A Highly Symmetrical Octapalladium(I) Compound: Crystal Structure of $\{[Pd(\mu\text{-}SC_6F_5)(\mu\text{-dppm})Pd](\mu\text{-}SC_6F_5)\}_4\cdot 2O(C_2H_5)_2$

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The chemistry of palladium in a formal oxidation state I is dominated[1,2] by binuclear compounds doubly bridged by bis(diphenylphosphino)methane (dppm) or related ligands.

Recently, Braunstein and co-workers have characterized[3] the tetranuclear $\{[Pd(\mu\text{-}Cl)(\mu\text{-dppm})Pd](\mu\text{-dppm})\}_2(BF_4)_2$, which contains two dipalladium(I) units.

Here, we describe the synthesis[4] of an octanuclear palladium(I) cluster containing four such moieties

$$2Pd_2(dba)_3\cdot CHCl_3 + 4Pd(SC_6F_5)_2dppm \xrightarrow{\text{ether}} \underset{\mathbf{1}}{\{[Pd(\mu\text{-}SC_6F_5)(\mu\text{-dppm})Pd](\mu\text{-}SC_6F_5)\}_4}\downarrow + 6dba + 2CHCl_3$$

The ^{19}F and ^{31}P NMR data[5] would be consistent with any formulation $\{[Pd(\mu\text{-}SC_6F_5)(\mu\text{-dppm})Pd](\mu\text{-}SC_6F_5)\}_n$ ($n \geq 2$), and indeed the highest observed peak in the mass spectrum[5] corresponds to $n = 2$. However, the structure of complex **1**, established by a single-crystal X-ray study,[6] shows this compound to be octanuclear ($n = 4$, Figure 1).

Taking into account the symmetry, the MS results, and preliminary reactivity studies, the compound can best be described as formed by four metal-metal bonded "$Pd(\mu\text{-}SC_6F_5)(\mu\text{-dppm})Pd$" units [$d$(Pd1-Pd2) = 2.581(3) Å] (Figure 2) which are bridged through four additional pentafluorobenzenethiolato groups to form a 12-membered puckered cycle, with the four dppm ligands sitting in turn above and below the ring, since the molecule lies on a crystallographic $\bar{4}$ axis; a further metal-metal interaction between palladium atoms in different binuclear units can be excluded, since the closest distance is d(Pd1a-Pd2) = 3.743(3) Å. Whereas the phosphorus and the S1 atoms show a pseudotetrahedral environment, the S2 atom bridging the two palladium centers of the asymmetric unit deviates strongly from this geometry, forming a Pd1-S2-Pd2 angle of 67.3°(2).

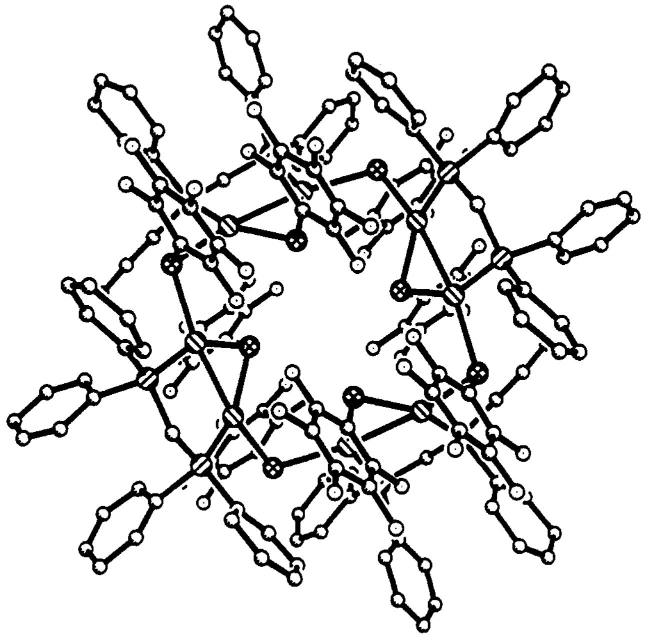

Figure 1. Molecular structure of compound **1**.

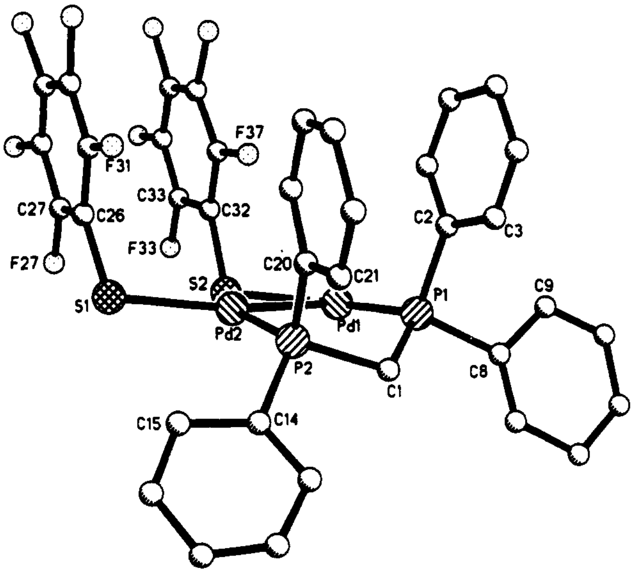

Figure 2. Numbering scheme for the asymmetric unit. Selected bond lengths (Å) and bond angles (deg): Pd1-P1 = 2.235(7), Pd2-P2 = 2.267(7), Pd1-S2 = 2.331(6), Pd2-S2 = 2.328(6), Pd1-S1a = 2.412(6), Pd2-S1 = 2.398(6); S2-Pd1-P1 = 148.9(2), S2-Pd2-P2 = 153.0(2), Pd2-S1-Pd1a = 102.2(2), P1-Pd1-S1a = 101.4(2), S1-Pd2-P2 = 101.0(2).

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(1) (a) Russell, M. J. H.; Barnard, C. F. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press Ltd.: Oxford, England, 1987, Vol. 5, p 1103. (b) Balch, A. L. *Comments Inorg. Chem.* **1984**, *3*, 51.

(2) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press Ltd.: Oxford, England, 1982, Vol. 6, p 265.

(3) Braunstein, P.; Luke, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 768.

(4) A mixture of $Pd_2(dba)_3\cdot CHCl_3$ (0.2588 g, 0.25 mmol) and $Pd(SC_6F_5)_2dppm$ (0.4445 g, 0.5 mmol) in diethyl ether (120 mL) was stirred in the dark for 7 days at room temperature. The resulting dark burgundy solid was filtered off, washed with Et_2O (10 × 2 mL), and dried in vacuo over P_2O_5. Yield: 63%. Anal. Calcd (found): C, 44.1 (44.6); H, 2.1 (2.2). IR (Nujol, $\bar{\nu}$ in cm^{-1}): SC_6F_5 groups 1084 s, 976 vs; ν(C-S) 848 vs; dppm 1437 vs, 1098 s, 999 m, 748 m, 691 vs.

(5) ^{19}F NMR (188.2 MHz, reference $CFCl_3$, saturated $CDCl_3$ solution, 20 °C): δ -127.3 (d, *o*-F), -129.7 (d, *o*-F), -159.0 (t, *p*-F), -164.7 (t, *p*-F), -165.5 (m, *m*-F), -165.8 (m, *m*-F). ^{31}P NMR (80.98 MHz, reference external 85% H_3PO_4): δ -5.5 ppm. MS (FAB^-, 3-nitrobenzylalcohol matrix): *m/e* 1990 ($M^+/2$, 11%), 1699 ($M^+/2$ - Pd - dppm + SC_6F_5, 11%), 1315 ($M^+/2$ - Pd - 2dppm + SC_6F_5, 6%), 1209 ($M^+/2$ - 2Pd - 2dppm + SC_6F_5, 5%), 917 ($M^+/2$ - Pd - 2dppm - SC_6F_5, 6%), 811 ($M^+/2$ - 2Pd - 2dppm - SC_6F_5, 15%), 700 ($M^+/2$ - 3Pd - 2dppm - SC_6F_5, 39%), 671 ($M^+/2$ - 3Pd - 2dppm - SC_6F_5 - S, 100%), 640 ($M^+/2$ - 3Pd - 2dppm - SC_6F_5 - 2S, 40%), 506($M^+/2$ - 3Pd - 2dppm - 2SC_6F_5, 82%), 476 ($M^+/2$ - 3Pd - 2dppm - 2SC_6F_5 - S, 65%).

(6) Crystals suitable for structure investigation were grown by slow diffussion of diethylether into a solution of **1** in chloroform at -28 °C. X-ray structure analysis: $Pd_8P_8S_8F_{40}C_{148}H_{88}\cdot 2OC_4H_{10}$; space group $I\bar{4}$; a = 17.906(9) Å, c = 24.736(6) Å, V = 7931(6) Å^3; Z = 2; size 0.38 × 0.30 × 0.30 mm^3; λ(Mo Kα) = 0.710 73 Å. T = 173 K; absorption correction (11 Ψ-scans with transmission factors 0.7918-0.8798); Siemens-Stoe AED2 four-circle diffractometer, ω-2θ scan method, 3° ≤ 2θ ≤ 51°; total number of reflections 4057; 2190 unique reflections with $F_o \geq 5.0\sigma(F_o)$; heavy atom method, refinement of F_o to R = 6.03%, R_w = 7.02%, gof = 1.06; Pd, S, P, F, C_1-C_7, and C_{20}-C_{25} anisotropic.

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In each unit, the two heavy atoms linked by the metal–metal bond, the S2, and the phosphorus atoms of the diphosphine are almost coplanar (mean deviation 0.0695 Å); the methylenic carbon deviates from this plane, resulting in an envelope conformation (dihedral angle 37.2°).

The Pd1–P1 and Pd2–P2 bonds are almost at right angles to the metal–metal bond (92.8(2) and 97.2(2)°, respectively). The torsion angle S1–Pd2–Pd1–S1a is −13.6°, i. e., the central ring is puckered.

A noteworthy feature is that the perfluorophenyl rings of the thiolato groups of each asymmetryc unit are parallel (dihedral angle 1.4°), and 3.20 Å apart; their rings are somewhat displaced, however. The rings are tilted, forming dihedral angles of 85.6 and 84.7° to the Pd1Pd2P1P2S2 plane; possibly weak residual interactions between the Pd1 and F37 (distance: 2.945(15) Å) atoms and Pd2 and F31 atoms (distance: 3.048(14) Å) are responsible for this geometry. The angles formed by any other contiguous pair of aryl rings are in the range 6–15°.

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Supplementary Material Available: Tables giving a summary of crystal structure determination data, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths and angles, and anisotropic thermal parameters for compound 1 (8 pages). Ordering information is given on any current masthead page.