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Isolation and X-ray characterization of a new crystal modification of $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-dppm})_3$ during the synthesis of the novel fluxional triangulo Pd(0) complex $[Pd_3(\mu_2\text{-}CO)_3(dppm)_2]_n$ ($n = 1$ or 2)

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Abstract—The one-step synthesis of a new type of fluxional Pd^0—CO—bis(diphenylphosphino)methane (dppm) cluster from Pd^{II} acetate is reported and the complex has been identified as $[Pd_3(\mu_2\text{-}CO)_3(\mu\text{-dppm})_2]_n$ ($n = 1$ or 2, **8**) on the basis of microanalytical and spectroscopic data. During repeated attempts to grow suitable crystals of this complex for X-ray analysis, a second crystal modification (**7**) of $Pd_6(\mu_2\text{-}CO)_3(\mu\text{-dppm})_3$ was isolated as a 0.5 toluene solvate. This modification contains two $Pd_6(\mu_2\text{-}CO)_3(\mu\text{-dppm})_3$ molecules in the asymmetric unit cell each showing minor structural differences from each other as well as from the previously characterized $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-dppm})_3 \cdot CH_2Cl_2$ (**6**). © 1997 Elsevier Science Ltd

Keywords: bis(diphenylphosphino)methane; cluster complexes; fluxionality; hydroborate reductions; palladium–carbonyl–phosphine complexes; X-ray structures.

Palladium [1] and platinum [2] cluster complexes in general have been under active investigation for some time and of particular interest (because the M_3 unit resembles [3] a fragment of a metal surface in its reactions) are triangulo systems which contain both CO and bis(diphenylphosphino)methane ligands [3]. Among the latter is the singly-capped 42e system $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**1**) [3–6], which is readily converted [5,7,8] into doubly-capped trinuclear systems such as $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3(\mu_3\text{-}X)]^+$ (**2**; X = CF_3COO, Cl, Br, I, SCN). The related complex $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3(CN)]^+$ (**3**), in which the CN group is terminal (but fluxional) rather than capping, has also been prepared [9] from **1** and Pt_3 complexes similar to **1**, **2** and **3** are also known [3,9]. The μ_3-CO ligand in **1** is also readily displaced by isonitriles to give [10] both mono- and di-isonitrile derivatives in which the isonitrile ligands have the unusual $\mu_3\text{-}\eta^1$-bonding mode. Recently, a Ni_3 analog of **2** has been reported [11]. Related trinuclear Pd— and Pt—CO—phosphine complexes containing M^0 have been less extensively investigated, although examples have been known for considerably longer than have **1**, **2** and **3**. The known complexes of this type for the most part contain monodentate phosphines and both the 42e systems $M_3(\mu_2\text{-}CO)_3(PR_3)_3$ (**4**) and the 44e systems $M_3(\mu_2\text{-}CO)_3(PR_3)_4$ (**5**, M = Pd [1], Pt [2]) have been thoroughly reviewed. Very recently, we reported [12] the synthesis and X-ray characterization of the interesting cluster $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-dppm})_3$ (**6**), which may be regarded as two units of type **4** linked face-to-face by the methylene bridges of the dppm ligands. Complex **6** was prepared, along with several other Pd—CO—dppm complexes, by the direct reduction of Pd^{IV} salts by $NaBH_4$ in the presence of dppm under CO and it is as an extension of this work, as well as a continuation of our general investigation [13] of the value of $M^{n+}/dppm/BH_4^-/CO$ reactions as a convenient synthetic route to low-nuclearity

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M—CO—dppm complexes, that we report here the X-ray structure of **7**, a new crystal modification of **6**, which is formed as a minor by-product in the synthesis of the unusual fluxional system $[Pd_3(\mu_2\text{-}CO)_3(dppm)_2]_n$ (**8**, $n = 1$ or 2).

EXPERIMENTAL

Materials

Bis(diphenylphosphino)methane (dppm), palladium(II) acetate and potassium hexachloropalladate(IV) were obtained from the Aldrich Chemical Corporation and were used without further purification. Palladium(II) chloride was obtained from Johnson Matthey. $NaBH_4$ (Aldrich) was stored under dry conditions. All solvents were reagent grade and were degassed prior to storage in a glove box.

Measurements

Samples and reagents were protected from exposure to air during weighing and data collection. Microanalyses for C and H were acquired in our laboratories with a Control Equipment Corp. Model 240XA analyzer using V_2O_5 as a combustion aid while those for P and Pd were provided by Guelph Chemical Laboratories Ltd, Guelph, Ontario. FT–IR spectra (Nujol mulls) were recorded on a Bruker IFS 66 spectrophotometer. A Bruker AC-E 200 NMR spectrometer equipped with a variable-temperature controller (BVT-1000S) was used to record ^1H and ^{31}P spectra in solution (CD_2Cl_2 for ^1H and CH_2Cl_2 for ^{31}P) at 200 and 81 MHz, respectively. Chemical shifts were measured as δ values with positive shifts downfield of Me_4Si for ^1H and downfield of the signal of external 85% H_3PO_4 for ^{31}P. For the ^{31}P spectra, the frequency lock was provided by a coaxial D_2O insert. Solid-state ^{31}P NMR spectra were acquired at 145.7 MHz using a Bruker AMX 500 spectrometer equipped with a wide-bore 360 MHz magnet for solid-state measurements. GC–HRMS analyses were carried out using a VG AutoSpec mass spectrometer equipped with a Hewlet–Packard model 5890 II gas chromatograph.

Syntheses

In a typical experiment, dppm (0.38 g, 1.0 mmol) was dissolved in toluene (10 cm^3) under a slow stream of CO, $Pd(PAc)_2$ (0.22 g, 1.0 mmol) was added in one portion and then CH_3CN (10 cm^3) was also added. The resulting orange solution was stirred at 20°C for 15 min under CO and $NaBH_4$ (0.09 g, 2.4 mmol) in ethanol (10 cm^3) was then added over 2 min. After this addition, the dark brown mixture was filtered and allowed to stand for 24 h. The dark red microcrystalline **8** deposited was washed with acetone (20 cm^3), water (20 cm^3) and acetone again (20 cm^3) and dried under reduced pressure (rotary pump) for 30 min. The resulting product (0.29 g, *ca* 24%) contained (^1H NMR) significant amounts of ethanol, acetone and toluene which could not be entirely removed by further pumping for extended periods and, in most syntheses, trace amounts (usually $<1\%$, as indicated by NMR evidence) of the Pd_6 system **6** (^{31}P NMR: δ 11.0) were also formed. Decomposition of **8** is rapid in most common organic solvents, except for dichloromethane in which it is sufficiently stable for NMR measurements to be made but not for recrystallization. Found (several solvated samples): C, 58.8–60.8; H, 4.0–4.6. Found (one solvated sample): P, 10.6; Pd, 26.3 (P : Pd atomic ratio 4.2 : 3). Calc. for unsolvated $C_{53}H_{44}O_3P_4Pd_3$: C, 54.3; H, 3.8; P, 10.6; Pd, 27.2%. ^{31}P ^1H NMR (ambient temperature) at 81 MHz: δ 13.6 (v. broad) in CH_2Cl_2. FT–IR (Nujol): ν(CO) 1854(s), 1839(s), 1760(m), 1747(m) cm^{-1}. Complex **8** can also be formed in comparable yields by similar methods from K_2PdCl_6 in ethanol/toluene (Pd : dppm : $NaBH_4$ ratios 1 : 1 : 4), but the product is usually contaminated with NaCl.

Many attempts were made to grow crystals of **8** for structural determination directly from the reaction filtrates by varying reaction conditions, but in all cases the crystals obtained were small, soft, variably solvated, of limited stability and diffracted very poorly. The one crystal (having the same color and general morphology as **8**) for which a data set was obtained proved to be a new modification (**7**) of the minor by-product **6**.

X-ray data collection, structure determination and refinement of a single crystal of $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-}dppm)_3 \cdot 0.5C_7H_8$ (**7**)

X-ray crystallographic data collection was carried out on an Enraf–Nonius CAD-4 diffractometer using graphite monochromated Mo-K_α radiation at 293 K. Unit-cell parameters were obtained by least squares analysis of 25 low-angle reflections. The stability of the crystal was measured by monitoring periodically three standard reflections; no systematic intensity variations were observed. Intensity data were corrected for Lorentz and polarization factors. All heavy atoms were found using direct methods. Cycles of Fourier and difference-Fourier calculations were used to find the remaining atoms. Calculated ideal locations for the hydrogen atoms of methylene carbon atoms and phenyl rings of dppm ligands and of the toluene solvent molecule were included but not refined. All atoms were refined isotropically except for the Pd and P atoms. Relevant data concerning the crystal, data collection and structure solution are found in Table 1. Atomic scattering factors were taken from tabulated values [14]. Calculations were performed on a 486 PC using NRCVAX and SHELX programs.

Table 1. Crystal data and structure refinement for $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-dppm})_3 \cdot 0.5C_7H_8$ (7)

Empirical formula	$C_{169}H_{139}O_{12}P_{12}Pd_{12}$
Formula weight	4010.24
Wavelength	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	P-1
Unit-cell dimensions	$a = 16.950(3)$ Å, $\alpha = 105.41(3)^\circ$ $b = 20.290(4)$ Å, $\beta = 97.26(3)^\circ$ $c = 25.090(5)$ Å, $\gamma = 96.76(3)^\circ$
Volume (Å^3)	8148(3)
Z	2
Density (calculated) (g cm^{-3})	1.635
Absorption coefficient (mm^{-1})	1.464
$F(000)$	3962
Theta range for data collection (°)	0.85–20.02
Index ranges	$-16 \leqslant h \leqslant 16, 0 \leqslant k \leqslant 19,$ $-23 \leqslant l \leqslant 23$
Reflections collected	13,640
Independent reflections	13,640 ($R_{int} = 0.0000$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13,640/0/948
Goodness-of-fit on F^2	1.056
Final R indices^a	$R_1 = 0.0999$, $wR_2 = 0.2394$ $[8564 F_o > 4\sigma(F_o)]$
R indices (all data)	$R_1 = 0.1555$, $wR_2 = 0.2662$
Largest difference peak and hole (e Å^{-3})	2.903 and -1.551

$^a R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

The several large peaks remaining, varying from 1.48 to 2.47 e A^{-3}, were at least 3 Å from both **7a** and **7b**, and attempts at resolving these as molecules of any of the solvents used in the isolation process (ethanol, acetone, acetonitrile and toluene) proved unsuccessful.

Atomic coordinates for **7** have been deposited with the Cambridge Crystallographic Data Center.

RESULTS AND DISCUSSION

Complex **8** is readily prepared, in one simple experimental step, by the direct reduction of either Pd^{II} acetate or K_2PdCl_6 by $NaBH_4$ in the presence of dppm and CO with the acetate giving a microcrystalline product which is always heavily solvated (ethanol, toluene, acetone all present). All attempts to grow crystals suitable for crystallography failed and, therefore, the principal structural features of **8** have been determined from chemical analyses, spectroscopic data and its reaction chemistry.

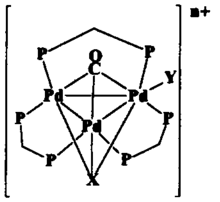
The P : Pd atomic ratio of 4 : 3 shows the presence of 2 dppm ligands per 3 Pd atoms and the FT–IR spectrum (Nujol) shows ν_{CO} at 1854(s), 1839(s), 1760(m), and 1747(m) cm^{-1}, which is a pattern consistent [1,2,12] with the presence of a zero-valent triangulo M_3 unit edge-bridged by CO groups. That it is indeed a Pd^0 complex is confirmed by several observations. Thus, the FT–IR, ^{1}H NMR and ^{31}P ^{1}H NMR spectra of samples prepared from Pd^{II} acetate, K_2PdCl_6, or the latter reagent to which has been added a large excess of bromide or iodide ion, are identical. Furthermore, neither the FT–IR spectrum nor the ^{1}H NMR spectrum shows the presence of a hydrido ligand or of a tetrahydroborato group. Other than this, ^{1}H spectra are of little structural value because of the presence of nonremovable solvent contamination and molecular fluxionality (see later discussion). ^{13}C NMR spectra could not be obtained at ambient or low temperatures because of the low solubility and the solution instability of **8**.

The presence of a triangulo Pd_3 unit is further supported by an unusual reaction in which **8** in dichloromethane reacts over several hours with the solvent to give a mixture of **2** (X = Cl) [7] and **6** [12] together with dppm dioxide and CO with the relative amounts of the two Pd_3-containing decomposition products varying from experiment to experiment. The CO evolved was detected by GC–HRMS analysis of the vapor above the solution and it is noteworthy that the presence of CO in CH_2Cl_2 solutions of **8** suppresses the decomposition. Clearly, oxidation of some of the Pd^0 atoms occurs under these conditions and such oxidations of Pd^0 systems by chlorinated solvents, with several possible outcomes, are not uncommon [15]. The variability in the product ratios from the solvent-induced decomposition can be rationalized as follows. If free dppm is added to a freshly prepared solution of **8** in CH_2Cl_2 not only is the rate of decomposition much slower but also decomposition eventually occurs to give **2** (X = Cl) and the mono- and dioxides of dppm when a chilled solution is allowed to come to room temperature. Since no **6** is formed during decomposition in the presence of dppm, the implication is that **2** and **6** are formed by different processes in the decomposition which occurs in the absence of an excess of dppm. The above data are therefore consistent with the formulation $[Pd_3(\mu_2\text{-CO})_3(\mu\text{-dppm})_2]_n$ (**8**).

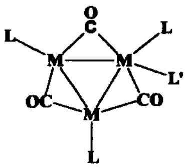
The fluxionality of **8** is clear from its ^{31}P ^{1}H NMR spectrum. At room temperature this shows a single very broad hump at δ 13.6 which resolves at 233 K into a complex pattern with three main signals at δ 25, 15 and 0, each of which shows fine structure with no easily recognizable coupling pattern. In this spectrum, the signal at δ 15 is about twice the area of each of the other signals. At temperatures higher than ambient, the broad room-temperature signal sharpens considerably but this could not be taken to the limit because of the thermal instability of the complex. These changes in the spectrum with temperature are reversible. The solid-state ^{31}P ^{1}H CP–MAS spectrum is similar to that obtained from solutions at low temperature except that no fine structure is apparent. The room-temperature fluxionality of **8** in solution is consistent with migration of the dppm ligands around a $Pd_3(\mu_2\text{-CO})_3$ core or, possibly, between two such cores within the same molecule.

Complex **8** is clearly related to either the M^0 trinuclear complexes **4** and **5** (M = Pd, Pt) or the hexanuclear Pd^0 system **6** which is, essentially, two units of type **4** linked by dppm bridges. While there have been relatively little X-ray structural and ^{31}P NMR data published on the Pd complexes of types **4** and **5**, the Pt complexes have received more attention and it has been shown that Pt-containing complexes of types **4** [16] and **5** [17] are planar triangulo systems in which the former bears one phosphine ligand on each Pt atom while the latter type bears two phosphines on one of the Pt atoms in the solid state. Complex **6** has been well characterized structurally [12]. Furthermore, it has been shown [18] by ^{31}P NMR methods that resolvable spectra are only obtainable for complexes of type **5** (M = Pt) at low temperatures (163–220 K) and that at room temperature, a rapid ligand exchange process occurs. It appears then that in order to maintain the electron count at 42e or more for the Pd_3 cores of **8** (n = 1 or 2), ligand migration around or between such cores rather than ligand dissociation is the operative process in solution and the extremes in the fluxionality for n = 1 or 2 are the 42e structure **8a**, the 42/44e structure **8c** and the 44e structures **8b** and **8d**. The appearance of the low-temperature ^{31}P ^{1}H NMR spectrum suggests that interconversion between structures is slow under these conditions.

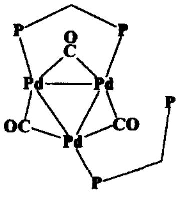
However, if n = 2, one would expect to be able to synthesize the complex (at least in dichloromethane solution) by treating **6** with additional dppm. Rather surprisingly, what was observed by ^{31}P NMR studies was a very rapid dppm-catalyzed decomposition of **6** to give **2** and the dioxide of dppm with no evidence for the formation of any adduct of **6** and dppm, fluxional or otherwise. This indicates that **8** is not formed in this reaction since, as noted above, **8** is stabilized in solution by additional dppm. Finally, it should be noted that the apparent nonformation of **6** during the slow decomposition of **8** in CH_2Cl_2 in the presence of an excess of dppm referred to earlier may not be an accurate deduction since **6** clearly decomposes much more rapidly than **8** under these conditions and would probably be consumed as it is formed. Thus, the weight of the evidence favors a molecular formula of $Pd_3(\mu_2\text{-CO})_3(dppm)_2$ for **8**.



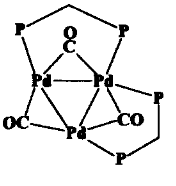
1: X, Y absent; n = 2
2: X = CF_3COO, Cl, Br, I, SCN; Y absent; n = 1
3: X absent; Y = CN; n = 1



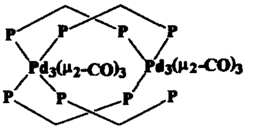
4: M = Pd, Pt; L = PR_3; L' absent
5: M = Pd, Pt; L = L' = PR_3



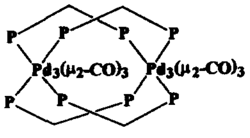
8a



8b



8c



8d

The very interesting reaction chemistry of **8** is under study and the results of this investigation will be reported in a separate publication.

The structure of **6**, the other structural variant of the hexanuclear Pd^0 complex reported in this paper, has been briefly described in a previous communication [12] and recently the Pt analog, isostructural with **6**, has been reported [19]. Complex **6** consists of two essentially parallel Pd_3 units with each pair of Pd atoms bridged by CO ligands. The Pd_3 units are almost eclipsed to form an approximate trigonal prism, with each trinuclear unit being linked only by the dppm ligands. As noted above, **7** is a different solvate and crystalline form of **6**. In fact the unit cell of **7** contains two hexanuclear units (**7a** and **7b**) which are not only different from each other but also different from **6**. Some of these differences are clear from the views illustrated in Figs 1 and 2. In Fig. 1, for

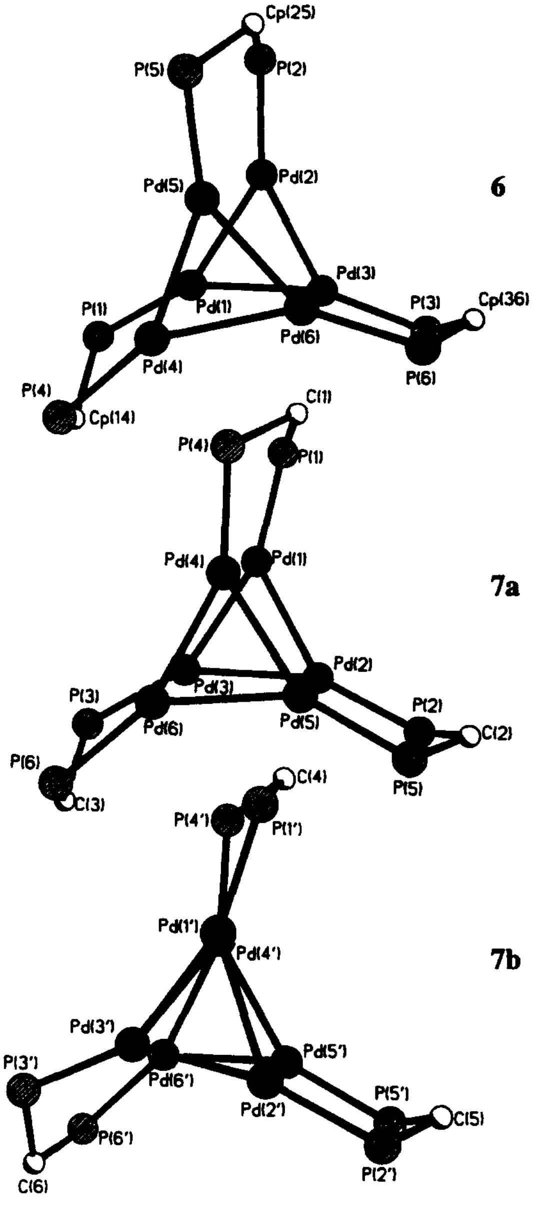


Fig. 1. View looking approximately down the pseudo three-fold axes of the trigonal prisms of **6** and the two structural variants (**7a** and **7b**) in the unit cell of **7**. The bridging CO ligands and the phenyl groups of the dppm ligands are omitted for clarity. To emphasize the structural differences, two of the Pd atoms and the P—C—P unit of a dppm ligand (all situated at the lower right of each diagram) are shown in the same relative orientation for each of the three structures.

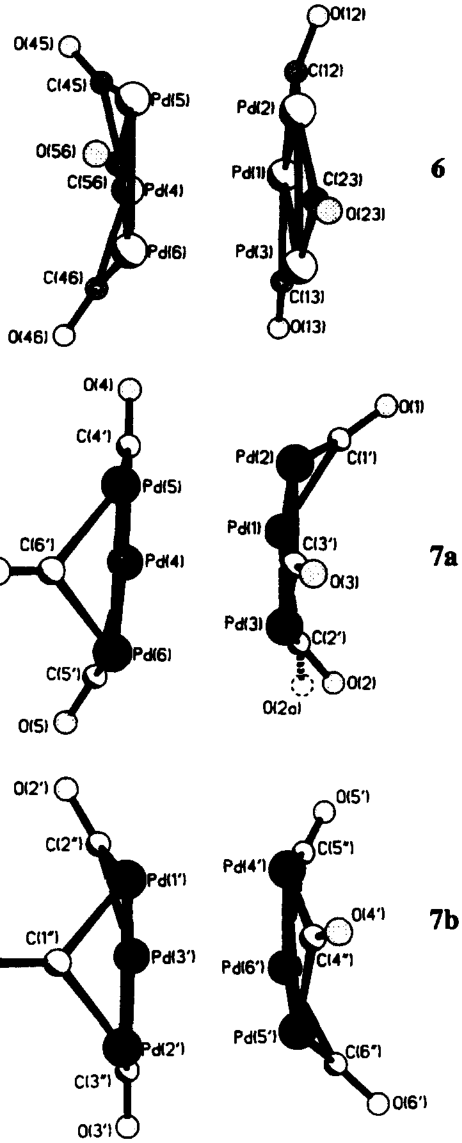


Fig. 2. View looking side-on at the trigonal prism formed by the six atoms in each of **6**, **7a** and **7b** showing the orientations of the CO ligands relative to each of the Pd_3 units. For comparison purposes, the pairs of Pd_3 units in the three structures are arranged with similar orientations and the dppm ligands are omitted. In **7a**, a disordered atom is shown for O(2).

comparison purposes, the hexanuclear units are oriented such that the two Pd atoms and the dppm ligand in the lower right-hand corner of each unit have the same relative configuration. The bridging CO groups and the phenyl rings have been omitted. The Pd_3 units are almost parallel to each other (deviations are 0.7, 4.5 and 3.3°, in **7a, 7b** and **6** [12], respectively). Similarly, deviations of the Pd_3 pairs from an eclipsed conformation in each of **6, 7a** and **7b** are 5.4, 11.3 and 10°, respectively. The different orientations of the methylene C atoms of the dppm ligands (two skewed in an anticlockwise manner and one clockwise in Fig. 1) in each of the structures should also be noted.

Figure 2 shows a side view of the Pd_6 framework and the six CO ligands for each of **6, 7a** and **7b**, with the dppm ligands omitted. Typically, one CO is approximately in the Pd_3 plane, the others being up to about 1 Å out of the plane and oriented towards the outside of the hexanuclear unit.

Selected bond lengths and angles, shown in Table 2, are quite similar to those found [12] for **6**.

Table 2. Selected bond lengths (Å) and angles (°) for $Pd_6(\mu_2\text{-}CO)_6(\mu\text{-dppm})_3 \cdot 0.5C_7H_8$ (7)

Pd(1)—Pd(3)	2.681(3)	Pd(1)—C(1′)	2.02(3)
Pd(1)—Pd(2)	2.734(3)	Pd(1)—C(2′)	2.05(3)
Pd(2)—Pd(3)	2.724(3)	Pd(2)—C(1′)	2.13(3)
Pd(4)—Pd(5)	2.688(3)	Pd(2)—C(3′)	2.13(3)
Pd(4)—Pd(6)	2.719(3)	Pd(3)—C(3′)	2.03(3)
Pd(5)—Pd(6)	2.673(3)	Pd(3)—C(2′)	2.05(3)
Pd(1′)—Pd(2′)	2.679(3)	Pd(4)—C(4′)	2.05(3)
Pd(1′)—Pd(3′)	2.693(3)	Pd(4)—C(5′)	2.09(3)
Pd(2′)—Pd(3′)	2.698(3)	Pd(5)—C(4′)	2.05(3)
Pd(4′)—Pd(6′)	2.715(3)	Pd(5)—C(6′)	2.10(3)
Pd(4′)—Pd(5′)	2.719(3)	Pd(6)—C(5′)	2.02(3)
Pd(5′)—Pd(6′)	2.691(3)	Pd(6)—C(6′)	2.10(3)
Pd(1)—P(1)	2.310(8)	Pd(1′)—C(1″)	1.98(3)
Pd(2)—P(2)	2.347(8)	Pd(1′)—C(2″)	2.07(3)
Pd(3)—P(3)	2.299(8)	Pd(2′)—C(3″)	2.03(3)
Pd(4)—P(4)	2.319(8)	Pd(2′)—C(1″)	2.06(3)
Pd(5)—P(5)	2.301(8)	Pd(3′)—C(3″)	2.04(3)
Pd(6)—P(6)	2.313(9)	Pd(3′)—C(2″)	2.04(3)
Pd(1′)—P(1′)	2.307(8)	Pd(3′)—P(3′)	2.316(8)
Pd(2′)—P(2′)	2.294(8)	Pd(4′)—C(5″)	2.05(3)
Pd(3′)—P(3′)	2.316(8)	Pd(4′)—C(4″)	2.10(3)
Pd(4′)—P(4′)	2.311(8)	Pd(5′)—C(6″)	2.07(3)
Pd(5′)—P(5′)	2.311(8)	Pd(5′)—C(4″)	2.05(3)
Pd(6′)—P(6′)	2.311(8)	Pd(6′)—C(6″)	2.08(3)
		Pd(6′)—C(5″)	2.07(3)

Pd(3)—Pd(1)—Pd(2)	60.40(9)	P(5)—Pd(5)—Pd(4)	152.0(2)
Pd(3)—Pd(2)—Pd(1)	58.84(9)	P(6)—Pd(6)—Pd(5)	142.6(2)
Pd(1)—Pd(3)—Pd(2)	60.76(9)	P(6)—Pd(6)—Pd(4)	153.0(2)
Pd(5)—Pd(4)—Pd(6)	59.25(8)	P(1′)—Pd(1′)—Pd(2′)	143.0(2)
Pd(6)—Pd(5)—Pd(4)	60.96(9)	P(1′)—Pd(1′)—Pd(3′)	154.3(2)
Pd(5)—Pd(6)—Pd(4)	59.78(9)	P(2′)—Pd(2′)—Pd(1′)	135.4(2)
Pd(2′)—Pd(1′)—Pd(3′)	60.29(9)	P(2′)—Pd(2′)—Pd(3′)	159.7(2)
Pd(1′)—Pd(2′)—Pd(3′)	60.12(8)	P(3′)—Pd(3′)—Pd(1′)	152.0(2)
Pd(1′)—Pd(3′)—Pd(2′)	59.59(9)	P(3′)—Pd(3′)—Pd(2′)	144.3(2)
Pd(6′)—Pd(4′)—Pd(5′)	59.37(8)	P(4′)—Pd(4′)—Pd(6′)	152.4(2)
Pd(6′)—Pd(5′)—Pd(4′)	60.25(8)	P(4′)—Pd(4′)—Pd(5′)	146.5(2)
Pd(5′)—Pd(6′)—Pd(4′)	60.39(8)	P(5′)—Pd(5′)—Pd(6′)	148.7(2)
Pd(1)—C(1′)—Pd(2)	82.5(12)	P(5′)—Pd(5′)—Pd(4′)	148.6(2)
Pd(1)—C(2′)—Pd(3)	81.5(10)	P(6′)—Pd(6′)—Pd(5′)	136.1(2)
Pd(3)—C(3′)—Pd(2)	81.6(11)	P(6′)—Pd(6′)—Pd(4′)	156.8(2)
Pd(5)—C(4′)—Pd(4)	82.0(11)	C(1′)—Pd(1)—C(2′)	133.6(12)
Pd(6)—C(5′)—Pd(4)	83.1(11)	C(1′)—Pd(1)—P(1)	98.1(9)
Pd(6)—C(6′)—Pd(5)	79.1(10)	C(2′)—Pd(1)—P(1)	115.1(8)
Pd(1′)—C(1″)—Pd(2′)	83.1(11)	C(1′)—Pd(1)—Pd(3)	103.6(9)
Pd(3′)—C(2″)—Pd(1′)	81.7(13)	C(2′)—Pd(1)—Pd(2)	108.0(8)
Pd(3′)—C(3″)—Pd(2′)	83.0(11)	C(1′)—Pd(2)—C(3′)	140.5(11)
Pd(5′)—C(4″)—Pd(4′)	81.6(11)	C(1′)—Pd(2)—P(2)	103.7(9)
Pd(4′)—C(5″)—Pd(6′)	82.4(11)	C(3′)—Pd(2)—P(2)	107.5(8)
Pd(6′)—C(6″)—Pd(5′)	81.0(11)	C(1′)—Pd(2)—Pd(3)	99.3(8)
C(2′)—Pd(1)—Pd(3)	49.2(8)	C(3′)—Pd(2)—Pd(1)	106.4(8)
C(1′)—Pd(1)—Pd(2)	50.4(9)	C(1′)—Pd(2)—Pd(5)	131.2(9)
C(3′)—Pd(2)—Pd(3)	47.6(8)	C(3′)—Pd(2)—Pd(5)	72.3(7)
C(1′)—Pd(2)—Pd(1)	47.1(9)	P(2)—Pd(2)—Pd(5)	90.6(2)
C(2′)—Pd(3)—Pd(1)	49.4(8)	Pd(3)—Pd(2)—Pd(5)	81.20(9)
C(3′)—Pd(3)—Pd(2)	50.8(8)	Pd(1)—Pd(2)—Pd(5)	98.35(10)
C(4′)—Pd(4)—Pd(5)	49.0(8)	C(3′)—Pd(3)—C(2′)	156.8(11)
C(5′)—Pd(4)—Pd(6)	47.4(8)	C(3′)—Pd(3)—P(3)	97.6(8)
C(6′)—Pd(5)—Pd(6)	50.5(8)	C(2′)—Pd(3)—P(3)	99.6(8)
C(4′)—Pd(5)—Pd(4)	49.0(8)	C(3′)—Pd(3)—Pd(1)	111.6(8)
C(6′)—Pd(6)—Pd(5)	50.4(8)	C(2′)—Pd(3)—Pd(2)	108.5(8)
C(5′)—Pd(6)—Pd(4)	49.6(8)	C(3′)—Pd(3)—Pd(6)	78.5(8)
C(1″)—Pd(1′)—Pd(2′)	49.7(8)	C(2′)—Pd(3)—Pd(6)	118.7(8)

Table 2. (*Continued*)

C(2″)—Pd(1′)—Pd(3′)	48.6(9)	P(3)—Pd(3)—Pd(6)	83.9(2)
C(1″)—Pd(2′)—Pd(1″)	47.2(8)	C(3′)—Pd(3)—Pd(4)	101.2(8)
C(3″)—Pd(2′)—Pd(3′)	48.7(2)	C(2′)—Pd(3)—Pd(4)	81.1(8)
C(2″)—Pd(3′)—Pd(1′)	49.7(9)	C(4′)—Pd(4)—C(5′)	152.4(11)
C(3″)—Pd(3′)—Pd(2′)	48.3(8)	C(4′)—Pd(4)—P(4)	97.0(8)
C(5″)—Pd(4′)—Pd(6′)	49.2(8)	C(5′)—Pd(4)—P(4)	105.5(8)
C(4″)—Pd(4′)—Pd(5′)	48.4(8)	C(5′)—Pd(4)—Pd(5)	105.4(8)
C(6″)—Pd(5′)—Pd(6′)	49.7(8)	C(4′)—Pd(4)—Pd(6)	108.2(8)
C(4″)—Pd(5′)—Pd(4′)	50.0(8)	C(4′)—Pd(5)—C(6′)	144.9(11)
C(6″)—Pd(6′)—Pd(5′)	49.3(8)	C(4′)—Pd(5)—P(5)	103.0(8)
C(5″)—Pd(6′)—Pd(4′)	48.4(8)	C(6′)—Pd(5)—P(5)	99.2(8)
P(1)—Pd(1)—Pd(2)	136.8(2)	C(4′)—Pd(5)—Pd(6)	110.0(8)
P(1)—Pd(1)—Pd(3)	158.2(2)	C(6′)—Pd(5)—Pd(4)	104.7(8)
P(2)—Pd(2)—Pd(3)	155.1(2)	C(5′)—Pd(6)—C(6′)	135.6(11)
P(2)—Pd(2)—Pd(1)	146.0(2)	C(5′)—Pd(6)—P(6)	109.0(9)
P(3)—Pd(3)—Pd(1)	148.9(2)	C(6′)—Pd(6)—P(6)	103.4(8)
P(3)—Pd(3)—Pd(2)	146.7(2)	C(5′)—Pd(6)—Pd(5)	108.1(8)
P(4)—Pd(4)—Pd(5)	144.7(2)	C(6′)—Pd(6)—Pd(4)	103.6(8)
P(4)—Pd(4)—Pd(6)	152.6(2)	C(1″)—Pd(1′)—C(2″)	127.2(12)
P(5)—Pd(5)—Pd(6)	146.8(2)	C(1″)—Pd(1′)—P(1′)	104.2(8)
C(2″)—Pd(1′)—P(1′)	110.7(9)		

The existence of three solid-states structural variants of the Pd_6 unit is possibly related to lattice solvent effects. Both **6** and **7** were obtained by reacting Pd salts (Pd^{IV} chloride for **6** and Pd^{II} acetate for **7**), dppm, $NaBH_4$ and CO in a mixture of ethanol and toluene (acetonitrile was also present in the reaction reported here from which traces of **7** were obtained). Both were isolated from the reaction mixture, although **6** was recrystallized from CH_2Cl_2 and its orthorhombic lattice contains a disordered CH_2Cl_2 molecule. Complex **7** was crystallized from the reaction filtrate and its triclinic lattice contains a disordered toluene molecule. It is possible that additional solvent molecules are also present, although attempts to resolve the residual peaks (>3 Å from both **7a** and **7b**) in the difference Fourier as ethanol, or any of the other solvents used in the isolation process, were not successful.

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REFERENCES

1. For a review, see Burrows, A. D. and Mingos, D. M. P., *Trans. Met. Chem.*, 1993, **18,** 129.
2. For a review, see Mingos, D. M. P. and Wardle, R. W. M., *Trans. Met. Chem.*, 1985, **10,** 441.
3. For reviews, see Puddephatt, R. J., Manojlović-Muir, Lj. and Muir, K. W., *Polyhedron*, 1990, **9,** 2767; Burrows, A. D. and Mingos, D. M. P., *Coord. Chem. Rev.*, 1996, **154,** 19.
4. Manojlović-Muir, Lj., Muir, K. W., Lloyd, B. R. and Puddephatt, R. J., *J. Chem. Soc., Chem. Commun.*, 1983, 1336.
5. Lloyd, B. R., Manojlović-Muir, Lj., Muir, K. W. and Puddephatt, R. J., *Organometallics*, 1993, **12,** 1231.
6. Lloyd, B. R., Bradford, A. and Puddephatt, R. J., *Organometallics*, 1987, **6,** 424.
7. Manojlović-Muir, Lj., Muir, K. W., Lloyd, B. R. and Puddephatt, R. J., *J, Chem. Soc., Chem. Commun.*, 1985, 536.
8. Ferguson, G., Lloyd, B. R., Manojlović-Muir, Lj., Muir, K. W. and Puddephatt, R. J., *Inorg. Chem.*, 1986, **25,** 4190.
9. Manojlović-Muir, Lj., Muir, K. W., Mirza, H. A. and Puddephatt, R. J., *Organometallics*, 1992, **11,** 3440.
10. Rashidi, M., Kristof, E., Vittal, J. J. and Puddephatt, R. J., *Inorg. Chem.*, 1994, **33,** 1497.
11. Jennings, M. C., Puddephatt, R. J., Manojlović-Muir, Lj., Muir, K. W. and Mwariri, B. N., *Inorg. Chim. Acta*, 1993, **212,** 197.
12. Holah, D. G., Hughes, A. N., Krysa, E. and Magnuson, V. R., *Organometallics*, 1993, **12,** 4721.
13. (a) Ahmed, S., Holah, D. G., Hughes, A. N. and Markewich, R. T., *Polyhedron*, 1993, **12,** 1101; (b) Elliot, D. J., Holah, D. G., Hughes, A. N., Magnuson, V. R., Moser, I. M. and Puddephatt, R. J., *Bull. Soc. Chim. Fr.*, 1992, **129,** 676; (c) Elliot, D. J., Holah, D. G., Hughes, A. N., Magnuson, V. R., Moser, I. M., Puddephatt, R. J. and Xu, W., *Organometallics*, 1991, **10,** 3933; (d) Elliot, D. J., Levy, C. J., Puddephatt, R. J., Holah, D. G., Hughes, A. N., Magnuson, V. R. and Moser, I. M., *Inorg. Chem.*, 1990, **29,** 5014; (e) Elliot, D. J., Ferguson, G., Holah, D. G., Hughes, A. N., Jennings, M. C., Magnuson, V. R., Potter, D. and Puddephatt, R. J., *Organometallics*, 1990, **9,** 1336; (f) Elliot, D. J., Holah, D. G., Hughes,

A. N., Mirza, H. A. and Zawada, E., *J. Chem. Soc, Chem. Commun.*, 1990, 32; (g) Holah, D. G., Hughes, A. N., Magnuson, V. R., Mirza, H. A. and Parker, K. O., *Organometallics*, 1988, **7**, 1233.

14. Cromer, D. T. and Waber, J. T., *International Tables for X-ray Crystallography*, Vol. 4. Kynoch Press, Birmingham, 1974.
15. Leoni, P., *Organometallics*, 1993, **12**, 2432, and refs therein.
16. Albinati, A., *Inorg. Chim. Acta*, 1977, **22**, L31.
17. Albinati, A., Carturan, G. and Musco, A., *Inorg. Chim. Acta*, 1976, **16**, L3.
18. Moor, A., Pregosin, P. S. and Venanzi, L. M., *Inorg. Chim. Acta*, 1982, **61**, 135.
19. Hau, L., Spivak, G. J., Xiao, J., Vittal, J. J. and Puddephatt, R. J., *J. Am. Chem. Soc.*, 1995, **117**, 7011.