Methanol Reduces an Organopalladium(II) Complex to a Palladium(I) Hydride. Crystallographic Characterization of a Hydrido-Bridged Palladium Complex

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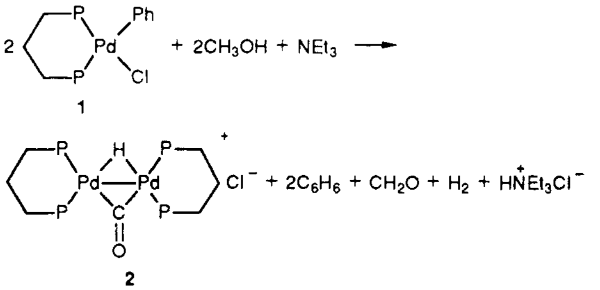
Summary: The organopalladium(II) complex **1** is reduced by methanol to the hydrido-bridged Pd(I) complex **2**, which was crystallographically characterized. A mechanism involving electrophilic attack of a cationic palladium hydride intermediate on a Pd(0) carbonyl complex is indicated.

Complexes of the type (phosphine)$_2$Pd(R)(X) (R = organyl; X = halide) are important intermediates in various palladium-catalyzed reactions. Alcohols are frequently involved in such reactions as reactants and/or solvents, e.g. in carbalkoxylation reactions of organic halides, olefins, and acetylenes.[1] We report here a facile, unusual reaction involving such a complex, 1, which is an intermediate in the Pd(dippp)$_2$ (dippp = 1,3-bis(diisopropylphosphino)propane) catalyzed reactions of aryl chlorides.[2] This unprecedented transformation takes place under conditions frequently used in palladium catalysis and should be considered in the mechanistic interpretation of such reactions. This reaction also results in a rare example of a structurally characterized hydrido-bridged palladium complex.

We have observed that carbonylation and vinylation reactions of aryl chlorides in alcoholic media frequently involve a color change from yellow to intense red, which persists throughout the reaction. Similarly, when a colorless solution of 1 in methanol containing 10 equiv of NEt$_3$ is heated to 60 °C, an intense red color develops immediately. GC analysis reveals quantitative formation of benzene, and formaldehyde is detected by the chromotropic acid test.[3] Evaporation of the solvent and analysis of the red solid[4] reveals that the Pd(I) complex 2 is formed. A Pd–Pd bond is invoked since the complex is diamagnetic. The overall stoichiometry of the transformation is presented in eq 1.



(1)

P = P(*i*-Pr)$_2$

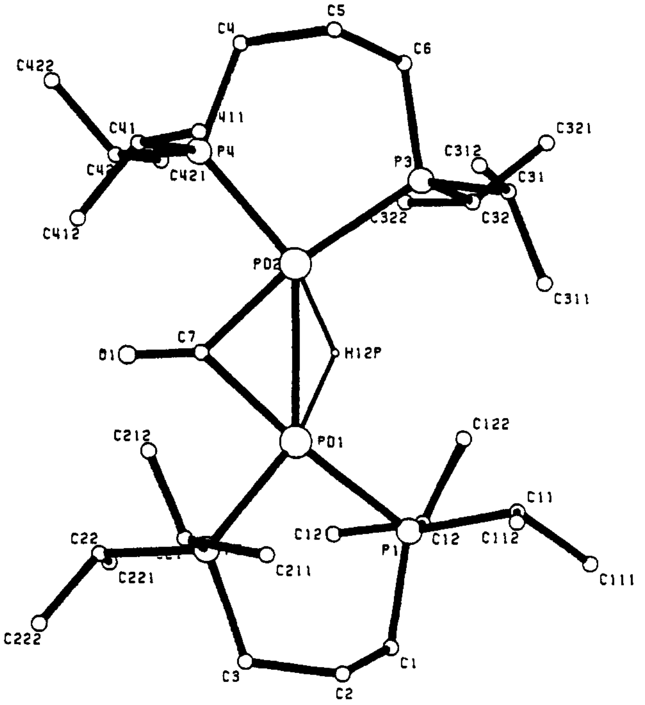


Figure 1. Molecular structure of 2. Selected bond distances (Å) and bond angles (deg): Pd(2)–Pd(1) = 2.767 (4), P(1)–Pd(1) = 2.371 (4), P(2)–Pd(1) = 2.331 (4), P(3)–Pd(2) = 2.367 (4), P(4)–Pd(2) = 2.326 (4), C(7)–Pd(1) = 2.028 (8), C(7)–Pd(2) = 2.021 (8), H–Pd(1) = 1.531 (11), H–Pd(2) = 1.540 (10), O(1)–C(7) = 1.163 (11); P(1)–Pd(1)–Pd(2) = 126.1 (2), Pd(1)–H–Pd(2) = 128.5 (7), Pd(2)–C(7)–Pd(1) = 86.2 (4), C(7)–Pd(1)–P(1) = 161.2 (2), P(2)–Pd(1)–H = 146.5 (4).

The structure of 2 is confirmed by an X-ray study of red crystals grown from toluene (Figure 1).[5]

Although palladium hydride complexes are postulated in various catalytic reactions,[1,6] very few palladium complexes containing bridging hydrides have been observed[6] and the first structural characterization of such a complex was described very recently.[6e] The crystal structure of a similar hydrido-bridged platinum complex is known.[7]

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(1) (a) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980.

(2) (a) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem. Soc.* **1989**, *111*, 8742. (b) *J. Chem. Soc., Chem. Commun.* **1989**, 1816.

(3) Feigel, F.; Auger, V. *Spot Tests in Organic Analysis*, 7th ed.; Elsevier: New York, 1966; p 434.

(4) 2: $^{31}P\{^1H\}$ NMR (methanol-d_4): δ 22.9 (s); ^1H NMR (methanol-d_4) δ 1.15 (bm 48 H, CH$_3$), 1.87 (bm, 8 H, P–CH$_2$), 2.11 (bm, 4 H, CH$_2$), 2.29 (d heptet, J_{P-H} = 13.6, J_{H-H} = 6.8 Hz, 8 H, CH), −5.17 (quintet, J_{P-H} = 41.1 Hz, 1 H, Pd–H–Pd); $^{13}C\{^1H\}$ NMR (methanol-d_4) δ 18.4 (bs, CH$_3$), 20.7 (bs, CH$_3$), 26.5 (bm, CH), 19.2 (bm, P–CH$_2$), 24.2 (bs, CH$_2$), 250.9 (quintet, J_{P-C} = 32 Hz, CO); IR ν(C≡O) 1789 cm^{-1}. Anal. Calcd: C, 44.86; H, 8.32; Cl, 4.3. Found: C, 44.45; H, 8.25; Cl, 4.5.

(5) Crystal data for 2: $C_{31}H_{69}OP_4Pd_2Cl{\cdot}C_7H_8$; M_r = 922.126, monoclinic, space group $C2/c$ (No. 15), a = 50.53 (2) Å, b = 11.263 (2) Å, c = 15.719 (3) Å, β = 90.44 (2)°, V = 8945 (4) Å^3; Z = 8, D_{calc} = 1.350 g/cm^3, μ(Mo Kα) = 10.21 cm^{-1}; crystal dimensions 0.4 × 0.3 × 0.2 mm. Data were measured on a Rigaku AFC5R diffractometer at 90 K. The hydrogen atoms were found from the difference Fourier map and refined with an overall temperature factor U_{over} = 0.032 (2) × 10^3 Å^2. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of R = 0.058 and R_w = 0.063. Details are given in the supplementary material.

(6) (a) Siedle, A. R.; Newmark, R. A.; Gleason, W. B *Inorg. Chem.* **1991**, *30*, 2005. (b) Young, S. J.; Kellenberger, B.; Reibenspies, J. H.; Himmel, S. E.; Manning, M.; Anderson, O. P.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 5744. (c) Zudin, V. N.; Chinakov, V. D.; Nekipelov, V. M.; Likholobov, V. A.; Yermakov, Y. I. *J. Organomet. Chem.* **1985**, *289*, 425. (d) Goel, R. G.; Ogini, W. O. *Inorg. Chim. Acta* **1980**, *44*, 2165. (e) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 4332.

(7) 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.

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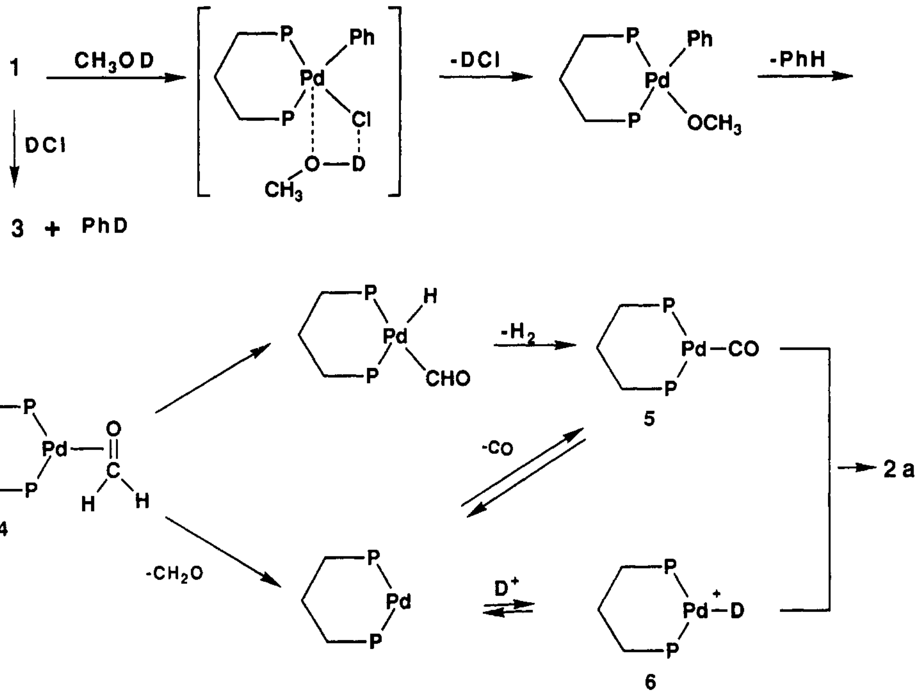
Scheme I



The palladium atoms of the cationic dimer **2** have a severely distorted planar configuration, the dihedral angle between the planes Pd(1)P(1)P(2) and Pd(1)C(7)H being 16.2 (8)°. The equivalence of the phosphorus atoms in solution, as observed by NMR spectroscopy, indicates a dynamic process. When the temperature is lowered to −80 °C, line broadening results but a limiting spectrum was not reached.

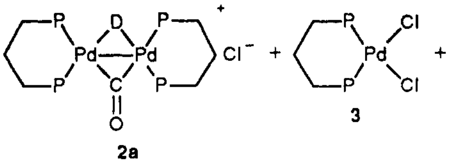
The Pd–Pd distance of 2.767 (4) Å confirms the presence of a strong single bond between these atoms.[8] The Pd–C–Pd angle of 86.2 (4)° is compatible with this bond; M–C(O)–M angles as large as 120° were observed in the absence of an M–M bond.[9] The relatively low stretching frequency of the bridging carbonyl reflects the high electron density on the metal center, as a result of the basic chelating phosphines.

The hydride ligand, which was located and refined, is at a Pd–H distance of 1.53 (11) Å, within the range reported for the few Pd–H complexes characterized crystallographically.[6e,10]

The carbonyl ligand exhibits a considerably higher trans influence than the hydride ligand, as manifested in Pd(1)–P(1) being significantly longer (by 0.04 Å) than Pd(1)–P(2). The same is true for a comparison of Pd(2)–P(3) and Pd(2)–P(4). The lower trans influence of bridging hydrides compared to that of terminal ones was noted before.[7,11]

Reaction of **1** with methanol proceeds at a comparable rate *even in the absence of* NEt_3, yielding complexes **2** and **3** in a 1:1 ratio. A similar reaction takes place with ethanol. Use of CH_3OD in this reaction leads exclusively to the *deuterido*-bridged complex **2a**[12] together with **3**,[13] benzene, and benzene-d_1 (as revealed by GCMS), the overall stoichiometry being that of eq 2. Exclusive formation of **2a** is observed also when CH_3OD is utilized in reaction 1.

$3\,\mathbf{1} + 2CH_3OD \longrightarrow$



$$2C_6H_6 + C_6H_5D + CH_2O + H_2 \qquad (2)$$

Scheme I outlines a plausible mechanistic interpretation of our results. Methanolysis of **1** in the presence of NEt_3 may involve methoxide attack at the metal center. In a neutral medium, a concerted process promoted by hydrogen bonding is more likely. β-Hydride elimination of the resulting methoxo complex would lead, after benzene reductive elimination, to the formaldehyde–Pd(0) complex **4**. Oxidative addition followed by hydride migration and H_2 reductive elimination would lead to the Pd(0) carbonyl complex **5**. A competing pathway involves formaldehyde dissociation followed by protonation to yield the Pd(II) complex **6**. Reaction of **5** with **6** could then lead to the observed Pd(I) product **2**. Formation of **3** and PhD is readily explained by reaction of the starting complex **1** with DCl.

Exclusive formation of **2a** when CH_3OD is used excludes methanol oxidative addition to **1**. Such a process was proposed for a Pt(II) complex.[14] **2** does not undergo H/D exchange with CD_3OD under the conditions of reaction 2.

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(8) 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, p 265.

(9) Colton, R.; McCormick, M. J.; Pannan, C. D. *J. Chem. Soc., Chem. Commun.* **1977**, 823.

(10) (a) DiBugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390. (b) Leoni, P.; Sommovigo, M.; Pasquali, M.; Midollini, S.; Braga, D.; Sabatino, P. *Organometallics* **1991**, *10*, 1038. (c) Kellenberger, B.; Young, S. J.; Stille, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 6105.

(11) Puddephatt, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 516.

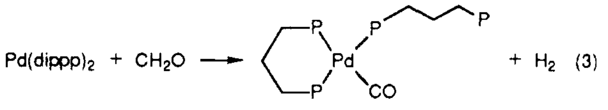
(12) **2a**: $^{31}P\{^1H\}$ NMR (methanol-d_4) δ 22.8 (triplet, 1:1:1, J_{P-D} = 5.9 Hz); $^2D\{^1H\}$ NMR (methanol-d_4) δ −5.17 (quintet, J_{P-D} = 6 Hz); IR ν(C=O) 1789 cm^{-1}.

(13) **3**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 38.3 (s); ^1H NMR ($CDCl_3$) δ 2.73 (d heptet, J_{P-H} = 10.0, J_{H-H} = 7.2 Hz, 4 H, CH), 1.96 (m, 2 H, CH_2), 1.53 (m, 4 H, P–CH_2), 1.37 (dd, J_{P-H} = 18.2, J_{H-H} = 7.3 Hz, 12 H, CH_3), 1.15 (dd, J_{P-H} = 14.8, J_{H-H} = 7.1 Hz, 12 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 27.8 (d, J_{P-C} = 30.7 Hz, CH), 21.4 (s, CH_2), 21.2 (s, CH_3), 18.4 (d, J_{P-C} = 2.8 Hz, CH_3), 15.2 (dd, J_{P-C} = 24.3, J_{P-C} = 8.0 Hz, P–CH_2).

(14) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159.

The strict stoichiometry of reaction 2 is readily explained by assuming that the hydrido complex **6** and the carbonyl complex **5** are in equilibrium with the 14e Pd(dippp), whereas the very stable **2** serves as a thermodynamic sink, its formation being essentially irreversible.

In support of the proposed mechanism we observe that paraformaldehyde undergoes decarbonylation with Pd(dippp)$_2$, leading to complex **7** (eq 3). Aldehyde oxidative addition to Pd(0) complexes is not common and may be driven to completion in this case by H_2 elimination.



7

In a probe of the feasibility of generation of **2** from **5** and **6**, Pd(dippp)$_2$ was reacted with 0.5 equiv of gaseous HCl, followed by reaction with CO. Immediate formation of **2** was observed. The same reaction takes place when CO is added prior to HCl (eq 4). A similar reaction of HPd(PPh$_3$)$_4^+$ and CO was reported.[6a,c] Although generation of a dimeric Pd(I) complex from the reaction between Pd(II) and unsaturated Pd(0) complexes is documented,[8] no reaction takes place between **3** and **5** to yield a chloro-bridged analogue of **2**. This suggests that the hydride plays an important role in the coupling process. Mechanistically, this can be viewed as an interaction between an electrophilic hydride and an unsaturated, electron-rich Pd(0) center, as contrasted with the well-known reaction involving coupling of a nucleophilic hydride with an electrophilic metal center.[15]

$$2\text{Pd(dippp)}_2 + \text{HCl} + \text{CO} \rightarrow \mathbf{2} + \text{dippp} \qquad (4)$$

Another point of interest is the role of dippp in this process. Equilibria involving chelate opening undoubtedly promote the β-elimination, migration, and reductive-elimination processes, all of which are dissociative with square planar Pd(II) complexes.[16] The ability of dippp to function in both mono- and bidentate modes plays an important role in Pd(dippp)$_2$ catalysis.[2] Compatible with this notion, we observe that reaction of (dippe)Pd(Ph)Cl (dippe = 1,2-bis(diisopropylphosphino)ethane) with methanol is considerably slower that that of **1**, although it eventually leads to an analogous complex.

Although the exact role of complex **2** and analogous Pd(I) complexes in catalysis is not yet clear,[17] the unprecented transformation reported here suggests that their formation and function should be considered in reactions involving organopalladium(II) intermediates in alcoholic media. If we take into consideration the high stability of **2**, an intriguing possibility is that some of these processes may actually involve binuclear catalysis.

The observation of reaction 1 has already led us to develop a method for efficient catalytic reduction of aryl chlorides under mild conditions using alcohol as the reducing agent.[18]

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Supplementary Material Available: Text describing the data collection, refinement, and crystal data and tables of atom coordinates, anisotropic temperature factors, hydrogen atom coordinates, bond lengths, bond angles, and torsion angles (11 pages); a table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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(15) (a) Albinati, A.; Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6825. (b) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064. (c) Paonessa, R. S.; Trogler, W. C. *Inorg. Chem.* **1983**, *22*, 1038. (d) Conroy-Lewis, F. M.; Simpson, S. J.; Brammer, L.; Orpen, A. G. *J. Organomet. Chem.* **1991**, *406*, 197.

(16) See, for example: Yamamoto A. *Organotransition Metal Chemistry*; Wiley: New York, 1985; pp 240–249.

(17) Participation of hydrido-bridged palladium complexes in catalysis has been proposed: (a) Reference 6c. (b) Min'kov, A. I.; Eremenko, N. K.; Merkur'eva, S. E.; Efimov, O. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1347. (c) Min'kov, A. I.; Efimov, O. A.; Eremenko, N. K.; Klimenko, E. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 2076.

(18) Ben-David, Y.; Portnoy, M.; Gozin, M.; Milstein, D. Submitted for publication.

Synthesis and Structure of Silicon-Containing Cage Molecules

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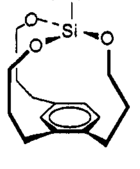
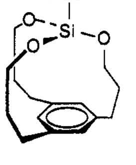
Summary: Triarmed cyclophanes **1** and **2** have been synthesized by *i*-Bu$_3$Al/TiCl$_4$-catalyzed cyclotrimerization of *t*-BuSi(OCH$_2$CH$_2$CH$_2$C≡CH)$_3$ and characterized by single-crystal X-ray, ^{1}H and ^{13}C NMR, and elemental analysis. Macrocyclic cage **1** has a distorted benzene ring, while that of **2** is nearly planar. In **1** and **2** the silicon atom is 3.50 and 3.58 Å above the mean plane of the benzene ring. Additional cyclotrimerization studies of this catalyst system are reported.



1



2

We wish to report the synthesis of **1** and **2**, the first examples of silicon-containing triarmed cyclophanes in which the silicon substituents are outside of the cage.[1] The syntheses of **1** and **2** are the first steps toward pre-

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[†] University of Colorado at Denver.

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(1) L'Esperance, R. P.; West, A. P., Jr.; Van Engen, D.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 2672–2676. This reference reports the first silicon-containing member of this series. Other related compounds are referenced in subsequent citations of Pascal and co-workers. In all of these studies, the hydrogen substituent is on the inside of the macrocycle.

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