Activation of dihydrogen by rhutenium, platinum and palladium complexes

Almeida-Lenero, K.Q.

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Chapter 4

Towards Palladium Hydride Complexes Via Heterolytic Splitting of Dihydrogen.

Abstract

Palladium complexes containing 2-pyridyl diphenylphosphine (PPh$_2$Py) and the wide bite angle diphosphines 9,9-dimethyl-4,5-bis(diphenylphosphino)-xanthene (Xantphos), 1,1'-diphenylphosphino ferrocene (dpf) and bis(2-diphenylphosphino-phenyl)-ether (DPEphos) were synthesized. The PPh$_2$Py coordinates as a bidentate ligand to form the bis-chelate complexes $[\eta^2$-diphosphine]Pd(η$^2$-PPh$_2$Py)]$^{2+}$ (1a-d). When Xantphos ($\beta_n = 111^\circ$) is used, the bis-chelate complex is in equilibrium with an isomer in which Xantphos coordinates in a tridentate P,O,P fashion and PPh$_2$Py is coordinated via the phosphorus atom only. Complexes containing DPEphos and Xantphos decompose under dihydrogen pressure. In the case of dpf slow heterolytic splitting of dihydrogen occurs to form the hydride complex $[(\text{dpf})\text{PdH}(\text{PPh}_2\text{PyH})](\text{OTf})_2$ (2a) which contains a protonated pyridylphosphine ligand. In solution, this compound slowly undergoes P-C bond cleavage of the PPh$_2$Py ligand to form $[(\text{dpf})\text{Pd}(\text{PHPh}_2)(\eta^1$-C$_5$H$_4$NH)](\text{OTf})_2$ (3a). When the 6-methyl-2-pyridyldiphenylphosphine ligand is used, the reaction with dihydrogen is very fast and the hydride complex immediately rearranges to the diphenylphosphino compound resulting from P-C bond splitting.
Chapter 4

Introduction

Palladium complexes have proven to be very efficient in a variety of catalytic reactions such as oxidations, reductions, isomerizations, carbonylations and coupling reactions.\(^1\)\(^-\)\(^2\) Hydride complexes have been proposed as key intermediates in the catalytic cycles of many of these transformations, but they have rarely been observed in catalytic reaction mixtures. In spite of their great importance, the number of palladium hydride complexes synthesized and characterized to date remains relatively small, compared to those of other transition metals.\(^3\) In contrast to their platinum counterparts, palladium hydrides are rather unstable and difficult to isolate.

An intense debate prevails over the intermediacy of palladium hydride species in the hydroxy and alkoxycarbonylation of alkenes and alkynes.\(^3\)\(^-\)\(^4\) Although in the case of alkenes most authors favor the hydride mechanism,\(^5\)\(^-\)\(^10\) the discussion remains open when alkynes are used as substrates.\(^11\)\(^-\)\(^17\) These reactions provide a clean route to either saturated or \(\alpha,\beta\)-unsaturated acids and esters, which can be used both as large scale chemical intermediates or in the synthesis of fine chemicals. A highly efficient catalyst for the methoxycarbonylation of propyne was developed by Drent et al.\(^15\)\(^,\)\(^18\)\(^-\)\(^22\) to produce methyl methacrylate (MMA), which is the monomer for the production of several polymers. This catalyst is prepared \textit{in situ} from Pd(OAc)\(_2\), 2-diphenylphosphinopyridine and excess of a strong acid, but its exact structure is unknown. The pyridyl substituent on the phosphine is essential for the catalyst to be highly active and selective. Substitution of PPh\(_2\)Py by triphenylphosphine causes a remarkable drop in both activity and selectivity. Furthermore, when the 6-position of the pyridyl moiety is substituted with a methyl group, the activity and selectivity of the catalyst is further increased. There is no agreement yet on the exact role played by this P-N ligand, and the mechanism of the alkoxycarbonylation of alkynes is still under discussion. Drent et al.\(^18\) have suggested the rate-determining step is the proton transfer from the protonated pyridylphosphine ligand to a Pd(II)-alkenyl species (Fig. 1A). On the other hand, Scrivanti et al.\(^14\) proposed that the pyridinium moiety of the PPh\(_2\)Py ligand directly protonates the alkyne coordinated to a Pd(0) center (Fig. 1B). Nevertheless, they do not exclude the possibility of protonation of the metal center to form a Pd-hydride species, which will immediately lead to alkyne insertion to form a \(\sigma\)-alkenyl species (Fig. 4-1C).
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Figure 4-1. Proposed mechanisms for the alkoxyocarbonylation of alkynes. A methoxycarbonyl intermediate. B. Direct protonation of coordinated alkyne C. Hydride migration to coordinated alkyne.

Stable palladium σ-alkenyl species have been isolated from the reaction of Pd(PPh₃Py)₃ with phenylacetylene in the presence of acid, while no reaction takes place without a proton source. This points towards the intermediacy of a hydride species. Indirect evidence for a hydride mechanism has also been provided by Petrov et al. and Inoue et al.

The very rich chemistry of pyridyolphosphine ligands has been widely investigated. Owing to the presence of both soft and hard donor atoms, they can stabilize metal ions in several oxidation states and geometries. When they act as chelating ligands they can stabilize a catalyst precursor, while the nitrogen atom de-coordinates easily to provide a vacant site for substrate binding and further reaction. These characteristics are very important in catalytic cycles, which often involve changes in the oxidation state and coordination number of the metal centers.

This prompted us to study the coordination chemistry of palladium complexes containing both a 2-diphenylphosphinopyridine and a wide bite angle diphosphine (Chart 4-1). The steric constraints imposed by these diphosphines have a pronounced effect on the structure
and catalytic activity of several transition metal complexes.\textsuperscript{28,29} In Chapter 3 it was shown that similar platinum complexes react smoothly with dihydrogen to produce platinum hydrides and a protonated pyridyl moiety, but these compounds react very slowly or not at all with unsaturated substrates. Considering the higher reactivity of palladium compared to platinum, the reactivity of the new palladium complexes towards dihydrogen is presented in this chapter.

**Results and Discussion**

**Coordination behavior of \([(diphosphine)Pd(PPh_2Py)]^{2+}\) complexes**

In order to compare the coordination chemistry of the palladium complexes with their platinum analogs described in the previous chapter, the same wide bite angle diphosphine ligands have been used (chart 4-1).

![Chart 4-1](image)

**Chart 4-1.** Schematic structure of the diphosphine ligands and natural bite angles in degrees. For dppf the value was taken from crystal structure, see ref 28.

The synthesis of palladium complexes containing a diphosphine and a chelating pyridylphosphine ligand 1a-d is outlined in chart 4-1. A complex containing dppf and 6-methyl-2-pyridylphosphine (1a-Me) was synthesized also. Reaction of the respective \([(diphosphine)PdCl_2]\) complexes with silver triflate in dichloromethane produces a deeply colored reaction mixture, red for Xantphos and DPEphos and green for dppf. The color of the latter complex suggests that a Pd-Fe interaction may exist in the dicationic species.\textsuperscript{30,31} Upon addition of the pyridylphosphine ligand, the reaction mixture becomes yellow-orange for the Xantphos type ligands and deep purple for dppf.
Scheme 4-1. **Synthesis of complexes** 1a, b and d. Phenyl groups on phosphorous atoms have been omitted for clarity, $P = PPh_2$.

The $^{31}$P NMR data for all complexes are shown in table 4-1. The $^1$H and $^{31}$P NMR signals in the spectra of complexes 1a and 1b are resolved at room temperature, but 1a-Me shows broad signals and 1d displays only a broad singlet in the $^{31}$P NMR spectrum at this temperature. For both 1a-Me and 1d sharp signals were observed when the spectra were measured at 233 K. As expected, complexes 1a and 1b give rise to an AMX spin system in the $^{31}$P NMR spectrum. The high field shift of $P_X$ confirms that the pyridylphosphine forms a four membered chelate ring. The chemical shifts and coupling constants are similar to those observed for the corresponding platinum complexes (chapter 3).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Complex</th>
<th>$\delta_{PA}$ (ppm)</th>
<th>$\delta_{PM}$ (ppm)</th>
<th>$\delta_{PX}$ (ppm)</th>
<th>$J_{PA-PM}$ (Hz)</th>
<th>$J_{PA-PX}$ (Hz)</th>
<th>$J_{PM-PX}$ (Hz)</th>
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<tr>
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<td>30.7</td>
<td>41.7</td>
<td>-42.3</td>
<td>8.5</td>
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<td>14</td>
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<td></td>
<td>1a-Me</td>
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<td>41.1</td>
<td>-40.8</td>
<td>n.r. b</td>
<td>389.4</td>
<td>12.2</td>
</tr>
<tr>
<td>DPEphos</td>
<td>1b</td>
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<td>20.1</td>
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<td>3.7</td>
<td>412</td>
<td>n.r. b</td>
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<td>18.8</td>
<td>-45.1</td>
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<td>388</td>
</tr>
<tr>
<td></td>
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<td>36.2</td>
<td>-</td>
<td>35.1</td>
<td>4.9</td>
<td>23.1</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 4-1.** $^{31}$P-$^1$H NMR data for complexes 1a-d. Spectra measured at 121.5 MHz in CD$_2$Cl$_2$ at 295 K unless otherwise stated. a at 233 K. b non resolved.

Although the purple color of 1a might suggest a Pd-Fe bond, no NMR spectroscopic evidence for such an interaction was found. The $^1$H NMR spectrum of 1a is very similar to that of [(dpff)Pt($\eta^2$-PPh$_2$Py)]$^{2+}$; the Cp protons of dpff display four signals (two protons each). By means of a COSY NMR experiment, the signals at $\delta=5.3$ and $\delta=3.6$ ppm were assigned to the $\alpha$ protons, while the signals at $\delta=4.8$ and $\delta=4.5$ ppm correspond to the $\beta$
protons. In principle, all Cp protons are magnetically unequivalent because the complex lacks a plane or axis of symmetry, so they should give rise to eight different signals. This is usually not observed owing to the rapid flip of both Cp rings around the Cp-Fe-Cp axis. Therefore, the pairs of protons at the α and β positions on each Cp ring are time averaged, resulting in just one NMR signal for each pair of α or β protons. One of the signals for the α protons (δ = 3.6 ppm), is shifted up-field by more than 1 ppm compared to the other signals, probably due to its proximity to one of the phenyl rings. These features are often observed in sterically congested dppf complexes.

Complex 1a-Me with the bulkier 6-methyl-2-pyridylphosphine ligand shows fluxional behavior at room temperature. The $^{31}$P NMR spectrum reveals an exchange process between the two phosphorus nuclei of dppf ($P_A$ and $P_M$, scheme 4-1). The extra steric bulk introduced by the methyl group induces easy de-coordination of the pyridyl moiety, probably assisted by the counterion or traces of free phosphine in solution. Rotation in the five-coordinated species is facile and results in exchange of the positions of $P_A$ and $P_M$ (scheme 4-2). Upon lowering the temperature all signals broaden further, but at 253 K they start to re-emerge from the base line. At 193 K the $^{31}$P NMR spectra shows a well resolved AMX pattern corresponding to $[(dp(f)Pd(η^2-\{2-(6-CH_3-C_5H_3N)PPh_2\})](OTf)_2$, indicating that the dissociation of the isomerization of the square planar complex is avoided at this temperature.

Scheme 4-2. Proposed mechanism for the exchange of $P_A$ and $P_M$ in 1a-Me. $Nu = OTf^-$, solvent or free phosphine.
Towards Pd Hydride Complexes

A second species is observed in the $^{31}$P NMR spectrum of 1a-Me at room temperature. It displays a doublet at $-14.9$ ppm and a triplet at $42.3$ ppm, with a coupling constant of $13.4$ Hz. The chemical shifts and the coupling constant are very similar to those reported by Sato et al. for $[(\eta^3\text{-dppe})\text{Pd}(\text{PPh}_3)](\text{BF}_4)_2$, which involves an Fe-Pd dative bond. Therefore we propose that the second species in solution is $[(\eta^3\text{-dppe})\text{Pd}(\text{PPh}_3)](\text{OTf})_2$. This product is not involved in the exchange process mentioned above, so it displays sharp NMR signals at room temperature. At 193 K, the signals for this product represent less than 5% of the total intensity. Remarkably, 1a-Me displays a very different behavior from its platinum counter part described in chapter 3. For the Pt complex, the species containing a chelating 6-methyl-2-pyridylphosphine $[(\text{dppf})\text{Pt}(\eta^3\{-2-(6-\text{CH}_3-\text{C}_5\text{H}_3\text{N})\text{PPh}_2\})](\text{OTf})_2$ and the one in which the coordinated pyridyl has been replaced by the anion do not exchange on the NMR time scale and separate sets of signals for each isomer are observed. Furthermore, a complex with a Fe-Pt bond was not detected at any temperature.

As stated before, the $^{31}$P NMR spectrum of the complex containing Xantphos (1d) displays only a broad singlet at room temperature, while the $^1$H NMR spectrum shows a slightly broad singlet for all methyl groups and broad signals for the aromatics. At low temperature, the singlet in the $^{31}$P NMR spectrum becomes less intense and other signals start to emerge from the base line. At 233 K two sets of signals can be distinguished in the $^{31}$P NMR spectrum: a doublet and a broad triplet with an intensity ratio of 2:1 (major product), and an AMX spin system (minor product) similar to that described above for complexes 1a-b. As observed for the platinum analog (chapter 3), the two sets of signals correspond to the cis and trans isomers of 1d (scheme 4-1). Thus the AMX spin system was assigned to the cis isomer containing a chelating pyridylphosphine. The second set of resonances corresponds to the trans isomer, in which Xantphos coordinates in a tridentate P-O-P fashion. In the $^1$H NMR spectrum three signals are observed for the methyl groups in the ligand backbone, two of equal intensity for the cis isomer ($\delta=1.9$ and $\delta=1.6$ ppm) and one ($\delta=1.7$ ppm) for the trans isomer. Integration of these signals shows a trans : cis ratio of 2.5, which was confirmed by integration of the $^{31}$P spectrum. At 193 K, the trans : cis ratio is 1.3, indicating that the formation of the pyridylphosphine chelate is favored at low temperature. For the analogous platinum complex (chapter 3), neither
exchange between the cis and trans isomers was observed at room temperature, nor did the ratio between the two isomers change with temperature.

A comparison of the NMR behavior of 1a-Me and 1d with that of the corresponding platinum complexes, indicates that the Pd-N bond is more labile than the Pt-N bond. This results in equilibrium between the chelating and monodentate coordination mode of the pyridylphosphine. In the case of the palladium complexes, these two species exchange on the NMR time scale, while for the platinum compounds both isomers can be observed separately, even at room temperature. In the platinum complexes containing an \( \eta^1 \)-coordinated \( \text{PPh}_2\text{Py} \), the fourth coordination site is occupied by an oxygen atom (from the backbone for the Xantphos containing complex or the triflate anion when dpf is used). Coordination of the anion is not observed in the palladium case.

Attempts to crystallize 1a, resulted in the formation of bright orange crystals from the purple solution. An X-ray structure determination showed that the crystals correspond to a Pd(I) dimer of formula \( [\text{Pd}_2(\text{PPh}_2\text{Py})_2(\text{OTf})_2] \) (4, fig. 4-2).

![Figure 4-2. ORTEP drawing of the palladium (I) dimer. The ellipsoids are drawn at 50% probability level. The hydrogen atoms and the triflate anions have been omitted for clarity. Selected bond lengths (Å): Pd1-N1 2.094(4), Pd2-N2 2.210(5), Pd1-P2 2.1968(14), Pd2-P1 2.3508(17), Pd1-Pd2 2.5407(10). Selected bond angles (°): N1-Pd1-Pd2 93.88(11), N1-Pd1-P2 170.64(12), P2-Pd1-Pd2 79.20(4), N2-Pd2-P1 171.55(11).](image-url)
This product has been prepared by Dervisi et al. The $^{31}$P NMR spectrum of the mother liquor showed two additional peaks at $\delta = -1.23$ and $\delta = 24.8$ ppm, apart from those of 1a. By comparison with the reported NMR data the signal at $\delta = -1.23$ ppm was assigned to the dimeric species. Generally, palladium (I) dimers with bridging pyridylphosphine ligands are prepared by conproportionation of a Pd(II) complex containing the PPh$_2$Py ligand and a Pd(0) source. In this case, the Pd(0) species probably was formed in situ. It is known that mono and diphosphines are able to reduce Pd(II) to Pd(0). Therefore, the formation of 4 probably involves de-coordination and oxidation of dppf with subsequent reduction of the palladium center. Thus the peak at $\delta = 24.8$ ppm was assigned to dppf-oxide, although this value is a bit lower than the reported 28 ppm. Dervisi et al. also reported the crystal structure of a compound similar to 4, but with TFA as counterion. The bond lengths and angles in the crystal structure of 4 are very similar to the ones reported for [Pd$_2$(PPh$_2$Py)$_2$(TFA)$_2$].

**Activation of Dihydrogen**

Even though the activation of dihydrogen by palladium complexes and the formation of palladium hydrides have been proposed to play an important role in the mechanism of the palladium catalyzed hydroformylation and hydrogenation very few hydride complexes have been prepared and isolated by this route. In fact, most of the known cationic palladium hydrides are prepared either by exchange of an anionic ligand by a neutral ligand, or by protonation of Pd(0) complexes.

NMR tube experiments have been performed in order to investigate the reactivity of compounds 1a-d towards the heterolytic splitting of dihydrogen. The test reactions were performed in a high pressure NMR tube and they were monitored by $^{31}$P and $^1$H NMR. As expected, the reaction of the palladium complexes with dihydrogen was much faster compared to the platinum complexes. When the bright orange solution containing [XantphosPd($\eta^2$-PPh2Py)](OTf)$_2$ was pressurized with 4 bar of H$_2$ at room temperature, the solution became immediately dark brown and extensive precipitation of palladium metal was observed. Nevertheless almost no change was observed in the $^1$H and $^{31}$P NMR spectra. The tube was subsequently heated to 40 °C and after one hour the peaks for the starting material had completely disappeared. Several multiplets were observed in the $^{31}$P
NMR spectrum, but no hydride signal could be detected. In order to avoid formation of palladium metal and the associated side reactions, the reaction was performed at low temperature. The solution in the high pressure NMR tube was cooled to $-60 \, ^\circ\text{C}$ before pressurizing to 4 bar with dihydrogen, and indeed neither precipitation nor color change was observed. The tube was then introduced in the pre-cooled NMR probe at 213 K. No change in the spectra was observed, even when the solution was warmed to 273 K. After increasing the pressure to 10 bar the reaction was followed at 253 K during 20 hours, but only after 15 hours various small new peaks could be observed. The solution was stored at room temperature for 24 hours and the NMR spectra were measured again at 253 K. [XantphosPd($\eta^2$-PPh$_2$Py)][OTf]$_2$ (1d) remains the main species in solution, but the $^1$H NMR spectrum shows very small peaks in the hydride region ($\delta= -9.1$ ppm), together with several broad peaks between $\delta= 13$ and $\delta= 15$ ppm. After a total time of 60 hours the starting material was still the major product, but the hydride signal could no longer be observed and several new peaks appeared in the $^{31}$P NMR spectrum, which resembled that of the reaction carried out at 40 $^\circ\text{C}$. Although it was not possible to assign all peaks in the $^{31}$P NMR spectrum, the observation of multiplets at $\delta= 220$ ppm points towards the formation of phosphido bridged dimers. These dimers are formed as a result of P-C bond cleavage in the PPh$_2$Py ligand (see below). Similar results were obtained from the reaction of [DPEphosPd($\eta^2$-PPh$_2$Py)][OTf]$_2$ with dihydrogen, but in this case extensive decomposition can already be observed after 14 hours at room temperature. Apparently, complexes 1d and 1b are unable to react with dihydrogen below room temperature, but above this temperature the hydride product reacts further forming unidentified products.

Different reactivity was observed for complexes 1a and 1a-Me bearing the dppf ligand. For 1a no reaction at all was observed under 4 bar of dihydrogen over a period of 8 hours. After 24 hours under 10 bar of H$_2$ about 30% conversion to a hydride containing product was observed. The high field region of the $^1$H NMR spectrum shows a broad doublet of doublets at $\delta= -6.7$ ppm, which resolves into a doublet of doublets of doublets upon cooling to 233 K. Four new signals for the Cp protons of dppf were observed between $\delta= 3.5$ and $\delta= 5$ ppm. A broad signal at 15.1 ppm was assigned to the protonated pyridyl moiety. The $^{31}$P NMR spectrum shows signals for the starting material together with a new triplet and a doublet of doublets ($\delta= 22.63$ and 32.22 ppm respectively).
These signals were assigned to the new palladium hydride [(dpdf)PdH(PPh$_2$PyH)][OTf]$_2$ \n2a (scheme 4-2). Complete conversion to \n2a can be obtained by carrying out the reaction \nin an autoclave under 10 bar of dihydrogen for 65 hours. \nIn contrast to this very slow reaction, complex \n1a-Me reacts immediately under 3 bar of \ndihydrogen at room temperature. The initial dark brown solution turns bright red within 15 \nminutes and small amounts of palladium metal are formed. Reduction to metallic palladium is avoided if the reaction is carried out at 0 °C. The \n$^1$H and $^{31}$P NMR spectra showed no starting material remaining. A small hydride signal could be observed in the \n$^1$H NMR spectrum, but its intensity was very small compared with the CH$_3$ and Cp protons, indicating that the main product does not contain a hydride ligand. The $^{31}$P/$^1$H NMR spectrum displays an AMX splitting pattern, similar to that of \n1a, but the disappearance of the signal at $\delta = -43.6$ ppm indicates the PPh$_2$Py is acting as a monodentate ligand. The proton-coupled $^{31}$P NMR spectrum reveals a strong P-H coupling in the same range as the \ntrans P-P coupling, giving raise to a pseudo-triplet. The $^1$H NMR spectrum shows a doublet of doublet of doublets centered at $\delta = 6.1$ ppm, which becomes a singlet upon phosphorus decoupling (Fig 4-3). The P-H coupling constant (360 Hz) points to the presence of a direct P-H bond. Furthermore, this product displays seven signals for the Cp rings of dpdf and a broad singlet at $\delta = 12$ ppm in the $^1$H NMR spectrum. The \n$^{13}$C/$^1$H/$^{31}$P NMR spectrum displays a singlet at $\delta = 179.5$ ppm which splits into a doublet of triplets when the spectrum is measured phosphorus-coupled (fig. 4-3). The value of the carbon-phosphorus coupling constants ($J_{CP}$ = 125 (d) and 12.6 (pt) Hz) indicate that an aryl group is coordinated to the palladium. After further characterization using $^1$H-$^1$H, $^1$H-$^{31}$P and $^1$H-$^{13}$C correlation NMR techniques, \n3a-Me was identified as a palladium-aryl complex arising from the cleavage of the phosphorus-pyridyl bond in the coordinated PPh$_2$Py ligand (scheme 4-3). Protonation of the nitrogen was confirmed by the broad singlet at $\delta = 12.2$ ppm, which shows a long-range correlation with the protons of the methyl group.
While trying to crystallize the hydride complex 2a, the light brown solution turned orange after several days at room temperature. The NMR spectra of the orange-red solid obtained after evaporation of the solvent showed very similar features to those of 3a-Me. Although we did not observe any sign of decomposition of 2a during its characterization in solution, it slowly decomposes to form the aryl complex 3a. No signs of the starting material (1a) were detected in the solution. This observation, together with the small amounts of hydride species observed upon reaction of 1a-Me with dihydrogen, indicate that a palladium hydride is indeed an intermediate in the conversion of 1a-Me to 3a-Me.

P-C bond cleavage in palladium phosphine complexes has been widely studied because it is responsible for catalyst deactivation as well as aryl redistribution in cross-coupling reactions. Two main mechanisms have been proposed for this reaction: oxidative addition of the phosphine-bound aryl to form a terminal phosphido group (which will usually react further to form dimeric compounds) or nucleophilic attack at a coordinated phosphorus, followed by addition of the cleaved aryl group. In this case the oxidative addition pathway can be discarded because no phosphido bridged products were observed by $^{31}$P NMR and there is no evidence of a Pd(IV) species.
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\[
\begin{array}{c}
\text{[Pd(PH$_2$)$_2$P$_2$N$_2$]$_2$}^{2+} + \text{H$_2$} \rightarrow \text{[Pd(PH$_2$)$_2$P$_2$N$_2$]$_2$}^{+} \rightarrow \text{[Pd(PH$_2$)$_2$P$_2$N$_2$]$_2$}^{+} \\
R = \text{H} \quad 1a \\
R = \text{Me} \quad 1a-\text{Me}
\end{array}
\]

Scheme 4-3. Reaction of complexes 1a and 1a-\text{Me} towards dihydrogen. The phenyl groups on the phosphorus have been omitted for clarity (P= PPh$_2$).

The hydride ligand in 2a (and the hypothetical 2a-\text{Me}) can act as an intramolecular nucleophile towards phosphorus. Because the nitrogen atom in 2a is protonated, the phosphorus-pyridinium bond is weakened, resulting in facile cleavage of this bond (scheme 4-4). This mechanism would explain the observation of a P-H bond in the final product and the fact that the P-C(pyridyl) is selectively cleaved. Novak and co-workers proposed a mechanism involving reductive elimination of a phosphonium salt to give a 14-electron Pd(0) species, followed by oxidative addition of a P-C bond.$^{50}$ Although this mechanism will result in the same final product as the nucleophilic substitution mechanism, the formation of a dicationic phosphonium salt seems unlikely, due to the positive charge in the pyridyl moiety.

\[
\begin{array}{c}
\text{[Pd(PH$_2$)$_2$P$_2$N$_2$]$_2$}^{+} \rightarrow \text{[Pd(PH$_2$)$_2$P$_2$N$_2$]$_2$}^{+} \\
\end{array}
\]

Scheme 4-4. Proposed mechanism for the formation of complex 3a and 3a-\text{Me}

This reaction pathway is in sharp contrast to that observed for the platinum hydrides described in the previous chapter, where the only decomposition observed was the loss of dihydrogen to regenerate the starting $\eta^2$-pyridylphosphine complex. One explanation for this difference may be the stronger $\sigma$ Pt-H bond compared to the Pd-H bond, which makes the nucleophilic attack at the phosphorus atom less likely in the platinum case.
Conclusions

The coordination mode of the pyridylphosphine ligand in [(diphosphine)Pd(PPh$_2$Py)]$^{2+}$ (1a-d) is governed by the steric demands of the diphosphine. Thus, stable bis-chelated complexes are formed with the smaller bite angle diphosphines (dppf and DPEphos) in spite of the strain imposed by the four-membered ring created by the PPh$_2$Py ligand. In solution, the complex containing Xantphos (1d) exists as an equilibrium mixture of a species containing a chelated and a species with a P-monocoordinated pyridylphosphine. The latter species is stabilized by coordination of the oxygen atom of the Xantphos backbone. The more bulky ligand, diphenyl-2-(6-methyl-pyridyl)phosphine, facilitates the de-coordination of the pyridyl moiety in the complex [(dppf)Pd{2-(6-CH$_3$-C$_5$H$_3$N)PPh$_2$})]$_2^+$ (1a-Me). In contrast to the analogous platinum compound, the anion does not coordinate to the palladium center. Thus, at low temperature only the bis-chelate complex [(dppf)Pd(η$_2$-{2-(6-CH$_3$-C$_5$H$_3$N)PPh$_2$})]$_2^+$ is observed. The interconversion of the η$^1$ and η$^2$ coordination modes of the pyridylphosphine ligands in 1a-Me and 1d is faster for palladium complexes than for the corresponding platinum ones (chapter 3).

Heterolytic splitting of dihydrogen is a possible route to palladium hydride complexes, but the stability of the products is highly dependent on the ancillary ligands. A hydride complex could only be isolated when [(dppf)Pd(PPh$_2$Py)]$^{2+}$ was used. When the other diphosphines are used, a hydride complex possibly forms, but it reacts immediately further to other products. The hydride product [(dppf)PdH(PPh$_2$PyH)](OTf)$_2$ (2a), slowly decomposes in solution via P-C bond cleavage. Substitution of the 6*-position of the pyridyl ring with a methyl group, accelerates the latter reaction and the hydride complex cannot be isolated.

The facile de-coordination of the pyridyl moiety may be relevant to the catalytic system described by Drent et al. for the alkoxy carbonylation of propyne.$^{15,18}$ They observed a significant increase in the activity and selectivity towards MMA when the diphenyl-2-(6-methyl-pyridyl)phosphine ligand was used. The limited lifetime of palladium hydride complexes containing a protonated PPh$_2$Py ligand renders a catalytic cycle starting with a hydride species unlikely. Nevertheless, if protonation of the Pd center occurs after coordination of the alkyne (see introduction, mechanism C), insertion into the Pd-H bond
will probably be much faster than the attack of the hydride to the phosphorous atom. The issue of ligand decomposition under actual catalytic conditions has not been addressed yet.

### Experimental Section

All manipulations were carried out under 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$_2$, diethyl ether, tetrahydrofuran, hexanes and pentane were distilled from sodium / benzophenone. (COD)PdCl$_2$,$^{51}$ DPEphos,$^{52}$ Sixantphos,$^{52}$ Xantphos$^{52}$ and 6-methyl-2-diphenylphosphinopyrine$^{53}$ 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-crystallised 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$_2$Cl$_2$ was dried over CaH$_2$, 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.

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

150 mg (0.205 mmol) of (dppf)PdCl$_2$ and 132 mg (0.512 mmol) of silver triflate were dissolved in 10 mL of CH$_2$Cl$_2$ in a Schlenk tube protected from light. The color of the solution changed immediately from orange to deep green and a white precipitate formed. The reaction mixture was stirred for 1 hour. The AgCl formed is allowed to settle and the solution was filtered into a Schlenk containing a solution of 65 mg (0.246 mmol) of diphenylphosphino-2-pyridyne in 5 mL of CH$_2$Cl$_2$. The color of the solution changed from green to purple. The reaction mixture was stirred for two hours and the solution was filtered over celite. The deep purple solution was evaporated in vacuum and the solid obtained was washed with diethyl ether (2x 5 mL) to yield 1a as a purple solid. The crude product was re-crystallised from CH$_2$Cl$_2$ / Et$_2$O to obtain pure 1a.
Yield = 200 mg (0.164 mmol), 80%.

**1H NMR** (300 MHz, CD$_2$Cl$_2$, 295 K): 8.08 (m, 1 H, Py-H$^5$), 7.97-7.07 (m, 33H, Ar), 5.28(s, 2H, αH Cp) 4.84(s, 2H, βH Cp), 4.47(s, 2H, βH Cp), 3.65 (s, 2H, αH Cp). **$^{31}$P{**$^1$H}$^\text{NMR}$ (121.5 MHz, CD$_2$Cl$_2$, 295 K): -42.3 (dd, P$_X$, J$_{PXP} = 408$ Hz, J$_{PXP}$ = 14 Hz), 30.7 (dd, P$_A$, J$_{PAPM}$ = 8.5 Hz), 41.7(t, P$_M$). **$^{13}$C {**$^1$H}$^\text{NMR}$ (125.7 MHz, CD$_2$Cl$_2$, 295 K): 148.4, 142.3 (CH, Py); 134.7, 134.6, 134.5, 134.1, 133.8, 133.6, 133.5, 133.3, 130.9, 130.8, 130.7, 130.6, 129.6, 129.5 (CH, Ar); 130.3, 129.8, 127.8, 127.5 (C, Ph); 121.2 (q, CF$_3$, J$_{CF}$ = 321.1 Hz); 119.7, 119.3 (C, Ph); 79.5 (d, CH, Cp, J$_{CP}$ = 12.7 Hz); 77.2 (d, CH, Cp, J$_{CP}$ = 9.4 Hz); 76.7 (d, CH, Cp, J$_{CP}$ = 9.3 Hz); 76.1 (d, CH, Cp, J$_{CP}$ = 10.6 Hz); 75.2 (d, CH, Cp, J$_{CP}$ = 7.6 Hz); 75.1 (d, C, Cp, J$_{CP}$ = 66.3 Hz); 66.0 (d, C, Cp, J$_{CP}$ = 58.5 Hz).

During the crystallization of this compound, orange plates were obtained by slow diffusion of pentane into a solution of 1a in THF. X-ray analysis of the crystals revealed they corresponded to [Pd(μ-PPh$_2$Py)OTf]$_2$.

dppf(6-methyl-2-diphenyl-pyridylphosphine)palladium (II) bis triflate (1a-Me)

This compound was prepared using the same procedure as described for 1a using 200 mg (0.273 mmol) of dppfPdCl$_2$ and 176 mg (0.683 mmol) of AgOTf in 10 mL of CH$_2$Cl$_2$, and 83.3 mg (0.301 mmol) of 6-methyl-2-diphenyl-pyridylphosphine in 5 mL of CH$_2$Cl$_2$. After working up as for 1a, a dark brown microcrystalline solid was obtained. Repeated crystallization from CH$_2$Cl$_2$ / pentane was necessary to obtain a pure product.

Yield = 260 mg (0.210 mmol), 77%.

**1H NMR** (300 MHz, CD$_2$Cl$_2$, 233 K): 7.93-7.00 (br. m, 33H, Ar), 4.77(s, 2H, Cp) 4.69 (s, 2H, H Cp), 4.33(br. s, 4H, Cp), 1.61 (br. s, 3 H, CH$_3$). **$^{31}$P{**$^1$H}$^\text{NMR}$ (121.5 MHz, CD$_2$Cl$_2$, 233 K): -43.6 (d, P$_X$, J$_{PXP} = 400$ Hz), 25.0 (d, P$_A$), 40.3 (P$_M$). **$^{13}$C {**$^1$H}$^\text{NMR}$ (125.7 MHz, CD$_2$Cl$_2$, 193 K): 166.0 (d, C, Py, J$_{CP}$ = 66.4 Hz); 162.1 (d, C, Py, J$_{CP}$ = 13.8 Hz); 141.9 (CH, Py); 134.4, 1333.8, 133.5, 132.7, 131.0, 130.9, 131.3, 130.2, 129.4, 129.2, 128.7 (CH, Ar); 128.9, 119.1, 118.8 (C, Ar); 120.7 (q, CF$_3$, J$_{CF}$ = 320.7 Hz); 119.7, 119.3 (C, Ph); 79.1 (m, CH, Cp); 71.6 (d, C, Cp, J$_{CP}$ = 74.4 Hz); 69.3 (d, C, Cp, J$_{CP}$ = 59.8 Hz); 24.9 (CH$_3$).

This product contained small amounts of [(η$^1$-dppf)Pd(η$^1$-(PPh$_2$Py(Me)))(OTf)]$_2$. 

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$^{31}$P{$^1$H} NMR (121.5 MHz, CD$_2$Cl$_2$, 233 K): 42.3 (t, PPh$_2$Py, $J_{PP}$ = 13.2 Hz); -14.9 (d, $\eta^3$-dppf).

Anal. Calcd. for C$_{54}$H$_{44}$P$_3$O$_6$NS$_2$F$_6$PdFe: C 52.47; H 3.59. Found: C 52.67; H 3.62.

DPEphos(diphenyl-2-pyridylphosphine)palladium (II) bis triflate (1b)

126 mg (0.176 mmol) of (DPEphos)PdCl$_2$ were suspended in 15 mL of CH$_2$Cl$_2$ and 113 mg (0.440 mmol) of silver triflate in 5 mL of CH$_2$Cl$_2$ were added. The dark yellow suspension was stirred overnight after which a bright orange solution had formed. The AgCl formed was allowed to precipitate and the solution was filtered into a Schlenk containing 55.6 mg (0.211 mmol) of diphenyl-2-pyridylphosphine in 5 mL of CH$_2$Cl$_2$. The reaction mixture was stirred for 16 hrs. The same work-up procedure as for 1a was used to obtain 1b as a fluffy bright yellow solid. Yield = 181 mg (0.150 mmol), 85%.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$, 295 K): 9.2 (m, 1 H, Py-H$^6$), 8.05-6.72 (m, 40 H, Ar), 6.56 (m, $^1$H, Py-H$^3$). $^{31}$P{$^1$H} NMR (121.5 MHz, CD$_2$Cl$_2$, 295 K): -46.0 (dd, P$_x$, $J_{PXP A}$ = 412 Hz), 20.05 (t, P$_M$), 20.49 (dd, P$_A$, $J_{PM A}$ = 3.7 Hz). $^{13}$C{$^1$H} NMR (125.7 MHz, CD$_2$Cl$_2$, 295 K): 169.1(d, C, Py, $J_{CP}$ = 86.1 Hz); 159.2, 158.3 (d, C-O); 148.8 (d, CH, Py, $J_{CP}$ = 12.2 Hz); 142.4 (CH, Py); 139.9, 136.6, 135.7, 135.1(CH, Ar); 134.8 (d, CH, $J_{CP}$ = 11.8 Hz); 134.5 (d, CH, $J_{CP}$ = 10.9 Hz); 134.2, 134.0 (d, CH, $J_{CP}$ = 2.9 Hz); 133.7(d, CH, $J_{CP}$ = 11.4 Hz); 133.3, 132.9, 132.3, 131.5 (d, CH, $J_{CP}$ = 4.6 Hz); 130.8 (d, CH, $J_{CP}$ = 11.81 Hz); 130.3 (d, CH, $J_{CP}$ = 11.4 Hz); 130.1, 129.9, 129.6 (d, CH, $J_{CP}$ = 12.2 Hz); 128.9, 127.1 (d, CH, $J_{CP}$ = 8.9 Hz); 126.0 (d, CH, $J_{CP}$ = 8.4 Hz); 125.0 (d, CH, $J_{CP}$ = 5.5 Hz); 127.4, 126.9, 125.9 (C$_r$); 125.6 (d, C$_r$, $J_{CP}$ = 12.0 Hz); 121.5 (q, CF$_3$, $J_{CF}$ = 321.5 Hz); 120.7 (d, C$_r$, $J_{CP}$ = 12.5 Hz); 120.3, 120.1, 119.7, 119.2, 118.77(C$_r$).

Anal. Calcd. for C$_{55}$H$_{42}$P$_3$O$_6$NS$_2$F$_6$Pd: C 54.76; H 3.51. Found: C 55.01; H 3.62.

Xantphos(diphenyl-2-pyridylphosphine)palladium (II) bis triflate (1d)

This compound was prepared using the same procedure as described for 1b using 231 mg (0.306 mmol) of XantphosPdCl$_2$ and 196 mg (0.764 mmol) of AgOTf and 96.6 mg (0.367 mmol) of diphenyl-2-pyridylphosphine in 5 mL of CH$_2$Cl$_2$. The same work-up procedure as for 1a was used to obtain an orange-yellow solid.

Yield = 362 mg (0.362 mmol), 90%.

$^1$H NMR (CD$_2$Cl$_2$ at 233 K, mixture of cis and trans complexes: 8.42-6.09 (m, 66 H, Ar), 1.91 (s, 1.2 H, CH$_3$ cis), 1.72 (s, 6 H, CH$_3$ trans), 1.55 (s, 1.2 H, CH$_3$ cis). $^{31}$P{$^1$H} NMR
High pressure NMR experiments

In a typical experiment the high pressure sapphire NMR tube was charged with the corresponding starting material (1a-d) and 2 mL of CD₂Cl₂ were added inside a glove box. The closed tube was then taken out of the box, cooled in an ethanol / N₂ bath when necessary, and pressurized with H₂. The tube was then transferred to the pre-cooled NMR probe at the desired temperature. The reactions were followed in time by ^1^H and ^31^P NMR spectroscopy.

dppf(diphenyl-2-pyridylphosphine)hydridopalladium (II) bis triflate (2a)

68 mg (0.056 mmol) of 1a were dissolved in 20 mL of CH₂Cl₂ and the purple solution was transferred to an autoclave under Ar. The autoclave was pressurized to 10 bar of H₂ and the solution was allowed to react during 65 hours. The reaction mixture was transferred to a Schlenk tube using H₂ pressure and the solvent was evaporated with a stream of H₂. The resulting light brown solid was washed with pentane (3x 5mL.) and finally dried under vacuum. Yield = 50 mg (0.041 mmol), 73.4 %.

^1^H NMR (300 MHz, CD₂Cl₂, 295 K): 15.1 (br., 1 H, NH), 8.5-7.1 (m, 34H, Ar), 4.96 (s, 2H, Cp), 4.64 (s, 2H, Cp), 4.33 (s, 2H, Cp), 3.69 (s, 2H, Cp), -6.7 (dd, J_{HPX} = 171 Hz, J_{HPA/PB} = 16, hydride). ^31^P{^1^H} NMR (121.5 MHz, CD₂Cl₂, 295 K): 22.63 (t, Pₓ, J_{PXPA/PB} = 26.9 Hz), 32.22 (dd, Pₓ/₁). Analytical Calcd. for C₅₄H₄₆P₃O₆NS₂F₆PdFe: C 52.00; H 3.62. Found: C 51.86; H 3.58.

dppf(diphenylphosphine)(pyridinium)palladium (II) bis triflate (3a)

This compound was obtained during the crystallization of 2a from CH₂Cl₂ / Et₂O at room temperature.

^1^H NMR (300 MHz, CD₂Cl₂, 295 K): 13.5 (br., 1 H, NH), 7.9- 7.07 (m, 34H, Ar), 6.0 ppm (ddd, P-H, J_HP = 370 Hz, J_HP = 16.8, 10.2 Hz), 5.16 (s, 1H, Cp), 4.76 (s, 1H, Cp), 4.65 (s, 2H, Cp), 3.39 (s, 1H, Cp), 4.33 (s, 1H, Cp), 4.15 (s, 1H, Cp), 3.82 (s, 1H, Cp). ^31^P{^1^H} NMR (121.5 MHz, CD₂Cl₂, 295 K): -1.6 (dd, Pₓ, J_{PXP} = 354 Hz, J_{PXM} = 34.0 Hz ), 17.86 (dd, Pₓ, J_{PXM} = 14.6 Hz), 26.71 (dd, Pₓ).
dppy(diphenyphosphine)(6-methyl-pyridynium)palladium (II) bis triflate (3a-Me)

A Fisher-Porter bottle equipped with a magnetic stirring bar was charged with 95 mg (0.077 mmol) of 1a-Me and 10 mL of CH₂Cl₂ were added. The dark-brown solution was cooled in an ice bath and the bottle was pressurized with 3 bar of H₂. The solution became light brown almost immediately and after 15 min, it turned bright red. The solution was kept under pressure for an additional 15 min and then transferred into a Schlenk tube. The solvent was evaporated in vacuum, the remaining solid was washed with pentane (3x5 mL.) and dried under vacuum. Yield = 71.4 mg (0.058 mmol), 75%.

¹H NMR (300 MHz, CD₂Cl₂, 193 K): 12.05 (br., 1 H, NH), 9.31-7.04 (m, 34H, Ar), 6.1 ppm (ddd, P-H, J₃₈= 375 Hz, J₃₉= 16.8, 10.2 Hz), 5.21(s, 1H, Cp) 4.69(s, 1H, Cp), 4.48(s, 4H, Cp), 4.41 (s, 1H, Cp), 4.35(s, 1H, Cp), 3.79(s, 1H, Cp), 1.53(s, 3H, CH₃).

³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂, 193 K): -2.2 (dd, Pₓ, Jₓ₁ₓ₂ = 350 Hz, Jₓ₁ₓ₃ = 36.5 Hz), 17.7 (dd, Pₓ, Jₓ₁ₓ₃ = 12.1 Hz), 27.2 (dd, Pₓ). ¹³C {¹H} NMR (100.6 MHz, CD₂Cl₂, 233 K): 179.5 (dt, C₂ Py, J_Cptrans = 125.5 Hz, J_Cpcis =12.6 Hz); 157.1(d, C₆ Py, J_Cp = 4.7 Hz); 141.2 (CH, Py); 136.3 (d, CH, J_Cp = 11.5 Hz); 134.8, 135.5, 134.3, 132.9, 132.6 (CH, Ar); 132.9 (d, CH, J_Cp = 52.4 Hz); 131.9, 131.7, 131.5, 131.3 (d, CH, J_Cp = 9.8 Hz); 130.7 (d, CH, J_Cp = 9.7 Hz); 130.5, 130.3 (d, CH, J_Cp = 11.1 Hz); 129.9 (d, CH, J_Cp = 11.1 Hz); 129.6 (d, CH, J_Cp = 9.2 Hz); 128.8, 128.6 (d, CH, J_Cp = 11.5 Hz); 128.2, 125.7, 125.2, 124.6 (C quat); 122.4 (CH); 121.0 (q, CF₃, J_Cf = 320.1 Hz); 120.8 (C quat, J_Cp = 51.9 Hz); 78.6 (d, CH, Cp, J_Cp = 22.2 Hz); 77.4 (d, CH, Cp, J_Cp = 11.2 Hz); 76.9 (d, CH, Cp, J_Cp = 7.6 Hz); 76.3 (d, CH, Cp, J_Cp = 4.2 Hz); 75.3 (d, CH, Cp); 74.3 (d, CH, Cp, J_Cp = 13.9 Hz); 74.0 (d, CH, Cp, J_Cp = 5.9 Hz); 72.6 (d, CH, Cp, J_Cp = 5.4 Hz); 70.6 (d, C₆ Cp, J_Cp = 59.5 Hz); 70.2 (d, C₆ Cp, J_Cp = 51.8 Hz); 20.1 (CH₃).

References

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