$Pd_6(\mu_3\text{-}CO)_4(PMe_3)_7$: The First Octahedral Hexapalladium Cluster Core

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Summary: $Pd(PMe_3)_4$ under 1 bar carbon monoxide at 50 °C is spontaneously transformed to the title compound. Its molecular structure contains a distorted Pd_6 octahedron with four face-bridging carbonyl ligands and seven terminally coordinated phosphines. In solution all ^{31}P nuclei appear isochronous by fast migration of phosphine ligands over the Pd_6 core. X-ray crystallographic data for $C_{25}H_{63}O_4P_7Pd_6$ (M_r = 1282.9): monoclinic, space group $P2_1/n$, a = 11.108 (3) Å, b = 22.831 (7) Å, c = 18.529 (6) Å, β = 93.60 (1),° V = 4689.8 Å^3, and Z = 4.

Introduction

Zerovalent palladium when surrounded by carbon monoxide ligands at room temperature requires the stabilizing assistance of phosphine ligands before carbonyl ligands can remain attached to the metal. $Pd(CO)(PPh_3)_3$ is one of the few mononuclear examples. With trimethylphosphine no stable complex of composition $Pd(CO)_n(PMe_3)_{4-n}$ (n = 1–3) has been described.[1] Our attempts to replace trimethylphosphine ligands of $Pd(PMe_3)_4$ by CO, which continue corresponding experiments with nickel as the central atom,[2] resulted in high yield spontaneous formation of the title cluster molecule 1. Structure and properties of 1 are the subject matter of this report.

Experimental Section

General Procedures and Materials. All air-sensitive material was handled by standard vacuum technique and kept under argon. Microanalyses were carried out by Dornis & Kolbe, Microanalytical Laboratory, Mülheim/Ruhr 1, FRG. Melting points (mp) and decomposition temperatures were obtained from sealed capillaries and are uncorrected. Trimethylphosphine[3] was prepared from triphenylphosphite and methylmagnesium chloride. Other chemicals (Merck-Schuchardt) were used as purchased. Infrared spectra from Nujol mulls betweeen KBr discs were recorded on a Perkin-Elmer, Type 397, spectrophotometer; ^1H-NMR spectra were obtained on a Bruker WM 300 (300 MHz) spectrometer, where ^{13}C (75.5-MHz) and ^{31}P (121.5-MHz) spectra were also recorded.

$Pd_6(\mu_3\text{-}CO)_4(PMe_3)_7$ (1). An 870-mg (2.12-mmol) sample of $Pd(PMe_3)_4$[4] in 60 mL of toluene was kept stirring under 1 bar CO for 3 h at 50 °C. The colorless solution turned dark red. Removing the volatiles in vacuo and extracting the dark red residue with 25 mL of pentane through a glass-sinter disk (G3) gave a red solution from which crystallized, at −25 °C, the dark red product. Its separation by decantation and washing by cold pentane delivered 300 mg of 1 (0.23 mmol, 65% yield), decomp pt > 180 °C. Anal. Calcd for $C_{25}H_{63}O_4P_7Pd_6$ (1283.1): C, 23.40; H, 4.95; P, 16.89. Found: C, 22.79; H, 4.89; P, 16.77. ^1H NMR (300 MHz, toluene-d_8, 98 K, Me_4Si external reference, δ O): δ(PMe$_3$) 1.47 (s). $^{13}C[^1H]$ NMR (75.5 MHz, toluene-d_8, Me_4Si external reference, δ O): 295 K, δ (PCH_3) 19.5 (m), δ(CO) 253.2 (s); 213 K, δ (PCH$_3$) 19.1 (pseudotriplet, $|^1J(PC) + {}^3J(PC)|$ = 16.3 Hz), δ(CO) 254.6 (s); 183 K, δ (PCH$_3$) 19.1 (pseudotriplet, $|^1J(PC) + {}^3J(PC)|$ = 15.6 Hz), δ(CO) 255.0 (s). $^{31}P[^1H]$ NMR (121.4 MHz, toluene-d_8, H_3PO_4 external reference, δ O): δ (PMe$_3$) −27.5 (s). IR (Nujol solution, 400–4000 cm^{-1}): 2800 m (ν_s(CH)); 1730 vs, 1708 vs (ν(CO)); 1416 s ($\delta_{as}(CH_3)$); 1298 m, 1279 s ($\delta_s(CH_3)$); 944 vs (br) ($\rho_1(CH_3)$); 840 w ($\rho_2(CH_3)$); 721 m ($\nu_{as}(PC_3)$); 665 s ($\nu_s(PC_3)$); 414 m (δ(CoCO)).

Crystal Structure Determination: $C_{25}H_{63}O_4P_7Pd_6$; M_r = 1282.9; red crystal sealed in a capillary; size 0.25 × 0.47 × 0.65 mm; monoclinic; space group $P2_1/n$ (No. 14); a = 11.108 (3) Å; b = 22.831 (7) Å; c = 18.529 (6) Å; β = 93.60 (1)°; V = 4689.8 Å^3; refined from 32 reflections $12 \le 2\theta \le 36°$; Z = 4; D_{calc} = 1.817 g cm^{-3}; λ(Mo Kα) = 0.71073 Å; μ = 2.49 mm^{-1}; T = 296 (1) K; Siemens R3 m/V diffractometer; graphite monochromator; ω–2θ scan; 11376 intensities collected $3 \le 2\theta \le 55°$; $-14 \le h \le 14$, $0 \le k \le 29$, $0 \le l \le 24$; 3 standards recorded every 400 showing 5% decrease, intensities adjusted accordingly; Lp-correction; empirical absorption correction via φ-scans; minimum/maximum transmission 0.11/0.17; after merging (R_{int} = 0.037) 10821 unique intensities, 6053 considered observed with $F > 4\sigma(F)$; structure solved by direct methods (Pd positions) and subsequent ΔF-maps; full-matrix least-squares refinement based on F and 342 parameters. Thermal displacement parameters indicated partial disorder of methyl-C and, to a lesser extent, of P(2). The disorder of C(22), C(51), and C(62) could successfully be treated by a split model with two half-occupied sites each. Anisotropic refinement of C(21)–C(23) and C(51)–C(71) led to no convergence. Isotropic H-atoms fixed at idealized positions; anisotropic refinement of remaining atoms converged at R = 0.053, R_w = 0.046, $1/w = \sigma^2(F) + 0.0001F^2$, S = 1.79, max (Δ/σ) = 0.001; secondary extinction correction $F^* = F(1 + 0.002\chi F^2/\sin(2\theta))^{-1/4}$, with χ = 0.00004, minimum/maximum height in final ΔF-map −0.92/0.85 e/A^3 near Pd positions. Scattering factors, structure solution, and refinement: SHELXTL-PLUS;[5] other programs, PARST.[6] Atomic coordinates are given in Table I, selected bond lengths and angles in Table II; Figure 2 shows the molecular structure.

Results and Discussion

From pale yellow $Pd(PMe_3)_4$[7] in toluene solution when kept under 1 bar CO at 50 °C, trimethylphosphine is liberated in a spontaneous condensation reaction according to eq 1 to a red solution containing the Pd_6 cluster 1 exclusively.

$$6PdL_4 + 4CO \rightarrow \underset{1}{Pd_6(CO)_4L_7} + 17L \qquad (1)$$

$$L = PMe_3$$

With its outer sphere of methyl groups, 1 is soluble in pentane, ether, toluene, or tetrahydrofuran. Solutions of 1 are instantaneously decomposed by oxygen and also are sensitive to daylight. Irradiation with a mercury lamp causes deposition of palladium metal within a few minutes. Crystals of 1 in air retain their shiny surface for some

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Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	*U* (eq)^a
Pd(1)	1842 (1)	6993 (1)	2339 (1)	43 (1)
Pd(2)	−159 (1)	6686 (1)	3040 (1)	45 (1)
Pd(3)	−366 (1)	5656 (1)	2227 (1)	44 (1)
Pd(4)	1637 (1)	5955 (1)	1530 (1)	43 (1)
Pd(5)	1757 (1)	5926 (1)	3025 (1)	48 (1)
Pd(6)	−248 (1)	6703 (1)	1551 (1)	43 (1)
P(1)	3318 (3)	7671 (2)	2499 (2)	75 (2)
P(2)	−1043 (3)	6886 (2)	4085 (2)	81 (3)
P(3)	−1415 (3)	4896 (2)	2664 (2)	69 (2)
P(4)	3432 (3)	5709 (2)	1097 (2)	70 (2)
P(5)	2990 (3)	5453 (2)	3824 (2)	74 (2)
P(6)	−863 (3)	7676 (2)	1516 (2)	75 (2)
P(7)	−984 (3)	6243 (2)	493 (2)	67 (2)
C(1)	1689 (9)	6795 (5)	3474 (5)	56 (7)
O(1)	2160 (6)	6995 (3)	4015 (4)	68 (5)
C(2)	1274 (10)	5214 (5)	2124 (6)	60 (8)
O(2)	1535 (7)	4708 (4)	2104 (5)	83 (7)
C(3)	−1606 (9)	6387 (5)	2353 (5)	56 (7)
O(3)	−2652 (6)	6425 (4)	2327 (4)	69 (6)
C(4)	1681 (9)	6865 (5)	1210 (5)	55 (7)
O(4)	2000 (7)	7120 (3)	709 (4)	76 (6)
C(11)	3903 (15)	8006 (7)	1733 (7)	189 (20)
C(12)	4659 (11)	7465 (6)	3046 (7)	128 (14)
C(13)	2915 (13)	8300 (5)	3001 (7)	112 (13)
C(21)	−2485 (19)	6709 (9)	4208 (10)	280 (13)
C(22)	−587 (20)	6338 (11)	4829 (12)	83 (8)*
C(222)	−2508 (30)	7411 (17)	3923 (18)	146 (13)*
C(23)	−495 (15)	7465 (8)	4626 (9)	191 (9)
C(31)	−740 (13)	4562 (6)	3471 (7)	139 (15)
C(32)	−1564 (13)	4247 (6)	2123 (7)	120 (13)
C(33)	−2901 (12)	4995 (6)	2906 (10)	157 (19)
C(41)	3659 (12)	5814 (7)	147 (6)	131 (14)
C(42)	3985 (11)	4977 (6)	1246 (7)	117 (13)
C(43)	4631 (11)	6115 (7)	1495 (8)	150 (17)
C(51)	3206 (25)	4653 (14)	3794 (15)	119 (12)*
C(512)	3748 (24)	4758 (13)	3523 (15)	87 (9)*
C(52)	2583 (14)	5417 (8)	4732 (8)	172 (8)
C(53)	4423 (13)	5774 (7)	4018 (8)	163 (7)
C(61)	−2420 (12)	7810 (7)	1390 (8)	158 (7)
C(62)	−38 (22)	8179 (12)	940 (13)	92 (9)*
C(622)	−628 (25)	8042 (13)	563 (15)	96 (9)*
C(63)	−544 (14)	8166 (8)	2270 (8)	183 (8)
C(71)	−1326 (15)	5461 (8)	442 (9)	205 (9)
C(72)	−2428 (10)	6487 (7)	107 (7)	112 (13)
C(73)	−93 (11)	6287 (8)	−270 (5)	115 (14)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. Values marked with an asterisk were determined with a split model, single occupancy factor 0.5 each.

Table II. Selected Bond Lengths (Å) and Angles (deg)

Pd(1)–Pd(2)	2.734 (1)	Pd(1)–Pd(4)	2.806 (1)
Pd(1)–Pd(5)	2.751 (1)	Pd(1)–Pd(6)	2.744 (1)
Pd(2)–Pd(3)	2.795 (1)	Pd(2)–Pd(5)	2.747 (1)
Pd(2)–Pd(6)	2.755 (1)	Pd(3)–Pd(4)	2.729 (1)
Pd(3)–Pd(5)	2.773 (1)	Pd(3)–Pd(6)	2.706 (1)
Pd(4)–Pd(5)	2.764 (1)	Pd(4)–Pd(6)	2.705 (1)
Pd(2)–Pd(1)–Pd(4)	89.8 (1)	Pd(2)–Pd(1)–Pd(5)	60.1 (1)
Pd(2)–Pd(1)–Pd(6)	60.4 (1)	Pd(4)–Pd(1)–Pd(5)	59.7 (1)
Pd(4)–Pd(1)–Pd(6)	58.3 (1)	Pd(5)–Pd(1)–Pd(6)	88.8 (1)
Pd(1)–Pd(2)–Pd(3)	90.1 (1)	Pd(1)–Pd(2)–Pd(5)	60.3 (1)
Pd(1)–Pd(2)–Pd(6)	60.0 (1)	Pd(3)–Pd(2)–Pd(5)	60.0 (1)
Pd(3)–Pd(2)–Pd(6)	58.3 (1)	pd(5)–Pd(2)–Pd(6)	88.7 (1)
Pd(2)–Pd(3)–Pd(4)	90.1 (1)	Pd(2)–Pd(3)–Pd(5)	59.1 (1)
Pd(2)–Pd(3)–Pd(6)	60.1 (1)	Pd(4)–Pd(3)–Pd(5)	60.3 (1)
Pd(4)–Pd(3)–Pd(6)	59.7 (1)	Pd(5)–Pd(3)–Pd(6)	89.2 (1)
Pd(1)–Pd(4)–Pd(3)	90.0 (1)	Pd(1)–Pd(4)–Pd(5)	59.2 (1)
Pd(1)–Pd(4)–Pd(6)	59.7 (1)	Pd(3)–Pd(4)–Pd(5)	60.6 (1)
Pd(3)–Pd(4)–Pd(6)	59.7 (1)	Pd(5)–Pd(4)–Pd(6)	89.4 (1)
Pd(1)–Pd(5)–Pd(2)	59.6 (1)	Pd(1)–Pd(5)–Pd(3)	90.2 (1)
Pd(1)–Pd(5)–Pd(4)	61.2 (1)	Pd(2)–Pd(5)–Pd(3)	60.8 (1)
Pd(2)–Pd(5)–Pd(4)	90.4 (1)	Pd(3)–Pd(5)–Pd(4)	59.0 (1)
Pd(1)–Pd(6)–Pd(2)	59.6 (1)	Pd(1)–Pd(6)–Pd(3)	91.8 (1)
Pd(1)–Pd(6)–Pd(4)	62.0 (1)	Pd(2)–Pd(6)–Pd(3)	61.6 (1)
Pd(2)–Pd(6)–Pd(4)	91.5 (1)	Pd(3)–Pd(6)–Pd(4)	60.6 (1)

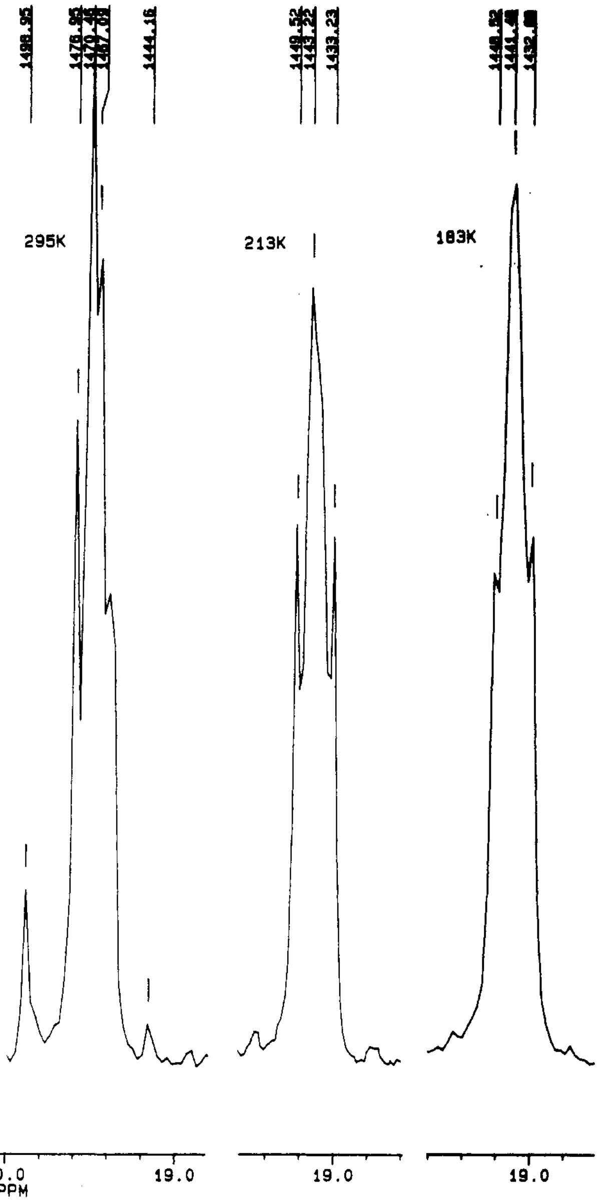

Figure 1. $^{13}C\{^1H\}$ NMR of 1 (PCH_3 region), signal at 19.9 pm as part of the $C_6D_5CD_3$ resonance.

minutes before oxidation starts to give white needles of trimethylphosphine oxide. Under argon in the dark, 1 and its solutions appear to be perfectly stable. In all NMR experiments single resonances of ^1H, ^{13}C, and ^{31}P nuclei are observed. While no dissociation of PMe_3 ligands is recognized from missing resonance of free ligands, a fast exchange of phosphine positions must be assumed. Accordingly a single ^{13}C resonance of the bridging carbonyl at $\delta = 254 \pm 1$ ppm is obtained from a time-averaged symmetric $Pd_6(CO)_4$ framework. The pseudotriplet ^{13}C resonance (Figure 1) represents strong PP coupling, indicating a strictly intramolecular process, because with intermolecular exchange a doublet or singlet (through P decoupling) would be expected.

The six palladium atoms in 1 adopt a distorted octahedral geometry in the solid (Figure 2). Four of eight faces of this metal atom octahedron are face-bridged by carbonyl ligands in an alternate sequence, and the ligand sphere is completed by seven PMe_3 groups in terminal positions. The distribution of the PMe_3 groups is one to each Pd atom and an additional one to atom Pd(6). The C and P donor atoms at the atoms Pd(1)–Pd(5) with two C and one P and at Pd(6) with two C and two P ligand atoms nearly

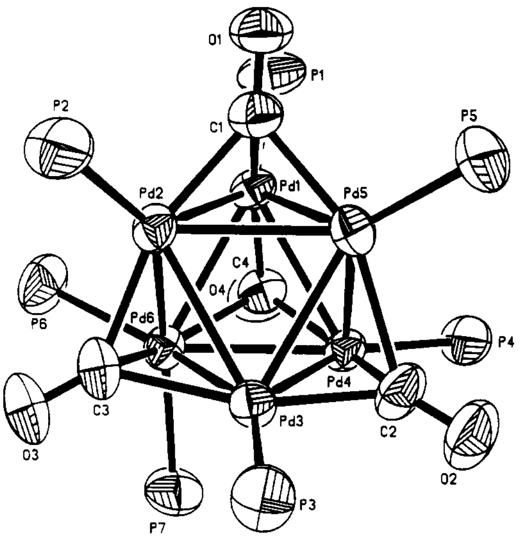

Figure 2. Molecular structure of 1 (methyl groups omitted for the sake of clarity).

generate a local C_{2v} symmetry. This C_{2v} symmetry-adapted pattern also is recognizable in the Pd_6 core of the twelve Pd–Pd edges. If the next neighbored four metal atoms are added as further ligand atoms at each palladium atom, the coordination number (CN) is 7 in the case of Pd(1)–Pd(5) and 8 in that of Pd(6). Finally, if the complete molecule is considered, there is no symmetry element with the exception of C_1 (identity).

As aforementioned the Pd_6 core is octahedrally distorted with extremal values of Pd–Pd–Pd angles between 58.3 (1)° and 62.0 (1)° instead of 60° on the one hand and 88.7 (1)° and 91.8 (1)° instead of 90° angles of an ideal octahedron on the other hand. Further distortions are visible from different Pd–Pd bond lengths between 2.705 (1) Å (Pd(4)–Pd(6)) and 2.806 (1) Å (Pd(1)–Pd(4)). Such metal–metal lengths observed are shorter, longer, or equal within the experimental error [see 2.744 (1) Å of Pd(1)–Pd(6)] compared to that of 2.745 (2) Å in palladium metal. Furthermore, the average Pd–Pd bond length of 2.751 (1) Å in 1 is somewhat shortened against that of 2.790 (2) Å in the octahedral part of the cluster $[Pd_7(CO)_7(PMe_3)_7]$ (2), showing a palladium atom octahedron monocapped by a $Pd(CO)_3PMe_3$ group.[7]

From the Pd atoms in 1, Pd(6), which has the higher CN of 8, should be affected by enlarged bond lengths with coordinated neighbor atoms. This is actually the case with the non-metal atoms C(3)–C(4) and P(6)–P(7), as expected (see Table II), but surprisingly changed for this Pd(6) with atoms Pd(3)–Pd(4) because these two metal–metal bond lengths of 2.706 (1) and 2.705 (1) Å are the shortest in the Pd_6 core. An explanation of the exceptional feature which might be originated from this Pd atom is given below. Besides both mentioned ligand-stabilized palladium clusters, other examples have been determined crystallographically like $[Pd_4(CO)_5(PPh_2Me)_4]$[8] (3) or $[Pd_{10}(CO)_{12}(PBu_3)_6]$[9] (4). From our knowledge the title cluster is the first palladium Pd_6 example with an octahedral metal core.

Empirical molecular orbital calculations indicate that such a system should have 43 valence molecular orbitals requiring a total count of 86 valence electrons (VE) to reach saturation.[10] This electron count and the number of framework bonding electrons of 14 VE is relatively unambiguous to characterize six-vertex transition-metal clusters.[11,12] The transition-metal atoms nickel, platinum, and rhodium next to palladium in the Periodic Table fulfill these requirements in the clusters $[Ni_6(CO)_{12}]^{2-}$ of trigonal antiprismatic near to octahedral,[13] $[Pt_6(CO)_{12}]^{2-}$ of close trigonal prismatic,[11-15] and $Rh_6(CO)_{16}$[16] of octahedral geometry.

All these topologies demand 14 metal–metal bonding electrons,[11] and, consequently, the octahedral metal arrangement in 1 should fulfill this requirement. But it remains to be explained the total electron count of 82 VE in 1 instead of 86 in the compared clusters. Such a deficiency of VE could account for the frequently observed tendency of palladium clusters having fewer total count of VE than predicted for the structure adopted. For example, the four-atom cluster 3 has 58 VE instead of 62, the ten-atom cluster 4 has 136 VE instead of 140, but the seven-atom cluster 2 having the expected 98 VE is probably supersaturated.[7] For such deficiency of VE, Lauher[10] has suggested that since the energies of the valence p (and to a lesser extent the s) orbitals become increasingly higher in energy with respect to the valence d orbitals on moving to the right of the transition element series, the p orbitals of the d^{10} metals are less available for bonding. A deficiency of CVMO results, and the structure undergoes a distortion. In the case of the C_{2v} symmetry-adapted Pd_6 core in 1, the distortion in the presence of four CO ligands having a larger π acceptor and seven PMe_3 ligands with a greater σ donor ability makes possible an enlargement of high lying orbitals from 11 to 13 on the cost of the mentioned 43 CVMO. Cluster 1 is, therefore, saturated, and in accordance with this assumption the average Pd–Pd bond lengths between 1 and 2 differ only about 0.039 (2) Å. To get an electron-precise count of 82 VE for a saturated cluster 1, a combination between the hypothetical nido cluster $[Pd_5(CO)_4(PPh_3)_5]^{2-}$ (70 VE) and such a capping group $[Pd(PPh_3)_2]^{2+}$ can be undertaken, but this is neither supported through the preparative pathway nor the structural features observed. Finally, the mentioned stronger involvement of the electron-rich Pd(6) atom in the metal–metal bonding, as observed, seems to be necessary to avoid an electron-deficient character in 1.

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Registry No. 1, 143618-49-9; $Pd(PMe_3)_4$, 55332-53-1.

Supplementary Material Available: Tables of positional and thermal parameters and bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

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