Formation of dinuclear palladium(I) hydride \([\text{Pd}_{2}(\text{-H})(\text{-CO})_{2}\text{BDPP}]\text{Cl}\) by methanolysis or hydrolysis of \(\text{Pd(COME)(Cl)(S,S)-BdPP}\)\((S,S)-\text{BDPP}=(2S,4S)-2,4\text{-bis(diphenylphosphino)pentane}\)
Formation of Dinuclear Palladium(I) Hydride

$[\text{Pd}_2(\mu-\text{H})(\mu-\text{CO})\{(S,S)-\text{BDPP}\}_2]\text{Cl}$ by Methanolation or Hydrolysis of $\text{Pd(COMe)}(\mu-\text{CO})\{(S,S)-\text{BDPP}\}_2$ $\{(S,S)-\text{BDPP} = (2S,4S)-2,4$-Bis(diphenylphosphino)pentane$\}$

Imre Töth* and Cornelis J. Elsevier*

J. H. van 't Hoff Research Institute, Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received October 26, 1993

Summary: The methanolation of acetyl palladium compound $\text{Pd(COMe)}(\mu-\text{CO})\{(S,S)-\text{BDPP}\}_2$ (1) in the presence or absence of CO results in the formation of a stoichiometric amount of methyl acetate as well as a 1/1 mixture of $\text{PdCl}_2(S,S)$-BDPP $\left(3\right)$ and the dinuclear $\mu$-hydrido-$\mu$-carbonyl complex $[\text{Pd}_2(\mu-\text{H})(\mu-\text{CO})\{(S,S)-\text{BDPP}\}_2]\text{Cl}$ (4). During this process, at least 1 equiv of methanol is decarboxylated, forming CO which ends up in the products methyl acetate and the $\mu$-hydrido-$\mu$-carbonyl compound 4.

Introduction

Palladium hydrides have been proposed as intermediates in various catalytic cycles, including those of asymmetric hydrocarboxylation and hydroesterification of prochiral olefins. These reactions, which are preferably catalyzed by palladium complexes containing chiral ligands, are of potential synthetic interest, although high enantioselectivities remain as yet to be realized. In order to understand the reason for the low enantioselectivities generally obtained when using $\text{PdCl}_2(S,S)$-BDPP, 3, or other similar dichloropalladium compounds as a chiral catalyst, it is particularly important to study the stereochemistry of the palladium hydrides which are involved in the olefin insertion steps of asymmetric hydrocarboxylation and hydroesterification cycles. However, mono- and dinuclear palladium hydrides of the type $\text{PdH(X)(L-L)}$, where $X$ = halide and $L$ = cis-chelating ligand, are difficult to isolate due to their facile reaction with $\text{HX}$ to give $\text{PdX}_2(L-L)$ and $\text{H}_2$. As shown in Scheme 1 for $\text{PdH(Cl)(S,S)}$-BDPP, 2, $\text{HX}$ is readily available in the hydride reaction mixtures by its partial elimination from the hydroxide complexes. For this reason, our attempt to isolate the mononuclear hydride, 2, has failed, although the compound has been recently detected in solutions of $\text{PdCl}_2(S,S)$-BDPP and $\text{HCl}$ at low temperatures. Zerovalent palladium compounds, $\text{PdL}_2$, as the products of $\text{HX}$ elimination from $\text{PdH(X)L}_2$, where $L_2$ = bis(monotertiary phosphine), ditertiary phosphine, are also known to undergo disproportionation reactions with the hydrides, giving dinuclear hydrido-bridged $\text{Pd}$ complexes. As demonstrated by using $\text{PPh}_3$ as the ligand, a hydrido-bridged dimer can be stabilized in the presence of CO by the formation of an additional carbonyl bridge. It has been proposed that such dinuclear compounds can also be catalytically active in olefin insertion or water gas shift reactions. By using the basic diteritary phosphine ligand 1,3-bis(diisopropylphosphino) propane (dipp), it...
As shown in Figure 1, when solutions of in situ formed or isolated acetyl compound 1 in neat MeOH or in solvent compositions containing at least 50% MeOH were heated under CO pressure, the formation of dichloro compound 3 and dinuclear bridging hydride 4 in exactly a 1/1 ratio could be observed by high pressure $^{31}$P NMR spectroscopy. In the process, concomitant with the methanolysis of compound 1, a stoichiometric amount of MeCOOMe was formed, as could be readily monitored by $^{13}$C NMR by using $^{13}$C enriched CO. Under the conditions shown in Figure 1 (80 °C, 25 bar of CO), the methanolysis of acetyl compound 1 requires about 2 h for completion. Due to their significantly different solubilities, compounds 3 and 4 could be readily separated by crystallization after the alcoholysis.

As illustrated in Scheme 1, the formation of both the dichloro compound 3 and bridging hydride 4 implies the intermediacy of mononuclear hydride 2. By the observed strictly stoichiometric ratio of the bridging hydride relative to compound 3, it is apparent that both products of the reductive elimination (eq 1) should be used up in the consecutive reactions (eqs 2–5) faster than they are formed; i.e. the reactions in eqs 2–5 should be faster than that in eq 1.

The dinuclear bridging hydride 4 can also be formed by the hydrolysis of the acetyl complex when the hydrolysis is carried out in solvents such as CD$_2$Cl$_2$ or CDC$_2$Cl in the presence of water. However, some dicarbonyl compound, Pd(CO)$_2$(BDPP)$_2$, is also produced in the latter case at the expense of the bridging hydride. By the use of less polar solvent compositions than above for alcoholysis or hydrolysis, such as toluene-$d_8$/dioxane-$d_8$/MeOH = 10/1, dioxane-$d_8$/water = 10/1, etc., the bridging hydride is not formed, instead the formation of an equimolar amount of the dicarbonyl compound is observed. Thus it seems that the Pd–Cl bond in mononuclear hydride intermediate 2 should be dissociated for the formation of bridging dimer 4. Otherwise, the reductive elimination of HCl from compound 2 yields the dicarbonyl compound in the presence of CO, as shown in eqs 1, 6, and 7.

Similarly to what has been observed with Pd(Ph)(Cl)- (dipp)$_2$, when acetyl compound 1 was heated in toluene-$d_8$/MeOH = 1/1 mixture under nitrogen atmosphere (in the absence of any added CO), the bridging dimer and dichloro compound 3 were also formed in exactly a 1/1 ratio. At 80 °C, the methanolysis of compound 1 required only several minutes for completion under a nitrogen atmosphere, in contrast with the observed 2 h reaction time under 25 bar of CO. Thus, as also found in the reaction of acetyl compound 1 with NaOMe, the presence of CO retards the rate of Me ester formation from the acetyl complex. The most plausible explanation for the finding is that CO occupies the formed free coordination site cis to the acetyl group in compound 1, which is available through the partial dissociation of the Pd–Cl bond, thus hindering the coordination of the MeOH or methoxide anion. The CO to from bridging hydride 4 in the absence of added CO might be available through the partial dissociation.

### Results and Discussion

As shown in Figure 1, when solutions of in situ formed or isolated acetyl compound 1 in neat MeOH or in solvent

---


under nitrogen atmosphere (at 80 °C in toluene-d$_5$MeOH)
Pd($^{13}$CO Me) (C$_1$) ( (S,S)-BDPP)J, which was carried out
that in the methanolysis of $^{13}$C0 enriched acetyl compound
Pd,7s9 bridging hydridocarbonyl compound
2332.
As
to form by decarbonylation of compound 1, decomposes
COOMe, as judged by $^{13}$C NMR spectroscopy. The methyl
compound Pd(Me)(Cl)( (S,S)-BDPP)14, which is expected
what has been shown previo~sly.~ Since both compounds
decomposition of thus formed alkyl complexes in MeOH
partial decarbonylation of acetyl compound 1. The
decarbonylation of similar acyl complexes15 and the
decomposition of thus formed alkyl complexes in MeOH
to mononuclear hydrides16 are well-known reactions in
decarbonylation of similar acyl complexes15 and the
recorded in CDZC12. (Clean binomial quintet patterns were
observed only at or above 323 K in other solvents.)

Figure 2. Temperature dependent $^1$H NMR spectra of [Pd$_2$-
($\mu$-H)($\mu$-CO)$[(S,S)$-BDPP]$]Cl (4) at the hydride region
recorded in CD$_2$Cl$_2$. (Clean binomial quintet patterns were
observed only at or above 323 K in other solvents.)

295 K
263 K
243 K
223 K

-4 -5 -6 ppm

Figure 3. Temperature dependent $^{13}$C NMR spectra of [Pd$_2$
($\mu$-H)($\mu$-CO)$[(S,S)$-BDPP]$]Cl (4) at the carbonyl region
recorded in toluene-d$_5$/MeOH = 1/1.

is about the mean value of the 92 Hz trans and 5.4 Hz cis
$^3$J$_{PC}$ couplings in the triplet of triplets (~5.01 ppm)
observed at 223 K. $^{13}$C NMR spectra of the bridging
hydride complex 4 containing a $^{13}$CO carbonyl bridge
showed a similar temperature dependence and patterns
for the carbonyl resonance (Figure 3). The quintet at 239.7
ppm produced by $^3$J$_{PC}$ couplings of 32.5 Hz of four
equivalent phosphorus atoms at room temperature
collapses at 263 K to give a triplet of triplet at 240.9 ppm at
223 K with trans and cis $^3$J$_{PC}$ couplings of 67 and 2.9 Hz.
(The small cis couplings are not resolved in the spectrum
shown in Figure 3). The triplet of triplet pattern for the
hydride and carbonyl bridge in $^1$H and $^{13}$C NMR,
respectively, and the AA'BB' pattern in $^{31}$P NMR indicates
a stable square-planar geometry for the complex at 223 K
or below.

Square-planar structures have also been found in the
solid state (crystal structures) and were inferred from some
low temperature solution NMR spectra of the analogous
Pd$^{7,9}$ and Pt$^{17}$ dimers. The observed equal $^2$J$_{PH}$ and $^2$J$_{PC}$
couplings on the bridging hydride and carbonyl, respec-
tively, in solution NMR spectra have been attributed to
dynamic equilibria involving the partial or complete
dissociation of square-planar hydroxycarbonyl bridged
compounds, i.e. to fast opening and closing of either the
carbonyl or both bridges.$^{7b,17}$

The complete dissociation (involving an equilibrium as
depicted in eq 5), which has been found to take place with
the analogous compound containing triphenylphosphine
in the presence of excess ligand,$^{7c}$ can be ruled out as an
explanation for the dynamic behavior of bridging hydro-
decarbonyl complex 4 for the following reasons. As it has
also been noted for the bridging dimer containing dippp,$^9$
the hydride resonance of compound 4 does not show H/D
exchange with CD$_3$OD in $^1$H NMR up to 80 °C. Fur-
thermore, when the isolated hydroxycarbonyl complex was
redissolved in MeOH or CH$_2$Cl$_2$, an extensive formation
of compound 3, thus a redistribution of the dimer through

\begin{footnotesize}
(15) Dekker, G. P. C. M.; Elsevier, C. J.; Vriese, K.; van Leeuwen, P.

1976, 993.

(17) Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F.; Saotake,
2332.
\end{footnotesize}
Scheme 2. Possible Mechanisms for CO Exchange in \([\text{Pd}_2(\mu^{-}\text{H})(\mu^{-}\text{CO})(\text{S,S}-\text{BDPP})_2\text{Cl}] (4)^a\)

\[
\text{CHCl}_3
\]
\[\begin{align*}
PdCl_2(\text{BDPP}) + H_2 + CO \rightarrow & \text{CO exchange} \\
\end{align*}
\]

Possibly, this is the reason for the fact that, despite its resistance to alkene insertion, the dinuclear hydride is not observed by high pressure NMR spectroscopy in operating catalytic systems of styrene hydroesterification by using dichloro compound 3 as the precursor, i.e. in the presence of in situ formed HCl.\(^6\) As mentioned above, the bridging carbonyl group of dimer 4 exchanges with free CO. The exchange is immeasurably fast at room temperature at 1 bar of CO pressure, as determined by observing the incorporation of \(^{13}\)CO enriched CO into the bridging carbonyl group of the dimer by \(^{31}\)P NMR spectroscopy. The CO exchange process slows down upon cooling; however, it is still well-detectable \((t_{1/2} \approx 2.5 \text{ h} \text{ under } 5 \text{ bar } \text{ CO} \text{ at } -50 \degree \text{C})\). As shown in Figures 1 and 2, the bridging dimer shows NMR spectra which are consistent with a stable (non-dynamic) square-planar structure at this temperature. \(^{31}\)P NMR spectra of compound 4 at 30 bar of CO pressure showed some line broadening at -50 \degree \text{C} or below, but an intermediate in the CO exchange (Scheme 2) could not be detected.

Some possible pathways for the CO exchange are shown in Scheme 2. As implied above, all the species involved in the exchange should be in an undetectably low concentration for NMR at or below -50 \degree \text{C}. Since the bridging carbonyl signal around 240 ppm does not exhibit a significant upfield shift (which could be expected in a fast exchange with compounds containing terminal carbonyl groups around 180 ppm) in \(^{13}\)C NMR spectra when the solution is heated to room temperature or even to 80 \degree \text{C} (283 ppm), the amount of such intermediates involved in CO exchange should be small. A CO exchange mechanism through short-lived intermediates in low concentrations can also be inferred from IR spectra of solutions of compound 4 in the presence of CO, which are completely blank in the region of terminal carbonyls, i.e. 1900-2100 cm\(^{-1}\). Since the exchange between the bridging carbonyl group and free CO remains slow on the \(^{13}\)C NMR time scale up to 80 \degree \text{C} (no coalescence of the two signals has been observed), at least one of the equilibria in either path of CO exchange must be slow for the NMR time scale. By the presented spectroscopic picture, the longer route in CO exchange (Scheme 2) through the intermediates A, B, and C, thus through at least three different undetectable species, cannot be excluded, although the shorter one through intermediates C and C' seems to be more feasible. In the latter case, instead of partial dissociation of compound 4, the observed dynamic behavior in the absence of CO could be readily explained by an equilibrium between square-planar and tetrahedral configurations. The availability of a so far unprecedented tetrahedral conformation for Pd hydrides might be supported by the facts that (i) the calculated energy barrier between a square-planar and a tetrahedral Pd\(^{II}\) compound is not large\(^9\) and (ii) most of the known Pd and Pt hydrides show strongly distorted square-planar conformations in the solid state as can be inferred from their crystal structures.\(^2\)

**Experimental Section**

NMR spectra were recorded on Bruker AMX-300 and Bruker AC-100 instruments in 10-mm quadrumuclear and multinuclear probes, respectively. High pressure NMR spectroscopy was carried out in a home-built assembly consisting mainly of a sapphire 10-mm high pressure tube and a titanium pressure head, which is similar to the one described by Roe.\(^12\) The NMR solvents were stored under \(N_2\) nondeuterated solvents were degassed before use. Microanalysis was performed by Dornis u. Kolbe, Mülheim, Germany. \(^{13}\)CO was purchased from Campro Scientific.

**Synthesis of PdCl(C(O)Me)((S,S)-BDPP)\(^{1}\) (1).** The synthesis of this compound has been described in ref 11. The isotopic derivative of 1 was prepared analogously by using \(^{13}\)CO instead of \(^{12}\)CO. Compound 1 can also be formed in situ, by the carbynylation of the methyl compound, Pd(Me)(Cl)(BDPP), under atmospheric or higher pressure of CO. The compounds Pd(Me)(Cl)(BDPP) and Pd(CO)\(_2\)(BDPP) have been characterized in ref 14. Compound 3 has been identified in the methanolsysis or hydrolysis reaction mixtures by comparing its NMR spectra to those of an authentic sample prepared separately.

**Synthesis of PdCl(C(H}}{{}_{2}}CN)\(_2\) and (S,S)-BDPP in benzene analogously to the procedure reported in ref 22 and was isolated as a white solid in 85% yield. Anal. Calcd for C\(_9\)H\(_{10}\)Cl\(_2\)Pd: C, 58.87; H, 4.86; P, 10.04. Found: C, 57.74; H, 4.95; P, 10.25. \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\), 293 K): \(\delta 24.2\) (s). \(^{1}H\) NMR (300 MHz, CDCl\(_3\), 293 K): \(\delta 7.90\) (dd, \(J_{PH} = 9.8\) Hz, \(J_{HH} = 7.3\) Hz, \(4H\)), 7.75 (dd, \(J_{PH} = 10.4\) Hz, \(J_{HH} = 7.8\) Hz, \(4H\)).


Synthesis of \([\text{Pd}_2(\mu-H)(\mu-\text{CO})(S,S)-\text{BDPP})\text{Cl}(4)\]. An amount of 450 mg (0.74 mmol) of \(\text{Pd}(\text{Me})(\text{Cl})(S,S)-\text{BDPP}\) was dissolved in 10 mL of a mixture of \(\text{MeOH}/\text{benzene} = 1/1\), and the formed colorless solution was poured into a 25-mL stainless steel autoclave. (The use of a cosolvent such as benzene or toluene was required due to the bad solubility of the methyl compound in MeOH). The autoclave was then charged to 10 bar of CO and heated to 80°C with stirring. After 3 h of stirring, the autoclave was cooled back to room temperature and the pressure was released. The formed brown-red solution was transferred into a Schlenk tube under Nz and concentrated under vacuo, yielding a brown-red inhomogeneous solid. The residue was then suspended in a CO saturated mixture of 5 mL of MeOH and 10 mL of ether. The formed white precipitate (compound 3) was filtered off and the obtained red mother liquid was concentrated again under vacuo. The crude product (\(~95\%\) purity) was recrystallized from 20 mL of toluene at \(-20\) °C giving 190 mg (0.16 mmol, 43%) of dark orange-red crystalline solid. Anal. Calcd for \(\text{C}_{18}\text{H}_{18}\text{OP}_{1/2}\text{ClPd}\): C, 61.19; H, 5.27; P, 10.71. Found: C, 60.08; H, 5.13; P, 10.66. IR (\(\nu_\text{CO}\)): 1821 (KBr) cm\(^{-1}\); 1835 (methanol/benzene = 1/1) cm\(^{-1}\). \(\text{^31P NMR}\) (121.5 MHz, \(\text{C}_6\text{D}_5\text{MeOH} = 1/1\)): \(\delta 18.1\) s (d, \(J_{\text{PC}} = 32.5\) Hz for \(4^*\)) at 323 K; 21.3 d, 11.8 d, \(J_{\text{PP}} = 32.5\) Hz (d, dd \(J_{\text{PC}} = 88\) Hz for \(4^*\)) at 223 K. \(\text{^31P NMR spectra of compound 4 at or below 223 K showed second order behavior at 40 MHz spectrometer frequency.}

**Notes**

With compound 4 have been monitored by high pressure NMR spectroscopy. Typical concentrations used in these experiments were about 0.05 mmol of compound 1 in 1.6 mL of a solvent composition containing at least 50% of an inert deuterated solvent specified above. In the CO exchange experiments, solutions (\(\text{CD}_2\text{D}_5\text{MeOH} = 1/1\)) of compound 4 (0.025 mmol/1.6 mL) or its derivative containing a \(^{13}\text{CO}\) carbonyl group, \(4^*\), were pressurized by \(^{13}\text{CO}\) or \(^{12}\text{CO}\), respectively, at dry ice temperature and were then heated to the desired temperature in the NMR probe. Since the CO exchange is fast at room temperature, compound \(4^*\) could also be conveniently obtained by bubbling \(^{13}\text{CO}\) (1 bar) into solutions of compound 4 at room temperature.

**Note:** Although the above described high pressure tubes have been used safely in our institute for years in the pressure range of 1–50 bars, it is absolutely recommended to avoid direct exposure to a charged high pressure tube while preparing, transporting, or immersing it into the NMR probe. To this effect we have conveniently employed an explosion-proof tube holder. Details may be obtained from one of the authors (C.J.E.).

**Standard NMR Experiments.** The reactions of compound 4 with styrene, \(\text{PPh}_3\), and HCl were studied in a standard 10-mm glass NMR tube by using 0.025 mmol of compound 4 and 1–2 equiv of reactants in 2 mL of \(\text{CD}_2\text{Cl}_2\).

**Acknowledgment.** We thank DSM Research, Geleen, The Netherlands, for financial support and Dr. J. G. de Vries (DSM Research) for his stimulating interest.

OM930737F