Formation of Dinuclear Palladium(I) Hydride $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)\{(S,S)\text{-}BDPP\}_2]Cl$ by Methanolysis or Hydrolysis of $Pd(COMe)(Cl)\{(S,S)\text{-}BDPP\}$ $\{(S,S)\text{-}BDPP$ = (2*S*,4*S*)-2,4-Bis(diphenylphosphino)pentane$\}$[†]

Imre Tóth*[,‡] 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

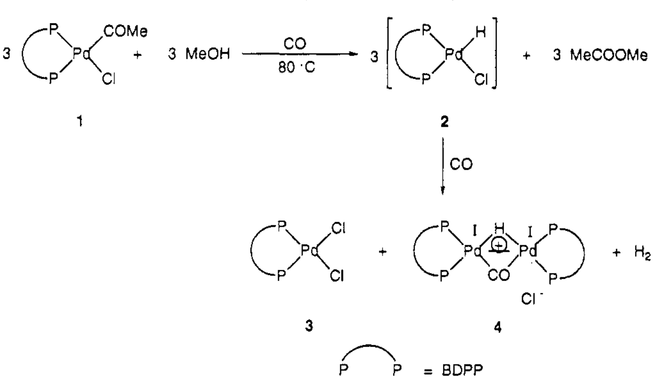
Received October 26, 1993[®]

Summary: The methanolysis of acetylpalladium compound Pd(COMe)(Cl){S,S)-BDPP} (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 $PdCl_2$ {(S,S)-BDPP} (3) and the dinuclear μ-hydrido-μ-carbonyl complex $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)\{(S,S)\text{-}BDPP\}_2]Cl$ (4). During this process, at least 1 equiv of methanol is decarbonylated, forming CO which ends up in the products methyl acetate and the μ-hydrido-μ-carbonyl compound 4.

Introduction

Palladium hydrides have been proposed as intermediates in various catalytic cycles,[1] including those of asymmetric hydrocarboxylation and hydroesterification of prochiral olefins.[2] 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.[3] In order to understand the reason for the low enantioselectivities generally obtained when using $PdCl_2\{(S,S)\text{-}BDPP\}$, **3**, or other similar dichloropalladium compounds[2b,c,4] 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, mononuclear palladium hydrides of the type PdH(X)(L-L), where X = halide and L-L = cis-chelating ligand, are difficult to isolate due to their facile reaction with HX to give PdX_2(L-L) and H_2.[5] As shown in Scheme 1 for PdH(Cl){*S,S*)-BDPP}, **2**, HX is readily available in the hydride reaction mixtures by its partial elimination from the hydride complexes. For this reason, our attempt to isolate the mononuclear hydride, **2**, has failed, although the compound has been recently detected in solutions of Pd{(*S,S*)-BDPP} and HCl at low temperatures.[6] Zerovalent palladium compounds, PdL_2 as the products of HX elimination from $PdH(X)L_2$, where L_2 = bis(monotertiary phosphine), ditertiary phosphine, are also known to undergo disproportionation reactions with the hydrides, giving dinuclear hydrido-bridged Pd^I complexes.[5] As demonstrated by using 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.[7] It has been proposed that such dinuclear compounds can also be catalytically active in olefin insertion or water gas shift reactions.[7a,8] By using the basic ditertiary phosphine ligand 1,3-bis(diisopropylphosphino)propane (dippp), it

Scheme 1. Formation of $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)\{(S,S)\text{-}BDPP\}_2]Cl$ (4)



$$Pd(H)(Cl)(BDPP) \rightleftharpoons Pd(BDPP) + HCl \qquad (1)$$

$$HCl + Pd(H)(Cl)(BDPP) \longrightarrow PdCl_2(BDPP) + H_2 \qquad (2)$$

$$Pd(BDPP) \xrightarrow[\text{MeOH}]{\text{(CO)}} Pd(CO)_n(BDPP) \quad n = 1,2 \qquad (3)$$

$$Pd(H)(Cl)(BDPP) \overset{\text{MeOH}}{\rightleftharpoons} [Pd(H)(BDPP)]^+Cl^- \qquad (4)$$

$$Pd(CO)_n(BDPP) + [Pd(H)(BDPP)]^+Cl^- \xrightarrow{\text{MeOH}} [Pd_2(\mu\text{-}H)(\mu\text{-}CO)(BDPP)_2]^+Cl^- \qquad (5)$$

$$Pd(BDPP) \xrightarrow[\text{dioxane}]{\text{CO}} Pd(CO)_2(BDPP) \qquad (6)$$

$$Pd(CO)_2(BDPP) + Pd(H)(Cl)(BDPP) \underset{\text{dioxane}}{\cancel{\longrightarrow}} [Pd_2(\mu\text{-}H)(\mu\text{-}CO)(BDPP)_2]Cl \qquad (7)$$

[†] Project sponsored by DSM Research, Geleen, The Netherlands.

[‡] Present address: DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands.

[®] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. J. *Principles and Application of Organotransition Metal Chemistry*; University Science Press: Mill Valley, CA, 1987; p 826.

(2) (a) Knifton, J. F. *J. Org. Chem.* **1976**, *41*, 2885. (b) Hayashi, T.; Tanaka, M.; Ogata, I. *J. Mol. Catal.* **1979**, *6*, 1. (c) Cometti, G.; Chiusoli, G. P. *J. Organomet. Chem.* **1982**, *236*, C 31.

(3) Ojima, I. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 232.

(4) (a) Consiglio, G.; Pino, P. *Chimia* **1976**, *30*, 193. (b) Consiglio, G. *J. Organomet. Chem.* 1977, *132*, C26. (c) Consiglio, G. *Helv. Chim. Acta* **1976**, *59*, 124.

(5) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: New York, 1982; Vol. 6, 243 and 265.

(6) Tóth, I.; Elsevier, C. J. To be published.

(7) (a) Zudin, V. N.; Chinakov, V. D.; Nekipelov, V. M.; Likholobov, V. A.; Yermanov, Yu. I. *J. Organomet. Chem.* **1985**, *289*, 425. (b) Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *Inorg. Chem.* **1991**, *30*, 2005.

(8) (a) Min'kov, A. I.; Eremenko, N. K.; Merkur'eva, S. E.; Efimov, O. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1347. (b) Min'kov, A. I.; Efimov, O. A.; Eremenko, N. K.; Klimenko, E. B. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 2076.

0276-7333/94/2313-2118$04.50/0

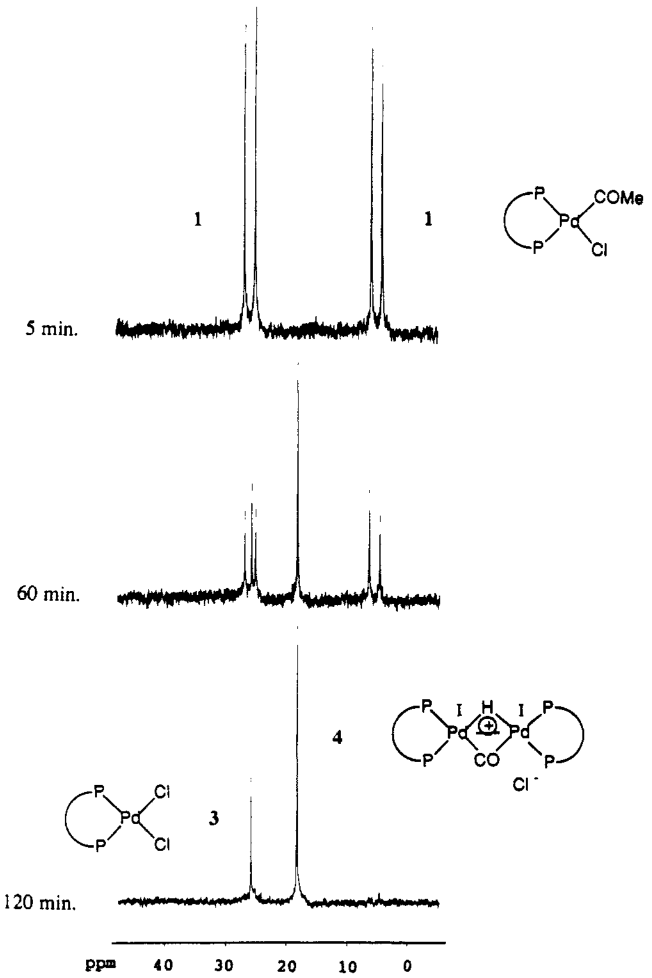


Figure 1. Formation of $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)\{(S,S)\text{-}BDPP\}_2]Cl$ (4) and $PdCl_2\{(S,S)\text{-}BDPP\}$ (3) by the methanolysis of $Pd(COMe)(Cl)\{(S,S)\text{-}BDPP\}$ (1) in toluene-d_8/MeOH = 1/1 under 25 bar of CO as observed by high pressure ^{31}P NMR spectroscopy.

has been shown recently that in the presence of a base, MeOH reduces Pd(Ph)(Cl)(dippp) to the dinuclear bridging hydridocarbonylpalladium(I) compound in the absence of added CO. A plausible mechanism for the latter process, which involves the in situ formation and subsequent recombination of PdH(Cl)(dippp), Pd(dippp), and CO, has been given.[9]

As part of our study on the mechanism of asymmetric hydroesterification and hydrocarboxylation, we have studied the alcoholysis and hydrolysis of an acetylpalladium complex, $Pd(COMe)(Cl)\{(S,S)\text{-}BDPP\}$ (1), as model reactions for the last partial step of the proposed catalytic cycle.[2a,10] Here we report that these reactions lead to the formation of the dinuclear bridging hydridocarbonyl complex $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)\{(S,S)\text{-}BDPP\}_2]Cl$ (4) which is, unlike the expected mononuclear hydride 2, thermally stable up to 80 °C and could be readily isolated.

Results and Discussion

As shown in Figure 1, when solutions of in situ formed or isolated acetyl compound 1[11] 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.[12] In the process, concomitant with the methanolysis of compound 1, a stoichoimetric 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_2Cl_2 or $CDCl_3$ in the presence of water.[13] However, some dicarbonyl compound, $Pd(CO)_2(BDPP)$,[14] 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)(dippp),[9] 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,[6] the presence of CO retards the rate of Me ester formation from the acetyl complex. The most plausible explanation for this finding is that CO occupies the formed free coordination site cis to the acetyl group in compound 1,[11] 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

---

[9] (a) Portnoy, M.; Frolow, F.; Milstein, D. *Organometallics* **1991**, *10*, 3960. (b) After submission of this paper, a full report appeared: Portnoy, M.; Milstein, D. *Organometallics* **1994**, *13*, 600.

[10] Cavinato, G.; Toniolo, L. *J. Organomet. Chem.* **1990**, *398*, 187.

[11] Tóth, I.; Elsevier, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 10388.

[12] Roe, D. C. *J. Magn. Res.* **1985**, *63*, 388.

[13] In contrast to the experience with Pd(Ph)Cl(dippp),[9] compound 4 was not formed when the *methyl* compound $Pd(Me)Cl\{S,S)\text{-}BDPP\}$[14] was heated in toluene-d_8/MeOH (1/1) at 80 °C under nitrogen. Instead, a slow but complete decomposition (ca. 15 h) to a mixture of unidentified compounds and 3 was observed. Similar treatment in the presence of 10 equiv (relative to Pd) of triethylamine resulted in the formation of a single species other than compound 4 in ca. 4 h. The structure of the latter complex is not known but probably is also a dinuclear species containing two BDPP ligands and a metal–metal bond, as was inferred from ^{31}P NMR (27.8 ppm, t, J_{PP} = 40 Hz; 20.8 ppm, t, J_{PP} 40 Hz at 353 K and a more complicated pattern at low temperatures).

[14] Tóth, I.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 529.

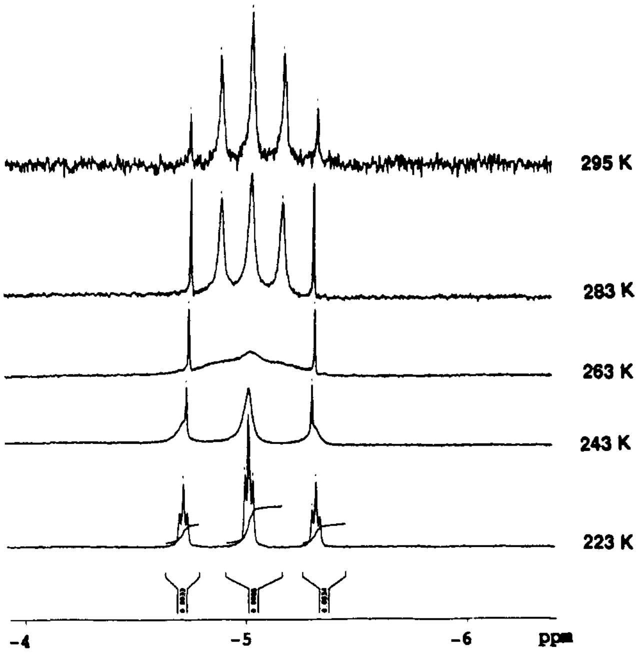


Figure 2. Temperature dependent ^{1}H NMR spectra of [Pd$_2$(μ-H)(μ-CO){(*S*,*S*)-BDPP}$_2$]Cl (4) at the hydride region recorded in CD$_2$Cl$_2$. (Clean binomial quintet patterns were observed only at or above 323 K in other solvents.)

partial decarbonylation of acetyl compound 1. The decarbonylation of similar acyl complexes[15] and the decomposition of thus formed alkyl complexes in MeOH to mononuclear hydrides[16] are well-known reactions in the literature. This seemed to be confirmed by the fact that in the methanolysis of ^{13}CO enriched acetyl compound Pd(^{13}COMe)(Cl){(*S*,*S*)-BDPP}, which was carried out under nitrogen atmosphere (at 80 °C in toluene-d_8/MeOH = 1/1), one-third of the total ^{13}CO of the acetyl complex ended up in the bridging dimer at the expense of Me^{13}COOMe, as judged by ^{13}C NMR spectroscopy. The methyl compound Pd(Me)(Cl){(*S*,*S*)-BDPP}[14], which is expected to form by decarbonylation of compound 1, decomposes very slowly under conditions identical to those above.[13] As the methyl compound is not observed in the reaction mixture after methanolysis (only compounds 3 and 4 are observed in a 1/1 ratio it seems that at least 1 equiv of MeOH was decarbonylated by the readily available Pd{(*S*,*S*)-BDPP} intermediate (Scheme 1) analogously to what has been shown previously.[9] Since both compounds 1[6] and 4 (vide infra) quickly exchange with free CO at 80 °C, ^{12}CO which is formed by the decarbonylation of MeOH could be freely incorporated into the bridging dimer and Me ester, giving rise to isotopic mixtures for these compounds.

Similarly to some analogous compounds with Pt[17] and Pd,[7,9] bridging hydridocarbonyl compound 4 shows dynamic behavior in its NMR spectra. Temperature dependent ^{1}H NMR spectra of the bridging hydride are shown in Figure 2. At 295 K, the hydride exhibits a quintet centered at −5.04 ppm with a $^2J_{PH}$ coupling of 44 Hz (indicating the presence of four equivalent P nuclei), which is about the mean value of the 92 Hz trans and 5.4 Hz cis $^2J_{PH}$ 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 $^2J_{PC}$ 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 $^2J_{PC}$ 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.

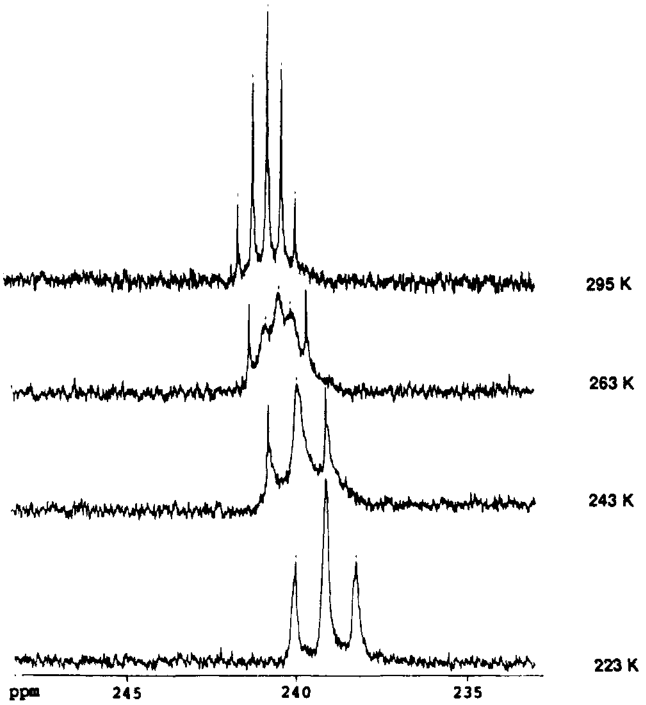


Figure 3. Temperature dependent ^{13}C NMR spectra of [Pd$_2$(μ-H)(μ-H)(μ-CO){(*S*,*S*)-BDPP}$_2$]Cl (4) at the carbonyl region recorded in toluene-d_8/MeOH = 1/1.

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 $^2J_{PH}$ and $^2J_{PC}$ couplings on the bridging hydride and carbonyl, respectively, in solution NMR spectra have been attributed to dynamic equilibria involving the partial or complete dissociation of square-planar hydridocarbonyl 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,[7a] can be ruled out as an explanation for the dynamic behavior of bridging hydridocarbonyl 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. Furthermore, when the isolated hydridocarbonyl complex was redissolved in MeOH or CH$_2$Cl$_2$, an extensive formation of compound 3, thus a redistribution of the dimer through

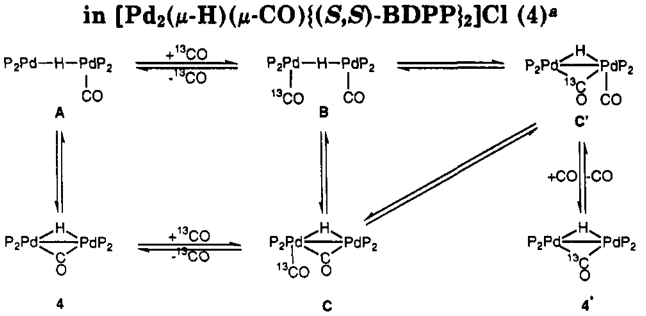
---

[15] Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598.

[16] Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.

[17] Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F.; Szostak, R.; Strouse, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1983**, *22*, 2332.

Scheme 2. Possible Mechanisms for CO Exchange in $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)\{(S,S)\text{-}BDPP\}_2]Cl$ (4)[a]



[a] P = (S,S)-BDPP, the counteranion Cl^- and charges at Pd have been omitted for clarity.

the intermediacy of compound 2 (Scheme 1) was not observed.[18] More importantly, compound 4 does not give an insertion reaction with styrene even after prolonged reaction times in the temperature range 248–295 K.[19] This is in sharp contrast to the experience with the in situ formed mononuclear hydride 2, which readily inserts styrene at −30 °C.[6] As observed for the analogous compound,[7a] dinuclear hydride 4 does react with PPh_3 or excess ligand to give a mixture of unidentified mono- and dinuclear hydrides but, as implicated above, probably not through the equilibrium in eq 5.

Thus it seems that compound 4 is not a catalytically active species in the hydrocarboxylation or hydroesterification of styrene derivatives. Like mononuclear hydride 2, bridging hydride 4 reacts with HCl to form dichloro compound 3, as shown in eq 8.

$$[Pd_2(\mu\text{-}H)(\mu\text{-}CO)(BDPP)_2]^+Cl^- + HCl \xrightarrow{CH_2Cl_2} PdCl_2(BDPP) + H_2 + CO \quad (8)$$

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}C 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 ($t_{1/2} \sim 2.5$ h under 5 bar CO) at −50 °C. As shown in Figures 1 and 2, the bridging dimer shows NMR spectra which are consistent with a stable (nondynamic) 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 °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 °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 °C (238 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 °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 theoretical tetrahedral Pd^{II} compound is not large[20] 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.[21]

Experimental Section

NMR spectra were recorded on Bruker AMX-300 and Bruker AC-100 instruments in 10-mm quadrunuclear 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 $PdCl\{C(O)Me\}\{(S,S)\text{-}BDPP\}$ (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 carbonylation 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 methanolysis or hydrolysis reaction mixtures by comparing its NMR spectra to those of an authentic sample prepared separately.

Synthesis of $PdCl_2\{(S,S)\text{-}BDPP\}$ (3). This compound was prepared by reaction of $PdCl_2(C_6H_5CN)_2$ 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 $C_{29}H_{30}Cl_2P_2Pd$: C, 58.37; 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): δ 24.2 (s). ^1H NMR (300 MHz, CDCl, 293 K): δ 7.90 (dd, $^3J_{PH} = 9.8$ Hz, $^3J_{HH} = 7.3$ Hz, 4*H*), 7.75 (dd, $^3J_{PH} = 10.4$ Hz, $^3J_{HH} = 7.8$ Hz, 4*H*),

---

[18] Compound 4 is moderately stable in solution in the absence of a CO atmosphere. Thus a few percent of compound 3 might be formed when compound 4 is dissolved in CO-free solvents.

[19] About 10% of compound 4 did transform to an unidentified species other than the mononuclear Pd alkyl compound after 16 h of standing at 248 K.

[20] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[21] See for example: (a) Di Bugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390. (b) Sommovigo, M.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *J. Organomet. Chem.* **1991**, *418*, 119.

[22] Hayashi, T.; Konishi, M.; Fukushimi, M.; Kanehira, K.; Hioki, T.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2195.

7.2–7.55 (m, 12*H*), 2.64 (m, not resolved, 2*H*), 2.12 (tt, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 6.4 Hz, 2*H*), 1.07 (dd, $^3J_{PH}$ = 14.1 Hz, $^3J_{HH}$ = 6.8 Hz, 6*H*).

Synthesis of [Pd$_2$(μ-H)(μ-CO){(*S,S*)-BDPP}$_2$]Cl (4). An amount of 450 mg (0.74 mmol) of Pd(Me)(Cl){(*S,S*)-BDPP} was dissolved in 10 mL of a mixture of MeOH/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 N_2 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 $C_{59}H_{61}OP_4ClPd$: C, 61.19; H, 5.27; P, 10.71. Found: 60.08; H, 5.13; P, 10.66. IR (ν_{CO}): 1821 (KBr) cm^{-1}; 1835 (methanol/benzene = 1/1) cm^{-1}. ^{31}P NMR (121.5 MHz, C_7D_8/MeOH = 1/1): δ 18.1 s (d, J_{PC} = 32.5 Hz for 4*) at 323 K; 21.3 d, 11.8 d, J_{PP} = 32.5 Hz (d, dd J_{PC} = 68 Hz for 4*) at 223 K. ^{31}P NMR spectra of compound 4 at or below 223 K showed second order behavior at 40 MHz spectrometer frequency.

High Pressure NMR Experiments. The methanolysis and hydrolysis of compound 1 and the CO exchange experiments 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 (C_7D_8/MeOH = 1/1) of compound 4 (0.025 mmol/1.6 mL) or its derivative containing a ^{13}CO carbonyl group, 4*, were pressurized by ^{13}CO or ^{12}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}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, 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 CD_2Cl_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