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Chapter 5

An NMR Study of Pt(II) hydride complexes containing S-N and P-S ligands.

Abstract

Oxidative addition of pyridine-2-thiol (HSpy) to [(dpf)Pt(trans-stilbene)] afforded a neutral platinum hydride complex containing a dangling pyridyl moiety. A faster reaction was observed under dihydrogen pressure, due to hydrogenation of the coordinated olefin. Protonation of [(dpf)PtH(Spy)] (2) with HOTf afforded complex 3 which contains a pyridinium group in close proximity to the hydride. Although no NMR evidence of a hydride-proton interaction was found, a weak interaction was detected by IR spectroscopy. [(dpf)PtH(PPh2Py)] (5) (dpf = 1-diphenylphosphinoethane-2-thiolate, PPh2Py = 2-diphenylphosphinopyridine) was prepared by reaction of the parent thiol (Hdpf) with Pt(PPh2Py)3 (4). The trans isomer of 5 is the kinetic product of the reaction, but cis-trans isomerization occurred above 193 K. In the presence of free pyridylphosphine, ligand scrambling takes place in 5 to form [PtH(PPh2Py)3] (6) and [Pt(dppe)2] (8). In absence of free pyridylphosphine in solution, complex 5 disproportionates to regenerate the starting material 4 and the bis-chelate complex 8. In spite of the tendency of thiolates to bridge two metal centers, no dimeric or polymeric compounds were detected.
Introduction

Heterobidentate ligands offer the possibility to combine different chemical attributes, for example hard and soft atoms, neutral and anionic donors, or $\sigma$- and $\pi$-donating or $\pi$-accepting properties. Therefore, many ligands combining donor atoms such as phosphorus, nitrogen, oxygen and sulfur have been developed. These atoms differ both in their electronic properties as well as in their steric demands, as phosphorus and nitrogen usually carry three substituents, while oxygen and sulfur generally bear two substituents. In the case of group 16 elements, the non-bonding electron pairs are available to form an extra bond, which opens the possibility to form dimeric and polymeric structures, especially in the case of sulfur.

The pyridine-2-thiolate (Spy) is a versatile ligand which can act as a monodentate, chelating and/or bridging ligand. Morris et al. have prepared a number of iridium hydride complexes containing Spy ligands in which the pyridine nitrogen is protonated (Fig. 5-1). The dangling pyridinium moiety forms intramolecular dihydrogen bonds with the hydride ligand (Fig. 5-1).1-3

![Figure 5-1](image)

Figure 5-1. Intramolecular dihydrogen bonds between a pendant pyridinium and a hydride ligand.

The hydride-proton interactions have been identified in solution, mainly by NMR, and in the solid state by X-ray diffraction. In complex A the Ir-H...H distances are shorter than 2 Å. The authors proposed that the dihydrogen bonds are essential for H/D exchange with D$_2$ gas. The exchange probably takes place via intramolecular proton transfer from the pyridinium to the hydride, yielding an $\eta^2$-H$_2$ intermediate that can then exchange with D$_2$.1
This exchange does not occur in the presence of a good hydrogen bond acceptor such as THF. In this case the pyridinium proton interacts with the oxygen atom instead of the hydride, and therefore it cannot assist the H/D exchange. The same research group investigated the influence of the phosphine ligand in the strength of the dihydrogen bond.\textsuperscript{4} When PCy\textsubscript{3} was replaced by PPh\textsubscript{3}, a weaker proton-hydride interaction was observed by NMR and IR. The effect was attributed to a decrease in the hydridic character of the hydride due to the less basic PPh\textsubscript{3}. A similar effect was observed when one of the hydrides was replaced by a CO ligand, which is a good π acceptor and therefore decreases the electron density of the metal center.

Pt(II) and Pd(II) complexes containing both a diphosphine and a Spy ligand with a pendant pyridyl arms have been recently prepared by Lobana \textit{et al.}\textsuperscript{5,6} An important difference between the pyridine-2-thiolate (Spy) and the 2-diphenylphosphino-pyridine (PPh\textsubscript{2}Py) ligand used in chapter 3, is the anionic character of the former. In chapter 3 it was shown that dihydrogen bonding does not occur in [(diphosphine)PtH(PPh\textsubscript{2}PyH)]\textsuperscript{2+}.

A possible explanation was the low hydridic character of the hydride, which precludes electrostatic interaction between the hydride and the proton. Although this might be intrinsic to platinum hydrides, this effect is enhanced by the dicationic character of the complex. As discussed above, an electron rich metal center may increase the polarization of the M-H bond and thus favor the formation of a dihydrogen bond. Therefore, a more electron rich system was investigated in which the neutral PPh\textsubscript{2}Py ligand was replaced by the anionic pyridylthiolate (Spy) ligand.

Another interesting class of heterobidentate ligands are those containing both phosphorus and sulfur donor atoms. Rhodium complexes containing 2-(diphenylphosphino)-ethanethiolate (dppet) and 2-(diphenylphosphino)-benzenethiolate (dppbt) have been successfully used for the carboxylation of methanol.\textsuperscript{7} The dppet ligand has also been used to prepare several Ni, Pd and Pt complexes, in which the phosphine and sulfur donors are in relative \textit{cis} positions.\textsuperscript{8-10} Owing to the different \textit{trans} influence of phosphorus and sulfur, these ligands open the possibility of regiospecific substitution reactions. Nevertheless, when the complexes contain other ligands apart from dppet, such as phosphines or coordinating anions, equilibria between chelating and monodentate coordination modes are often observed. These equilibria result in isomerization of the complexes and may lead to polymeric structures and ligand scrambling. All these
processes would have a negative effect on the selectivity of a potential catalyst. It was therefore interesting to study the solution behavior of platinum complexes containing a chelating phosphinothiolate ligand and a hemilabile pyridylphosphine.

In this chapter, the chemistry of neutral platinum (II) hydride complexes containing either the pyridine-2-thiolate (Spy) or the 2-(diphenylphosphino)ethanethiolate (dppet) ligands is described. The behavior of these complexes in solution as well as the formation of dihydrogen bonds is compared with the results obtained for complexes containing a PPh2Py ligand described in chapter 3.

**Results and Discussion**

Complexes containing a pyridine-2-thiolate ligand

The oxidative addition of pyridine-2-thiol to a Pt(0) precursor is a convenient synthesis route to neutral hydride complexes. [(dppf)Pt(trans-stilbene)] (1) is an air and temperature stable, easy to synthesize precursor. Reaction of 1 with pyridine-2-thiol (HSpy) afforded the hydride complex [(dppf)PtH(Spy)] (2, scheme 5-1). Performing the reaction under dihydrogen pressure accelerates the reaction, probably due to partial hydrogenation of the stilbene. GC-MS analysis of the reaction mixture indicated the presence of both stilbene and 1,2-diphenylethane.

![Scheme 5-1. Preparation of neutral platinum hydrides containing a pyridinethiolate ligand.](image)

When the reaction was performed under D2, no deuterium was incorporated into complex 2, indicating that the hydride is indeed formed by oxidative addition of the S-H moiety and not by heterolytic cleavage of dihydrogen gas. Although the reaction between 1 and HSpy also proceeds without dihydrogen, an excess of HSpy as well as a longer reaction time (4
Platinum Complexes with N,S and P,S Ligands

h) and heating (40 °C) are needed to drive the reaction to completion. This leads to the formation of about 30 % of side products, which probably contain two molecules of pyridinethiolate coordinated to platinum.

The hydride complex 2 shows a doublet of doublets at $\delta = -3.7$ ppm ($J_{HP} = 18, 192$ Hz, $J_{HPt} = 882$ Hz) in the $^1$H NMR spectrum, indicating that dppe is coordinated in a cis geometry and the hydride is cis to the sulfur atom. The $^{31}$P NMR spectrum displays two doublets ($\delta = 23.4, 27.1$ ppm) with the corresponding platinum satellites. The signal at $\delta = 27.1$ ppm has the smaller Pt-P coupling constant ($J_{PPt} = 2016$ Hz), thus it was assigned to the phosphorus atom trans to the hydride ligand ($P_x$). The resonance at $\delta = 27.1$ ppm displays a coupling constant of 3369 Hz which is typical for phosphorus atoms trans to sulfur ligands.11

In order to investigate the potential dihydrogen bonding in complex 2, the pyridine moiety was protonated with HOTf at low temperature to afford the cationic compound 3 (scheme 5-2). Spectroscopic data for complexes 2 and 3 are shown in table 1.

Protonation of complex 2 can occur at the nitrogen atom, the hydride, the sulfur or the platinum center. Equilibria between complexes protonated at the sulfur atom (hydride-thiol) and the tautomeric dihydrogen-thiolate, resulting from protonation of the hydride, occur readily in ruthenium and osmium complexes.12-14

![Scheme 5-2](image)

**Scheme 5-2.** Protonation of hydride complex 2.

The $^1$H NMR spectrum of the reaction mixture of 2 with HOTf, shows one hydride signal only at $\delta = -5.58$ ppm (doublet of doublets), which is slightly broader than the one of the parent compound 2 (Fig. 5-2). There are no significant differences in the values of the H-P and H-Pt coupling constants (table 5-1). A signal at $\delta = 13.9$ ppm in the $^1$H NMR spectrum, integrating in a 1:1 ratio with respect to the hydride, was assigned to the pyridinium proton. These features indicate that protonation occurred at the nitrogen atom.
only. Upon warming above 0 °C several decomposition products are formed, which do not contain any hydride ligand.

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Table 5-1. $^1$H and $^{31}$P($^1$H) NMR spectroscopic data for complexes 1 and 2. All spectra were measured in C$_7$D$_8$ at 273 K.

The chemical shift of the hydride in 3 is very similar to that of [(dpff)PtH(PPh$_2$Py)]$^{2-}$ (δ = -5.72 ppm, chapter 3). The value of the platinum hydride coupling constants in 2 and 3 (J = 900 Hz) are significantly higher than that for [(dpff)PtH(PPh$_2$Py)]$^{2-}$ (J_{HPt} = 762 Hz). This probably reflects a stronger σ-interaction between the hydride and the metal center in the complexes with the pyridinethiolate ligand. The $^{31}$P NMR spectrum shows that mainly one product was formed, but minor peaks of unidentified impurities were also observed. The spectrum displays two doublets, and again the resonance with the smallest P-Pt coupling was assigned to the phosphorus atom $trans$ to the hydride (P$_X$). This resonance shifts very little compared to that of 2, but the signal for P$_A$ ($trans$ to sulfur) is shifted up-field by almost 5 ppm (table 5-1). The protonated pyridyl moiety is a strongly electron-withdrawing substituent that causes electron density to shift from the sulfur atom to the aromatic ring, thus changing the properties of the sulfur donor. The increase in the P$_A$-Pt coupling constant from 3369 Hz in 2 to 3500 Hz in 3 reflects this change. Another important difference between products 2 and 3 concerns the protons of the Cp rings of dpff. The $^1$H NMR spectra of complex 2 displays four separate resonances for these protons, integrating for two protons each. One of the signals is shifted down-field (δ = 4.5 ppm) relative to the other three resonances that appear between δ = 4.0 and δ = 3.8 ppm. Upon protonation, one of the latter signals shifts down field, while the other two coincide into one broad singlet at δ = 3.9 ppm. This indicates that protonation of the pyridyl moiety causes a structural re-arrangement of the whole molecule and not only of the thiopyridine.
Dihydrogen Bonding

In order to investigate a possible hydride-proton interaction in complex 3, VT-NMR and IR experiments were carried out. The first remarkable difference between 2 and 3 is the upfield shift of almost 2 ppm of the hydride signal upon protonation (Figure 5-1). Morris et al. reported that the chemical shift of the hydride in \([\text{IrH}_2(\eta^1-\text{SC}_5\text{H}_4\text{NH})_2(\text{PCy})_3]\text{BF}_4 \) changes by almost 1 ppm when the hydrogen bonding between the hydride and the pyridinium proton is disrupted. The signals for the hydride ligand in 3 do not show a significant shift upon lowering the temperature, but the signal for the NH proton shifts by 1.3 ppm on going from 273 to 203 K. Below this temperature both signals are too broad to be measured accurately.

The minimum relaxation time of the hydride ligand in 2 is 576 ms at 233 K. For complex 3, the \(T_{1\text{min}}\) of the hydride is 689 ms (253 K), while for the pyridinium proton it is 425 ms (253 K). These relaxation times are rather long compared to those usually reported for protons involved in dihydrogen bonds. For example, the \(T_{1\text{min}}\) in the iridium complex A are 168 ms for Ir-H and 178 ms for the N-H proton (233 K). A dihydrogen bond between the hydride and the pyridinium proton would bring the two atoms into close proximity, causing an increase of the dipole-dipole relaxation. Thus a shorter relaxation time is expected.\(^{3,15}\)

A NOE difference experiment showed no change in the N-H signal when the hydride resonance was irradiated. This result, together with the high \(T_{1\text{min}}\) values for both the hydride and the N-H proton in 3, and the observed increase of the \(T_{1\text{min}}\) of the hydride upon protonation indicate that no dihydrogen interaction occurs.

![Figure 5-2. Hydride region of the \(^1\text{H}\) NMR spectrum of complexes 2 (top) and 3 (bottom).](image-url)
On the other hand, the IR spectrum (toluene, 295 K) shows a shift of the v(Pt-H) band from 2087 cm\(^{-1}\) in 2 to 2075 cm\(^{-1}\) in 3 (slightly broad). Additionally, the spectrum of 3 shows a broad band at 3309 cm\(^{-1}\). Although these IR features have been related to the presence of a hydrogen bonding interaction, the N-H band falls in the range of weak hydrogen bonding. If a weak dihydrogen bond exists in 3, the H-bonded form of complex 3 may not be detectable in the NMR spectrum. In this case, the shift of the hydride ligand may be attributed to electronic changes of the platinum center caused by the electron-withdrawing pyridinium ring or to the change of polarity of the solvent upon addition of the acid. Indeed, when the spectrum of 2 is measured in CD\(_2\)Cl\(_2\), the hydride resonance appears at \(\delta = -5.06\) ppm, which is 1.32 ppm up-field compared to the one observed in toluene-d\(_8\).

**Complexes with the diphenylphosphinoethanethiolate ligand**

Oxidative addition of the diphenylphosphinoethanethiol (Hdppe) to Pt(PPh\(_2\)Py)_3 in dichloromethane yields a mixture of the cis and trans isomers of [(dppet)PtH(PPh\(_2\)Py)] (5a and 5b, scheme 5-3).

![Scheme 5-3. Synthesis of platinum hydrides containing a phosphino-thiolate ligand. The phenyl groups on the phosphorus atoms were omitted for clarity, P= PPh\(_2\).](image)

The trans isomer 5a can be obtained in pure form by performing the reaction at \(-80^\circ\)C and adding pentane at this temperature to precipitate the product. After filtration, the yellow solid was re-dissolved in CD\(_2\)Cl\(_2\) taking care that the product was always kept at \(-80^\circ\)C. The \(^1\)H and \(^{31}\)P NMR spectra measured at 193 K show the presence of one compound only. The high field region of the \(^1\)H NMR spectrum displays a doublet of doublets at \(\delta = -7.10\) ppm with two small H-P couplings (9 and 18 Hz), indicating that the hydride is trans to the sulfur atom (Fig. 5-3A). The \(^{31}\)P NMR spectrum displays two doublets at \(\delta = 36.6\) and \(\delta = \ldots\)
69.9 ppm (Fig.5-4A). The latter chemical shift is characteristic for phosphine ligands in five membered rings, thus the resonance at 69.9 ppm is assigned to the phosphorus of the dppet ligand. The strong P-P coupling (358 Hz) and the very similar P-Pt coupling constants (2918 and 2920 Hz) indicate that the two phosphorus atoms are trans to one another. The NMR spectra of this complex did not change on standing at 193 K over a period of 12 hours. However, when the sample was allowed to stand at room temperature for 6 hours, a second species was observed by NMR (193 K). The new product displays a doublet of doublets at $\delta = -4.06$ ppm with one large and one small H-P coupling constant, of 184.6 and 24.0 Hz respectively (Fig. 5-3B). The $^{31}$P NMR spectrum shows, in addition to the signals for the trans complex 5a, two doublets at $\delta = 27.1$ and $\delta = 59.3$ ppm ($J_{PP} = 10.9$ Hz). The P-Pt coupling constants are 3093 and 1995 Hz, respectively (Fig. 5-4B). These signals correspond to the cis isomer, 5b. The small P-Pt coupling constant of the resonance at $\delta = 59.3$ ppm indicates this phosphorus atom is trans to the hydridic ligand.

If an NMR sample of isolated 5a is prepared at room temperature, and then cooled to 193 K in the NMR probe, a mixture of cis and trans 5 is observed, indicating that the equilibration of the two isomers is relatively fast at 295 K. Performing the reaction at $-80^\circ$C in an NMR tube (without eliminating the excess of PPh$_2$Py) affords an initial cis : trans ratio of 1: 6. Upon warming, the intensity of the signals for 5b slowly increases at the expense of the resonance of the trans isomer. At 273 K, the ratio is 1: 2.3 and it does not change further when the sample is cooled again to 193 K. When the reaction was carried out at room temperature, a mixture of the cis and trans isomers of 5 in a 1: 2.4 ratio was observed by $^1$H NMR. Apparently, formation of the trans isomer is kinetically favored, and 5a can be precipitated selectively at low temperature. This indicates that the reaction does not involve a coordinated thiol as intermediate, followed by proton transfer to the metal. In this case, the cis isomer 5b will be the kinetic product. Upon increasing the temperature, isomerization of 5a to 5b is observed, but once the thermodynamic equilibrium is reached, the ratio between the two species does not change with temperature.

The course of the reaction of 4 with Hdppe was followed in an NMR tube (reaction performed at room temperature) over a period of six days. Owing to the presence of free PPh$_2$Py stemming from 4, the exchange between the latter and coordinated pyridylphosphine causes broadening of the resonances in the NMR spectra. This exchange is slow enough at 193 K to allow for assignment of the different peaks and therefore all the
spectra in the subsequent discussion were measured at this temperature. Figure 5-3 and 5-4 show the change in time of the $^1$H and $^{31}$P NMR spectra respectively. Immediately after reaction (Fig. 5-3B), the cis and trans isomers of 5 are the only hydride species in solution. The singlet at $\delta=59.36$ with a Pt-P coupling constant of 2899 Hz corresponds to the biscalixate complex $[\text{Pt(SCH}_2\text{CH}_2\text{PPh}_2)]^9$ (8). The singlet at $\delta = 24.4$ ppm, which does not display Pt satellites was assigned to the 2-pyridylphosphine oxide $\text{P(O)}\text{Ph}_2\text{Py}$.  

![Chemical structures](image)

**Figure 5-3.** Evolution of complex 5 in solution (CD$_2$Cl$_2$). $^1$H NMR spectrum (high field region), at 193 K. A: isolated product 5a. B: reaction mixture of 4 and dppet immediately after mixing at RT. C: after 2 days at RT. D: after 6 days at RT. P = PPh$_3$.  

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After two days of standing at room temperature, signals of four hydride species can be observed in the \( ^1\text{H} \) NMR spectrum (Fig. 3C). Two of the signals correspond to \( 5a \) and \( 5b \). The major new product (6), displays a doublet of triplets at \( \delta = -5.1 \) ppm \((J_{PP} = 162, 12, \text{Hz}, J_{PP} \approx 775 \text{Hz})\). The minor species (7) shows a doublet of doublets at \( \delta = -3.8 \) ppm \((J_{HP} = 7.5, 161.0 \text{Hz}, J_{PP} = 846 \text{Hz})\), which is broadened at the base because they coincide with the Pt satellites of 6. The ratio between the four species is \( 1 \) (6): \( 0.71 \) (5b): \( 0.36 \) (5a):\( 0.03 \) (7).

![Figure 5-4](image)

**Figure 5-4.** Evolution of complex 5 in solution (CD\(_2\)Cl\(_2\)). \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum at 193 K. For product numbering see figure 5-3. A: isolated product. B: reaction mixture of 4 and Hdppe immediately after mixing at RT. C: after 2 days at RT. D: after 6 days at RT. * denotes P(O)PPh\(_2\)Py.

The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of the reaction mixture shows signals for complexes 5a, 5b and 8, as well as for free PPh\(_2\)Py and P(O)Ph\(_2\)Py. Additionally, a triplet \((\delta = 23.7 \text{ ppm})\) and a doublet \((\delta = 33.5 \text{ ppm})\) integrating for one and two phosphorus atoms respectively are observed (Fig. 5-4C). These signals show a correlation (HMOC \(^1\text{H}-^{31}\text{P}\)) with the hydride resonance of 6. Therefore, complex 6 was identified as [PtH(PPh\(_2\)Py)\(_3\)]\(^+\).
In order to verify the assignments for 6, the product was synthesized separately by protonation of Pt(PPh$_2$Py)$_3$ with HBARF in CH$_2$Cl$_2$ (scheme 4). The $^1$H and $^{31}$P NMR spectra of the isolated product correspond to the resonances observed in the spectra of the reaction mixture. In the in-situ experiments, the counter ion is probably a chloride stemming from the solvent (CD$_2$Cl$_2$). Indeed, if the reaction is performed in acetonitrile-d$_3$, signals for complex 6 are not observed (for the experiments in CD$_3$CN the spectra were recorded at 295 K for solubility reasons).

![Scheme 5-4](image)

**Scheme 5-4.** Synthesis of complex 6 by protonation of the Pt(0) precursor. The phenyl groups on the phosphorus atoms were omitted for clarity, P = PPh$_2$.

After two days of standing at room temperature, the $^{31}$P NMR spectrum shows additionally a small doublet at $\delta = 97.0$ ppm with platinum satellites ($J_{PP} = 27.9$ Hz, $J_{P-Pt} = 2402$ Hz). A $^1$H-$^{31}$P NMR correlation experiment showed that this phosphorus is trans to the hydride signal at $-3.8$ ppm (7). From the doublet pattern in the $^{31}$P NMR spectrum and the doublet of doublets of the hydride signal, 7 should contain a second phosphorus atom coordinated to platinum. However, this second phosphorus could not be identified using correlation experiments. Nevertheless, a broad resonance at $\delta = 80$ ppm could correspond to this phosphorus atom. The chemical shift of the phosphorus nucleus at $\delta = 97.0$ ppm and the P-Pt coupling constant is similar to those observed for platinum phosphinito complexes [PPh$_3$PtH$_2$P(O)Ph$_2$]$_2$(Ph$_2$POH)].$^{16,17}$ These complexes were synthesized by oxidative addition of Ph$_2$POH to Pt(PPh$_3$)$_3$. For the reaction under investigation, slow hydrolysis of free or coordinated PPh$_2$Py could be the source of diphenylphoshinious acid. We propose that complex 7 contains at least one phosphinito ligand responsible for the resonance at $\delta = 97.0$ ppm.

Apart from the hydride signals, the $^1$H NMR spectrum of the reaction mixture in CD$_2$Cl$_2$ shows a remarkable signal with platinum satellites at $\delta = 16.6$ ppm ($J_{HP} = 39$ Hz), which is not observed above 233 K. The integration of this signal roughly corresponds to that of the
hydride signal of 7. Moreover, this resonance shows a long-range correlation with the phosphorus signal at $\delta = 97.0$ ppm. Very similar signals were observed by Pregosin et al. in Pt(II) complexes having a "pseudo-agostic bond" N-H ---Pt.$^{18}$ Therefore, 7 may contain a protonated pyridylphosphine whose pyridinium proton interacts with the platinum center. Alternatively, the resonance at $\delta = 16.6$ ppm may correspond to the OH proton of the phosphinito ligand.$^{19}$ In this case, the platinum satellites observed may arise from a through-bond Pt-P-O-H coupling. Hence, complex 7 is tentatively assigned the formula [PtH(PPh$_2$OH)(P(O)Ph$_2$L)]. The L ligand can be a solvent molecule or a pyridine stemming from hydrolysis of 2-diphenylphosphinopyridine to form diphenylphosphinous acid (PPh$_2$OH) and pyridine.

When the reaction mixture of 4 and Hdppet (in CD$_2$Cl$_2$) was checked after standing for six days at room temperature, the $^1$H NMR spectrum shows complete disappearance of 5a and 5b. Product 6 is apparently the only hydride species in solution (Fig. 5-3D). The $^{31}$P NMR spectrum shows a considerable increase of the signals for 6 and 8, and of the singlet of phosphine oxide (Fig. 5-4D). The $^{31}$P-decoupled $^1$H NMR spectrum revealed a small signal for complex 7 concealed under the Pt satellites of 6. In the $^{31}$P NMR spectrum the doublet at $\delta = 97.0$ ppm can still be observed. Two singlets with Pt satellites are now observed in the high field region of the $^1$H NMR spectra, the above mentioned signal at $\delta = 16.56$ ppm, and a new signal at $\delta = 16.85$ ppm ($J_{HPt}= 42$ Hz).

![Diagram of complexes](image)

Scheme 5-5. Products formed from the reaction of 4 with Hdppet. The phenyl groups on the phosphorus atoms were omitted for clarity, P= PPh$_2$. 
In order to investigate the role of free PPh$_2$Py in the reactions described above, the fate of the isolated product 5a in CD$_2$Cl$_2$ was followed. The $^1$H NMR spectrum measured two days after dissolution of 5a at room temperature showed no hydride signal any more. Signals of the starting material 4, the bis-chelate complex 8 and pyridylphosphine oxide were identified in the $^{31}$P NMR spectrum. Additionally, two doublets at $\delta=21.8$ and $\delta=57.1$ ppm ($J_{PP}=12.8$ Hz, $J_{PP}\_1=2794$, 3463 Hz) were observed. These signals are similar to those reported for cis[(dppet)PdCl(PPh$_3$)]$^8$ and thus were assigned to cis[(dppet)PtCl(PPh$_2$Py)] (9). This product was separately synthesized by reaction of [PtCl$_2$(PPh$_2$Py)$_2$] and Hdppet.

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Table 5-2. Spectroscopic data for complexes 4-9. All spectra were measured at 300 MHz for $^1$H in CD$_2$Cl$_2$ at 193 K. * tentatively assigned.

Apparently, the reaction between Pt(PPh$_2$Py)$_3$ (4) and Hdppet is reversible. If an excess of PPh$_2$Py is present, slow ligand redistribution occurs in complex 5 to form mainly [PtH(PPh$_2$Py)$_3$]$^+$ (6) and [Pt(dppet)$_2$] (8). Without free pyridylphosphine, product 5 disproportionates to the starting material 4 and the bis-chelate complex 8. It seems that [(dppet)PtH(PPh$_2$Py)] is the kinetic product of the reaction, but if the reaction is allowed to proceed long enough, the thermodynamically stable products 6 and 8 will form eventually.
Scheme 5-6. Evolution of products 5a and 5b in solution, with (top) and without (bottom) excess PPh₂Py.

As stated before, complex 6 can be obtained by protonation of the Pt(0) precursor (4) with a strong acid (HBARF). On the other hand, no strong acid is present in solutions containing 5a, 5b and PPh₂Py, which eventually yield [PtH(PPh₂Py)₃]⁺ (6). One possibility is that 6 is formed in situ by protonation of 4 by small amounts of H₂O or HCl stemming from the solvent. Alternatively, 4 could react with the dihydrogen formed during the decomposition of the hydride complexes 5a and 5b to form 8. In order to investigate these possibilities, the reactions of 4 with H₂O and H₂ were carried out. Ten equivalents of H₂O were added to a solution of Pt(PPh₂Py)₃ (4) in CD₂Cl₂ and the reaction was monitored by NMR. No reaction or decomposition of the starting material was observed, even after heating to 40 °C for 45 min. Only after heating overnight to 40 °C, new signals were observed in the hydride region of the ¹H NMR spectrum. The new signal at δ=-3.9 ppm (Jpp=21, 186 Hz) does not correspond to either compound 6 or 7. After four days at 40 °C the starting material 4 was completely consumed, but extensive decomposition to metallic platinum was also observed. In both the ¹H and ³¹P NMR spectra, signals corresponding to 6 were observed, but the low intensity of the signals and the poor quality of the spectra precluded assignment of the remaining signals. The large excess of H₂O and the drastic
conditions needed to form \(6\) from \(4\) and \(H_2O\) suggest that direct protonation of \(4\) by water is not the source of complex \(6\). The formation of significant amounts of HCl in solution seems unlikely, since HCl should react fast with Pt(PPh2Py)3 (4) to form product 6.

The reaction of Pt(PPh2Py)3 (4) with dihydrogen was also investigated. A solution of 4 in CD2Cl2 was pressurized to 10 bar of \(H_2\) in a high pressure NMR tube and the reaction was followed by NMR spectroscopy. No reaction was observed at room temperature during 4 hours. After heating the NMR tube to 50 °C for 1.5 hours, small peaks corresponding to complex 6 were detected. Complete conversion to \([\text{PtH(PPh}_2\text{Py)}_3]+\) (6) was achieved after 12 hours at 50 °C. In contrast to the reaction with water, no precipitation of metallic Pt was observed. The \(^{31}\text{P}\) NMR spectrum displays the expected signals for 6, a singlet corresponding to P(O)Ph2Py and free PPh2Py. Surprisingly, a doublet at \(\delta = 96.4\) ppm was also observed. The \(^1\text{H}\) NMR spectrum showed a second hydride resonance at \(\delta = -3.8\) ppm and a signal at \(\delta = 16.5\) ppm with Pt satellites (\(J_{\text{PH}} = 39\) Hz). These results further suggest that these three signals belong to the same product, previously assigned to 7, and that complex 7 does not contain a phosphorus atom stemming from dppet.

Once again, the harsh conditions needed for reaction of Pt(PPh2Py)3 (4) with \(H_2\) to form 6, make it unlikely that this reaction also occurred in an NMR tube at ambient pressure. Thus, transformation of 5a and 5b into 6 probably does not involve reaction with dihydrogen.

Considering the last two experiments and the fact that an excess of free PPh2Py is needed to form 6 from a mixture of 5a and 5b, the most probable pathway for the reaction is proton transfer from 5 to a free pyridylphosphine. This species can then protonate another platinum center, containing either a monocoordinated dppet or only pyridylphosphine ligands. Equilibria between the chelating and monodentate coordination modes of phosphino-thioether ligands in Pt(II) and Pd(II) complexes have been observed by Del Zotto et al.\(^{20}\). Decoordination of the sulfur donor was favored in the presence of anions or phosphines. Although stronger coordination is expected for a thiolate than for a thioether, this possibility cannot be ruled out, especially in the presence of a large excess of free phosphine. Owing to the higher stability of 6 compared to 5, ligand scrambling will eventually result in formation of 6 and 8. The very small amounts of complex 7 observed at any time may indicate that it is a decomposition product not participating in the process described above.
Conclusions

Platinum complexes containing a thiolate ligand can be synthesized by oxidative addition of the parent thiol to a Pt(0) precursor. The complexes with a thiolate ligand (2, 3 and 5) have a stronger Pt-H σ-bond than the dicationic hydrides containing only phosphorus co-ligands presented in chapter 3. This is reflected in the values of the Pt-H coupling constants, which are up to 150 Hz higher than those for [(PP)PtH(PPh₂PyH)]²⁺.

Protonation of the dangling pyridine moiety in complex 2 causes a significant up-field shift of the hydride resonance. This shift is probably due to the change of solvent polarity in the presence of strong acid. No NMR evidence of dihydrogen bonding between the hydride and the pyridinium proton was found. Although the anionic thiolate ligand increases the electron density at the platinum center and enhances the hydridic character of the hydride, this is not sufficient to induce strong Pt-H---H-N interactions.

Oxidative addition of diphenylphosphinoethanethiol (Hdppet) to Pt(PPh₂Py)₃ yields the neutral hydride trans-[(dppet)PtH(PPh₂Py)] (5a) as the kinetic product. In solution this complex re-arranges to its cis isomer (5b). Further ligand scrambling occurs at room temperature resulting eventually in [PtH(PPh₂Py)]⁺ (6) and [Pt(dppet)₂] (8) which are the thermodynamically favored products. Free pyridylphosphine in solution is essential for ligand scrambling, probably by acting as a proton transfer agent between different platinum centers. In the absence of free PPh₂Py, the hydride complex 5 reverts to the starting material and dppet forms stable [Pt(dppet)₂] (8).

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 CaH₂. Diethyl ether, tetrahydrofuran, hexane and pentane were distilled from sodium / benzophenone and toluene was distilled from sodium. Dppf and pyridine-2-thiol were purchased from Aldrich Chemical Co. and used as received. HBARF (H[B(3,5-(CF₃)-C₆H₃)₄])₂¹ and Hdppet²² and Pt(PPh₂Py)₃²³ were synthesized according to literature procedures. Diphenyl-2-pyridylphosphine was
purchased from Aldrich Chemical Co. and re-crystallized from hot hexanes prior to use. Reactions under dihydrogen pressure were carried out in Fischer-Porter bottles. NMR spectra were recorded on a Bruker DPX 300 or a Bruker AMX 400. $^{195}$Pt NMR chemical shifts were measured using an HMQC $^1$H-$^{195}$Pt-$^{31}$P experiment, with H$_2$PtCl$_6$ in D$_2$O as external reference ($\delta=0$ ppm). CD$_2$Cl$_2$ was dried over CaH$_2$ and CD$_3$CN over P$_2$O$_5$, they were vacuum transferred, degassed and stored over molecular sieves. Toluene-d$_8$ was dried over molecular sieves and degassed. Elemental analyses were performed by the Service de Microanalyse du LCC-CNRS, Toulouse.

(dppf)Pt(stilbene) (1)

This product was synthesized using a procedure similar to that reported for [(PPh$_3$)$_2$Pt(trans-stilbene)].$^{24}$ The reaction was carried out under air.

0.5 mL of N$_2$H$_4$·H$_2$O were added to a suspension of 500 mg (0.609 mmol) of (dppf)PtCl$_2$ in 7 mL ethanol. After a few minutes a dark orange solution was formed. The solution was filtered into a flask containing 150 mg (0.832 mmol) of trans-stilbene, and the reaction mixture was heated to 60 °C. After 5 min. evolution of N$_2$ was observed and a yellow precipitate formed. The flask was cooled in an ice-bath. The precipitate was recovered by filtration, washed with cold methanol (3 x 2 mL) and dried in vacuum. Yield : 363 mg (0.390 mmol). 64 %. The spectroscopic characteristics of this product correspond to that reported.$^{25}$

$^1$H NMR (300 MHz, Tol-d$_8$, 295 K): 7.72 (br. s, 4H, Ar); 7.26 (br. s, 4H, Ar); 7.1-6.9 (m, 22H, Ar); 4.19 (d, 2H, PhC$_2$H$_2$Ph, $J_{HP}= 2.4$ Hz, $J_{HPt}= 60$ Hz); 4.14 (s, 2H, Cp), 4.04 (s, 2H, Cp), 3.82 (s, 2H, Cp), 3.79 (s, 2H, Cp). $^{31}$P NMR (121.5 MHz, Tol-d$_8$, 295 K): 21.41 (s, $J_{PP} = 3758.9$ Hz).

(dppf)(2-mercaptopyridine)hydridoplatinum (II) (2)

100 mg (0.108 mmol) of (dppf)Pt(stilbene) and 12 mg (0.108 mmol) of pyridine-2-thiol were introduced in a Fischer-Porter bottle equipped with a magnetic stirrer. The bottle was evacuated and pressurized to 1 bar with H$_2$ and placed in an ice bath. 10 mL of cold toluene, previously saturated with H$_2$, were introduced in the Fischer-Porter bottle and the dihydrogen pressure was increased to 3 bar. The initial yellow suspension turned slowly into a bright yellow solution. After 30 min. the pressure was reduced to 1 bar. 15 mL of pentane (saturated with H$_2$) were slowly added in order to form two layers. The pressure
was increased to 3 bar of H$_2$ and the bottle was stored at -20 °C. After one night, an off-white precipitate had formed. After carefully reducing the pressure to 1 bar, the solution was filtered. The solid was re-dissolved in 3 mL CH$_2$Cl$_2$ and transferred to a Schlenk vessel. The solvent was evaporated with a dihydrogen stream and the remaining solid was dried under vacuum. To avoid decomposition of the product, it should not be put under vacuum while it is in solution. Yield: 65 mg (0.076 mmol), 70 %.

$^1$H NMR (300 MHz, Tol-d$_8$, 273 K): 8.33 (m, 1H, H$_6$, Py); 8.10 (m, 4H, Ar); 7.87 (m, 5H, Ar); 7.26-7.17 (m, 10H, Ar); 6.93-6.71 (m, 3H, Ar); 6.17 (m, 1H, Ar); 4.46 (d, 2H, Cp, J$_{HP}$=1.2 Hz); 4.00 (d, 2H, Cp, J$_{HP}$=1.2 Hz); 3.9(s, 2H, Cp); 3.78 (s, 2H, Cp); -3.74 (dd, 1H, hydride, J$_{Hpcis}$=8.0 Hz, J$_{Hpt}$=192.1 Hz, J$_{HP}$= 882.4 Hz). $^{31}$P NMR (121.5 MHz, Tol-d$_8$, 273K): 23.4 (d, J$_{PP}$= 16.4 Hz, J$_{PP}$= 3369 Hz); 27.1 (d, J$_{PP}$= 2016 Hz).

$^{13}$C NMR (75.5 MHz, Tol-d$_8$, 273K): 137.0 (C$_{quat}$), 135.4, 135.3, 135.2, 135.1, 130.5 (CH, Ar); 129.0 (C$_{quat}$), 128.5, 128.0 (CH, Ar); 76.5 (d, C$_t$, Cp, J$_{CP}$= 75.2 Hz); 75.9 (d, CH, Cp, J$_{CP}$= 11.3 Hz); 75.1 (d, CH, Cp, J$_{CP}$= 9.8 Hz); 74.0 (d, C$_t$, Cp, J$_{CP}$= 37.8 Hz); 72.8 (d, CH, Cp, J$_{CP}$= 6.0 Hz); 71.9 ((d, CH, Cp, J$_{CP}$= 6.7 Hz). $^{195}$Pt NMR (85.6 MHz, Tol-d$_8$, 273 K): -4905.

IR (nujol mull): 2087 cm$^{-1}$ (vPt-H).

Anal. Calc. for C$_{39}$H$_{33}$P$_2$NSFePt: C 54.43 %, H 3.86 %. Found : 54.05 %, H 3.94 %.

Protonation of 2

26 mg (0.028 mmol) of 2 were dissolved in 0.75 mL of toluene-d$_8$. The solution was cooled to -80 °C in an ethanol / liquid N$_2$ bath and 2.5 µL (0.028 mmol) of HOTf were added using a microsyringe. After a few minutes, some orange precipitate forms. The bright yellow solution is filtered and transferred to an NMR tube at -80 °C. $^1$H, $^{31}$P NMR and T$_1$ were measured at this temperature and at 20 °C intervals up to 22 °C.

$^1$H NMR (300 MHz, Tol-d$_8$, 273 K): 13.93 (br s, 1H, NH); 8.44 (br, 3H, Ar); 8.01 (m, 8H, Ar); 7.74 (br, 2H, Ar); 7.34-6.77 (m, 8H, Ar); 5.96 (m, 2H, Ar); 5.62 (m, 2H, Ar); 4.43, 4.40 (s, 4H, Cp); 3.96 (s, 4H, Cp); -5.58 (dd, 1H, hydride, J$_{Hpcis}$=19.5 Hz, J$_{Hpt}$=190.6 Hz, J$_{HP}$= 909.4 Hz). $^{31}$P NMR (121.5 MHz, Tol-d$_8$, 273K): 18.7 (d, J$_{PP}$= 16.4 Hz, J$_{PP}$= 3500 Hz); 26.2 (d, J$_{PP}$= 2018 Hz). $^{195}$Pt NMR (85.6 MHz, Tol-d$_8$, 273 K): -4833.

IR (toluene): 2075 v(Pt-H), 3309 v(N-H).
[(dppet)PtH(PPh₂Py)] (5)

128 mg (0.133 mmol) of Pt(PPh₃)₃ were dissolved in 4 mL of CH₂Cl₂. In a separate Schlenk vessel 33 mg (0.133 mmol) of 2-(diphenylphosphino)ethanethiol (Hdppet) were dissolved in 2 mL of CH₂Cl₂. Both solutions were cooled to −80 °C in an ethanol / liquid N₂ bath. The solution containing Hdppet was added drop wise to the bright orange solution of Pt(PPh₃)₃ and the reaction mixture became pale yellow. When addition was complete, the reaction mixture was stirred for 1 h at −80 °C. 10 mL of pentane were added and the biphasic mixture was stored at −20 °C. After several hours, a fine yellow precipitate had formed. The solution was filtered and the solid was dried in vacuum. Yield: 49 mg (0.069 mmol), 52 %.

Anal. Calc. for C₃₁H₂₉P₂SNPt: C 52.84 %, H 4.15 %, N 1.99 %. Found: C 52.95 %, H 3.86 %, N 2.01 %.

trans product. ¹H NMR (300 MHz, CD₂Cl₂, 193 K): 8.73 (s, 1H, H₆, py); 8.25 (m, 1H, py); 7.84-7.09 (m, 22H, Ar); 2.63 (br. m, 4H, CH₂), -7.10 (dd, 1H, hydride, J₆P = 9.0, 18.0 Hz, J₆Pt = 978 Hz). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 193 K): 36.6 (d, J₆P = 385.2 Hz, J₆Pt = 2918 Hz); 69.9 (d, J₆Pt = 2920 Hz). ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂, 193 K): 157.3 (d, Cp, J₆C = 71.9 Hz); 150.9 (d, CH, py, J₆C = 13.2 Hz); 136.7 (d, CH, J₆C = 10.0 Hz); 135.1 (d, CH, J₆C = 12.5 Hz); 133.8 (d, CH, J₆C = 12.5 Hz); 132.8 (C₆); 132.1 (C₆); 131.0 (C₆); 130.0 (C₆); 129.0 (d, CH, J₆C = 12.1 Hz); 128.7 (d, CH, J₆C = 10.4 Hz); 125.1 (CH); 41.0 (CH₂).

cis product. ¹H NMR (300 MHz, CD₂Cl₂, 193 K): -4.06 (dd, 1H, hydride, J₆Pt = 24.0 Hz, J₆Pt = 978 Hz), 8.40 (br. d, 1H, py, J=3.9 Hz); 8.23 (br. d, 1H, py, 4.2Hz); 7.77 (br. s, 8H, BARF); 7.57-7.01 (m, 40H, Ar + BARF); 6.74 (br. d, 2H, Ar.

[tris(2-diphenylphosphinopyridine)hydridoplatinum](BARF) (6)

54 mg (0.055 mmol) of Pt(PPh₂Py)₃ and 61 mg (0.055 mmol) of HBARF·2Et₂O were placed in a Schlenk vessel, which was cooled to −80 °C. 5 mL of pre-cooled CH₂Cl₂ were added and the reaction mixture was slowly warmed to room temperature over 1 h. The solvent was evaporated in vacuum, the resulting oily solid was washed with pentane (3 x 5 mL) and dried in vacuum. Yield: 100 mg (0.052 mmol), 94 %.

¹H NMR (300 MHz, CD₂Cl₂, 203 K): 8.32 (br. d, 1H, py, J=3.9 Hz); 8.23 (br. d, 1H, py, 4.2Hz); 7.77 (br. s, 8H, BARF); 7.57-7.01 (m, 40H, Ar + BARF); 6.74 (br. d, 2H, Ar,
Platinum Complexes with N,S and P,S Ligands

J=7.8 Hz); 6.35 (br. d, 1H, Ar, J=7.5 Hz); -5.11 (dt, 1H, hydride, J_{HP_{cis}}= 12.0 Hz, J_{HP_{trans}}= 162.1 Hz, J_{HP}= 777 Hz). $^{31}$P{$^1$H} NMR (121.5 MHz, CD$_2$Cl$_2$, 203 K): 33.1 (d, 2P, J$_{PP}= 18.5$ Hz, J$_{PP}= 2933$ Hz); 24.0 (t, 1P, J$_{PP}= 2327$ Hz). $^{13}$C{$^1$H} NMR (75.5 MHz, CD$_2$Cl$_2$, 193 K): 157.3 (d, C$_i$, py, J$_{CP}= 71.9$ Hz); 150.9 (d, CH, py, J$_{CP}= 13.2$ Hz); 136.7 (d, CH, J$_{CP}= 10.0$ Hz); 135.1 (d, CH, J$_{CP}= 12.5$ Hz); 133.8 (d, CH, J$_{CP}= 12.5$ Hz); 132.8 (C$_{quat}$); 132.5 (CH); 132.1, 132.0 (C$_{quat}$); 131.6 (CH); 131.4 (C$_{quat}$, J$_{CP}= 3.1$ Hz); 131.2 (CH); 129.0 (d, CH, J$_{CP}= 12.1$ Hz); 128.7 (d, CH, J$_{CP}= 10.4$ Hz); 125.1 (CH); 41.0, 40.5 (CH$_2$).
References