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$[Pd_3(PPh_3)_4]^{2+}$, a New Palladium Triphenylphosphine Complex

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Triphenylphosphine has been featured prominently in metal coordination chemistry.[1] Palladium triphenylphosphine complexes, in particular, have attracted their share of interest as a result of their numerous applications in organic synthesis and catalysis.[2] Here we report a previously unknown binary palladium triphenylphosphine complex with an unprecedented triphenylphosphine bonding mode.

Yellow $[(PPh_3)_2Pd(\mu\text{-}OH)]_2(BF_4)_2$[3] is only slightly soluble in CH_2Cl_2 but rapidly dissolves to give a red solution when ethanol is added. Examination of the red solution by ^{31}P NMR spectroscopy reveals formation of Ph_3PO and a new complex with a pair of multiplets centered at 43.51 and 9.58 ppm. The new complex is also produced with other alcohols including MeOH, ^iPrOH, and ^tBuOH,[4] but the process slows markedly with the more hindered alcohols. Reduction of the CH_2Cl_2/ROH solvent volume followed by cooling gives beautiful transparent red and yellow crystals of $[Pd_3(PPh_3)_4](BF_4)_2$ (**1**) (89% yield). The ratio of the yellow to red crystals changes with the alcohol. With EtOH, only a few yellow crystals are observed, whereas with ^iPrOH, ca. 30% of the crystal mass is yellow. All of the crystals become opaque minutes after separation from the mother liquor. A red EtOH crystal and a red and a yellow ^iPrOH crystal were examined by X-ray diffraction after rapid transfer from the mother liquor to the N_2 cold stream of an X-ray diffractometer. The centrosymmetric Pd_3 cation structure shown in Figure 1 was revealed for all three crystals.[5] The red ^iPrOH crystal gave the best quality structure, and data for this structure are given here.[6] The $[Pd_3(PPh_3)_4]^{2+}$ cation consists of a $Ph_3P-Pd-Pd-Pd-PPh_3$ linear chain sandwiched by two head-to-tail $Ph_2P-C_6H_6$ groups each bonded through the P atom to one Pd atom and to two Pd atoms through a phenyl ring.[7] Although PPh_3 has been observed to bridge two metal centers through the P atom and a Ph ring,[8] a three-metal-center bridge as in **1** is without precedent.

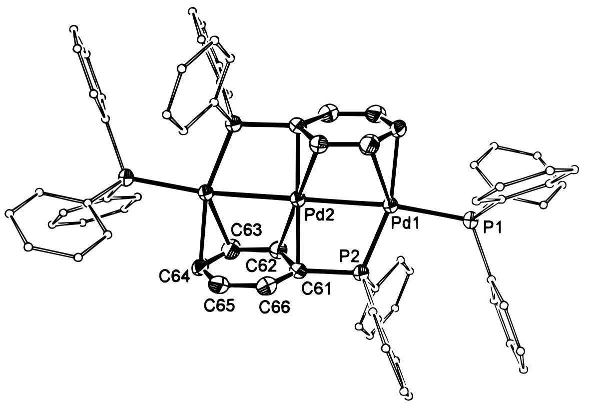

Figure 1. ORTEP drawing of the cationic portion of $[Pd_3(PPh_3)_4](BF_4)_2$ (**1**). Selected distances (Å) and angles (deg): Pd1−Pd2, 2.6587(3); Pd1−P1, 2.345(1); Pd1−P2, 2.255(1); Pd1−C63, 2.397(5); Pd1−C64, 2.288(4); Pd2−C61, 2.183(4); Pd2−C62, 2.317(4); P2−C61, 1.813(4); C61−C62, 1.434(7); C62−C63, 1.406(6); C63−C64, 1.405(7); C64−C65, 1.413(7); C65−C66, 1.377(7); C66−C61, 1.437(6); Pd1−Pd2−Pd1, 180; P1−Pd1−Pd2, 172.27(3); P2−Pd1−Pd2, 71.08(3); P1−Pd1−P2, 101.35(4); Pd1−P2−C61, 110.30(15); P2−C61−Pd2, 91.6(2); C66−C61−C62, 117.0(4); C61−C62−C63, 120.4(4); C62−C63−C64, 121.3(5); C65−C64−C63, 117.9(4); C64−C65−C66, 122.1(5); C65−C66−C61, 120.7(5).

The arene rings bond to the Pd centers through four carbon atoms, bridging the two Pd atoms as $\mu\text{-}\eta^2{:}\eta^2$-diene units (see Figure 1). Structural diagrams for **1** and related complexes are shown in Scheme 1. Arene bonding similar to that in **1** has been observed in the Pd_2 complexes **2**[9] and **3**.[10] Closely related to **1** is **4**,[11] where the MeNC ligands of **4** replace the P atom and the arene diene unit of the bridging phosphane ligands. In complexes **1** and **4** the Pd oxidation states in the chain may be described as Pd(I)−Pd(0)−Pd(I).

The formation of **1** involves Pd(II) reduction. While it is possible to write a balanced reaction where PPh_3 is the only reducing agent, the alcohol is most likely involved. Reduction of Pt(II) and Pd(II) complexes by alcohols has long been known.[12] To gain more information, the EtOH reaction was repeated in CD_2Cl_2 and monitored by ^1H NMR and ^{31}P NMR spectroscopies under both an air atmosphere and a dinitrogen atmosphere. In both cases, the simultaneous formation of **1** and $CH_3C(O)H$ was observed, confirming that EtOH is the reducing agent. Under the dinitrogen atmosphere, only traces of $OPPh_3$ were observed, and although **1** was the major product, there were many minor products. In air, clean formation of **1**, $CH_3C(O)H$, and $OPPh_3$ is observed. Thus, the alcohol is the reducing agent and free PPh_3 is scavenged by air oxidation, thereby improving the yield of **1**.

^1H and ^{13}C NMR data for **1** indicate either more symmetric bonding of the phenyl ring in solution or fluxional behavior. Instead of the expected six signals only four signals, are observed for the bound Ph ring in the ^{13}C NMR spectrum. Five signals are expected in the ^1H NMR spectrum, but only three are

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[1] McAuliffe, C. A.; Levason, W. *Phosphine, Arsine, and Silbene Complexes of Transition Elements*; Elsevier: Amsterdam, 1979; Vol. 1. Stelzer, O. In *Topics in Phosphorus Chemistry*; Griffith, E. J., Grayson, M., Eds.; Wiley: New York, 1977; pp 1−229.

[2] Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: San Diego, CA, 1985. Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 1995.

[3] Bushnell, G. W.; Dixon, K. R.; Hunter, R. G.; McFarland, J. J. *Can. J. Chem.* **1972**, *50*, 3694.

[4] Isomeric impurities may be responsible for the Bu^tOH reaction.

[5] The crystal color difference appears to result from a different packing alignment of the cations. In the yellow crystals, the Pd−Pd−Pd axes are all parallel, whereas in the red crystals, the Pd−Pd−Pd axes are alternately parallel and perpendicular.

[6] X-ray data (−100 °C): red crystals of $\mathbf{1}\cdot 2Pr^iOH\cdot CH_2Cl_2$ from CH_2Cl_2/Pr^iOH, monoclinic ($C2/c$), $a = 23.1169(13)$ Å, $b = 15.0359(8)$ Å, $c = 21.0036(12)$ Å, $\beta = 108.7850(10)°$, $Z = 4$, $R = 0.0480$, GOF = 1.121.

[7] There may also be bridge bonding of the P atom (P2) to the central Pd atom (Pd2) as proposed for $[(dppp)Pd]_2(OTf)_2$: Budzelaar, P. H. M.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *Organometallics* **1992**, *11*, 23−25.

[8] Examples of bridging arylphosphine complexes: Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1973**, *60*, C11−C13. Alyea, E. C.; Ferguson, G.; Somogyvari, A. *Organometallics* **1983**, *2*, 668−674. Luck, R.; Morris, R. H.; Sawyer, J. F. *Organometallics* **1984**, *3*, 1009−1014. Elschenbroich, C.; Heikenfeld, G.; Wunsch, M.; Massa, W.; Baum G. *Angew. Chem., Int. Ed. Engl.*, **1988**, *27*, 414−416. Cotton, F. A.; Luck, R. L.; Morris, R. H. *Organometallics* **1989**, *8*, 1282−1287. Cotton, F. A.; Kibala, P. A.; Shang, M.; Wojtczak, W. A. *Organometallics* **1991**, *10*, 2626−2630. Cotton, F. A.; Wojtczak, W. A. *Inorg. Chim. Acta* **1994**, *217*, 187−190. Singewald, E. T.; Mirkin, C. A.; Stern C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1624−1627. Elschenbroich, C.; Isenburg, T.; Behrendt, A.; Frenzen, G.; Harms, K. *J. Organomet. Chem.* **1995**, *501*, 129−144.

[9] Allegra, G.; Casagrande, G. T.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289−294.

[10] Dupont, J.; Pfeffer, M.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *Organometallics* **1989**, *8*, 1116−1118.

[11] Balch, A. L.; Boehm, J. R.; Hope, H.; Olmstead, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 7431−7432.

[12] Hartley, F. R. *The Chemistry of Platinum and Palladium;* Applied Science: London, 1973; pp 29, 51. Belluco, U. *Organometallic and Coordination Chemistry of Platinum;* Academic: London, 1974; p 2. Maitlis, P. M. *The Organic Chemistry of Palladium*; Maitlis, P. M., Stone, F. G. A., West, R., Eds.; Academic: New York, 1971; Vol. 1, pp 10−11.

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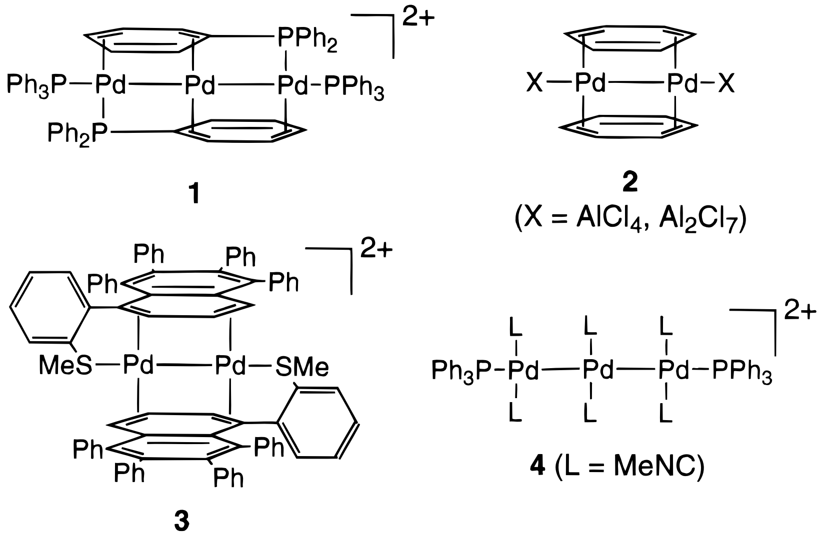
Scheme 1



1

2
(X = $AlCl_4$, Al_2Cl_7)

3

4 (L = MeNC)

observed. The observed signals are strongly upfield shifted out of the aromatic region consistent with the bonding description in **A**.[13] A facile fluxional process involving tilting of the ring back and forth along the P−C bond axis would exchange the bound and unbound sides of the arene and seems the most likely explanation for the reduced number of NMR signals.

The extremely low PPh_3/Pd ratio of **1** suggests that **1** may be a potential source of unsaturation. As a first test of this we added 8 equiv of PPh_3 to a CH_2Cl_2 solution of **1** and monitored the mixture by ^{31}P NMR spectroscopy. Remarkably, there is only a slow reaction at ambient temperatures with **1** persisting for hours after the addition.[14] Final products after several days include $[(Ph_3P)_3PdCl]^+$ and $Pd(PPh_3)_x$. There is no reaction between **1** and CO (1 atm) or MeI at ambient temperatures.

In conclusion, we have isolated an unexpected new palladium triphenylphosphine complex. The novel triphenylphosphine bridging to three metal centers is surprisingly robust and resists degradation at ambient temperatures. The low PPh_3/Pd ratio does, however, suggest that **1** may be a useful precursor in stoichiometric and catalytic reactions. Complex **1** may also represent an intermediate in carbon−phosphorus bond cleavage reactions previously observed in Pt and Pd arylphosphine chemistry.[15] The thermolysis of **1** as well as its use as a catalytic and stoichiometric reagent are under investigation.

Acknowledgment. We thank the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant No. DF-FG02-88ER13880), for support of this work. Grants from the National Science Foundation provided a portion of the funds for the purchase of X-ray (CHE-9011804) and NMR (PCM-8115599 and CHE 89-08304) equipment.

Supporting Information Available: An X-ray crystallographic file for **1** in CIF format. See any current masthead page for ordering and Internet access instructions.

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(13) Spectroscopic data for $[Pd_3(PPh_3)_4](BF_4)_2$ (**1**): ^1H NMR (CD_2Cl_2, 250 MHz, 20 °C, ppm) 4.83 (t, $J = 7.6$ Hz, 4H, H2,6 of PPh−Pd), 6.00 (t, $J = 6.4$ Hz, 4H, H3,5 of PPh−Pd), 7.02 (br m, 2H, H4 of PPh−Pd), 7.26−7.53 (m, 50H, PPh); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 63 MHz, 20 °C, ppm) 41.3 (dt, $J = 43$, 4 Hz, C1 of PPh−Pd), 88.3 (t, $J = 9$ Hz, C4 of PPh−Pd), 107.3 (t, $J = 5.6$ Hz, C2,6 of PPh−Pd), 117.1 (t, $J = 3$ Hz, C3,5 of Ph−Pd), 125.1 (d, $J = 51$ Hz, C1 of PPh_2 or PPh_3), 129.6 (m, C3,5 of PPh_2 and PPh_3), 131.5 (s, C4 of PPh_3), 132.9 (s, C4, PPh_2), 133.7 (t, $J = 6.4$ Hz, C2,6 of PPh_3), 135.71 (t, $J = 7$ Hz, C2,6 of PPh_2). Assignments are tentative. Many of the peaks are second-order patterns but approximate the first-order patterns given. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101 MHz, 20 °C, ppm): 43.51 (P_A, Ph_3PPd; 9.58 (P_B, Ph_2PPh−Pd). The second-order AA′BB′ signals appear as approximate triplets of doublets with $J \approx 23$, 5 Hz. Simulation gives approximate values of $J_{AA'} = 78.0$ Hz, $J_{BB'} = 17$ Hz, $J_{AB} = -45$ Hz, $J_{AB'} = 43$ Hz. UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)): 382 (11 700), 340 (22 700), 488 (51 200).

(14) A feature of this reaction is the absence of a ^{31}P NMR signal for PPh_3, even at the beginning of the reaction. This is presumably a result of line broadening due to chemical exchange although the signals for **1** remain unaltered.

(15) Berry, D. E.; Bushnell, G. W.; Dixon, K. R.; Moroney, P. M.; Wan, C. *Inorg. Chem.* **1985**, *24*, 2625−2634 and references therein.