Activation of dihydrogen by rhutenium, platinum and palladium complexes
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Chapter 3

Heterolytic Activation of Dihydrogen with Platinum (II) Diphosphine Complexes

Abstract

Wide bite angle diphosphine ligands were used to prepare [(diphosphine)Pt(PPh$_2$Py)]$^{2+}$ complexes (1a-d). Except for the ligand with the largest bite angle, the pyridylphosphine coordinates in a bidentate mode leading to bischelate complexes. In the case of Xantphos (9,9-dimethyl-4,5-bis(diphenylphosphino)-xanthene, $\beta_n = 111^\circ$) two types of complexes are formed, in which the pyridylphosphine ligand coordinates in a mono or bidentate fashion, respectively. The crystal structures of three of the complexes was determined. The X-ray crystal structure of [(Xantphos)Pt(PPh$_2$Py)]$^{2+}$ shows that Xantphos coordinates in a tridentate P,O,P fashion. Under dihydrogen pressure, the pyridyl moiety in complexes 1a-d can de-coordinate to provide a vacant coordination site at the metal center. Furthermore it can act as an internal base to assist the heterolytic splitting of dihydrogen. The reaction yields a platinum hydride complex with a protonated pyridine moiety in close proximity to one another. The structure as well as the reactivity of compounds 1a-d towards dihydrogen is governed by the steric requirements of the diphosphines. The crystal structure of [(dppl)PtH(PPh$_2$PyH)](OTf)$_2$ (2a) has been determined. Additionally, the complexes [(diphosphine)Pt(NH$_2$(CH$_2$)$_n$Py))]$^{2+}$ (n= 0,1) (3a, 3d) containing an aminopyridine ligand have been prepared. The heterolytic splitting of dihydrogen assisted by compounds 3a and 3d yields hydride bridged dimers [Pt$_2$H$_3$(diphosphine)$_2$][OTf]$_2$ (5d) and the corresponding ammonium salt.
Introduction

The activation of HX molecules (X=H, SiR$_3$) by transition metal complexes is a key step in the mechanism of many catalytic reactions.$^{1-7}$ It can either occur via oxidative addition, for example in catalytic hydrogenation, hydroformylation or hydrosilylation, or via heterolytic splitting as in processes such as hydrogen metabolism,$^{8-11}$ nitrogen fixation$^{12}$ or D$_2$/H$^-$/exchange.$^{13-16}$

![Figure 3-1. Two pathways for the activation of dihydrogen.](image)

The heterolytic activation of HX is usually achieved using metal centers in medium or high oxidation states and requires the assistance of a Brønsted base. Some ligands act as intramolecular bases to assist the splitting of H$_2$. This has been reported for complexes containing sulfides,$^{17}$ thiolates,$^{13}$ amines,$^{18}$ or nitrosyl groups.$^{19}$ During the cleavage of the HX bond the main interaction involved is σ donation from HX to an empty d orbital of the metal. Hydride and/or dihydrogen species are often involved either as precursors or as intermediates in the reaction. It has been proposed that heterolytic cleavage can occur by prior coordination of molecular hydrogen, followed by deprotonation of the corresponding η$^2$-H$_2$ complex.$^{20-24}$ The enhancement of the acidity of dihydrogen upon coordination to a metal ion is a well established fact.$^{25}$ The vast majority of η$^2$-H$_2$ complexes reported to date are d$^6$ octahedral complexes. Dihydrogen complexes with metals in a d$^8$ electron configuration are still relatively rare.$^{26,27}$ Recently Stahl et al. observed the activation of a coordinated dihydrogen molecule in the Pt(II) complex trans[($\text{PCy}_3$)$_2$PtR(η$^2$-H$_2$)]$^+$ (R= CH$_3$, Ph). This complex easily eliminates either methane or benzene to form trans[($\text{PCy}_3$)$_2$Pt(H)(S)]$^+$, (S= solvent).$^{26}$
Another important interaction that sometimes occurs prior to the H-X bond splitting is a proton-hydride interaction, or dihydrogen bonding.\textsuperscript{28,29} The interaction between a weakly acidic proton (NH or OH) and a transition metal hydride has a substantial strength (3-7 Kcal mol\textsuperscript{-1}), which lies in the range observed in conventional hydrogen bonds. Therefore it can influence the structure and reactivity of metal hydride complexes. It has been shown that dihydrogen bonded adducts can be formed prior to proton transfer from HA to a metal hydride to form a dihydrogen complex. This reaction is the reverse of the heterolytic splitting of H\textsubscript{2}; thus complexes exhibiting H---H interactions can be considered as intermediates in the activation process.\textsuperscript{30-32}

The ancillary ligands (usually phosphines) have an important influence on dihydrogen bond formation. Morris \textit{et al.} compared the strength of intramolecular IrH---H bonds in complexes with PCy\textsubscript{3} and PPh\textsubscript{3}. The stronger dihydrogen bond was formed in complexes containing PCy\textsubscript{3}, which increases the basicity of the hydride.\textsuperscript{33} Crabtree, Eisenstein \textit{et al.}\textsuperscript{18} found that while PPh\textsubscript{3} favors the heterolytic splitting of dihydrogen by iridium complexes (assisted by a pendant amino group), more basic alkylphosphines form an \eta\textsuperscript{2}-H\textsubscript{2} complex. When two different sites are available for hydrogen bonding, the steric bulk of the phosphine can affect the regioselectivity of the dihydrogen bond. Berke \textit{et al.} studied the interaction of [ReH\textsubscript{2}(NO)(CO)L\textsubscript{2}] with fluoroalcohols and observed that when L= PMe\textsubscript{3} the proton donor interacted mainly with one of the hydrides. As the steric bulk of the phosphine was increased (L=\textsuperscript{3}P\textsubscript{3}Pr\textsubscript{3}) the interaction was switched to the NO ligand to form a conventional NO---HA hydrogen bond.\textsuperscript{34,35} DuBois \textit{et al.} investigated the effect of the chelate bite size in the reactivity of a series of palladium triphosphine complexes. They observed that only the compounds with the widest bite angle ligands were able to react with dihydrogen to form a hydride complex. From theoretical calculations on [Pd(PH\textsubscript{3})\textsubscript{2}H]\textsuperscript{+} they concluded that with increasing P-M-P angle, the energy of the LUMO of the complex decreases; thus facilitating electron transfer to this orbital. Therefore they proposed that wider bite angles would promote heterolytic cleavage of dihydrogen.\textsuperscript{36}

In our research group, a series of wide bite angle diphosphine ligands has been developed. Much effort has been made towards the understanding of the influence of diphosphine ligands on the reactivity and catalytic performance of transition metal complexes.\textsuperscript{37-39} We are now interested in the reactivity of platinum complexes with wide bite angle diphosphine ligands towards the heterolytic activation of dihydrogen. In this chapter, the synthesis and characterization of [Pt(diphosphine)(PPh\textsubscript{2}Py)]\textsuperscript{2+} complexes is described. The
hemilabile diphenyl-2-pyridylphosphine ligand is able to provide an empty coordination site by de-coordination of the pyridyl moiety and at the same time acts as an intramolecular base to assist the heterolytic cleavage of H₂. The resulting complexes contain both a hydride and a protonated pyridyl moiety in close proximity to one another, which makes them potential candidates for dihydrogen bonding.

Results and discussion

Synthesis of [(diphosphine)Pt(PPh₂Py)]²⁺ complexes. (1a-d)

Chart 3-1 shows the diphosphine ligands used for this study, together with their calculated, so-called natural bite angles (Bₙ), as defined by Casey et al. It has been shown in our group that there is a significant influence of the bite angle of diphosphine ligands on reactions such as rhodium catalyzed hydroformylation, palladium catalyzed allylic alkylation and cross-coupling reactions, and nickel catalyzed hydrocyanation. Recently van Haaren et al. found that an increase in the bite angle results in larger cone angles of the ligands, which leads to an increased steric interaction of the diphosphine with the other ligands in the coordination sphere of the metal.

The Xantphos-type diphosphines can form either cis or trans complexes depending on the co-ligands present. Xantphos can also act as a tridentate P,O,P ligand.

The dicationic Pt complexes containing a chelating pyridylphosphine ligand were prepared by reaction of the corresponding (diphosphine)PtCl₂ with silver triflate followed by addition of the pyridylphosphine ligand (scheme 3-1). When silver triflate is added to a
CH₂Cl₂ solution containing the dichloride precursor, the color changes from colorless or pale yellow, to bright yellow or red (dppf). After a few minutes precipitation of AgCl is observed. Upon addition of the diphenyl-2-pyridylphosphine, the color changes immediately to pale yellow (orange for dppf).

![Scheme 3-1. Synthesis of complexes 1a-d. Phenyl groups on phosphorous atoms have been omitted for clarity, P= PPh₂](image)

Complexes 1a-d were characterized in solution by multinuclear NMR spectroscopy. ³¹P NMR spectroscopic data are summarized in Table 3-1. The ³¹P{¹H} NMR spectra display an AMX spin system (fig. 3-2) for the cis isomer and an A₂X system for the trans isomer. For complexes 1a-c only the cis isomer was observed, whereas for complex 1d containing the Xantphos ligand, a mixture of the cis and trans isomers was obtained. The AMX spin system is consistent with a structure in which the diphosphine is coordinated in a cis fashion and the pyridylphosphine acts as a chelating ligand. Bidentate coordination of the PPh₂Py ligand is confirmed by the large up-field shift of PX which show resonances between δ = −38 and δ = −40 ppm. The value of the P-Pt coupling constant (= 2000 Hz) is small compared to the values observed for the other two phosphorus nuclei. Both the chemical shift and the JPX-Pt coupling are characteristic of a strained four-membered ring.⁵⁰,⁵¹

![Figure 3-2. ³¹P{¹H} NMR spectrum of 1b.](image)
The platinum-phosphorus coupling constant for the phosphorus *trans* to the pyridine nitrogen \((J_{PM,P})\) is significantly larger than that for the phosphorus *trans* to another phosphorus atom \((J_{PA,P})\), which is a better \(\pi\)-acceptor.

The \(^{31}\)P spectrum of \(1d\) displays a triplet \((P_A)\) and a doublet \((P_X)\) with an intensity ratio of 2:1, in addition to the AMX system described. This system corresponds to the *trans* isomer of \(1d\), in which the pyridylphosphine acts as a monodentate ligand (Scheme 3-1). For compound *trans*-\(1d\), the phosphorus atom of the pyridylphosphine ligand \((P_X)\) displays a very large Pt-P coupling constant of \(J_{PX,P} = 4447\) Hz. This value is commonly observed for phosphorus atoms *trans* to oxygen donor ligands.\(^{52}\) Furthermore, while the chemical shift of the \(^{195}\)Pt nuclei in all *cis* complexes does not vary by more than 20 ppm, \(\delta_{P}\) of *trans*-\(1d\) is about 100 ppm higher than the average value of the former complexes (table 3-1), indicating that there is an important difference in the environment of the platinum nucleus in *cis* and *trans*-\(1d\). This points to an interaction between the platinum center and the oxygen of the Xantphos backbone, indicating that Xantphos coordinates as a tridentate ligand. This P,O,P type of coordination for Xantphos has been observed in cationic Rh and Pd complexes. It has been suggested that the metal-oxygen interaction can stabilize the *trans* isomer with respect to the *cis* one in which this interaction is not present.\(^{47,49}\) The tridentate coordination of Xantphos was confirmed by single crystal X-ray diffraction, which will be discussed later.

| Complex | \(J_{PA,PM}\) (Hz) | \(J_{PA,PX}\) (Hz) | \(J_{PM,PN}\) (Hz) | \(J_{PA,PA}\) (Hz) | \(J_{PM,PM}\) (Hz) | \(J_{PX,PX}\) (Hz) | \(\delta_{PA}\) (ppm) | \(\delta_{PM}\) (ppm) | \(\delta_{PX}\) (ppm) | \(\delta_{Pi}\) (ppm) |
|---------|----------------------|------------------|------------------|------------------|------------------|------------------|----------------|----------------|----------------|----------------|           |
| \(1a\)  | 12.0                 | 364              | 19.5             | 2737             | 3496             | 2058             | 24.0           | 9.16           | -38.3          | -4083          |           |
| \(1b\)  | 16.3                 | 372              | 15.8             | 2829             | 3536             | 2143             | 15.2           | -7.5           | -39.2          | -4063          |           |
| \(1c\)  | 19.3                 | 360              | 15.2             | 2772             | 3563             | 2142             | 12.8           | -6.6           | -40.1          | -4082          |           |
| \(1d\)  |                      |                  |                  |                  |                  |                  |                |                |                |                |           |
| *cis*   | 24.3                 | 358              | 12.2             | 2800             | 365              | 2118             | 12.0           | -6.5           | -41.3          | -4073          |           |
| *trans* | ---                  | 12.1             | ---              | 2503             | ---              | 4447             | 39.2           | ---            | 16.3           | -3972\(^{a}\) |           |

*Table 3-1. \(^{31}\)P spectroscopic data for complexes \(1a-d\). All spectra were measured in CD\(_2\)Cl\(_2\) at room temperature.\(^a\) Value for \(1d'\)-Me.*
Table 3-1 reveals that there is a trend in the chemical shifts and P-P coupling constants going from \textbf{1a} to \textbf{1d}. With increasing bite angle, the coupling constant $J_{PA,PM}$ increases as well, while $J_{PM,PX}$ shows the reverse trend. Regarding the chemical shifts, dppf shows the highest while Xantphos shows the smallest coordination shifts in the $^{31}P$ NMR spectra. Furthermore, there is a continuous trend on increasing the bite angle. The chemical shift of heavy elements is difficult to calculate and predict accurately,\textsuperscript{53} so usually empirical correlations are used. The ring size and flexibility of dppf has often been compared with that of dppb.\textsuperscript{54} It can be considered that dppf forms a seven membered chelate ring while the Xantphos-type ligands form eight membered rings. Hence the higher coordination shift of \textbf{1a} may reflect the more favorable conformation of a seven-membered ring.

The chelating coordination of the 2-pyridylphosphine is usually reflected in the $^1H$ NMR spectrum of the corresponding metal complexes, by a downfield shift of the proton ortho to the nitrogen (H$_6$) in the pyridine moiety. When the pyridine nitrogen coordinates, the resonance of H$_6$ shifts to higher frequencies compared to the free ligand\textsuperscript{55,56} (above $\delta$=9 ppm for the chelate vs. $\delta$= 8.72 ppm for the free ligand in CDCl$_3$). Although for complexes \textbf{1a-d} the resonance for H$_6$ is clearly separated from the rest of the aromatic signals, it appears at a lower value than expected. A similar trend was observed by James and co-workers,\textsuperscript{57} who studied ruthenium complexes containing the 2-pyridylphosphines PPh$_3$-$\alpha$-(Py)$_x$ (x =1-3). PPy$_3$ acted as a tridentate ligand with the phosphorus atom and two of the pyridine nitrogens coordinated to ruthenium. They observed that the signals for H$_6$ in the coordinated pyridyl rings appeared down-field compared to the resonance of H$_6$ in the non-coordinated pyridine. This may be due to the proximity of the phenyl groups of the diphosphines to the pyridyl ring, causing an unusual shielding of H$_6$. As it will be discussed later, the phenyl groups of wide bite angle diphosphines tend to embrace the metal ion and cause important steric interactions with the other coordinated ligands.

For complex \textbf{1a} containing dppf, the $^1H$ NMR spectrum shows four signals for the hydrogen atoms in the Cp rings, each integrating for 2 protons. The signals at $\delta$= 5.2 and $\delta$= 3.7 ppm are assigned to the $\alpha$ protons, and the signals at $\delta$= 4.9 and $\delta$= 4.8 ppm correspond to the $\beta$ protons. The signals were assigned using a COSY NMR experiment. Given that the complex lacks a plane or axis of symmetry all Cp protons are magnetically inequivalent, so they should give rise to eight different signals. Nevertheless this is seldom
observed because both rings flip rapidly around the Cp-Fe-Cp axis; thus the pairs of α and β protons on each ring are time averaged. This results in just one NMR signal for each pair of α or β protons on each cyclopentadienyl.\textsuperscript{54,58,59} One of the signals for the α protons (δ = 3.64 ppm), is shifted up-field by more than 1 ppm compared to the other signals, indicating that it is in close proximity with one of the phenyl rings which have a shielding effect. These features are often observed in sterically congested dppf complexes.\textsuperscript{60,61}

The \textsuperscript{1}H NMR spectrum of complex 1d with the Xantphos ligand displays two signals for the methyl groups in the backbone at δ = 1.77 and δ = 1.82 ppm. Integration of these signals indicates the cis and trans isomers are present in a 1:1 ratio. This ratio does not change with temperature, indicating that the equilibrium between the two isomers is temperature independent. For complex 1c, which exists as the cis isomer only, one signal (δ = 0.78 ppm) was observed for the CH\textsubscript{3} groups in the backbone.

Analogs of complexes 1a and 1d using the very bulky BARF [B(3,5-(CF\textsubscript{3})\textsubscript{2}-C\textsubscript{6}H\textsubscript{3})\textsubscript{4}] anion (1a' and 1d') and the diphenyl-2-(6-methyl-pyridyl)phosphine ligand (1a-Me and 1d'-Me) were also prepared. (chart 3-2). Complexes 1a' and 1d' were synthesized in the same way as 1a-d, but using NaBARF instead of silver triflate. The \textsuperscript{31}P NMR data for these complexes are summarized in table 3-2. Both the \textsuperscript{1}H and \textsuperscript{31}P NMR spectra of 1a' (dppf) are essentially the same as for 1a, but complex 1a-Me with the bulkier diphenyl-2-(6-methyl-pyridyl)phosphine ligand gave rise to very broad signals at room temperature.

<table>
<thead>
<tr>
<th>Diphosphine</th>
<th>P,N ligand</th>
<th>Anion</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>dppf</td>
<td><img src="image" alt="Diphosphine" /></td>
<td>BARF</td>
<td>1a'</td>
</tr>
<tr>
<td>dppf</td>
<td><img src="image" alt="Diphosphine" /></td>
<td>OTf</td>
<td>1a-Me</td>
</tr>
<tr>
<td>Xantphos</td>
<td><img src="image" alt="Diphosphine" /></td>
<td>BARF</td>
<td>1d'</td>
</tr>
<tr>
<td>Xantphos</td>
<td><img src="image" alt="Diphosphine" /></td>
<td>BARF</td>
<td>1d'-Me</td>
</tr>
</tbody>
</table>

Chart 3-2.
In a variable temperature NMR experiment the signals of 1a-Me sharpened upon lowering the temperature. At -40 °C, two distinct sets of signals were observed in the $^{31}$P NMR spectrum in a 1 : 1 ratio. The first set corresponds to a complex analogous to 1a in which the pyridylphosphine coordinates in a chelating fashion. Thus, its spectroscopic properties are very similar to those described for 1a-c (Table 3-2).

The second set of signals is an ABX spin system for which both the chemical shifts and the P-Pt coupling constants indicate that the pyridylphosphine acts a P-coordinating monodentate ligand. The ABX spin system rules out a trans structure similar to trans-1d or a dimeric structure. The $^1$H NMR spectra shows two signals ($\delta$=1.59 and $\delta$=2.40 ppm) for the methyl groups of the pyridyl moiety, and a total of seven signals for the Cp protons. Two of the signals (4 protons in total) appear at $\delta$= 3.26 and $\delta$= 3.23 ppm and are shifted up-field by more than 1 ppm, as observed for 1a. The remaining signals (integrating for 12 protons) appear between $\delta$= 5.09 and $\delta$= 4.27 ppm. This indicates that in both products dppf is coordinated in a cis fashion (scheme 3-2).

![Scheme 3-2.](image)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$J_{PA-PM}$ (Hz)</th>
<th>$J_{PA-PX}$ (Hz)</th>
<th>$J_{PM-PX}$ (Hz)</th>
<th>$J_{PL-PA}$ (Hz)</th>
<th>$J_{PL-PM}$ (Hz)</th>
<th>$\delta_{PA}$ (ppm)</th>
<th>$\delta_{PM}$ (ppm)</th>
<th>$\delta_{PX}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-Me I</td>
<td>12</td>
<td>354</td>
<td>21</td>
<td>2728</td>
<td>3533</td>
<td>20.9</td>
<td>5.0</td>
<td>-40.0</td>
</tr>
<tr>
<td>1a-Me II</td>
<td>$J_{PA-PB}$</td>
<td>$J_{PA-PX}$</td>
<td>$J_{PB-PX}$</td>
<td>$J_{PL-PA}$</td>
<td>$J_{PL-PX}$</td>
<td>$\delta_{PA}$</td>
<td>$\delta_{PB}$</td>
<td>$\delta_{PX}$</td>
</tr>
<tr>
<td></td>
<td>425</td>
<td>15</td>
<td>19</td>
<td>3461</td>
<td>2538</td>
<td>16.4</td>
<td>23.2</td>
<td>15.8</td>
</tr>
<tr>
<td>1d'-Me</td>
<td>---</td>
<td>17</td>
<td>---</td>
<td>2476</td>
<td>---</td>
<td>37.7</td>
<td>---</td>
<td>-0.49</td>
</tr>
</tbody>
</table>

Table 3-2. $^{31}$P{$^1$H} Spectroscopic data from the complexes with the diphenyl-2-(6-methyl-pyridyl)phosphine ligand.
In the second product, the 6-methyl-2-pyridinephosphine is not chelating and the fourth coordination position is probably occupied by the triflate anion. The IR spectrum shows two split bands for $v(\text{SO}_3)$ at 1260 and 1005 cm$^{-1}$. These bands have been previously assigned to mono-coordinated sulfonates. Although triflates are known to be weakly coordinating anions, the IR data and the fact that the microanalysis of a sample containing both products is correct shows that both compounds have the same composition (see experimental section). The broad spectra observed at room temperature indicates exchange between the two species.

Changing the anion from OTf to BARF in the Xantphos containing compounds did not result in any significant difference in the spectroscopic behavior of 1d$'$ compared to 1d. When the 6-methyl-2-pyridylphosphine ligand is used, only the trans isomer (1d$'$-Me) is formed. This indicates that the steric interaction of the methyl group of the P,N ligand with the phenyl groups of Xantphos destabilizes the coordination of the pyridine nitrogen, shifting the equilibrium to the trans isomer.

**Solid state structures of complexes 1b-d**

Complexes 1b-d were further characterized by single crystal X-ray diffraction. Suitable crystals were grown by slow diffusion of diethyl ether or hexanes into dichloromethane solutions of the corresponding complex. Selected bond distances and angles are presented in table 3-2. The structures found in the solid state are in agreement with those proposed in solution from the NMR data discussed above. Thus, complexes with DPEphos (b) and Sixantphos (c) form cis complexes, while for Xantphos (d) both cis and trans isomers are present in solution. In the latter case, only the trans isomer could be crystallized. The X-ray structure of trans 1d confirms the P,O,P coordination mode of Xantphos, which was proposed based on the $J_{\text{Pt-PN}}$ coupling constant and the $^{195}\text{Pt}$ chemical shift. The solid state structures of 1b and 1c show that there is considerable interaction between the phenyl groups of the diphosphine ligand and those of the pyridylphosphine. This interaction becomes more important as the bite angle increases. In the case of the Xantphos ligand the pyridylphosphine is forced to act as a monodentate ligand. The “embracing effect” of the phenyl rings in wide bite angle diphosphines in palladium allyl complexes was studied by van Haaren et al. 43

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For complexes 1b and 1c the coordination sphere of the platinum atom consists of a cis coordinated diphosphine ligand and a chelating pyridylphosphine. As commonly observed in complexes containing a chelating pyridylphosphine, the bond angles involving the four-membered Pt1-N1-C1-P1 ring show an important deviation from the ideal 90° value. The P1-Pt-N1 angles of 68.9(3)° for 1b and 69.1(11)° for 1c, are slightly smaller than those reported for other platinum complexes (70.8(5)° for [PtCl(η²-Ph₂PPy)(PPh₂PPy)]⁺ and 70.4(5)° in [PtMe(η²-Ph₂PPy)(PPh₂PPy)]⁺).

Figure 3-3. Molecular structure of [(η²-DPEphos)Pt(η²-Ph₂PPy)][OTf]₂ (1b). The ellipsoids are drawn at 50% probability level. The hydrogen atoms and the triflate anions have been omitted for clarity.
The smaller bite angle of the pyridylphosphine ligand may be due to steric bulk of the diphosphine, compared to the smaller methyl and chloride ligands. The intrachelate angles (P1-C1-N1 103.6(7)° in 1b and 103.4(3)° in 1c) and Pt-P1-C1 (83.3(4)° and 83.35(16)°, respectively) show the same deviation from the ideal values as observed in the above mentioned complexes.

**Figure 3-4.** Molecular structure of [(η^5^-Sixantphos)Pt(η^2^-Ph₂PPy)][OTf]₂ (1c). The ellipsoids are drawn at 50% probability level. The hydrogen atoms and the triflate anions have been omitted for clarity.

The Pt-N1 distance in 1b/c is almost 0.1 Å longer than the one reported by Jain et al. and Farr et al. in the above mentioned platinum complexes, but in the same range as those observed in [Ru(η^2^-Ph₂PPy)(CO)₂Cl₂]⁶⁵ and [PdCl(η^2^-Me₂PPy)(PMe₂PPy)]⁺.⁶⁶
Heterolytic Activation of H₂ with Pt complexes

The platinum atom in 1b is shifted 0.124 Å away from the least-squares plane determined by itself, the three phosphorus atoms and the nitrogen atom, while the deviation is only 0.043 Å in 1c. Especially for the complex 1b (DPEphos), the deviation from the coordination plane is much larger than the 0.017 Å or the 0.026 Å observed in [PtMe(η²-Ph₃Ppy)(PP₃Ppy)][BPh₄]₆⁴ and [Ru(η²-Ph₃Ppy)(CO)₂Cl₂]₆⁵ respectively. The larger deviation from the coordination plane may be due to the presence of the additional chelating ligand, while in the two other complexes reported the additional ligands are monodentate and therefore can coordinate at an angle near the ideal 90° value. Because DPEphos (b) and Sixantphos (c) have natural bite angles larger than 100°, they will force a geometry with a more open P2-Pt-P3 angle which leads to further distortion around the Pt center. In fact, the P2-Pt-P3 angle is smaller (98.96(10)° in 1b and 94.95(5)° for 1c) than expected from these wide bite angle diphosphines. Particularly for the Sixantphos complex (1c), the value of 94.95(5)° is at the lower end of the flexibility range for this ligand (93-130°).⁶⁷ In complex 1b the P2-Pt-P3 angle is slightly smaller than the P-Pd-P angle observed in palladium complexes containing DPEphos prepared in our group (from 100.82° to 103.93°).⁶⁶-⁶⁷ Again, the smaller bite angle may be caused by the steric interaction between the phenyl rings of the diphosphine and those on the PPh₃Ppy ligand (figures 3-3 and 3-4).

The backbone of the DPEphos ligand is highly bent (fig. 3-3); the planes containing the aromatic rings form an angle of 102.9°. This conformation has been observed in other square planar complexes of DPEphos.⁶⁶⁷ In case of complex 1c, (fig. 3-4) one of the aromatic rings of the Sixantphos backbone is bent to the back, the angle between the planes formed by (C4 to C9) and (C10 to C15) is 40.2°.

The Pt-O distance in 1b is 3.4888(5) Å, but it is considerably shorter in 1c (2.725(3) Å). The latter distance is only slightly longer than the 2.714(3) Å reported for [SixantphosPd(4-C₆H₄CN)Br]⁶⁷ in which the diphosphine ligand adopts a trans geometry, and thus forces the oxygen atom close to the metal. This is, to a lesser extent, also the case in 1c. Because of the rigidity of Sixantphos, the Pt-O bond cannot be much longer. A weak platinum-oxygen bond was proposed in a Pt(II)-β-diketonato complex in which the Pt-O distance was 2.796(6) Å.⁶⁸ Similar Pd-O distances have been reported in five-coordinated palladium (II) complexes⁶⁹-⁷⁰ and thus the short distance observed in 1c might also indicate the presence of a weak Pt-O interaction.
### Table 3-3. Selected bond distances (Å) and bond angles (°) for complexes 1b-d

<table>
<thead>
<tr>
<th></th>
<th>DPEphos (1b)</th>
<th>Sixantphos (1c)</th>
<th>Xantphos (1d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-P1</td>
<td>2.324(3)</td>
<td>2.3011(14)</td>
<td>2.2387(7)</td>
</tr>
<tr>
<td>Pt-P2</td>
<td>2.279(3)</td>
<td>2.2638(13)</td>
<td>2.3171(5)</td>
</tr>
<tr>
<td>Pt-P3</td>
<td>2.337(3)</td>
<td>2.3852(13)</td>
<td>2.2976(5)</td>
</tr>
<tr>
<td>Pt-O1</td>
<td>3.488(5)</td>
<td>2.725(3)</td>
<td>2.1889(18)</td>
</tr>
<tr>
<td>Pt-N1</td>
<td>2.112(8)</td>
<td>2.109(4)</td>
<td>---</td>
</tr>
<tr>
<td>P1-C1</td>
<td>1.814(11)</td>
<td>1.818(5)</td>
<td>1.833(2)</td>
</tr>
<tr>
<td>(\angle) P1-Pt-P2</td>
<td>99.32(10)</td>
<td>99.42(5)</td>
<td>96.90(2)</td>
</tr>
<tr>
<td>(\angle) P2-Pt-P3</td>
<td>98.96(10)</td>
<td>94.95(5)</td>
<td>162.22(2)</td>
</tr>
<tr>
<td>(\angle) P3-Pt-N1</td>
<td>92.3(3)</td>
<td>96.50(11)</td>
<td>---</td>
</tr>
<tr>
<td>(\angle) P1-Pt-N1</td>
<td>68.9(3)</td>
<td>69.08(11)</td>
<td>---</td>
</tr>
<tr>
<td>(\angle) P2-Pt-N1</td>
<td>168.1(3)</td>
<td>168.49(11)</td>
<td>---</td>
</tr>
<tr>
<td>(\angle) P1-Pt-P3</td>
<td>157.29(10)</td>
<td>164.89(5)</td>
<td>100.22(2)</td>
</tr>
<tr>
<td>(\angle) Pt-P1-C1</td>
<td>83.3(4)</td>
<td>83.35(16)</td>
<td>110.78(11)</td>
</tr>
<tr>
<td>(\angle) P1-C1-N1</td>
<td>103.6(7)</td>
<td>103.4(3)</td>
<td>---</td>
</tr>
<tr>
<td>(\angle) P2-Pt-O1</td>
<td>---</td>
<td>---</td>
<td>80.97(4)</td>
</tr>
<tr>
<td>(\angle) P3-Pt-O1</td>
<td>---</td>
<td>---</td>
<td>82.37(4)</td>
</tr>
<tr>
<td>(\angle) P1-Pt-O1</td>
<td>---</td>
<td>---</td>
<td>174.69(4)</td>
</tr>
</tbody>
</table>

In complex 1d (fig. 3-5), Xantphos acts as a tridentate ligand. The Pt-O distance is 2.1189(18) Å, which is slightly shorter than the 2.1537(14) Å observed in \textit{trans-}[XantphosPd(4-C₆H₄CN)]⁺.47 This is probably caused by the larger \textit{trans} influence of the aryl ligand compared to the phosphine in 1d. The geometry around the metal is square planar. Because of the rigidity of the Xantphos ligand, P2 and P3 are bent down from the coordination plane and the P2-Pt-P3 angle is 162.22(2)°. The O-Pt-P1 angle (174.69(4)°) is closer to the ideal value of 180°. The Xantphos backbone is also bent, the angle between the aromatic rings (C4 to C9) and (O1,C9 to C12) is 8.3°, while the angle between the latter and the (C11 to C16) plane is 10.6°. The Pt-P2 and Pt-P3 distances are similar to
those observed in other \textit{trans} coordinated Pt(II) complexes. The Pt-P bond length in 1d (2.2387(7) Å) is similar to those observed in platinum complexes in which the PPh$_2$Py ligand acts as P-monodentate. This bond is also considerably shorter than those in 1b/c.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-5.png}
\caption{Molecular structure of [(\textit{η}$_1$-Xantphos)Pt(\textit{η}$_1$-Ph$_2$Py)][OTf]$_2$ (\textit{trans}1d). The ellipsoids are drawn at 50\% probability level. The hydrogen atoms and the triflate anions have been omitted for clarity.}
\end{figure}

Two factors play an important role in the coordination chemistry of 1a-d; the natural bite angle of the diphosphine ligands, and the steric constraints imposed by the chelation of the pyridylphosphine. While dppf and DPEphos can easily coordinate in a \textit{cis} fashion, the bite angle of Sixantphos and particularly of Xantphos is too large for the ideal 90° P-M-P angle in a \textit{cis} coordinated square planar complex, but neither of them is large enough for ideal
trans coordination. In fact, the crystal structure of 1d, as well as the other reported structures with a trans coordinated Xantphos ligand, show that the P-M-P angle is always less than 165° with the phosphorus atoms bent away from the plane. As stated before, diphosphines with a wide bite angle also have a large cone angle, which results in less free space around the metal center for coordination of other ligands. As the chelation of the pyridylphosphine increases the steric bulk around the metal center, bidentate coordination of the PPh₂Py ligand becomes less favored as the bite angle increases. Furthermore, chelation of the pyridylphosphine is unfavorable by the intrinsic strain of the four-membered ring. Nevertheless, the PPh₂Py acts as a chelating ligand in 1a-d. Obviously, the Pt-N bond is strong enough to stabilize the highly strained geometries in 1a-c, especially in the case of 1c in which the Sixantphos ligand is forced to adopt an uncommonly small bite angle. But as the steric hindrance in 1d becomes more important, chelation of the pyridylphosphine is more difficult, and a mixture of cis and trans -1d is formed. The additional steric bulk in 1d-Me results in the exclusive formation of the trans isomer. In the latter case, the Pt-N bond has been replaced by a Pt-O bond. In general, ethers are known to coordinate only weakly to platinum, but in trans-1d the oxygen atom is forced to be close to the metal, thus favoring an interaction with the Pt center. The weak coordinating abilities of both the triflate anion and the dichloromethane, may also contribute to the formation of the Pt-O bond. Thus, the structure of complexes 1a-d is a compromise between the steric hindrance induced by the bite angle of the diphosphine and the stabilization due to the chelation of the pyridylphosphine.

Heterolytic activation of H₂

Complexes 1b-d react with dihydrogen under mild conditions (4 bar, 40 °C, 16 h) to afford cationic platinum hydrides 2b-d according to scheme 3-3.

\[
\begin{align*}
1a-d & \quad \begin{array}{c}
\text{(OTf)}_2 \\
\text{(CH₂Cl₂)}
\end{array}
\quad \xrightarrow[4 \text{bar} / 40 \degree \text{C}]{\text{H₂}} \\
2a-d & \quad \begin{array}{c}
\text{(OTf)}_2 \\
\text{(CH₂Cl₂)}
\end{array}
\end{align*}
\]

Scheme 3-3. Reaction of complexes 1a-d with dihydrogen. P= PPh₂
In this reaction, the coordinated pyridine moiety acts as hemilabile ligand to provide a vacant coordination site as well as an internal base to assist the heterolytic splitting of the dihydrogen molecule. The new hydride complexes were characterized by multinuclear NMR spectroscopy. The \(^1\)H and \(^{31}\)P NMR data are presented in tables 3-4 and 3-5, respectively. The \(^1\)H NMR spectrum of 2b-d shows a characteristic hydride signal between \(\delta = -5\) and \(\delta = -8\) ppm (figure 3-6). The shape of the signal depends on the ligand used. For complexes 2b and 2c containing DPEphos and Sixantphos respectively, all the H-P couplings are resolved and the hydride signal appears as a doublet of doublets of doublets, with the corresponding Pt satellites. For complex 2d (Xantphos), the two cis H-P couplings are not well resolved, the hydride signal appears as a slightly broad doublet of triplets, with Pt-satellites. Protonation of the pyridine moiety was confirmed by the broad signal at about 15 ppm, with an integration ratio with the hydride of 1:1. This signal broadens and shifts slightly to higher field on lowering the temperature.

![Figure 3-6. High field region of the \(^1\)H NMR spectrum of 2b](image)

The new complexes show an ABX spin system in the \(^{31}\)P NMR spectrum, in which the AB part is formed by the two phosphines \textit{trans} to one another and \(P_X\) corresponds to the phosphorus \textit{trans} to the hydride ligand. This assignment is confirmed by the relatively small \(P_X\)-Pt coupling constant (\(J_{P_X-Pt} \approx 2200\) Hz), which is normally observed for nuclei \textit{trans} to hydrides. At the same time, the increase of more than 1000 Hz of the \(P_P\)-Pt coupling constant indicates a release of the ring strain. Complete spectroscopic data are shown in tables 3-4 and 3-5. The \(^1\)H and \(^{31}\)P spectra did not change significantly on lowering the temperature, apart from some broadening of the signals below 233 K. At 203 K, the N-H proton is not longer observed.
Table 3-4. \(^1\)H\(^{31}\)P NMR data for the hydride complexes 2a-d. NMR spectra were measured at 300 MHz in CD\(_2\)Cl\(_2\) at room temperature, unless otherwise stated. \(^a\) At 233 K. \(^b\) n.r. not resolved.

Table 3-5. \(^{31}\)P\(^1\)H NMR spectroscopic data for the hydride complexes 2a-d. All spectra were measured at 121.5 MHz in CD\(_2\)Cl\(_2\) at room temperature, unless otherwise stated. \(^a\) At 233 K. \(^b\) chemical shifts and coupling constants calculated with gNMR. \(^c\) At 160.5 MHz.

As observed for the precursors 1a-d, the \(^{31}\)P coordination shift of P\(_A\) and P\(_B\) are higher for complexes containing dppf than for those with the Xantphos-type phosphines. Although this may be attributed to the size of the chelate ring, an electronic contribution of the iron atom in dppf can not be excluded. The chemical shift of P\(_X\) is considerably higher for 2a and 2a-Me than that of 2b-d, the variation of \(\delta_{P_X}\) is much smaller within the Xantphos-type ligands.

A similar trend is observed in the \(^1\)H NMR spectra, in which the hydride ligand shifts upfield as the bite angle of the diphosphine increases. Wander et al. calculated that on
increasing the P-M-P angle in [PdH(\text{PH}_3)_2], electron density moves from the hydride ligand into the LUMO of the metal fragment.\textsuperscript{36} The same authors observed an up-field shift of the resonance of the hydride in [PdH(R\_2P(CH\_2\_n)\_nPPh(CH\_2\_n)\text{PR}_2]\textsuperscript{+} as the bite angle of the triphosphine ligand increased.

Surprisingly, the complex with the dppf ligand 1a did not react with dihydrogen, not even at 10 bar and 50 °C. The use of a more basic solvent such as acetone leads to complete decomposition of the starting material without formation of the desired hydride product. If one equivalent of external base (Et\_2NH or DIPEA) is used, a hydride complex is formed together with the salt of the amine under the same reaction conditions as for 1b-d. This complex can be protonated afterwards with HOTf to afford 2a, in which the pyridine moiety is protonated. Although the bite angle and the basicity of dppf are similar to those of DPEphos, 1a and 1b show a strikingly different reactivity towards the heterolytic activation of dihydrogen.

More information on the electronic properties of the metal center was sought by means of \textsuperscript{195}Pt NMR. The chemical shift of \textsuperscript{195}Pt nuclei are sensitive to the ligands present in the coordination sphere and is therefore a useful probe of the electronic environment of the metal.\textsuperscript{72,73} Nevertheless, as can be seen in table 3-1, the \textsuperscript{195}Pt chemical shift for complexes 1a and 1c is not significantly different, indicating that there are no large differences in the coordination environment of these two complexes.

The explanation for the different reactivity of 1a compared to 1b may lay in the smaller cone angle of dppf (229.7°) compared to that of DPEphos (240.2°). For allylic alkylation reactions van Haaren \textit{et al}. observed an important difference in the activity and selectivity of the palladium catalysts with dppf compared to the one with DPEphos.\textsuperscript{46} In the case of 1b-d, the steric interaction between the phenyl groups of the Xantphos-type ligands with the pyridylphosphine may labilize the Pt-N bond, whereas in 1a the stronger coordination of the pyridyl moiety results in lack of reactivity. The driving force for the formation of the hydride complexes is probably the release of the ring strain in the diphenyl-2-pyridylphosphine ligand. Indeed, when the latter ligand was replaced by 3-diphenylmethylpyridylphosphine, which forms a 6-membered metallacycle, the reaction with dihydrogen was very slow. The built-in base in complexes 1b-d does not accelerate the reaction. Indeed the reaction of [(DPEphos)\text{Pt}(\text{PPh}_3)](\text{OTf})_2 with dihydrogen and one equivalent of external base (DIPEA) is as fast as the reaction of complex 1b. This indicates
that either the rate of de-coordination of the pyridyl moiety is the rate-limiting step rather than the actual heterolytic splitting of the dihydrogen molecule, or that the low equilibrium concentration of the tricoordinate species causes the low rate for H₂ splitting.

Complex 1a' with the bulky and non coordinating BARF anion showed the same lack of reactivity towards dihydrogen without an external base. Complex 1a-Me (cis and trans) did react under the same conditions as 1b-d to give a mixture of two hydride species. The reaction mixture displays very broad signals in the ¹H and the 3¹P NMR spectra at room temperature. On lowering the temperature to 233 K relatively sharp multiplets appeared and it was possible to identify three sets of peaks. One set corresponds to unreacted starting material (1a-Me-I) which is present in about 10 %. The second set of signals corresponds to the major species in solution and it is characterized by a doublet of doublets at δ = -5.61 ppm in the ¹H NMR spectrum and an ABX spin system in the 3¹P NMR spectrum. The splitting pattern, coupling constants and chemical shifts are similar to those observed for complexes 2a-d and therefore this species was assigned to a hydride cis[dppfPtH{2-(6-CH₃-C₅H₃NH)PPh₂}]²⁺ (cis 2a-Me, scheme 3-4). Protonation of the pyridine moiety was confirmed by a broad peak at 14.3 ppm. When the solution containing this mixture was filtered over celite, the peaks for cis 2a-Me disappeared almost completely, which enabled the identification of the third product. The ¹H NMR spectrum of this product displays a sharp doublet of triplets at δ = -5.11 ppm, while the 3¹P NMR spectrum shows a doublet and a triplet coupled to one another. The relative intensity of these signals is 2:1. Apart from the hydride peaks, the ¹H NMR spectrum shows also a signal at δ = 2.1 ppm for the CH₃ of the diphenyl-2-(6-methyl-pyridyl)phosphine ligand and several signals between 4.5 and 3.5 ppm for the Cp protons in dppf, confirming the presence of these two ligands in the product. From these data the third product was assigned to an isomer of 2a-Me in which dppf is coordinated in a trans fashion while the pyridylphosphine is trans to the hydride (scheme 3-4).

Scheme 3-4. Products formed from the reaction of 1a-Me with dihydrogen.
Similar results were observed for the reaction of [XantphosPt(6-methyl-diphenyl-2-pyridylphosphine)](BARF)₂ (1d'Me) with dihydrogen. The ¹H NMR spectrum displays two hydride signals (both doublets of triplets) with coupling constants similar to those observed for the rest of the hydride complexes. The broadness of the signals in the ³¹P NMR spectrum at all temperatures, however, did not allow further identification of the products.

**X-Ray Crystal Structure of 2a-Me.**

Crystals suitable for X-ray diffraction where obtained by slow diffusion of diethyl ether into a dichloromethane solution of 2a-Me. Figure 3-7 shows the crystal structure of [(dpff)PtH{2-(6-CH₃-C₅H₃NH)PPh₂}]₂[OTf]₂. The most relevant bond distances and angles are presented in table 3-6. The four ligands around the platinum are arranged in a plane, for which the maximum deviation from the least-squares plane defined by P1-H1-P1-P2-P3 is 0.089 Å. The geometry is strongly distorted from the ideal 90° angles expected for a square plane. The more important deviations are the H1-Pt-P1 angle (76.3(18)°) and the H1-Pt-P3 angle (77.9(18)°). The bite angle of dpff (P2-Pt-P3 is 99.24(4)°) is very similar to the 99.3(1)° observed in [(dpff)PtCl₂]₇⁴ and falls within the standard range for Pt(II)-dpff complexes.₅⁴ The preference of dpff for bite angles larger than 90° as well as the steric interaction between dpff and the pyridylphosphine ligand force P1 and P3 to bend towards the small hydride ligand, causing the rather small P1-Pt-P3 angle (153.57(4)°). The Cp rings of dpff are only slightly tilted, the angle between the two planes being 2.2°, which is relatively small for square planar complexes. The Pt-P1 and Pt-P3 bond lengths are normal for this type of Pt complexes; the Pt-P3 distance of 2.2897(11) Å is in the range normally observed in (dpff)Pt(II) complexes. In contrast, the Pt-P2 bond is significantly longer (2.3410(12) Å) than other Pt-P bonds observed for phosphines trans to a hydride ligand, for example 2.304(3)Å in [PtH(SiPh₃)(PEt₃)₂]₇⁵ and 2.278(2) Å in [PtH(CH₂CMe₂)(Cy₂PCH₂CH₂PCy₂)].₇⁶ The latter two complexes contain alkyl phosphines, which might explain the shorter Pt-P bond compared with the one in 2a-Me.
Figure 3-7. Molecular structure of [(dpdpf)PtH{2-(6-CH3-C5H5NH)PPh2}][OTf]2 (2a-Me). The ellipsoids are drawn at 50 % probability level. The triflate anions and the hydrogen atoms (except for the hydride ligand) have been omitted for clarity.

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-H1</td>
<td>1.64(6)</td>
</tr>
<tr>
<td>Pt-P1</td>
<td>2.2737(11)</td>
</tr>
<tr>
<td>Pt-P2</td>
<td>2.3410(12)</td>
</tr>
<tr>
<td>Pt-P3</td>
<td>2.2897(11)</td>
</tr>
<tr>
<td>P1-C1</td>
<td>1.840(4)</td>
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<td>θ H1-Pt-P1</td>
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<td></td>
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<tr>
<td></td>
<td>θ H1-Pt-P3</td>
</tr>
<tr>
<td></td>
<td>θ P1-Pt-P2</td>
</tr>
<tr>
<td></td>
<td>θ P2-Pt-P3</td>
</tr>
<tr>
<td></td>
<td>θ P1-Pt-P3</td>
</tr>
</tbody>
</table>

Table 3-6. Selected bond distances (Å) and bond angles (°) for complex 2a-Me
One of the phenyl rings of the pyridylphosphine ligand (P1) is parallel to one of the phenyl rings of P2. The angle between the rings (N1, C1-C5) and (C18-C23) is only 5.5° and the distance between their centroids is 3.493Å, which probably indicates a π-staking interaction.

The Pt-H bond is relatively long (1.64(6) Å) compared with the one reported for \([\text{PtH(CH}_2\text{CMe}_3)(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)]^7\) (1.56(5) Å), and to the Pt-H(terminal) distance determined by neutron diffraction in \([(\text{dppe})\text{PtH(μ-H)}_2\text{Pt(dppe)}]^+\) (1.610(2)).

**Dihydrogen Bonding**

Compounds 2a-d are potential candidates for dihydrogen bonding because they possess a protonated pyridyl moiety (hydrogen bond donor) and a metal hydride (hydrogen bond acceptor) in close proximity. The presence of a dihydrogen interaction has been characterized in the solid state by X-ray crystallography and neutron diffraction, and in solution by NMR and IR spectroscopy. Normally, the infrared spectra of hydrogen bonded systems shows that the metal-hydride and the NH or OH vibration bands broaden and shift to lower frequencies compared to compounds in which no hydrogen bonding occurs. The \(^1\text{H}\) NMR spectrum usually displays low field shifts for the X-H resonance (X= O or N), low minimum T\(_1\) values and sometimes even hydride-proton couplings. In order to investigate whether dihydrogen bonding occurred in the platinum compounds 2a-d, various NMR experiments were carried out. The \(^1\text{H}\) NMR spectra of 2a-d did not change significantly with temperature and neither coupling nor coalescence between the NH and the hydride was observed. The T\(_1\) of the two signals remains long at all temperatures (T\(_1\)\(_{\text{min}}\) ≈ 500 ms for the hydride) and no T\(_1\) coalescence was observed. No exchange or through-space interactions could be detected using NOE and Spin Saturation Transfer experiments. It was therefore concluded that the protonated pyridine and the hydride do not interact with one another. An explanation for the lack of interaction may be the low hydridic character of the hydride ligand in complexes 2a-d. It is known that dihydrogen bonding is an electrostatic interaction between a negatively charged hydride and a positively charged proton. However, in some cases Pt(II)-hydrides are not considered to be negatively charged or nucleophilic. Extended Hückel calculations by Wander \textit{et al.} on \([\text{Pd(PH}_3)_3\text{H}]^+\) showed that the P-M-P angle has a large influence on the partial charge of
the hydride. They calculated that when the P-M-P angle increases from 80° to 100°, the charge on the hydride decreases from -0.51 to -0.27. The origin of this effect was attributed to a decrease of the energy of the LUMO of the [Pd(PH₃)₃]²⁻ fragment as the bite angle increases, causing the electron density to shift from the hydride ligand into this orbital. This result implies that hydride complexes with phosphine ligands enforcing wide bite angles will be more acidic than analogous complexes with small bite angle ligands. Considering that all the ligands used enforce bite angles over 90°, it is expected that the hydride complexes 2a-d have small negative charges and therefore the interaction with the pyridinium proton will be weak.

From the crystal structure of 2a-Me it can be seen that the pyridyl fragment of the PPh₂Py ligand points away from the hydride. However, the Pt-P bond can rotate in solution and at some point the hydride and the pyridinium proton may be close enough to one another to establish an interaction. If this interaction is not strong enough to stabilize this particular conformation over the others, the potential dihydrogen bond will not be detectable by NMR.

Reactivity Studies

If dichloromethane solutions of the hydride complexes 2b-d are allowed to stand at room temperature, they lose dihydrogen slowly reforming the starting compounds 1b-d. When the solution is allowed to stand for a few days, precipitation of metallic platinum is also observed. The loss of dihydrogen is faster for complex 2d containing Xantphos, which reverts completely to 1d in 12h, even at 0°C. If this solution is re-pressurised with 3 bar of dihydrogen for 16h, the hydride complex 2d is re-formed cleanly, showing that the loss of H₂ is reversible.

Complex 2d was tested as catalyst for the hydrogenation of several unsaturated substrates. 2d is able to hydrogenate 1-hexene under 3 bar of H₂ at 40 °C, but the reaction is very slow (ratio 2d : 1-hexene = 1:100). After 16 h reaction time, only 90 % conversion to hexane was observed. ¹H and ³¹P NMR spectroscopy of the reaction mixture revealed the presence of mainly 2d in solution, in addition small amounts of 1d (both cis and trans) and free phosphine were observed. The hydride complex 2d is completely inactive towards acetone, acetophenone or heptaldehyde. As before, the NMR spectra of the solutions after reaction
showed a mixture of 2d and 1d; but free phosphine was not observed. The stoichiometric 
reaction of 1-hexene with 2d (without dihydrogen) was followed by NMR. Immediately 
after the addition of 1-hexene to a solution of 2d in CD$_2$Cl$_2$, the $^1$H NMR spectrum shows 
signals for hexane at 0.88 and 1.30 ppm, integration of these signals compared to those for 
the olefin indicates about 10% conversion to hexane. In addition, small peaks for 2-hexene 
were also identified. Heating the NMR tube to 35 °C leads to an increase of the signals for 
2-hexene, and after 1 day at room temperature complete isomerisation from 1-hexene to 2-
hexene was observed, while the signals for hexane did not change any further. Neither the 
proton nor the phosphorus spectra show important changes in the signals of 2d during the 
reaction. Small peaks for 1d are visible after 24 h, but these may result from normal 
decomposition of 2d in solution, as explained above.

**Platinum(II) complexes with aminopyridine ligands**

The occurrence of dihydrogen bonding in iridium hydride complexes with aminopyridine 
and related ligands has been widely studied by Crabtree *et al.*$^{15,29,83}$ In complexes 2a-d, 
the electron poor pyridinium moiety in PPh$_2$PyH$^+$ withdraws electron density from the 
phosphorus atom. Thus, the PPh$_2$PyH$^+$ ligand reduces the electron density on the metal, 
which in turns decreases the partial negative charge of the hydride. Furthermore, the 
terminal amine is a better base than pyridine. Therefore, replacing the pyridylphosphine 
ligand by an aminopyridine offers the possibility of studying these effects on the platinum 
complexes described in this chapter. The complexes [(diphosphine)Pt(N,N)]$^{2+}$ containing a 
2-(aminomethyl)pyridine (3a and 3d) or a 2-aminopyridine (4d) were synthesized by a 
similar route to that used for 1a-d.

![Chart 3-3. Platinum complexes with amino-pyridine ligands](image-url)
Chapter 3

Complexes 3a and 4d display broad signals at room temperature in both the \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectra. Upon lowering the temperature to 193 K the signals for 3a resolve, but those for 4d remain broad. In contrast, the \(^{31}\text{P}\) spectrum of 3d is sharp at 295 K but the proton signals are very broad. Complexes 3a (193 K) and 3d (295 K) display very similar \(^{31}\text{P}\) NMR spectra: 2 doublets with \(^{195}\text{Pt}\) satellites. The P-P coupling constant (\(J_{pp} = 21.5\) Hz 3a, 22.6 Hz 3d) indicates a cis conformation of the diphosphine ligand. The very similar Pt-P coupling constants for both phosphorus nuclei (\(J_{pp} = 3508, 3484\) Hz for 3a and 3552, 3536 Hz for 3d) show that they are trans to a ligand of similar trans influence, pointing to a chelating aminopyridine ligand. The \(^1\text{H}\) NMR spectrum of 3a and 3d is not completely resolved even at 193 K. Complex 3a shows two broad signals for the Cp and the NH\(_2\) protons together, and a separate signal for the methylene protons. Complex 3d shows two signals for the methyl groups in the diphosphine ligand backbone, a broad signal for the CH\(_2\) group and two broad signals for the NH\(_2\) protons. The broadness of the methylene protons of the aminopyridine ligand suggests restricted rotation, and thus confirms the hypothesis that the N,N ligand is coordinated in a chelating fashion. Because of the broad signals of the NMR spectra of 4d no further investigation was carried out.

Activation of H\(_2\) using complexes 3 and 4

The reactivity of these complexes towards dihydrogen was investigated. Complexes 3a and 3d and 4d did not react with dihydrogen under the conditions used for 1a-d (3 bar, 40 °C). After 16 hours the starting material was recovered unchanged. When the reaction of 3d with H\(_2\) was followed in a high pressure NMR tube, new signals were observed after 12 hours at 10 bar and 50 °C. After 18 hours, about 30 % of a new hydride-containing product (5d) was formed. Performing the reaction in an autoclave under the same conditions afforded a quantitative yield of the new hydride product 5d after 65 hours. This product is air stable in the solid state and in solution over a period of several hours. Reaction of 3a and 4d with 10 bars of dihydrogen at 50 °C afforded a similar product. The high field \(^1\text{H}\) NMR spectrum of 5d shows five equally spaced quintets centered at \(\delta = -7.2\) ppm (fig. 3-8), with a P-P coupling constant of 42 Hz and a platinum-hydride coupling constant of 429 Hz. The \(^1\text{H}\) NMR spectrum of the reaction mixture shows signals for the aminopyridine ligand and a broad signal at 12.5 ppm, which could correspond to the protonated amine. When the product was isolated and re-crystallized, the latter signals were no longer observed, suggesting that 5d does not contain an aminopyridine ligand. The coupling
pattern of the hydride signal and the small value of $^{1}J_{H, Pt}$ compared to the values observed for 2a-d (about 700 Hz), point to a hydride bridged dimer containing four equivalent phosphorus and three equivalent hydrides.\textsuperscript{84-86} Integration of the $^{1}$H NMR spectrum shows a ratio between the hydrides: CH$_{3}$ : aromatics of 3: 12: 52, indicating 5d contains three hydrides and two Xantphos ligands. A $^{1}$H-coupled $^{195}$Pt-INEPT experiment gave an antiphase quartet, which confirms that 5d contains three equivalent hydrides in the NMR time scale. The pattern observed both in the $^{1}$H and $^{31}$P NMR spectra is very similar to that observed by Tulip et al.\textsuperscript{86} for [Pt$_{2}$H$_{3}$]($t$-Bu)$_{2}$P(CH$_{2}$)$_{3}$P($t$-Bu)$_{2}$][BPh$_{4}$] and by Knobler et al.\textsuperscript{85} for [(dppe)$_{2}$H$_{3}$Pt$_{2}$][BPh$_{4}$]. Although NMR spectroscopy of these complexes indicates that all hydrides are equivalent in solution, both bridging and terminal hydrides are observed by IR. The neutron diffraction crystal structure of the latter complex confirms the presence of one terminal and two bridging hydrides.\textsuperscript{77} Since then, many cationic hydride-bridged dimers with bidentate ligands have been reported in which the hydrides remain equivalent on the NMR-time scale even at low temperature.\textsuperscript{87} Based on this information we propose for 5d the dimeric structure shown in chart 3-4.

![Chart 3-4. Proposed structure for dimer 5d.](image)

The shape of the hydride signal can be explained by considering the natural abundance of the NMR active $^{195}$Pt nuclei (33.8 %). Isotopomer A corresponds to 44 % of the molecules containing no $^{195}$Pt nuclei, in this case only H-P coupling is observed. The other two isotopomers contain one (B, 44.8 %) or two (C, 11%) $^{195}$Pt nuclei and thus display coupling to both phosphorus and platinum. Thus, the quintet of quintets pattern observed arises from the superposition of the resonances of the three isotopomers. Similarly, the observed $^{31}$P NMR spectrum (figure 3-8) results from the superposition of the resonances of the above mentioned isotopomers. Accordingly, isotopomer A displays only one singlet, while in isotopomer B with just one $^{195}$Pt nuclei, the phosphorus atoms on each platinum become non-equivalent and give rise to an $A_{2}A'_{2}X$ spin system. This system produces a first order doublet of triplets pattern for each of the A and A' phosphorus, so the P-P and
the one and three-bond Pt-P coupling constants can be directly calculated from the spectrum\textsuperscript{86} ($^3J_{P,P} = 13$ Hz, $^1J_{P,P} = 3374$ Hz, $^3J_{P,Pt} = 238$ Hz). Isotopomer C gives rise to an $A_2A'_{2XX'}$ spin system, which displays a second order spectrum. The main feature of this spectrum is a doublet of separation $N = ^1J_{P,Pt} + ^2J_{P,Pt}$ (fig. 3-8). This type of spectrum was analyzed in detail by Tulip \textit{et al.} \textsuperscript{86}

![Figure 3-8. $^1$H NMR (left) and $^{31}$P-$^1$H (right) NMR spectra of 5d. A isotopomer with no $^{195}$Pt (43.8%). B isotopomer with one $^{195}$Pt (44.8%). C isotopomer with two $^{195}$Pt (11.4%).]

The formation of the dimeric species can be formally regarded as an attack of a dihydride intermediate to an unsaturated Pt species or a species containing a weakly coordinated ligand, in this case the aminopyridyne (Scheme 3-5).

![Scheme 3-5. Possible pathway for the formation of dimer 5d.]

In fact, diphosphine platinum complexes containing pyrazole ligands or a coordinated solvent molecule are commonly used as precursors to form hydride-bridged dimers.\textsuperscript{85,88}
Thus, the ease of formation of this type of dimers is determined by the ability of the N,N ligand to dissociate from the platinum.

Conclusions

The coordination mode of the hemilabile pyridylphosphine ligand in a series of [(diphosphine)Pt(PPh$_2$Py)]$^{2+}$ complexes is determined by the steric demands of the diphosphine ligand. With increasing bite angle the phenyl rings of the diphosphine "embrace" the platinum center, leaving less space for the coordination of other ligands, and thus destabilizing bidentate coordination of the PPh$_2$Py. If the diphosphine becomes too bulky as in the case of Xantphos, P-monodentate coordination of the pyridylphosphine becomes favorable, resulting in a mixture of cis and trans-1d.

The same steric factors influence the reactivity of 1a-d towards the heterolytic cleavage of dihydrogen. Accordingly, the ligand with the smallest bite and cone angle (ddpf) forms complexes in which the pyridyl moiety is strongly coordinated to the platinum center and thus is unable to provide the vacant coordination site required for the coordination and splitting of dihydrogen.

Complexes 2a-d contain a hydride as well as a proton donor in the same molecule, but no dihydrogen bonds are formed. It has been proposed that wide bite angle ligands reduce the partial negative charge on the hydride ligand. In the case of 2a-d, the decrease of the hydridic character induced by the bite angle of the diphosphines, results in a too weak an electrostatic interaction between the hydride and the pyridinium proton.

While complexes 1b-d (pyridylphosphine) react with dihydrogen to form mononuclear hydride species, complexes 3a, 3d and 4d (aminopyridine) do not react at all under the same conditions. At increased pressure and temperature, hydride bridged dimers are formed. The difference in reactivity seems to arise from the different strength of the Pt-P bond compared to the Pt-N bond. The soft phosphorus atom coordinates strongly to the soft platinum center, thus preventing dissociation of the PPh$_2$Py ligand. In contrast, the hard nitrogen atoms in the aminopyridine ligand de-coordinate easier from the platinum center, especially in the protonated species. Thus, coordinatively unsaturated species are formed which are able to form dinuclear products.
Experimental section

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove box techniques. All solvents were dried and freshly distilled under nitrogen prior to use. Dichloromethane was distilled from CaH\textsubscript{2}, diethyl ether, tetrahydrofuran, hexanes and pentane were distilled from sodium / benzophenone. DPEphos\textsuperscript{,37} Sixantphos\textsuperscript{,37} Xantphos\textsuperscript{,37} 6-methyl-diphenyl-2-pyridylphosphine\textsuperscript{,89} (CH\textsubscript{3}CN)\textsubscript{2}PtCl\textsubscript{2}\textsuperscript{m} and Na[B(3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})]\textsuperscript{91} were synthesized according to literature procedures. Dppf was purchased from Aldrich Chemical Co. and used as received. Diphenyl-2-pyridylphosphine was purchased from Aldrich Chemical Co. and re-crystallized from hot hexanes prior to use. High pressure reactions were carried out in home-made stainless steel autoclaves fitted with a glass liner, or in a Fisher-Porter bottle for reactions up to 3 bar. NMR spectra were recorded on a Bruker DPX 300, Bruker DRX 300, Bruker AMX 400 or Varian Innova 500. CD\textsubscript{2}Cl\textsubscript{2} was dried over CaH\textsubscript{2}, vacuum transferred, degassed by three freeze-thaw cycles and stored over molecular sieves. Elemental analyses were performed by the Service de Microanalyse du LCC-CNRS, Toulouse, France. X-ray diffraction studies were performed by the National NWO-CW Single Crystal Service Facility, Universiteit Utrecht, The Netherlands; or by the Service de Diffraction des Rayons X du LCC-CNRS, Toulouse, France.

dppf(diphenyl-2-pyridylphosphine)platinum (II) bis triflate (1a)

652 mg (0.759 mmol) of (dppf)PtCl\textsubscript{2} and 511 mg (1.99 mmol) of silver triflate were dissolved in 20 mL dry CH\textsubscript{2}Cl\textsubscript{2}. The color of the solution changes almost immediately from orange to deep red and a white precipitate forms. The reaction mixture was stirred for three hours with protection from light. A solution of 251 mg (0.954 mmol) of 2-diphenyl-2-pyridylphosphine in 10 mL CH\textsubscript{2}Cl\textsubscript{2} was added via cannula and the reaction mixture was stirred overnight. The formed AgCl was allowed to settle and the solution was filtered through celite. The clear orange solution was evaporated in vacuum and the solid obtained was re-crystallized from CH\textsubscript{2}Cl\textsubscript{2} / diethyl ether to yield 1a as a microcrystalline orange solid. Yield: 950 mg (0.724 mmol), 95 %.

\textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 295 K): 8.22 (m, 1 H, Py-H\textsuperscript{6}), 8.03-7.11 (m, 33H, Ar), 5.2, 4.86, 4.77, 3.65 (s, 8H, Cp). 31P{\textsuperscript{1}H} NMR (121.5 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 295 K): -38.3 (dd, P\textsubscript{X}, J\textsubscript{NPX} = 364 Hz, J\textsubscript{PXP} = 19 Hz, J\textsubscript{PXP} = 2058 Hz), 9.16 (t, P\textsubscript{M}, J\textsubscript{PMP} = 12 Hz, J\textsubscript{PMP} = 3496 Hz); 24.0 (dd, P\textsubscript{A}, J\textsubscript{PAP} = 2737 Hz). 13C {\textsuperscript{1}H} NMR (125.7 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 295 K): 67.1,
Heterolytic Activation of \( \text{H}_2 \) with Pt complexes

71.9 (d, \( \text{C}_1 \), \( \text{Cp} \), \( J_{\text{CP}} = 77 \text{ Hz} \)), 78.1 (d, \( \text{CH} \), \( \text{Cp} \), \( J_{\text{CP}} = 12 \text{ Hz} \)), 77.2 (d, \( \text{CH} \), \( \text{Cp} \), \( J_{\text{CP}} = 9 \text{ Hz} \)), 76.5 (d, \( \text{CH} \), \( \text{Cp} \), \( J_{\text{CP}} = 11 \text{ Hz} \)), 75.7 (d, \( \text{CH} \), \( \text{Cp} \), \( J_{\text{CP}} = 8 \text{ Hz} \)), 117.7 (d, \( \text{C}_1 \), \( \text{Ph} \), \( J_{\text{CP}} = 59 \text{ Hz} \)), 121.5 (q, \( \text{CF}_3 \), \( J_{\text{CF}} = 321 \text{ Hz} \)), 127.6 (d, \( \text{C}_1 \), \( \text{Ph} \), \( J_{\text{CP}} = 55 \text{ Hz} \)), 129.2 (d, \( \text{C}_1 \), \( \text{Ph} \), \( J_{\text{CP}} = 70 \text{ Hz} \)), 129.7, 129.9, 131.1, 131.3, 131.4, 133.2, 134.0, 134.1, 134.4, 134.9, 135.0 (CH, \( \text{Ph} \)), 143.5 d, 148.3 (d, \( \text{CH} \), \( \text{Py} \), \( J_{\text{CP}} = 13 \text{ Hz} \)), 170.7 (d, \( \text{C} \), \( \text{Py} \), \( J_{\text{CP}} = 69 \text{ Hz} \)).

Anal. Calcd. for \( \text{Cs}_5\text{H}_2\text{Pt}_2\text{F}_6\text{NS}_2\text{Fe} \): C 48.56; H 3.23. Found: C 48.13; H 3.21.

dppf(diphenyl-2-pyridylphosphine)platinum (II) bis BARF (1a')

100 mg (0.122 mmol) of (dppf)PtCl\(_2\), 238 mg (0.268 mmol) of NaBARF and 35.3 mg (0.134 mmol) of 2-diphenyl-2-pyridylphosphine were dissolved in 10 mL CH\(_2\)Cl\(_2\). After a few minutes, the reaction mixture became orange-red and a fine white precipitate was observed. The reaction mixture was stirred overnight and then filtrated over celite to remove the NaCl formed. After evaporation of the solvent and washing with pentane (2 x 5 mL), pure 1a' was obtained as a finely orange solid. Yield: 317.2 mg (0.116 mmol), 95%.

\(^1\text{H NMR} (300 \text{ MHz, CD}_2\text{Cl}_2, 233 \text{ K}): 7.74, 7.50 (s, \text{BARF}), 8.1-7.0 (m, \text{Ar}) 4.82, 4.67 (br S, 4H, \text{Cp}), 4.37, 3.51 (s, 4H, \text{Cp}). \(^{31}\text{P}\{^1\text{H}\} \text{NMR} (121.5 \text{ MHz, CD}_2\text{Cl}_2, 233 \text{ K}): -38.5 (dd, \text{P}_x, J_{\text{PXPA}} = 358 \text{ Hz}, J_{\text{PXP M}} = 19.5 \text{ Hz}, J_{\text{PX Pt}} = 2066 \text{ Hz}), 8.72 (dd, \text{P}_M, J_{\text{PMPA}} = 11 \text{ Hz}, J_{\text{PMPt}} = 3486 \text{ Hz}); 23.1 (dd, \text{P}_A, J_{\text{PA Pt}} = 2717 \text{ Hz}).


dppf(diphenyl-2-(6-methyl-pyridyl)phosphine)platinum (II) bis triflate (1a-Me)

This compound was prepared as described for 1a using 250 mg (0.305 mmol) of (dppf)PtCl\(_2\) and 196 mg (0.762 mmol) of silver triflate dissolved in 20 mL CH\(_2\)Cl\(_2\) and adding a solution of 93 mg (0.335 mmol) of 6-methyl- diphenyl 2-pyridylphosphine in 5 mL CH\(_2\)Cl\(_2\). Yield: 354 mg (0.275 mmol), 90%.

\(^1\text{H NMR} (300 \text{ MHz, CD}_2\text{Cl}_2, 233 \text{ K}): 8.10 - 6.67 (m, \text{Ar, both products}); 5.03, 4.90, 4.75, 4.71 (s, 2H each, \( \text{Cp prod. 2} \)); 4.37, 4.29, 3.31 (s, 8H total, \( \text{Cp prod. 1} \)); 2.48 (s, 3H, \( \text{CH}_3 \), \( \text{prod. 2} \)); 1.72 (s, 3H, \( \text{CH}_3 \), \( \text{prod. 1} \)). \(^{31}\text{P}\{^1\text{H}\} \text{NMR} (121.5 \text{ MHz, CD}_2\text{Cl}_2, 233 \text{ K}): \text{Product 1, AMX spin system: -40.0 (dd, \text{P}_x, J_{\text{PXPA}} = 354 \text{ Hz}, J_{\text{PXP M}} = 20.7 \text{ Hz}, J_{\text{PX Pt}} = 2075 \text{ Hz}); 5.04 (dd, \text{P}_M, J_{\text{PMPA}} = 12.2 \text{ Hz}, J_{\text{PMPt}} = 3533 \text{ Hz}); 20.9 (dd, \text{P}_A, J_{\text{PA Pt}} = 2728 \text{ Hz}). \text{Product 2, ABX spin system: 15.84 (dd, \text{P}_x, J_{\text{PA PA}} = 14.6 \text{ Hz}, J_{\text{PAPB}} = 19.4 \text{ Hz}, J_{\text{PAPt}} = 3764 \text{ Hz}); 16.38 (AB, \text{P}_A, J_{\text{PAPB}} = 425 \text{ Hz}, J_{\text{PA Pt}} = 3461 \text{ Hz}); 23.23 (AB, \text{P}_B, J_{\text{PB Pt}} = 2538 \text{ Hz}). IR (KBr pellet): v(SO\(_3\)) 1260 and 1005 cm\(^{-1}\).

**Chapter 3**

**DPEphos(diphenyl-2-pyridyldiphosphine)platinum (II) bis triflate (1b)**

This compound was prepared as described for 1a using 125 mg (0.157 mmol) of (DPEphos)PtCl₂ and 100 mg (0.392 mmol) of silver triflate in 10 mL of CH₂Cl₂. The reaction mixture changed from colorless to bright yellow. After 3 hours stirring 45.4 mg (0.172 mmol) of 2-diphenyl-2-pyridylphosphine in 5 mL of CH₂Cl₂ were added via cannula, and the reaction mixture turned pale yellow. The light gray solid obtained was recrystallized from CH₂Cl₂/diethylether to yield 1b as a white powder.

Yield: 180 mg (90 %). Crystals suitable for X-ray analysis were obtained by layering a concentrated CH₂Cl₂ solution of the pure product with 20 mL of hexane.

**¹H NMR (300 MHz, CD₂Cl₂, 295 K):** 8.23 (m, 1 H, Py-H⁶), 7.98-6.80 (m, 39 H, Ar), 6.66 (m, 1 H, Py-H⁵), 6.38 (m, 1 H, Py-H⁴). **³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 295 K):** -39.2 (dd, Pₓ, JₓPₓ = 372 Hz, JₓPₓₓ = 15.8 Hz, JₓPₓₓₓ = 2143 Hz); -7.5 (t, Pₓ, JₓPₓₓₓ = 16.3 Hz, JₓPₓₓₓₓ = 3536 Hz); 15.8 (dd, Pₓ, JₓPₓₓₓ = 2829 Hz).

**¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂, 295 K):** 118.0, 118.4, 118.7 (Cₓ), 119.0 (d, CH, JₐC = 7.5 Hz), 121.5 (q, CF₃, JₓC = 321.5 Hz), 123.4, 125.9 (Cₓ), 125.9, 126.1 (CH), 127.5 (d, CH, JₐC = 7.5 Hz), 126.5 (d, Cₓ, JₐC = 38.1 Hz), 129.9, 130.8, 131.1, 133.2, 133.5, 133.7, 133.9, 134.4, 134.8, 135.6, 136.1, 137.7, 143.5 (d, CH, Py, JₐC = 5.0 Hz), 148.5 (d, CH, Py, JₐC = 8.0 Hz), 158.9, 159.1 (d, C-O, JₐC = 7 Hz), 170.4 (d, Cₓ, Py, JₐC = 67.9 Hz).


**Sixantphos(diphenyl-2-pyridyldiphosphine)platinum (II) bis triflate (1c)**

This compound was prepared as described for 1a using 502 mg (0.583 mmol) of (Sixantphos)PtCl₂ and 374.8 mg (1.46 mmol) of silver triflate in 25 mL of CH₂Cl₂, and adding 169 mg (0.642 mmol) of 2-diphenyl-2-pyridyldiphosphine in 10 mL of CH₂Cl₂. A yellow solid was obtained and recrystallized from CH₂Cl₂/pentane to yield 1c as a white microcrystalline solid. Yield: 696 mg (0.515 mmol), 88 %. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated CH₂Cl₂ solution of the pure product, at room temperature.

**¹H NMR (300 MHz, CD₂Cl₂, 295 K):** 8.20 (m, 1 H, Py-H⁶), 8.05-6.97 (m, 38 H, Ar), 6.82 (m, 1 H, Py-H⁵), 0.77 (s, 6H, CH₃). **³¹P{¹H} NMR (CD₂Cl₂ at 295 K):** -40.1 (dd, Pₓ, JₓPₓ = 360 Hz, JₓPₓₓ = 15.2 Hz, JₓPₓₓₓ = 2142 Hz); -6.6 (t, Pₓ, JₓPₓₓₓₓ = 19.3 Hz, JₓPₓₓₓₓ = 3563 Hz); 12.8 (dd, Pₓ, JₓPₓₓₓ = 2772 Hz). **¹³C{¹H} NMR (125.7 MHz, CD₂Cl₂, 295 K):** -2.4 (s, Si-CH₃), 114.3 (d, Cₓ, JₓC = 66.5 Hz) 115.7 (d, Cₓ, JₓC = 69.3 Hz), 121.5 (q, CF₃, JₓC = 321.5 Hz), 126.0 (d, Cₓ, C-O, JₓC = 15.1 Hz), 126.2 (d, CH, JₓC = 7.8 Hz), 126.5 (d, Cₓ, JₓC = 38.1 Hz), 130.8, 131.1, 133.5, 133.7, 133.9, 134.4, 134.8, 135.6, 136.1, 137.7, 143.5 (d, CH, Py, JₓC = 5.0 Hz), 148.5 (d, CH, Py, JₓC = 8.0 Hz), 158.9, 159.1 (d, C-O, JₓC = 7 Hz), 170.4 (d, Cₓ, Py, JₓC = 67.9 Hz).

Heterotypic Activation of H₂ with Pt complexes

Hz), 127.3, 129.8, 129.9, 130.1, 131.0, 131.1, 133.0, 133.3, 133.9, 134.2, 134.6, 135.7, 139.5, 139.8, 143.2 (d, CH, Py, J_Cp = 5.0 Hz), 148.9 (d, CH, Py, J_Cp = 13.0 Hz), 170.7 (d, C, Py, J_Cp = 56.4 Hz).

Anal. Calcd. for C_{57}H_{46}P_{3}O_{2}NS_{2}F_{6}SiPt.CH_{2}Cl_{2} : C 49.0; H 3.21. Found: C 49.71; H 3.40.

Xantphos(diphenyl-2-pyridylphosphine)platinum (II) bis triflate (1d)
This compound was prepared as described for 1a using 250 mg (0.296 mmol) of (Xantphos)PtCl₂ and 190.2 mg (0.740 mmol) of silver triflate in 15 mL of CH₂Cl₂, and adding 86 mg (0.330 mmol) of diphenyl-2-pyridylphosphine in 5 mL of CH₂Cl₂. A yellow solid is obtained and recrystallized from CH₂Cl₂/Ether to yield 1d as a light yellow powder. Yield: 335 mg (0.251 mmol) 85%. Crystals suitable for X-ray analysis were obtained by layering a concentrated CH₂Cl₂ solution of the pure product with 10 mL of hexane.

^1H NMR (300 MHz,CD₂Cl₂, 295 K): 8.44 – 6.12 (m, Ar, 40H); 1.95 (s, CH₃, cis prod); 1.72 (s, CH₃, 1d-trans); 1.62 (s, CH₃, 1d-cis), 6H total for the three signals. ^31P{^1H} NMR (121.5 MHz, CD₂Cl₂, 295 K): 1d-cis: -41.3 (dd, P_x, J_{PXPA} = 358 Hz, J_{PXPM} = 12.2 Hz, J_{PXPt} = 2118 Hz); -6.5 (dd, P_M, J_{PMPA} = 24.3 Hz, J_{PMPt} = 3654 Hz); 12.0 (dd, P_A, J_{PAPT} = 2800 Hz). 1d-trans: 16.3 (t, P_x, J_{PAPX} = 12.1 Hz, J_{PXPt} = 4447 Hz), 39.2 (d, P_A, 2P, J_{PAPT} = 2503 Hz).

Anal. Calcd. for C_{58}H_{46}P_{3}O_{2}NS_{2}F_{6}Pt : C 52.18; H 3.47; N 1.05. Found: C 52.05; H 3.35.

Xantphos(diphenyl-2-pyridylphosphine)platinum (II) bis BARF (1d')
This compound was prepared as described for 1a' using 100 mg (0.118 mmol) of (Xantphos)PtCl₂, 210 mg (0.237 mmol) of NaBARF and 31.2 mg of diphenyl-2-pyridylphosphine in 10 mL dry CH₂Cl₂. A light pink foamy solid was obtained.

Yield (crude product): 270 mg (0.098 mmol, 83%).
The ^1H and ^31P NMR spectra of this product are the same as for 1d.

Xantphos(diphenyl-2-(6-methyl-pyridyl)phosphine )platinum (II) bis BARF (1d'-Me)
This compound was prepared as described for 1a' using 100 mg (0.118 mmol) of (Xantphos)PtCl₂, 210 mg (0.237 mmol) of NaBARF and 36 mg of 6-methyl-diphenyl-2-pyridylphosphine in 10 mL dry CH₂Cl₂. A light red oil was obtained which after washing with pentane (2 x 5mL.) becomes a pink foamy solid.

Yield: 311 mg (0.112 mmol), 95%.
1H NMR (500 MHz, CD2Cl2, 295 K): 7.83-6.80 (m, 63 H, Ar), 2.36 (s, 3H, Py-CH3), 1.76 (s, 6H,CH3). 31P{1H} NMR (CD2Cl2 at 295 K): -0.49 (d, P_A, 2P, J_{PAP} = 17.4 Hz, J_{PAP} = 2476 Hz); 37.70 (t, P_X, J_{XPX} = 4322 Hz). 13C {1H} NMR (75.5 MHz, CD2Cl2, 295 K): 24.3 (s, C-CH3), 33.4 (s, CH3 -Py), 117.8 (CH), 121.5 (q, CF3, J_{CF} = 321.5 Hz), 123.1, 123.4, 129.0, 129.4 (C_i), 129.5 (d, CH, J_{CP} = 15.1 Hz), 130.4 (t, CH, J_{CP} = 16 Hz), 133.8 (t, CH, J_{CP} = 7.5 Hz), 134.4, 134.7, 134.9, 135.1, 137.3 (CH), 161.4, 162.8 (d, C, Py, J_{CP} = 50.0 Hz).

dppf(diphenyl-2-pyridylphosphine)hydridoplatinum (II) bis triflate (2a)
43 μL of diethylamine were added to a solution of 540 mg (0.412 mmol) of 1a in 20 mL CH2Cl2. This solution was introduced into a stainless steel autoclave under argon, and purged 3 times with H2, after which the autoclave was pressurized to 4 bar of H2 and heated to 40 °C overnight. After reducing the pressure to 1 bar and cooling to room temperature, the reaction mixture was transferred to a Schlenk under 1 bar of H2. The yellow brown solution was evaporated under vacuum to obtain an amber sticky solid, which after thorough washing with diethyl ether (5 x 10 mL) and drying under vacuum afforded a golden powder. The ammonium salt was removed by crystallization from CH2Cl2 / Et2O.

100 mg (0.076 mmol) of this complex were dissolved in 10 mL of CH2Cl2 and the solution was frozen in an acetone / liquid nitrogen bath. 10.1 μL (17.16 mg, 0.114 mmol) of HOTf were added using a microsyringe. The Schlenk was shaken to dissolve the acid and the reaction mixture was slowly warmed to room temperature. After 1 hr. at room temperature, the solvent was evaporated in vacuum. The oily orange product was washed several times with diethyl ether to obtain a dark orange solid. Yield: 80 mg (0.061 mmol), 72 %.

1H NMR (300 MHz, CD2Cl2, 295 K): 15.1 (br, NH), 8.54 (br, 1 H, Py-H\textsuperscript{\textdegree}), 8.35 (br, 1 H) 7.84-7.07 (m, 32 H, Ar), 4.87 (s, 2H, Cp); 4.61(s, 2H, Cp); 4.30 (s, 2H, Cp); 3.62(s, 2H, Cp); 5.72 (s, 1H, hydride, J_{HPA} = 11.7, J_{HPB} = 18.45 Hz, J_{HPX} = 154 Hz J_{HPY} = 762 Hz). 31P{1H} NMR (121.5 MHz, CD2Cl2, 295 K): 22.9 (P_X, J_{PXPA} = 10.81 Hz, J_{PXPB} = -8.8 Hz, J_{PXPA} = 2310 Hz); 21.8 (P_B, J_{PAPB} = 364 Hz, J_{PPB} = 2755 Hz); 28.7 (P_A, J_{PAPI} = 3033Hz). IR ν(Pt-H) = 2078 cm\textsuperscript{-1}. 80
dppf(diphenyl-2-(6-methyl-pyridyl)phosphine) hydridoplatinum(II) bis triflate (2a-Me)

100 mg (0.075 mmol) of 1a-Me were dissolved in 10 mL CH$_2$Cl$_2$ and introduced into a stainless steel autoclave under Ar and purged 3 times with H$_2$. The autoclave was pressurised to 4 bar of H$_2$ and heated to 40 °C overnight. After cooling to room temperature and reducing the pressure to 1 bar, the reaction mixture was transferred to a Schlenk under 1 bar of H$_2$. The orange solution was evaporated under vacuum and the remaining solid was washed with 10 mL of pentane and re-crystallized from CH$_2$Cl$_2$/Et$_2$O to afford 2a-Me as a dark orange solid. Yield: 93 mg (0.070 mmol), 93%.

$^1$H NMR (300MHz, CD$_2$Cl$_2$, 295 K): Hydride region, 2a-Me cis $\delta$5.61 (ddd, $J_{HPA} = 10.5$ Hz, $J_{HPB} = 22.5$ Hz, $J_{HPX} = 150.0$ Hz, $J_{HP} = 750$ Hz), 2a-Me trans $\delta$5.11 (dt, $J_{HPA} = 13.5$ Hz, $J_{HPX} = 162.0$ Hz, $J_{HP} = 797$ Hz). $^{31}$P{${^1}$H} NMR (121.5 MHz, CD$_2$Cl$_2$, 295 K): 2a-Me cis, 20.7 (P$_B$, J$_{PBP} = 372$ Hz, J$_{PBPX} = -21.9$ Hz, J$_{PBP} = 3079$ Hz), 29.9 (P$_A$, J$_{PAP} = 2750$ Hz). 2a-Me trans, 22.9 (P$_X$, J$_{PXP} = 19.4$ Hz, J$_{PXP} = 2255$ Hz, J$_{PXP} = 2255$ Hz), 25.3 (P$_A$, J$_{PAP} = 2863$ Hz).

DPEphos(diphenyl-2-pyridylphosphine) hydridoplatinum (II) bis triflate (2b)

This compound was prepared as described for 2a-Me using 200 mg (0.155 mmol) of 1b dissolved in 20 mL CH$_2$Cl$_2$. The crude off-white solid was washed with 10 mL of pentane and re-crystallized from CH$_2$Cl$_2$/Et$_2$O to afford pure 2b as a white solid. Yield: 170 mg (0.131 mmol), 85%.

$^1$H NMR (300MHz, CD$_2$Cl$_2$, 295 K): 8.50 (d, 1 H, Py-H$^6$), 7.77-6.87 (m, 38 H, Ar), 6.78 (t, 1H, Py, J= 7.3 Hz), 6.61 (t, 1H, Py, J= 9.5 Hz), 6.07 (m, 1H, Py), -6.81 (s, 1H, hydride, $J_{HPA} = 13.0$ Hz, $J_{HPB} = 16.5$ Hz, $J_{HPX} = 163.1$ Hz $J_{HP} = 739$ Hz). $^{31}$P{${^1}$H} NMR (121.5 MHz, CD$_2$Cl$_2$, 295 K): 16.4 (P$_B$, J$_{PBP} = 361$ Hz, J$_{PBPX} = -10.5$ Hz, J$_{PBP} = 2944$ Hz); 16.5 (P$_X$, J$_{PXP} = 31.7$ Hz, J$_{PXP} = 2217$ Hz); 23.4 (P$_A$, J$_{PAP} = 2905$ Hz).

Anal. Calcd. for C$_{55}$H$_{44}$P$_3$O$_7$NS$_2$F$_6$Pt: C 50.93; H: 3.42. Found: C 51.05; H 3.45

Sixanthphos(diphenyl-2-pyridylphosphine) hydridoplatinum (II) bis triflate (2c)

This compound was prepared as described for 2a-Me using 200 mg (0.148 mmol) of 1c. The crude off-white product was re-crystallized from CH$_2$Cl$_2$/pentane to afford pure 2c as a white solid. Yield: 180 mg (0.133 mmol) 90%. 

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**Xantphos(diphenyl-2-pyridylphosphine)hydridoplatinum (II) bis triflate (2d)**

This compound was prepared as described for 2a-Me using 250 mg (0.187 mmol) of 1d. The crude pale yellow product was re-crystallized from CH₂Cl₂/pentane to afford pure 2d as a white solid. Yield: 230 mg (0.172 mmol) 92 %.

**1H NMR (300 MHz, CD₂Cl₂, 295 K):** 15.4 (br, NH), 9.17 (m, 1 H, Py-H), 8.50-6.90 (m, 39 H, Ar), 1.83 (s, 6H, CH₃).

**31P{1H} NMR (121.5 MHz, CD₂Cl₂, 295 K):** 15.8 (Pₓ, JₓPA = 16.3 Hz, JₓPB = -19.6 Hz, JₓPₓP = 2298 Hz), 17.7 (Pᵧ, JᵧPA = 375 Hz, JᵧPB = 2937 Hz); 23.0 (Pₐ, JₐPₓP = 3045 Hz). **195Pt NMR (HMQC, 64.19 MHz, CD₂Cl₂, 273 K):** -5090. IR ν(Pt-H) = 2099 cm⁻¹.


**dppf(2-aminomethylpyridine)platinum (II) bis triflate (3a)**

107 mg (0.131 mmol) of (dppf)PtCl₂ and 84 mg (0.327 mmol) of silver triflate were dissolved in 10 mL of CH₂Cl₂. The solution became deep red and a white precipitate formed. The reaction mixture was stirred for 4 hours with protection from light. 14 µL (0.131 mmol) of 2-(aminomethyl)pyridine were added using a microsyringe, after which the reaction mixture was bright yellow. After stirring overnight, the AgCl formed was allowed to precipitate and the solution was filtered over celite. The clear solution was evaporated in vacuum and the solid obtained was washed with Et₂O (3 x 5 mL) to yield 3a as a yellow solid.

**1H NMR (300 MHz, CD₂Cl₂, 233 K):** 8.10-7.32 (m, 24H, Ar); 6.72 (m, 1H, NH); 4.07 (br. s, 7H, Cp + NH); 4.25 (s, 2H, Cp); 3.34 (s, 2H, CH₂). **31P{1H} NMR (121.5 MHz, CD₂Cl₂, 233 K):** 8.6 (JₓPₓ = 21.48 Hz, JₓPᵧ = 3485 Hz); 14.6 (JᵧPᵧ = 3508 Hz).
Xantphos(2-aminomethylpyridine)platinum (II) bis triflate (3d)
This compound was prepared as described for 3a using 100 mg (0.118 mmol) of XantphosPtCl₂ and 76 mg (0.296 mmol) of silver triflate in 10 mL CH₂Cl₂ to afford a bright yellow suspension. After 3 hrs of stirring at room temperature, 12.21 µL of 2-(aminomethyl)pyridine were added and the reaction mixture was stirred overnight. The crude product was re-crystallized from CH₂Cl₂/ Et₂O. Yield: 129 mg (0.110 mmol), 93 %.

¹H NMR (300 MHz, CD₂Cl₂, 193 K): 7.95-6.51 (m, 30 H, Ar), 5.82 (br, 1H, NH), 5.18 (br, 1H, NH), 4.29 (br, 2H, CH₂), 1.99 (s, 3H, CH₃), 1.62 (s, 3H, CH₃). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 295 K): -13.9 (J_PP = 22.6 Hz, J_Pp₂ = 3536 Hz), -6.0 (J_Pp₂ = 3552 Hz).

dppf(2-aminopyridine)platinum (II) bis tetraphenylborate (4a)
150 mg (0.183 mmol) of (dppf)PtCl₂ and 156 mg (0.457 mmol) of sodium tetraphenylborate were dissolved in 10 mL of CH₂Cl₂. After 1 hour the solution became deep red and a white precipitate formed. After addition of 17.2 (0.183 mmol) of 2-aminopyridine the reaction mixture became bright yellow. After stirring for 1.5 hours, the solution was filtered over celite. The clear solution was evaporated in vacuum and the obtained solid was re-crystallized from CH₂Cl₂ / to yield 4a as a light orange solid. Yield: 220 mg (0.148 mmol), 81 %.

¹H NMR (300 MHz, CD₂Cl₂, 295 K): 8.03-7.36 (m, 24H, Ar); 7.37-6.89 (m, 20H, BPh₄); 6.37 (m, ¹H, NH); 6.01 (m, 1H, NH); 5.02 (br. s, 3H, Cp); 4.87 (s, 1H, Cp); 4.79 (s,1H, Cp); 4.74 (s, 1H, Cp); 3.69 (s, 1H, Cp); 3.61 (s, 1H, Cp). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 295 K): 8.3 (J_PP = 14.6 Hz, J_Pp₂ = 2324 Hz); 19.7 (J_Pp₂ = 3705 Hz).

Xantphos(2-aminopyridine)platinum (II) bis triflate (4d)
This compound was prepared as described for 3d using 250 mg (0.296 mmol) of XantphosPtCl₂ and 190 mg (0.742 mmol) of silver triflate. 30 mg (0.319 mmol) of 2-aminopyridine were dissolved in 5 mL of CH₂Cl₂ and added to the reaction mixture via cannula. The crude product was re-crystallized from CH₂Cl₂/ Et₂O. Yield: 273 mg (0.233 mmol), 79 %.

¹H NMR (300 MHz, CD₂Cl₂, 193 K): 8.03-6.67 (m, 30 H, Ar), 6.07 (br, 2H, NH₂), 2.01 (br. s, 3H, CH₃), 1.82 (s, 3H, CH₃). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 295 K): -18.4 (J_Pp₂ = 3911 Hz); -12.2 (J_Pp₂ = 3728 Hz).
bis(Xantphos)trihydrido platinum(II) triflate (5d)

100 mg (0.098 mmol) of 4d were dissolved in 20 mL of CH₂Cl₂ and introduced into a stainless steel autoclave under Ar. The autoclave was purged 3 times with H₂, pressurized to 10 bar of H₂, and heated to 50 °C for 65 hours. After reducing the pressure to 1 bar and cooling to room temperature, the reaction mixture was transferred to a Schlenk under 1 bar of H₂. The golden solution was evaporated under vacuum and the solid was washed with 10 mL of pentane and re-crystallized from CH₂Cl₂/Et₂O to afford 5b as a golden brown solid. Yield: 75 mg (0.044 mmol), 90 %.

¹H NMR (300 MHz, CD₂Cl₂, 295 K): 7.67 (m, 4H, Ar); 7.29-7.02 (m, 42H, Ar); 6.29 (m, 4H, Ar); 1.78(s, 12H, CH₃); -7.20 (m, 3H, hydride, J_H-Pt = 42 Hz, J_H-Pt = 429 Hz).

³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 295 K): isotopomer A 22.94(s); isotopomer B ³J_Pp = 13 Hz, ³J_PP = 3374 Hz, ³J_PP = 238 Hz); isotopomer C, N= 3598.8 Hz, ³²J_PP = 224.8 Hz).

¹³C{¹H} NMR (75.5 MHz, 295 K): 155.5 (C_q, C-O); 135.3, 134.0, 132.5, 131.2 (CH, Ph); 128.6 (pt, C_r, J_CF = 7.5 Hz); 127.9; 125.2 (pt, C_r, J_CF = 8.0 Hz); 121.5 (q, CF₃, J_CF = 321.5 Hz), 27.2 (CH₃).

¹⁹⁵Pt{³¹P} NMR (INEPT, 85.6 MHz, CD₂Cl₂, 295 K): -4812 (J_Pt-H = 428 Hz). IR ν(Pt-H) = 2121 cm⁻¹.

Heterolytic Activation of $\text{H}_2$ with Pt complexes

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