of 12 in toluene.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): δ (ppm) 1.35 (s, $^2J_{PH} = 87.9$ Hz, 6H, Pt(CH$_3$)$_2$), 2.12 (s, 3H, CH$_3$CN), 4.94 (dd, $^2J_{PH} = 15.3$ Hz, $^2J_{RHH} = 2.4$ Hz, 1 H, H$_{benz}$), 7.10 (d, $^3J_{HH} = 7.3$ Hz, 2 H, H$_{ar}$), 7.29 – 7.42 (m, 10 H, H$_{ar}$), 7.42 – 7.52 (m, 6 H, H$_{ar}$), 7.56 (br s, 4 H, BAr$_F$), 7.58 – 7.67 (m, 4 H, H$_{ar}$), 7.72 (br s, 8 H, BAr$_F$), 7.88 – 7.95 (m, 4 H, H$_{ar}$), 8.15 (d, $^3J_{HH} = 7.6$ Hz, 2 H, H$_{ar}$). – $^{13}$C NMR (75.5 MHz, CD$_2$Cl$_2$): δ (ppm) 3.29 (s, 1 C, CH$_3$CN), 9.97 (s, 2 C, Pt(CH$_3$)$_2$), 45.63 (d, 2 C, C$_{olefintrip}$), 50.80 (d, $^1J_{CP} = 27.3$ Hz, 1 C, CH$_{benz}$), 95.93 (s, 2 C, C≡CPh), 117.86 (s, BAr$_F$), 121.71 (s, 2 C, C$_{quat}$), 123.17 (s, 2 C, C≡CPh), 126.78 (s, 1 C, CH$_3$CN), 128.38 (s, 2 C, CH$_{ar}$), 128.66 (q, BAr$_F$), 128.70 (d, $^1J_{CP} = 39.7$ Hz, 2 C, C$_{quat}$), 129.34 (d, $^3J_{CP} = 10.6$ Hz, 4 C, CH$_{ar}$), 129.55 (s, 4 C, CH$_{ar}$), 129.99 (s, 2 C, CH$_{ar}$), 130.25 (d, $^4J_{CP} = 6.7$ Hz, 2 C, CH$_{ar}$), 130.89 (q, BAr$_F$), 131.22 (s, 4 C, CH$_{ar}$), 132.35 (d, 2 C, CH$_{ar}$), 132.81 (s, 4 C, CH$_{ar}$), 132.94 (d, $^3J_{CP} = 8.6$ Hz, 2 C, C$_{quat}$), 133.29 (d, $^2J_{CP} = 10.5$ Hz, 4 C, CH$_{ar}$), 135.18 (s, BAr$_F$), 135.50 (d, 2 C, C$_{quat}$), 162.13 (q, $^1J_{BC} = 49.7$ Hz, BAr$_F$). – $^{31}$P NMR (121.5 MHz, C$_6$D$_6$): δ (ppm) 91.26 (d, $^1J_{PRH} = 197.9$ Hz, $^2J_{PP} = 537.9$ Hz, 1 P, tropP). – $^{19}$F NMR (188.3 MHz, C$_6$D$_6$): δ (ppm) -62.83 (s, 24 F, BAr$_F$). – $^{11}$B NMR (C$_6$D$_6$): δ (ppm) -6.60 (s,
$^{103}$Rh NMR (15.8 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) -7304 (d, $^1$J$_{RhH}$ = 200.3 Hz). $^{195}$Pt NMR (64.4 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) -3196 (dd, $^2$J$_{PtP}$ = 538.0 Hz, $^1$J$_{PtRh}$ = 109.3 Hz).

$[^{\text{PhC≡C-TropPPh}}_2]Rh(OTf)Pt(CH_3)_2$ \((13)\)
MF: C$_{47}$H$_{39}$F$_3$O$_3$PPtRhS

MW: 1069.84

10 (50.0 mg, 0.053 mmol) was stirred with AgOTf (13.7 mg, 0.053 mmol) in THF (3 mL) for 3 hours. The precipitate of silver (I) chloride was removed by filtration over Celite. The filtrate solution was layered with n-hexane and after recrystallization orange crystals were obtained. The solution was removed and the product was washed with n-hexane and dried in vacuo. Yield: 37.0 mg (69 %).

$^1$H NMR (300 MHz, THF-d$_8$): $\delta$ (ppm) 1.47 (d, $^2$J$_{PH}$ = 90.1 Hz, 6 H, Pt(CH$_3$)$_2$), 5.14 (d, $^2$J$_{PH}$ = 14.3 Hz, 1 H, H$_{benz}$), 7.12 (d, $^3$J$_{HH}$ = 7.6 Hz, 2 H, H$_{ar}$), 7.19 – 7.39 (m, 10 H, H$_{ar}$), 7.50 – 7.57 (m, 6 H, H$_{ar}$), 7.69 – 7.73 (m, 4 H, H$_{ar}$), 7.96 – 8.02 (m, 4 H, H$_{ar}$), 8.22 (d, $^3$J$_{HH}$ = 7.8 Hz, 2 H, H$_{ar}$). $^{13}$C NMR (75.5 MHz, THF-d$_8$): $\delta$ (ppm) 10.11 (s, 2 C, Pt(CH$_3$)$_2$), 45.27 (d, $^1$J$_{CRh}$ = 2.1 Hz, 2 C, C$_{olefin-trop}$), 50.41 (d, $^1$J$_{CP}$ = 28.9 Hz, 1 C, CH$_{benz}$), 91.95 (s, 2 C, C≡CPh), 94.66 (s, 2 C, C≡CPh), 123.71 (s, 2 C, C$_{quat}$), 128.48 (s, 2 C, CH$_{ar}$), 128.67 (s, 2 C, CH$_{ar}$), 128.95 (d, $^3$J$_{CP}$ = 10.4 Hz, 4 C, CH$_{ar}$), 128.99 (d, $^4$J$_{CP}$ = 3.0 Hz, 4 C, CH$_{ar}$), 129.26 (s, 2 C, CH$_{ar}$), 129.83 (d, $^1$J$_{CP}$ = 46.6 Hz, 2 C, C$_{quat}$), 129.97 (s, 2 C, CH$_{ar}$), 130.83 (d, $^4$J$_{CP}$ = 6.4 Hz, 2 C, CH$_{ar}$), 130.92 (s, 2 C, CH$_{ar}$), 131.96 (d, $^3$J$_{CP}$ = 2.7 Hz, 2 C, CH$_{ar}$), 133.31 (s, 4 C, CH$_{ar}$), 134.95 (d, $^2$J$_{CP}$ = 10.1 Hz, 4 C, CH$_{ar}$), 137.19 (d, $^2$J$_{PH}$ = 2.8 Hz, 2 C, C$_{quat}$). $^{31}$P NMR (121.5 MHz, THF-d$_8$): $\delta$ (ppm) 91.60 (d, $^1$J$_{PRh}$ = 211.8 Hz, $^2$J$_{Ppt}$ = 519.0 Hz, 1 P, tropP). $^{19}$F NMR (188.3 MHz, THF-d$_8$): $\delta$ (ppm) -78.4 (s, OTf). $^{103}$Rh NMR (15.8 MHz, THF-d$_8$): $\delta$ (ppm) -6737 (d, $^1$J$_{PRh}$ = 210.6 Hz). $^{195}$Pt NMR (64.4 MHz, THF-d$_8$): $\delta$ (ppm) -3263 (dd, $^2$J$_{Ppt}$ = 519.4 Hz, $^1$J$_{PtRh}$ = 94.5 Hz).

$[^{\text{PhC≡C-TropPPh}}_2]Rh_2Pt_2((CH_3)_2(\mu-Cl))BAr^F$ \((14)\)
MF: C$_{122}$H$_{82}$BClF$_{24}$P$_2$Pt$_2$Rh$_2$

MW: 2708.09

7 (100.0 mg, 0.11 mmol) was stirred with NaBAr$^F$ (47.1 mg, 0.053 mmol) in THF (5 mL). After 1 hour, the reaction mixture was filtrated over Celite. The solvent was removed and the
product was washed with n-hexane and dried under vacuum. Yield: 79.9 mg (38%). Red crystals were grown by slow diffusion of n-hexane in a solution of 9 in toluene.

$^1$H NMR (300 MHz, THF-d$_8$): δ (ppm) 1.47 (s, 6 H, Pt(CH$_3$)$_2$), 5.28 (d, $^2$J$_{PH}$ = 14.6 Hz, 1 H, H$_{benz}$), 7.12 – 7.38 (m, 12 H, H$_{ar}$), 7.48 – 7.53 (m, 6 H, H$_{ar}$), 7.57 (br s, 4 H, BAr$^f$), 7.79 (br s, 8 H, BAr$^f$), 7.80 – 7.85 (m, 4 H, H$_{ar}$), 7.92 – 8.00 (m, 4 H, H$_{ar}$), 8.16 (d, $^3$J$_{HH}$ = 7.8 Hz, 2 H, H$_{ar}$). – $^{13}$C NMR (75.5 MHz, THF-d$_8$): δ (ppm) 10.12 (s, 2 C, Pt(CH$_3$)$_2$), 48.09 (d, 2 C, C$_{olefin trop}$), 49.48 (d, $^1$J$_{CP}$ = 27.7 Hz, 1 C, CH$_{benz}$), 91.54 (s, 2 C, C≡CPh), 92.49 (s, 2 C, C≡CPh), 117.20 (s, BAr$^f$), 121.29 (s, 2 C, C$_{quat}$), 125.62 (s, 2 C, CH$_{ar}$), 127.50 (d, $^1$J$_{CP}$ = 38.7 Hz, 2 C, C$_{quat}$), 127.85 (d, $^3$J$_{CP}$ = 10.9 Hz, 4 C, CH$_{ar}$), 129.55 (s, 4 C, CH$_{ar}$), 128.77 (s, 4 C, CH$_{ar}$), 128.92 (q, BAr$^f$), 129.17 (q, BAr$^f$), 129.48 (s, 4 C, CH$_{ar}$), 129.56 (d, $^1$J$_{CP}$ = 6.8 Hz, 2 C, CH$_{ar}$), 130.60 (d, 2 C, CH$_{ar}$), 132.02 (s, 4 C, CH$_{ar}$), 133.79 (d, $^2$J$_{CP}$ = 10.0 Hz, 4 C, CH$_{ar}$), 132.24 (d, $^3$J$_{CP}$ = 4.6 Hz, 2 C, C$_{quat}$), 134.62 (s, BAr$^f$), 135.58 (d, $^3$J$_{CP}$ = 2.7 Hz, 2 C, C$_{quat}$), 161.84 (q, $^1$J$_{BC}$ = 49.6 Hz, BAr$^f$). – $^{31}$P-NMR (121.5 MHz, THF-d$_8$): δ (ppm) 88.76 (d, $^1$J$_{PPh}$ = 215.6 Hz, $^2$J$_{PP}$ = 505.7 Hz, 1 P, tropP). – $^{19}$F-NMR (188.3 MHz, THF-d$_8$): δ (ppm) -62.87 (s, 24 F, BAr$^f$). – $^{11}$B NMR (THF-d$_8$): δ (ppm) -6.46 (s, 1B, BAr$^f$). – $^{103}$Rh NMR (15.8 MHz, THF-d$_8$): δ (ppm) -7491 (d, $^1$J$_{PPh}$ = 209.1 Hz). – $^{195}$Pt NMR (64.4 MHz, THF-d$_8$): δ (ppm) -3321 (br).

$$\left[\left(\text{PhCe}-\text{TropPPh$_2$}\right)\text{Rh$_2$Pt$_2$}(\text{CH$_3$)$_2$}2(\mu-\text{CITICI})\right]\text{BAr}^f (15)$$

MF: C$_{122}$H$_{82}$BCl$_2$F$_{24}$P$_2$Pt$_2$Rh$_2$Ti
MW: 2947.94

7 (8.8 mg, 0.0094 mmol) and TlBAr$^f$ (10.3 mg, 0.0096 mmol) were combined in 1 mL benzene and stirred for 1 hour. The reaction mixture was filtered over Celite and the filtrate was layered with n-hexane. Slow diffusion resulted in crystallisation of the orange product.

$^1$H NMR (300 MHz, THF-d$_8$): δ (ppm) 1.50 (s, 6 H, Pt(CH$_3$)$_2$), 5.28 (d, $^2$J$_{PH}$ = 14.6 Hz, 1 H, H$_{benz}$), 7.17 (d, $^3$J$_{HH}$ = 6.3 Hz, 2 H, H$_{ar}$), 7.19 – 7.41 (m, 10 H, H$_{ar}$), 7.48 – 7.51 (m, 6 H, H$_{ar}$), 7.57 (br s, 4 H, BAr$^f$), 7.78 (br s, 8 H, BAr$^f$), 7.83 – 7.91 (m, 4 H, H$_{ar}$), 7.95 (m, 4 H, H$_{ar}$), 8.14 (d, $^3$J$_{HH}$ = 7.8 Hz, 2 H, H$_{ar}$). – $^{31}$P NMR (121.5 MHz, THF-d$_8$): δ (ppm) 90.12 (d, $^1$J$_{PPh}$ = 218.9 Hz, $^2$J$_{PP}$ = 513.6 Hz, 1 P, tropP). $^{13}$C, $^{195}$Pt and $^{103}$Rh NMR were not measured, since there was not enough compound to measure a decent spectrum.
Catalytic hydrogenation of N₂O

In a screw cap Schlenck were added compound X, mesitylene and THF/benzene (2 mL) in the quantities described in table x. After degassing the solution by three freeze pump thaw cycles the flask was charged with 1 bar N₂O. The reaction solution was frozen and 1 bar of H₂ was added. After stirring for 22 hours at room temperature the solution was degassed and the amount H₂O and TON were determined by ¹H NMR of the reaction solution using mesitylene as internal standard (table 10).

Table 10. Quantities of complex 10-14 and mesitylene used in the catalytic hydrogenation of nitrous oxide in different solvents. The amount of H₂O and TON were determined using mesitylene as internal standard.

<table>
<thead>
<tr>
<th>Compound X</th>
<th>Quantity compound (mg, μmol)</th>
<th>Quantity mesitylene (mg, μmol)</th>
<th>Quantity H₂O (μmol)</th>
<th>TON based on H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 in THF</td>
<td>7.5 mg, 8.0 μmol</td>
<td>8.4 mg, 69.9 μmol</td>
<td>85.2 μmol</td>
<td>11</td>
</tr>
<tr>
<td>11 in THF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>No reaction</td>
</tr>
<tr>
<td>12 in THF</td>
<td>11.4 mg, 6.3 μmol</td>
<td>7.8 mg, 64.9 μmol</td>
<td>65.2 μmol</td>
<td>11</td>
</tr>
<tr>
<td>12 in Benzene</td>
<td>10.5 mg, 5.8 μmol</td>
<td>8.5 mg, 70.7 μmol</td>
<td>269.2 μmol</td>
<td>47</td>
</tr>
<tr>
<td>13 in THF</td>
<td>8.1 mg, 7.6 μmol</td>
<td>10.6 mg, 88.2 μmol</td>
<td>464.2 μmol</td>
<td>62</td>
</tr>
<tr>
<td>14 in Benzene</td>
<td>8.7 mg, 3.2 μmol</td>
<td>9.6 mg, 79.9 μmol</td>
<td>21.0 μmol</td>
<td>6</td>
</tr>
<tr>
<td>13 in THF, 3 days</td>
<td>5.2 mg, 4.9 μmol</td>
<td>10.0 mg, 83.2 μmol</td>
<td>2080.0 μmol</td>
<td>430</td>
</tr>
</tbody>
</table>
5. Appendix

List of Abbreviations

ACN  Acetonitrile
BARF  Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
Cu-ZSM-5  Copper Zeolite Socony Mobil–5
DCM  Dichloromethane
DSC  Differential Scanning Calorimetry
HMQC  Heteronuclear multiple-quantum coherence
Me  Methyl
n-Hex  n-Hexane
NMR  Nuclear magnetic resonance
OTf  Triflate
Ph  Phenyl
Qimid  Quasi multiple ion detection
RT  Room temperature
SEM  Scanning electron microscope
TGA  Thermogravimetric analysis
THF  Tetrahydrofuran
TMS  Trimethylsilyl
Tol  Toluene
TON  Turnover number
Trop  5-dibenzosuberene
XRD  X-ray diffraction
6. References


