Preparation and Structure of Tetrakis(μ_3-carbonyl)tris(μ-carbonyl)heptakis(trimethylphosphine)heptapalladium, $[Pd_7(CO)_7(PMe_3)_7]$

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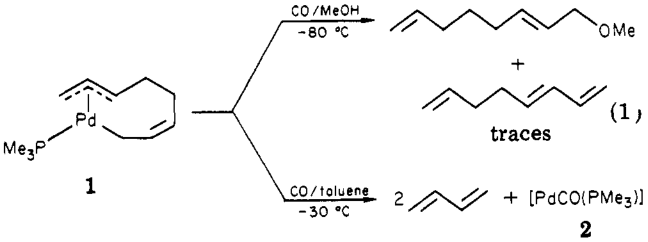
The title compound has been prepared by reaction of $[Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PMe_3)]$ with carbon monoxide and has been shown by X-ray crystallography to have a structure in which a face-capped octahedron of palladium atoms interacts with phosphine molecules and both face- and edge-bridging carbonyl groups. A model in which the capping palladium atom of the metal skeleton is disordered in three positions above a triangular face of the octahedron, reducing the overall symmetry of the molecule from C_{3v} to C_s, shows a satisfactory agreement with the 1509 observed ($I > 2.0\sigma(I)$) X-ray intensity data ($R = 0.06$). The compound crystallizes in the trigonal space group $R3m$ ($Z = 1$) with cell constants $a = 11.098$ (2) Å and $\alpha = 103.94$ (3)°.

Introduction

In the course of our investigations into the mechanism of the transition-metal-catalyzed transformation of 1,3-dienes, we have recently prepared $[Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PMe_3)]$ (1) and shown that compounds of this type are probably involved as intermediates in the palladium-catalyzed oligomerization, cooligomerization, and telomerization of butadiene.[2,3] As part of its chemical characterization, 1 was treated with carbon monoxide. Whereas in methanol reaction with CO occurs at −80 °C to give 1-methoxy-2,7-octadiene and traces of 1,3,7-octatriene (eq 1), in toluene a slow reaction is observed first at −30 °C with elimination of butadiene (80%) (similar behavior has been observed on reacting the analogous nickel complexes with triphenylphosphine[4]) and formation of a dark red crystalline material (2) whose structure is the subject of this publication.



Results and Discussion

The infrared spectrum of 2 as a KBr disk (ν_{CO} 1685 (s), 1750 (s), 1770 (s), 1785 (sh), 1800 (vs), 1825 (s) cm^{-1}) suggests that the molecule contains bridging but not terminal carbonyl groups. The low solubility prevented a cryoscopic determination of the molecular weight and the heptameric nature was deduced from a X-ray structural determination.

Table I. Selected Bond Lengths (Å) with Estimated Standard Deviations in Parentheses

Pd1-Pd1	2.756 (3)	Pd1-C1	2.19 (2)
Pd1-Pd2	2.798 (2)	Pd1-C2	2.08 (2)
Pd2-Pd2	2.809 (1)	Pd2-C2	2.16 (2)
Pd2-Pd3	2.729 (5)	C1-O1	1.09 (3)
Pd2· · ·Pd3	3.180 (5)	C2-O2	1.28 (3)
Pd1-P1	2.275 (5)	P1-C11	1.88 (2)
Pd2-P2	2.39 (1)	P1-C12	1.89 (4)
Pd2-P21	2.10 (2)	P3-C31	1.86 (5)
Pd3-P3	2.314 (7)		

Table II. Selected Bond Angles (deg) with Estimated Standard Deviations in Parentheses

Pd1-Pd1-Pd1	60.0	Pd1-Pd2-P2	95.4 (3)
Pd1-Pd1-Pd2	60.5 (1)	Pd1-Pd2-P21	109.5 (6)
Pd1-Pd1-Pd2	90.5 (1)	Pd3-Pd2-P2	132.8 (3)
Pd2-Pd1-Pd2	60.3 (1)	Pd3-Pd2-P21	117.0 (7)
Pd1-Pd1-P1	130.1 (2)	Pd3· · ·Pd2-P2	130.3 (7)
Pd2-Pd1-P1	139.0 (2)	Pd3· · ·Pd2-P21	146.6 (3)
Pd1-Pd1-C1	51.0 (6)	Pd2-Pd2-Pd2	147.3 (2)
Pd2-Pd1-C1	111.1 (6)	Pd2-Pd2-P21	149.9 (5)
P1-Pd1-C1	94.7 (6)	Pd1-Pd2-C2	105.9 (6)
Pd1-Pd1-C2	109.8 (6)	Pd2-Pd2-C2	49.4 (6)
Pd2-Pd1-C2	49.9 (6)	Pd3-Pd2-C2	83.4 (6)
P1-Pd1-C2	108.9 (6)	Pd3· · ·Pd2-C2	102.8 (6)
C1-Pd1-C2	156.4 (8)	Pd2-Pd3-Pd2	62.0 (1)
Pd2-Pd2-Pd2	60.0	Pd2-Pd3-P3	148.3 (2)
Pd2-Pd1-Pd2	59.0 (1)	Pd1-C1-Pd1	78.0 (8)
Pd2-Pd2-Pd1	59.9 (1)	Pd1-C1-O1	133 (2)
Pd2-Pd2-Pd1	89.5 (1)	Pd1-C2-Pd2	82.7 (8)
Pd1-Pd2-Pd3	117.8 (1)	Pd2-C2-Pd2	81.3 (7)
Pd2-Pd2-Pd3	70.1 (1)	Pd1-C2-O2	127 (2)
Pd2-Pd2· · ·Pd3	53.8 (1)	Pd2-C2-O2	132 (2)
Pd1-Pd2· · ·Pd3	113.4 (1)		

The seven palladium atoms adopt a monocapped octahedral geometry with one trimethylphosphine group attached to each metal atom. Four of the carbonyl groups face bridge the octahedral part of the cluster while the other three are edge bridging. The structure is shown in Figure 1, and selected bond lengths and bond angles are brought together in Tables I and II.

The octahedral part of the cluster has an almost ideal geometry with Pd–Pd bond distances that, within experimental error, are all equal, and the average value of 2.79 (2) Å is only slightly longer than that found in palladium metal (2.745 Å).[5]

The position of the molecule in the crystal requires that its symmetry be $3m$ (C_{3v}). However, as a result of disorder of the seventh palladium atom on one of the triangular

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[1] Dedicated to the memory of Rolly Pettit with whom P. W. J. had the enjoyable experience of working as a post-doc during 1966–1967.

[2] Part of the doctoral thesis of K.-P. S. submitted to the Ruhr-Universität, Bochum, in 1982.

[3] Döhring, A.; Jolly, P. W.; Mynott, R.; Schick, K.-P.; Wilke, G. *Z. Naturforsch., Anorg. Chem., Org. Chem.* 1981, *36B*, 1198.

[4] Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vol II, Chapter III.

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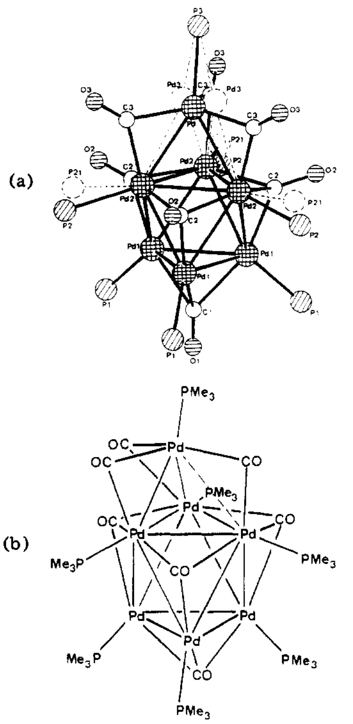

Figure 1. Structure of $[Pd_7(CO)_7(PMe_3)_7]$ (**2**): (a) determined in the X-ray experiment; (b) idealized structure.

faces of the octahedron, the symmetry of the individual molecules is reduced to C_s (*m*) (see Experimental Section). The remainder of the discussion will be limited to a description of the idealized molecule represented in Figure 1b.

Two different Pd–Pd distances involving the palladium atom Pd3 can be clearly differentiated. One Pd–Pd bond length at 3.180 (5) Å is appreciably longer than the others (2.729 (5) Å), and the angle between the planes defined by the three Pd2 atoms and the triangle Pd2–Pd2–Pd3 is 83.6°.

The three trimethylphosphine phosphorous atoms P1 are located 1.52 Å below the basal plane defined by Pd1, so that the Pd–P bond is bent 41.9° out of the plane. The phosphorous atoms attached to the three palladium atoms Pd2 are disordered in the crystal in two positions, at P2 and P21. A difference Fourier synthesis without these atoms revealed that the occupancy of P2 is twice that of P21, which suggests that P2 is bonded to the palladium atom nearest to Pd3. P21 thus appears to be bonded to the single Pd2 atom that makes the long Pd–Pd bond with Pd3. The phosphorous atom P2 lies 0.56 Å below the plane defined by Pd2, whereas P21 lies 0.1 Å above it in the direction of Pd3. The unique carbonyl group C1–O1 appears to be symmetrically bonded to the palladium triad defined by Pd1, and the carbonyl groups C2–O2 are similarly bonded to the Pd2–Pd2–Pd1 faces. The average Pd–C distance is 2.14 (6) Å.

As a consequence of the 3-fold disorder of the molecule in the crystal, the edge-bridging carbonyl groups C3–O3 appear disordered in three positions. The fact that only an average position of C3 could be obtained from a difference Fourier synthesis precludes a detailed discussion of these groups.

The cluster described here not only represents an example of a ligand-stabilized palladium carbonyl cluster[6] (other examples that have been investigated crystallographically include $[Pd_4(CO)_5(PPh_2Me)_4]$,[7] $[Pd_4(OAc)_4(CO)_4(AcOH)_2]$,[8] $[Pd_4(OAc)_4(CO)_2(phen)_4]$,[9] and $[Pd_{10}(CO)_{12}(PBu_3)_6]$[10]) but also belongs to the relatively rare class of seven-atom clusters.

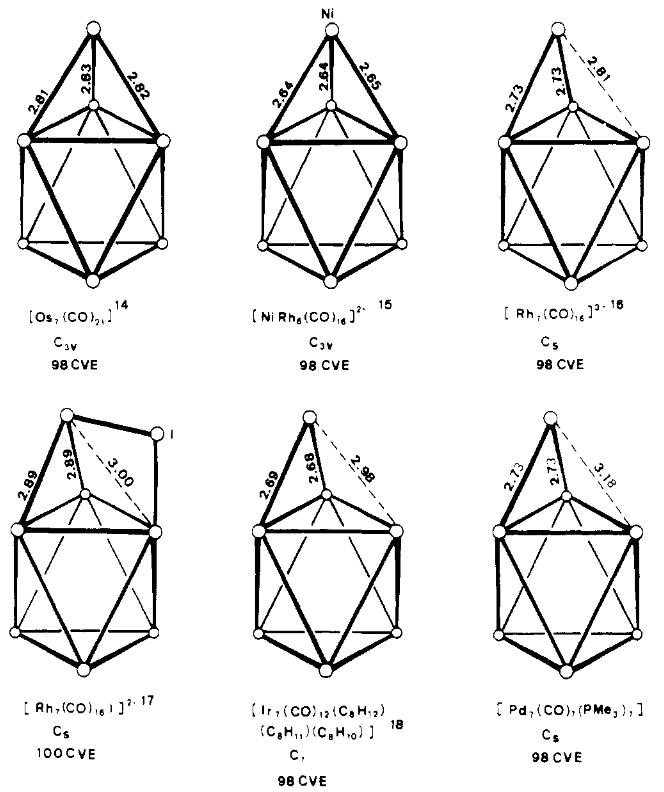

Figure 2. The structures of some seven-atom clusters.

In all but one case, viz., $[Pt_7(C_9H_9N)_{12}]$,[11] the metal atoms in seven-atom clusters appear to adopt a monocapped octahedral arrangement. Examples of structures containing this geometry are given in Figure 2.

Empirical molecular orbital calculations by Lauher[12] indicate that such a system should have 49 cluster valence molecular orbitals (CVMO's) requiring 98 cluster valence electrons (CVE's) to reach saturation. Only for $[Rh_7(CO)_{16}I]^{2-}$ has a monocapped octahedral cluster been reported in which the number of CVE's is 100.[17] As can be seen from Figure 2, among the clusters having 98 CVE's only the osmium complex and the nickel–rhodium complex have C_{3v} symmetry.[13] In the remainder an increase in the

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[6] See: Johnson, B. F. G., Ed. "Transition Metal Clusters"; Wiley: New York, 1980.

[7] Dubrawski, J.; Kriege-Simondson, J. C.; Feltham, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2089.

[8] Moiseev, L. I.; Stromnova, T. A.; Vargaftig, M. N.; Mayer, G. J.; Kuzmina, L. G.; Struchkov, Y. T. *J. Chem. Soc., Chem. Commun.* **1978**, 27.

[9] Vargaftic, M. N.; Stromnova, T. A.; Khodashova, T. S.; Poray-Koshits, M. A.; Moiseev, I. *Izv. Akad. Nauk. SSSR., Ser. Khim.* **1980**, 1960.

[10] Mednikov, E. G.; Eremenko, N. K.; Mikhailov, V. A.; Gubin, S. P.; Slovokhotov, Y. L.; Struchkov, Y. T. *J. Chem. Soc., Chem. Commun.* **1981**, 989.

[11] Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Chem. Lett.* **1979**, 391.

[12] Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305; **1979**, *101*, 2604; *J. Catal.* **1980**, *66*, 237; *J. Organomet. Chem.* **1981**, *213*, 25.

[13] The discussion on page 333 of ref 15 is rather misleading since according to the table of bond distances and the atomic positional coordinates of this compound the three Ni–Rh bond lengths appear almost equal.

[14] Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1977**, 385.

[15] Fumagalli, A.; Longoni, G.; Chini, P.; Albinati, A.; Brückner, S. *J. Organomet. Chem.* **1980**, *202*, 329.

[16] Albano, V. G.; Bellon, P. L.; Chiani, G. F. *J. Chem. Soc., Chem. Commun.* **1969**, 1024.

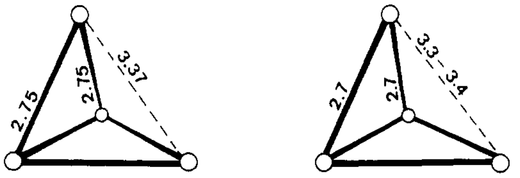

Figure 3. Partial structures of [$Pd_4(CO)_5(PPh_2Me)_4$] (**3**)[10] and [$Pd_{10}(CO)_{12}(PBu_3)_6$] (**4**).[7]

length of one bond in the tetrahedral part of the cluster results in a reduction of symmetry to approximately C_s.

This is presumably associated with the occupation of a low-lying antibonding molecular orbital and can be visualized by comparing [$Rh_7(CO)_{16}$]$^{3-}$ (98 CVE's) with [$Rh_7(CO)_{16}I$]$^{2-}$ (100 CVE's): whereas the number of CVMO's remains constant, the presence of iodide introduces two extra electrons which must be accommodated in an antibonding molecular orbital. As a result the bond length in the tetrahedral part of the molecule increases by 0.2 Å.

Lauher has suggested[12] 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 series, the p orbitals of the d^{10} metals are less available for bonding. A deficiency of CVMO's results, and the structure undergoes a distortion. In other words a symmetrical seven-atom palladium cluster having 98 CVE's is probably supersaturated.

Such an explanation would also account for the frequently observed tendency of palladium to form clusters having fewer CVE's than predicted for the structure adopted. For example, the four-atom cluster **3** had 58 CVE's instead of the expected 62 while the ten-atom cluster **4** has 136 CVE's instead of 140 (Figure 3).

Interestingly, **3** and **4** also contain a tetrahedral element in which one edge is elongated, while a further similarity with the title compound is the identical arrangement of bonding carbonyl groups.

Experimental Section

Preparation of [$Pd_7(CO)_7(PMe_3)_7$] (2). [$Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PMe_3)$] (0.77 g, 2.66 mmol) was suspended in toluene (3 mL) at −78 °C and attached to a gas burette filled with CO. A 62-mL sample of CO (0.96 mol/Pd) was absorbed over a period of 12 h. A gas sample was taken and the volatile fraction of the reaction mixture condensed into a cold trap. GC analysis indicated the formation of a total of 231 mg (4.26 mmol, 80%) of butadiene with traces of C_8-hydrocarbons. The dark red powder left after removal of the volatile components was recrystallized. Anal. Calcd for [$PdPC_4H_9O$]$_n$: Pd, 50.55; P, 14.71; C, 22.82; H, 4.32; O, 7.60. Found: Pd, 50.62; P, 14.78; C, 22.89; H, 4.25; O, 7.46 (difference).

Table III. Crystallographic Data for [$Pd_7(CO)_7(PMe_3)_7$]

Crystal Data	
formula	$C_{28}H_{63}O_7P_7Pd_7$
M_r	1470.9 g mol^{-1}
crystal size, mm	0.55 × 0.22 × 0.4
cryst system	trigonal
space group	$R3m$
a, Å	11.098 (2)
α, deg	103.94 (3)
V, Å^3	1221.1
Z	1
D_{calcd}, g cm^{-3}	2.0
Measurement of Data	
monochromated (graphite) Mo Kα X radiation	$\lambda = 0.710\,69$ Å
reflectns measd	5102 [$\pm h,\pm k,l$]
μ(Mo Kα)	27.42 cm^{-1}
takeoff angle, deg	$\theta = 6.15$
θ limits, deg	$2.0 < \theta < 26.6$
$\theta - 2\theta$ scan technique (48 steps)	
horizontal detector aperture, mm	($5.0 + 1.25 \tan\theta$)
vertical aperture, mm	4.0
Ω scan range	$0.8 + 0.35 \tan\theta$
$\sigma(F)$	$(\sigma(I)_{poisson}{}^2 + (Ik)^2)^{1/2}/2F$, $k = 0.02$
no. of variables	78
obsd reflctns	1509, $I > 2.0\sigma(I)$
R	0.064
R' ($w = I/\sigma^2(F_o)$)	0.065

Crystal Structure Determination. A suitable crystal was obtained by recrystallization from benzene and sealed in a Lindemann glass capillary under an atmosphere of argon. Intensity data were collected on a Nonius CAD-4 diffractometer using graphite-monochromated Mo K_α X radiation. A total of 5100 reflections were collected in a range ($2.0 < \theta < 26.6$, [$\pm h,\pm k,l$]) by using a θ–2θ scan technique with the scan speeds varying from 1.3 to 10.0° min^{-1}, depending on the standard deviation to intensity ratio of a preliminary 10° min^{-1} scan. The intensity of a reflection and its standard deviation were calculated from INT − 2(BGL + BGR) and (INT + 4(BGL + BGR))$^{1/2}$ respectively, where INT, BGL, and BGR are the peak intensity and the left and the right backgrounds. The time spent measuring the backgrounds was half that taken to measure the peak. A Zr filter was inserted in front of the detector if the peak count was greater than 50 000 counts s^{-1}. The intensity of the three monitor reflections remeasured after every 90 min of X-ray exposure showed no significant variation during the course of data collection. Intensities were corrected for Lorentz and polarization effects,[19] but no absorption correction was applied (μ = 27.4 cm^{-1}). The Laue symmetry of the diffracted intensities was $3m$, and as there was no systematic absence, the possible space groups are $R32$ (No. 155), $R3m$ (No. 160), and $R\bar{3}m$ (No. 166). Equivalent reflections were averaged, $R = (\sum(F - \langle F\rangle)^2/\sum\langle F\rangle^2(m-1))^{1/2} = 0.028$, where m is the number of equivalent reflections averaged, and yielded a total of 1509 observed intensities ($I > 2.0\sigma(I)$) that were used in the solution and refinement of the structure. Pertinent crystal data are given in Table III; the cell parameters were obtained by least-squares fit to the θ values of 75 automatically centered reflections ($11 < \theta < 23°$).

The structure was solved by Patterson and Fourier methods. First, the positions of the palladium atoms in the octahedral part of the cluster were determined from a Patterson synthesis. From the distribution of maxima it was possible to exclude $R32$ as a possible space group. A subsequent Fourier synthesis using the phases calculated from the two independent palladium atom positions Pd1 and Pd2 in the noncentrosymmetric space group ($R = 0.32$, $R_w = 0.31$)[20] revealed Pd3 to be positionally disordered about the exact 3-fold axis passing through the octahedron. Each palladium atom sits on a crystallographic mirror plane and was constrained to do so during the remaining refinement cycles. Consistent with this, Pd1 and Pd2 were given occupancy factors of a half and Pd3 was given an occupancy factor of one-sixth. In addition, the z positional parameters of Pd2 was fixed at 0.0. Refinement allowing the metal atoms isotropic thermal motion gave $R = 0.24$ and $R_w = 0.28$, and a Fourier synthesis calculated at this stage enabled the phosphorus atoms to be located. The phosphorus atoms attached to Pd2 appeared in the Fourier synthesis as two peaks with relative heights of 2:1. The positions of these peaks were included in the model as P2 and P21 and given the relative weights of 2:1. An attempt to refine the population parameters was unsuccessful, and in successive refinement cycles the population of P2 grew at the expense of P21 and the two atoms moved closer together. (The P2–P21 distance at the end of refinement is 0.7 Å.) Refinement of the palladium and phosphorus

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[17] Albano, V. G.; Ciani, G.; Martinengo; Chini, P.; Giordano, G. *J. Organomet. Chem.* **1975**, *188*, 381.

[18] Pierpont, C. G.; Stunty, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 616. Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 2972.

[19] Computer programs used in the data reduction include DATAP written by Coppens, Leiserovitz, and Rabinovich.

[20] Agreement indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

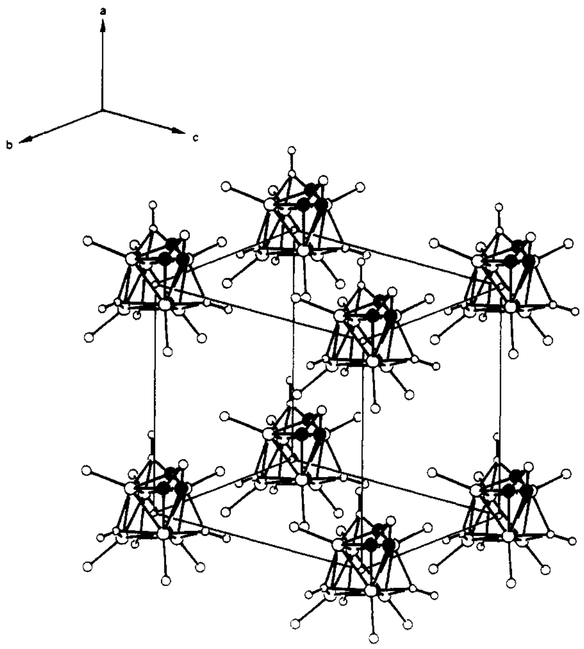

Figure 4. The contents of the unit cell of **2**. The disordered Pd3 atoms are shown as black spheres. The edge-bridging carbonyl groups C3–O3 have been omitted for clarity.

atoms allowing anisotropic thermal motion converged at $R = 0.101$ and $R_w = 0.105$. Positional and thermal parameters were constrained to be equal in accord with the respective symmetry of the special position of each atom. C1, O1, C2, O2, C11, and C22 were then located on a Fourier synthesis map, and further refinement of the structure including these atoms with anisotropic thermal parameters gave $R = 0.065$ and $R_w = 0.068$. A difference Fourier synthesis failed to reveal more than an average position for C3. Disorder of the phosphorus atom bonded to Pd2 also made the unambiguous assignment of the methyl carbon atoms attached to this atom difficult, and these were included in the refinement at calculated positions (C–P = 1.85 Å, Pd–P-C = 110°).

Elemental analysis of the compound had clearly shown the molecular formula to be $[PdPC_4H_9O]_n$, and the model at this stage of refinement supported the heptameric nature of the compound, so a model containing seven carbonyl groups was sought. As there was no evidence of either face-capping or terminally bonded carbonyl groups attached to the metal tetrahedron containing Pd3 in the difference Fourier synthesis, a model was adopted, whereby the three carbonyl groups C3–O3 were in bridging positions between Pd2 and Pd3. An average position for C3 was taken from the difference Fourier synthesis, and its attended oxygen atom O3 was incorporated at a calculated position, C–O = 1.15 Å. Inclusion of these atoms at positions agreement indices, which converged at $R = 0.064$ and $R_w = 0.065$.

Table IV. Atomic Positional Parameters ($\times 10^4$) with Estimated Standard Deviations in Parentheses

atom	x	y	z
Pd1	−1109 (1)	−1109 (1)	466 (1)
Pd2	1606 (1)	1606 (1)	0
Pd3	2569 (3)	2569 (3)	3112 (4)
P1	−2766 (4)	−2766 (4)	486 (6)
P2	1968 (9)	1968 (9)	−1942 (10)
P21	2371 (17)	2371 (17)	−1314 (25)
P3	4374 (5)	4374 (5)	4374 (5)
O1	−2457 (17)	−2457 (17)	−2457 (17)
O2	−179 (17)	−179 (17)	3433 (14)
C1	−1672 (20)	−1672 (20)	−1672 (20)
C2	4 (19)	4 (19)	2385 (20)
C11	−4438 (16)	−2754 (19)	−387 (20)
C12	−2793 (28)	−2793 (28)	2183 (32)
C31	4627 (41)	4627 (41)	6142 (64)
C21	1852	3579	−2002
C22	672	672	−3417
C23	2413	4141	−899
C24	1482	1482	−2953
C3	3206	3206	1094
O3	3965	3965	883

The function minimized was $\sum\omega(F_o - F_c)^2$ with $\omega = 1/\sigma^2(F_o)$.[21] In the final refinement cycle the mean shift to error ratio 0.05, and the final Fourier synthesis was essentially featureless except for several peaks ($\leq$1.8 e Å^{-3}) in the vicinity of the palladium and phosphorus atoms, with much smaller values elsewhere. Neutral atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber,[22] and anomalous scattering factors for Pd and P were taken from ref 23. Refinement of the enantiomorphic structure gave no significant improvement in the weighted R factor. Final positional parameters appear in Table IV. These together with a table of the thermal parameters and a list of observed and calculated structure amplitudes can be obtained as supplementary material.

2 crystallizes as independent molecules separated by distances greater than the sum of van der Waals radii of the relevant atoms. Figure 4 gives the contents of the unit cell.

Registry No. **1**, 80181-65-3; **2**, 83632-51-3.

Supplementary Material Available: Tables of positional and thermal parameters and a list of observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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(21) Refinement of the structure was carried out by using the program SHELX 76, G. M. Sheldrick, unpublished.

(22) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(23) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.