Reactions of Palladium(IV), Bis(diphenylphosphino)methane (dppm), and $NaBH_4$ in the Presence of CO: Structure of $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-}dppm)_3$

David G. Holah,*[1a] Alan N. Hughes,[1a] Elizabeth Krysa,[1a] and
Vincent R. Magnuson[1b]

*Departments of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1,
and University of Minnesota—Duluth, Duluth, Minnesota 55812*

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Summary: The synthesis and structural characterization of the title compound are reported. It is a new type of palladium(0) hexamer consisting of two almost planar $Pd_3(\mu_2\text{-}CO)_3P_3$ units bridged by the $-CH_2-$ groups of the three dppm ligands in such a way that the two almost planar Pd_3 units are only approximately 10° from being eclipsed.

The two basic types of known complexes containing Pd, CO, dppm, and X are dimers of the type $Pd_2(\mu_2\text{-}CO)(\mu\text{-}dppm)_2X_2$[2–5] (**1**; X = Cl, Br, I, N_3, NCO, SCN, CF_3COO) and the singly capped trimer $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]X_2$[6–8] (**2**; X = CF_3COO), which reacts with suitable reagents to produce doubly capped trimers such as $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)(\mu_3\text{-}X)]Y$ (**3**; X = CF_3COO, Cl, Br, I, Y = CF_3COO;[7,9] X = SCN, Y = PF_6;[10] X = CO, Y = $(PF_6)_2$[11]). Compounds of type **1** are typically prepared by the carbonylation of $Pd_2(dppm)_2X_2$,[2,4] while the key to the successful synthesis of **2** involves reactions of palladium acetate, dppm, and CO in the presence of CF_3COOH.[6–8] In the Pd/CO/dppm/X system, there appear to be no complexes known with Pd nuclearities greater than 3, although there are many such examples (e.g., Pd_{4-6}, Pd_8) involving monodentate phosphines.[12–18] Also, while Pd(0)/CO/dppm complexes have been implicated[6] as intermediates in trimer formation, we know of no examples of such species with appreciable stability. This may be because the most widely used route to such systems is via substitution reactions of the parent carbonyls $M_x(CO)_y$, which are unknown for M = Pd.

In previous work, we have shown that reactions between metal(II) halides and $NaBH_4$ in the presence of CO and dppm are a particularly convenient route to M/CO/phosphine complexes (e.g., M = Co[19], Ni[20]). Also, while it has been reported briefly[4] that the closely related reactions of $PdCl_2(dppm)$, $NaBH_4$, and CO lead only to the formation of **1**, more recent studies with Pt(II), bulky phosphines (monodentate), $NaBH_4$, and CO have produced a series of Pt_3 and Pt_4 clusters,[21] and therefore, we undertook a detailed examination of similar Pd(IV) reactions in the presence of dppm.[22]

When K_2PdCl_6, dppm, $NaBH_4$, and CO are reacted together, **1** is only one of five products formed. The others are, depending on conditions, the new hexamer[23] $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-}dppm)_3$ (**4**), $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3Cl]Cl$ (**3**, X = Y = Cl), the known[24] compound $Pd_2(\mu\text{-}dppm)_3$ (**5**), and the fluxional Pd/dppm/CO complex **6**, which has not yet been identified. Using X-ray crystallography, the structure of compound **4**[25] has been determined. It is both the first characterized example of a stable Pd(0)/dppm/CO complex and a hitherto unknown type of Pd hexamer (Figure 1) in which two almost planar $Pd_3(\mu_2\text{-}CO)_3P_3$ trimeric units are bridged by the $-CH_2-$ groups of dppm in such a way that the two almost parallel trimers are only ~10° away from being eclipsed. Figure 1 shows two views of the inner core of the six Pd atoms arranged in a distorted trigonal prism. As shown in the caption for Figure 1, the trigonal faces are of nearly perfect symmetry with the range of Pd–Pd distances being 2.658(2)–2.724(2) Å and the range of the interior angles of the Pd atoms on the triangular faces being 59.23(6)–60.72(6)°. All pairs of Pd atoms on the trigonal faces are bridged by carbonyl groups, and each Pd atom is linked to a Pd atom on the other trigonal face by a bridging dppm ligand. The Pd atoms

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[1] (a) Lakehead University. (b) University of Minnesota—Duluth.

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[23] Conditions: Pd salt:dppm:$NaBH_4$ ratio of 1:1:16; CO atmosphere; in toluene/ethanol (1:1) at 20 °C for 15 minutes; pure solid obtained from the filtrate after 24 h; yield 75%. Anal. Calcd for $C_{81}H_{66}O_6P_6Pd_6$: C, 49.7; H, 3.4. Found: C, 49.3; H, 3.7. $^{31}P\{^1H\}$ NMR at 81 MHz: δ 11.0 in CH_2Cl_2. FTIR (Nujol): $\nu(CO)$ 1876 (s, sh), 1884 (m), 1841 (s, sh), 1826 (m), 1818 (m) cm^{-1}. Recrystallization from CH_2Cl_2/hexane yielded CH_2Cl_2-solvated black crystals suitable for X-ray studies.

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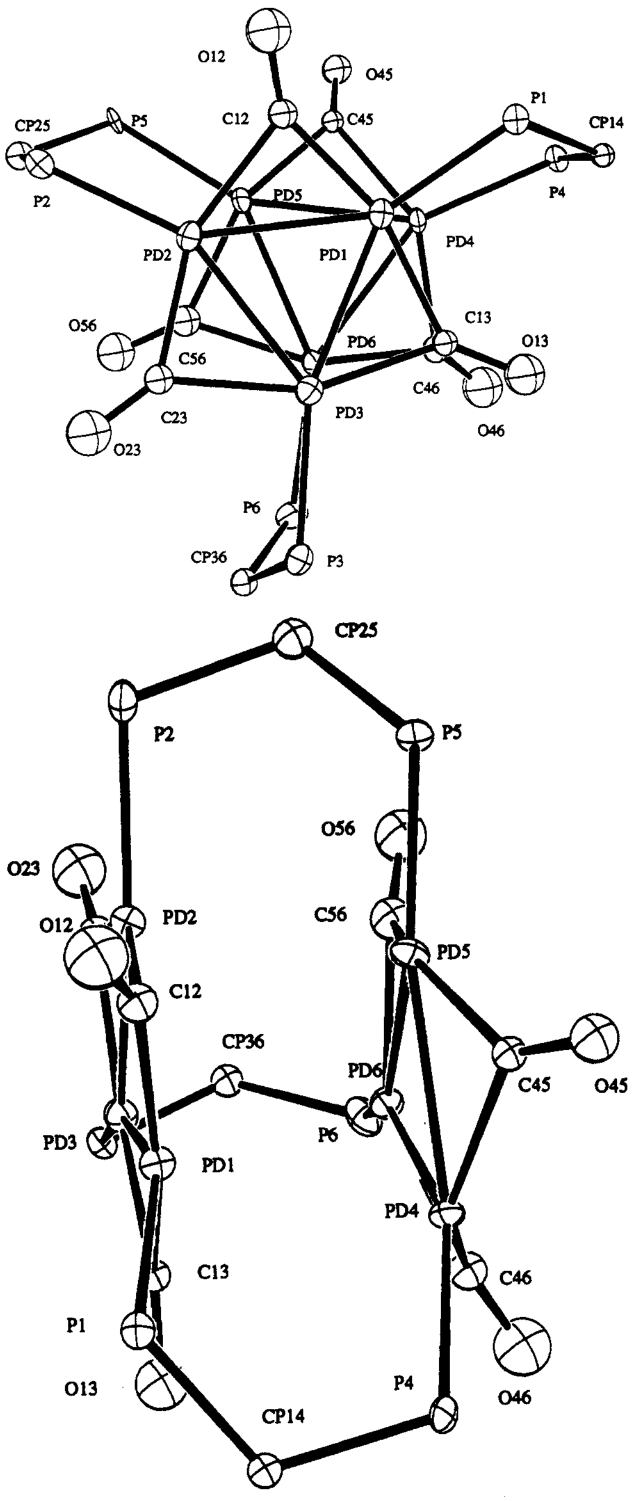

Figure 1. Two views of the molecular structure of 4. Phenyl carbon and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd1–Pd2, 2.680(2); Pd2–Pd3, 2.698(2); Pd1–Pd3, 2.658(2); Pd4–Pd5, 2.720(2); Pd5–Pd6, 2.696(2); Pd4–Pd6, 2.724(2); Pd1–P1, 2.305(6); Pd2–P2, 2.309(6); Pd3–P3, 2.306(6); Pd4–P4, 2.353(5); Pd5–P5, 2.297(6); Pd6–P6; 2.325(6); Pd1–C12, 1.96(2); Pd1–C13, 2.02(2); Pd2–C12, 2.13(2); Pd2–C23, 2.02(2); Pd3–C23; 2.06(2); Pd3–C13, 2.02(2); Pd4–C45, 2.12(2); Pd4–C46, 2.07(2); Pd5–C56, 2.03(2); Pd5–C45, 2.03(2); Pd6–C56, 2.04(2); Pd6–C46, 2.08(2); C12–O12, 1.21(3); C23–O23, 1.19(3); C13–O13, 1.21(3); C45–O45, 1.13(2); C56–O56, 1.20(3); C46–O46, 1.19(3); Pd1–Pd2–Pd3, 59.23(6); Pd2–Pd1–Pd3, 60.72(6); Pd1–Pd3–Pd2, 60.05(6); Pd4–Pd5–Pd6, 60.39(6); Pd5–Pd4–Pd6, 59.37(6); Pd4–Pd6–Pd5, 60.24(6).

Pd1, Pd2, and Pd3 of one trigonal face make an angle of 3.1° with the plane of Pd atoms Pd4, Pd5, and Pd6, on the other face. In addition, the two planes are rotated approximately 10° relative to one another. The atoms P2, P3, C13, O13, C23, and O23 all lie within ±0.120 Å of the Pd1–Pd2–Pd3 plane with P1, C12, and O12 displaced 0.539, 0.228, and 0.728 Å away from the core of Pd atoms. On the other hand, P4 is located 0.560 Å away from the Pd4–Pd5–Pd6 plane and toward the Pd1–Pd2–Pd3 plane. The other atoms that fall near this plane, P5, P6, C45, C56, C46, O45, O56, and O46, are all oriented away from the Pd4–Pd5–Pd6 plane and away from the Pd hexamer core. Distances across the long edges of the distorted trigonal prism of Pd atoms are Pd1–Pd4 = 3.030(2) Å, Pd2–Pd5 = 3.010(3) Å, and Pd3–Pd6 = 2.948(3) Å.

Each of the trimeric units has 42 valence electrons, and the average Pd–Pd distance within a trimeric unit is at the high end of the range found in other 42-electron trimers[26] and longer than Pd–Pd distances in **3**.[7–9] The structure is different from those of the known Pd_6 clusters[27] (containing CO and phosphines), which are based on either (i) the octahedron[13] or (ii) two trimers with one Pd on each bridged by two chlorides[17] or two trimers in which two Pd atoms on each ring are each bridged by one Cl,[12] with a resulting "chair" arrangement in both cases. The other known example[28] of a Pd_6 cluster with a distorted-trigonal-prismatic arrangement is $Pd_6(\mu_4\text{-}Se)_3(\eta^3\text{-}C_4H_7)_6$.

Work is continuing on elucidating the reaction chemistry (and the catalytic potential, particularly of 4 with its exposed Pd_3 faces) of these compounds and the identification of 6.

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Supplementary Material Available: A table giving a summary of crystal data, data collection parameters, and refinement details, tables of positional and thermal parameters and interatomic distances and bond angles, and an additional figure for the X-ray structural analysis of $Pd_6(\mu_2\text{-}CO)_6(\mu_2\text{-}dppm)_3$ (4) (18 pages). Ordering information is given on any current masthead page.

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(25) Crystal data: $Pd_6P_6O_6C_{81}H_{66}\cdot CH_2Cl_2$; M_r = 2044.6; orthorhombic, $Pna2_1$; a = 39.836(13) Å, b = 15.587(4) Å, c = 12.165(4) Å; D_{calcd} = 1.80 g/cm^3; Z = 4; λ(Mo Kα) = 0.710 69 Å; T = 172 K; μ = 16.3 cm^{-1}. A total of 7385 independent reflections were collected on an Enraf-Nonius CAD4 diffractometer using the ω-scan technique ($2\theta_{max}$ = 50°); 5852 reflections with $I > 2.5\sigma(I)$ were used in the structure refinement. An empirical absorption correction was carried out using ψ curves for three reflections, the ratio of the maximum to minimum transmission factors being 1.216. Structure solution was by direct methods for the Pd atoms; the remaining nonhydrogen atoms were located through least-squares refinement and difference Fourier synthesis. Pd and P atoms were refined anisotropically. Hydrogen atom positions were not located in the structure, but their contributions were included in the refinements. The final difference Fourier map had several moderately strong residual peaks, with the largest at 2.7 e Å^{-3}, approximately 1.0 Å from the Pd core atoms. Each of the six Pd atoms had two nearby residual peaks nearly coplanar with the plane of the Pd atoms in each trimeric unit. The refined C–Cl distances in the solvent molecule, CH_2Cl_2, were 1.83(4) and 1.57(4) Å. Attempts to include disorder or partial occupancy for the solvent molecule and the Pd atom trimeric units were unsuccessful. The residual R and R_w values are 0.067 and 0.090, respectively. All calculations were performed on a PC Express 486 computer using NRCVAX software: Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

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