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Mechanism of Formation of the Cluster Complex $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^{2+}$ and Its Halide Adducts

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The cluster complex $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$, **1**, dppm = $Ph_2PCH_2PPh_2$, is prepared in 90% yield by reaction of $Pd(OAc)_2$, dppm, and CO in acetone/CF_3CO_2H/H_2O solvent, followed by recrystallization in the presence of NH_4PF_6. The complexes $[Pd(O_2CCF_3)_2(dppm)]$, **3**, $[Pd_2(O_2CCF_3)_2(\mu\text{-dppm})_2]$, **4**, $[Pd_2(O_2CCF_3)_2(\mu\text{-}CO)(\mu\text{-dppm})_2]$, **5**, and $[Pd_3(\mu\text{-}O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]$, **2a**, have been identified in the reaction medium by using ^{31}P NMR to monitor the reactions. It is suggested that a short-lived palladium (0)–dppm complex is formed, which may then react with **3** to give **4** or **5**, and then with **4** or **5** to give **2a**. The cluster complex $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ is coordinatively unsaturated and reacts quantitatively with anions X^- to give $[Pd_3(\mu\text{-}X)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$, **2a**, X = O_2CCF_3; **2b**, X = Cl; **2c**, X = Br; **2d**, X = I. It is shown by a series of spectral titrations that the binding ability follows the series $I^- > Br^- > Cl^- > CF_3CO_2^-$ and that a ligand higher in the sequence will quantitatively displace one lower in the sequence. The structure of **2d** has been determined by X-ray structure analysis. Crystals of $[Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][O_2CCF_3]\cdot(CH_3)_2CO\cdot H_2O$ (**2d**) are monoclinic, space group $P2_1/n$, with $a = 15.009(2)$ Å, $b = 26.851(4)$ Å, $c = 18.911(2)$ Å, $\beta = 94.22(1)°$, $R = 0.043$ for 10 018 observed reflections $[I > 3\sigma(I)]$. The Pd–I bonds, with lengths of 2.951(1)–3.083(1) Å, appear to be unusually weak.

Introduction

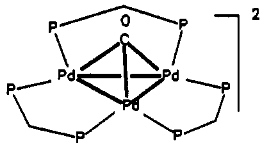
The coordinatively unsaturated cluster complexes $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, **1**, M = Pd or Pt, dppm = $Ph_2PCH_2PPh_2$, are perhaps the best mimics for triangles of metal atoms on a metal surface. They bind many small organic and inorganic molecules, and there are close analogies to chemisorption of these molecules on metal surfaces, in terms of both structure and dynamics.[2a] Because of their interesting chemistry, a detailed study of the mechanism of formation of the cluster complexes has been carried out and is reported below. This article also gives details of the synthesis of the complex **1**, M = Pd, and a study of its adducts with halide and trifluoroacetate ions. Preliminary accounts of parts of this work have been published.[2b–4]

Results and Discussion

Synthesis of Pd_3 Clusters. After numerous unsuccessful attempts to synthesize trinuclear palladium clusters containing the $Pd_3(\mu\text{-dppm})_3$ unit, a very simple, high-yield synthesis was found.[2] It relies on the reaction of palladium(II) acetate with dppm and CO in aqueous acetone containing excess trifluoroacetic acid. The overall stoichiometry of the reaction is shown in eq 1. This predicts formation of 0.67 mol of CO_2 for each mole of $Pd(OAc)_2$ used, while 0.78 mol of CO_2 was observed experimentally. The agreement is reasonable, and the slight discrepancy may indicate some catalysis of the water gas shift reaction by intermediate palladium complexes.

$$3Pd(OAc)_2 + 3dppm + 3CO + 2H_2O + 2CF_3CO_2H \rightarrow \underset{\textbf{2a}}{[Pd_3(O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+} + CF_3CO_2^- + 2CO_2 + 6AcOH \quad (1)$$

The reaction can be carried out at room temperature using 1 atm of CO and then takes about 1 day for completion or it can be carried out in a pressure reactor using 10 atm of CO and is complete in 10 h. The isolated yield of cluster is ca. 90% by either method.



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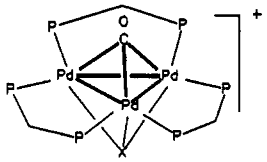
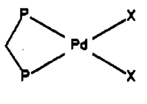


2a, X = CF_3CO_2

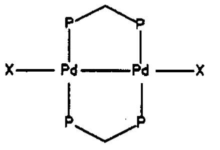
2b, X = Cl

2c, X = Br

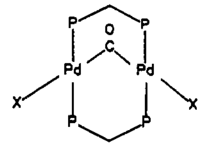
2d, X = I



3, X = CF_3CO_2



4, X = CF_3CO_2



5, X = CF_3CO_2

In the trifluoroacetate derivative, **2a** (eq 1), one trifluoroacetate is weakly bound to the Pd_3 triangle while the other is present as a counterion (see later).[2a] However, treatment with $NH_4[PF_6]$ gives the cluster $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, **1a**, as the salt with $[PF_6]^-$ counterions.

Mechanism of Cluster Formation. The formation of clusters from simple precursors under such mild

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(1) (a) University of Western Ontario. (b) University of Glasgow.

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conditions as described above is unusual and gave an opportunity to study the reaction route. The initial reaction of $Pd(OAc)_2$ with dppm in the presence of excess trifluoroacetic acid gives $[Pd(O_2CCF_3)_2(dppm)]$, **3**, which can be isolated in high yield. It contains chelating dppm and monodentate trifluoroacetate groups as shown by the spectroscopic data and by a recent X-ray structure determination.[5] Further studies of the reaction were carried out using preformed **3**, for simplicity.

The reduction of **3**, in acetone solution containing free trifluoroacetic acid in a 10-mm NMR tube, by CO/H_2O was monitored by using ^{31}P NMR spectroscopy. If 1 mol of CO was used for each mole of **3**, the reaction occurred according to eq 2.

$$2[Pd(O_2CCF_3)_2(dppm)] + CO + H_2O \rightarrow [Pd_2(O_2CCF_3)_2(\mu\text{-dppm})_2] + CO_2 + 2CF_3CO_2H \quad (2)$$

The singlet in the ^{31}P NMR spectrum due to **3** at $\delta = -48.2$ ppm decayed over a period of 6 h while a new singlet due to $[Pd_2(O_2CCF_3)_2(\mu\text{-dppm})_2]$, **4**, grew at $\delta = -9.4$ ppm. If instead excess CO was used, the peak at $= -9.4$ ppm was not observed but the decay of the peak at $\delta = -48.2$ ppm was accompanied by growth of a peak at $\delta = 18.3$ ppm due to $[Pd_2(O_2CCF_3)_2(\mu\text{-CO})(\mu\text{-dppm})_2]$, **5**. The complexes **4** and **5** could be isolated in pure form from these reaction mixtures and characterized by comparison of their spectroscopic properties with those of similar complexes.[6,7] The complexes **4** and **5** are easily interconverted by addition or loss of CO (eq 3). These observations[3] have recently been confirmed by two other research groups, and the structures of both **4** and **5** have been determined crystallographically.[8,9]

$$\underset{\mathbf{4}}{[Pd_2(O_2CCF_3)_2(\mu\text{-dppm})_2]} + CO \quad \underset{\mathbf{5}}{[Pd_2(O_2CCF_3)_2(\mu\text{-CO})(\mu\text{-dppm})_2]} \quad (3)$$

In the reaction of **3** with excess CO, complex **5** is not formed quantitatively since, as the concentration of **5** builds up, further reaction occurs to give **2a**, which is characterized by a singlet in the ^{31}P NMR spectrum at $\delta = -16.5$ ppm. A series of ^{31}P NMR spectra recorded during one such reaction is shown in Figure 1, and it can be seen that formation of **2a** is essentially quantitative after 15 h at room temperature. The pure complex **4** is reduced under the same conditions to give **2a**, but the reaction is somewhat slower, taking 24 h to reach completion. Qualitatively, the reaction of **3** or **4** to give **2a** occurs more rapidly if the concentration of water is increased but is retarded by increasing the concentration of CF_3CO_2H. In the absence of CF_3CO_2H, some palladium metal was formed. The system is too complex to permit a detailed kinetic analysis. The overall stoichiometry for reduction of **4** is given in eq 4, $X = CF_3CO_2$.

$$3[Pd_2X_2(\mu\text{-dppm})_2] + 3CO + H_2O \rightarrow 2[Pd_3(\mu_3\text{-X})(\mu_3\text{-CO})(\mu\text{-dppm})_3]X + 2HX + CO_2 \quad (4)$$

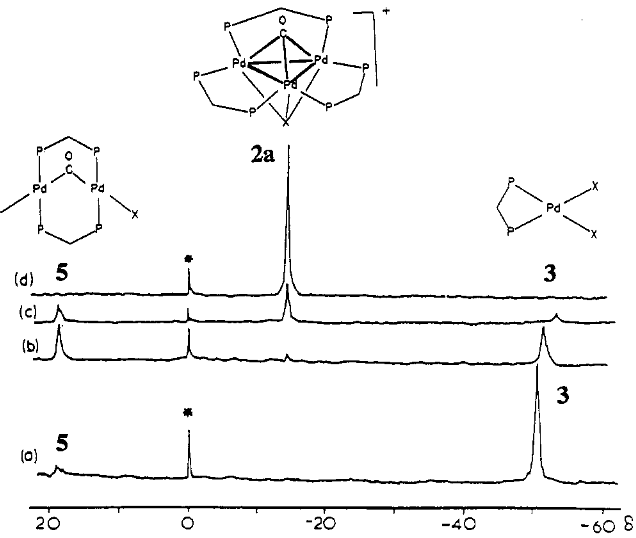

Figure 1. ^{31}P NMR spectra of the reaction mixture obtained by reaction of complex **3** with CO/H_2O in acetone at times: (a) 0; (b) 1 h; (c) 4 h; (d) 15 h. The numbers **2a**, **3**, and **4** label the peaks due to these complexes and the peak labeled with an asterisk (*) is due to the reference $(MeO)_3PO$.

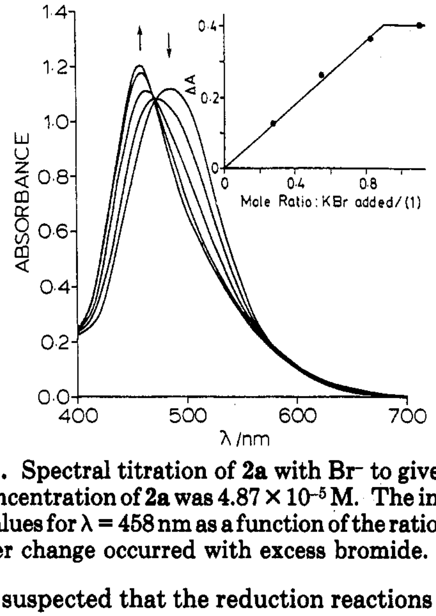

Figure 2. Spectral titration of **2a** with Br^- to give **2c**. The initial concentration of **2a** was 4.87×10^{-5} M. The inset shows the ΔA values for $\lambda = 458$ nm as a function of the ratio $[Br^-]/\mathbf{2a}$; no further change occurred with excess bromide.

It was suspected that the reduction reactions gave one or more intermediate, short-lived palladium(0) complexes, $[Pd(dppm)(CO)_x]$ or $[Pd_2(\mu\text{-dppm})_2(CO)_y]$, which then reacted rapidly with Pd(II) or $Pd(I)_2$ species. Therefore some model reactions were carried out with preformed $[Pd_2(\mu\text{-dppm})_3]$.[10] The reactions with complexes **3** and **4** are shown in eqs 5 and 6, $X = CF_3CO_2$.

$$2[PdX_2(dppm)] + [Pd_2(\mu\text{-dppm})_3] + CO \rightarrow [Pd_3(X)(\mu_3\text{-CO})(\mu\text{-dppm})_3]X + [Pd(dppm)_2]X_2 \quad (5)$$

$$4[Pd_2X_2(\mu\text{-dppm})_2] + [Pd_2(\mu\text{-dppm})_3] + 3CO \rightarrow 3[Pd_3(X)(\mu_3\text{-CO})(\mu\text{-dppm})_3]X + [Pd(dppm)_2]X_2 \quad (6)$$

These reactions show that the palladium(0) complex will react rapidly with either **3** or **4** to give **2a**. Some of the very stable, inert complex $[Pd(dppm)_2]^{2+}$ is formed, as the trifluoroacetate salt, as a result of the presence of an additional dppm ligand in the palladium(0) complex

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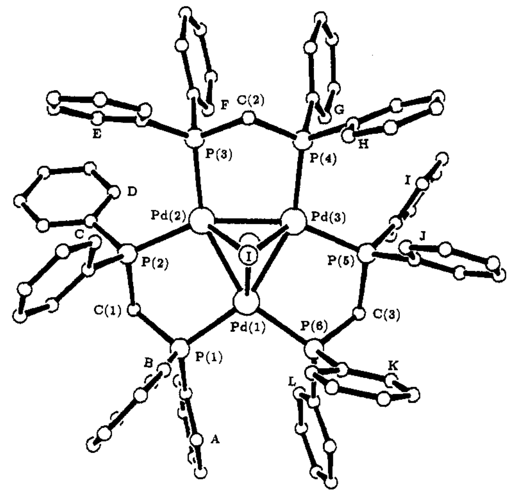

Figure 3. The **2d** cation viewed down the normal to the Pd_3 plane. Phenyl carbon atoms are numbered in sequence $C(n1)\cdots C(n6)$, (n = A–L), starting with the P-substituted atom. Ring labels are placed adjacent to $C(n2)$. Atoms are represented by spheres of arbitrary size.

$[Pd_2(\mu\text{-dppm})_3]$. No intermediates were detected when these reactions were monitored by ^{31}P NMR spectroscopy. These observations lend support to the hypothesis of palladium(0) intermediates in the cluster formation.

The complex $[Pd_2(\mu\text{-dppm})_3]$ can also act as a precursor to **2a** according to eq 7, X = CF_3CO_2.

$$3[Pd_2(\mu\text{-dppm})_3] + 8HX + CO \rightarrow [Pd_3(X)(\mu_3\text{-CO})(\mu\text{-dppm})_3]X + 3[Pd(dppm)_2]X_2 + 4H_2 \quad (7)$$

Overall, it seems that in the acetone/CF_3CO_2H/H_2O/CO system used, the stable product when there is a 1:1 ratio of Pd:dppm is the cluster **2a**, though if the ratio of Pd:dppm = 1:2 the stable complex is $[Pd(dppm)_2]^{2+}$. The formation of **2a** from $[Pd_2(\mu\text{-dppm})_3]$ involves formal oxidation of Pd(0) to Pd(+2/3) and occurs rapidly, while the formation of **2a** from $[PdX_2(dppm)]$ or $[Pd_2X_2(\mu\text{-dppm})_2]$ and CO involves reduction of palladium from Pd(II) or Pd(I) to Pd(2/3) and occurs more slowly. However, the reduction of $[PdX_2(dppm)]$ or $[Pd_2X_2(\mu\text{-dppm})_2]$ by Pd(0) is rapid. In addition, the rearrangement of dppm ligands which must occur as the nuclearity changes and which requires cleavage and formation of Pd–P bonds must also occur rapidly. Thus it seems that the slow steps in the overall reaction of eq 1 must be the steps which require reduction by CO/H_2O and also that complex **3** is reduced more easily than **4** or **5**. The formation of Pd(0) species probably occurs according to eq 8 or 9, X = CF_3CO_2. It is not surprising that (9) is slower than (8) since it involves reduction of palladium(I).

$$[PdX_2(dppm)] + (x + 1)CO + H_2O \rightarrow [Pd(CO)_x(dppm)] + 2HX + CO_2 \quad (8)$$

$$[Pd_2X_2(\mu\text{-dppm})_2] + (y + 1)CO + H_2O \rightarrow [Pd_2(CO)_y(\mu\text{-dppm})_2] + 2HX + CO_2 \quad (9)$$

The nature of these proposed Pd(0) species is uncertain. However, it should be noted that nickel forms stable complexes such as $[Ni(CO)_2(dppm\text{-}P)_2]$ and $[Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2]$, with the mononuclear and binuclear derivatives interconverting easily, and that mixed carbonyl(phosphine) complexes of palladium(0) are known.[11] Hence it is at least likely that carbonyl(dppm) derivatives of Pd(0) are formed and that they would be labile. The reductions do not occur if X = halide rather than trifluoroacetate, which is attributed to the ability of CO to displace CF_3CO_2 but not halide from palladium, to give a cationic carbonyl which is then attacked by water. There are numerous precedents for this mechanism of reduction by CO/H_2O and it is often a key step in catalysis of the water gas shift reaction.[12] The likely steps are shown for reduction of $[PdX_2(dppm)]$ in eq 10, X = CF_3CO_2.

$$[PdX_2(dppm)] \xrightarrow{CO} [PdX(CO)(dppm)]^+X^- \xrightarrow{H_2O,\,-HX} [PdX(CO_2H)(dppm)] \xrightarrow{-CO_2} [PdXH(dppm)] \xrightarrow{xCO,\,-HX} [Pd(CO)_x(dppm)] \quad (10)$$

Finally, the products are formed by reaction of the Pd(0) species, which may be either mononuclear or binuclear, with complex **3** and then **4** or **5**, perhaps according to eqs 11 and 12, X = CF_3CO_2. The mechanism proposed above suggests a route to prepare mixed Pd_2Pt or $PdPt_2$ clusters, for example by reaction of $[PdX_2(dppm)]/[Pt_2(\mu\text{-dppm})_3]$/CO. Several such possible combinations were tested, but none gave the mixed clusters $[Pd_nPt_{3-n}(\mu_3\text{-X})(\mu_3\text{-CO})(\mu\text{-dppm})_3]X$. Instead, mixtures of the homonuclear clusters (along with unidentified complexes) were usually formed as identified by their ^{31}P NMR spectra.

$$[PdX_2(dppm)] + [Pd(CO)_x(dppm)] \xrightarrow{-xCO} [Pd_2X_2(\mu\text{-dppm})_2] \xrightarrow{CO} [Pd_2X_2(\mu\text{-CO})(\mu\text{-dppm})_2] \quad (11)$$

$$[Pd_2X_2(\mu\text{-CO})(\mu\text{-dppm})_2] + [Pd(CO)_x(dppm)] \xrightarrow{-xCO} [Pd_3(\mu_3\text{-X})(\mu_3\text{-CO})(\mu\text{-dppm})_3]X \quad (12)$$

To summarize, the reduction of the Pd(II) complex **3** by CO/H_2O is rapid and gives an equilibrium mixture of the $Pd(I)_2$ complexes **4** and **5**, which are reduced more slowly to give the $Pd(2/3)_3$ cluster **2a**. Qualitative rate data indicate that short-lived Pd(0) complexes are formed as primary reduction products, but they were not formed in high enough concentration for direct detection to be possible. The good leaving group trifluoroacetate is needed for the reduction of **3** or **4** to occur; this is due to the requirement for an intermediate cationic carbonyl to be formed, which then undergoes nucleophilic attack by water to give CO_2, HX, and the Pd(0) intermediate. Model studies with preformed Pd(0) support this reaction route, but the reactions are more complex than expected. Within

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Table I. Selected Distances (Å) and Angles (deg)

Pd(1)–Pd(2)	2.599(1)	Pd(1)–Pd(3)	2.599(1)
Pd(1)–I	2.951(1)	Pd(1)–P(1)	2.320(2)
Pd(1)–P(6)	2.316(2)	Pd(1)–C(CO)	2.137(8)
Pd(2)–Pd(3)	2.591(1)	Pd(2)–I	3.083(1)
Pd(2)–P(2)	2.317(2)	Pd(2)–P(3)	2.309(2)
Pd(2)–C(CO)	2.192(8)	Pd(3)–I	3.031(1)
Pd(3)–P(4)	2.301(2)	Pd(3)–P(5)	2.325(2)
Pd(3)–C(CO)	2.160(8)	O(CO)–C(CO)	1.114(9)
O(S)–C(1S)	1.255(15)	C(1S)–C(2S)	1.50(3)
C(1S)–C(3S)	1.493(18)	O(1A)–C(1A)	1.243(13)
O(2A)–C(1A)	1.054(15)	F(1A)–C(2A)	1.285(16)
F(2A)–C(2A)	1.168(15)	F(3A)–C(2A)	1.275(12)
C(1A)–C(2A)	1.692(12)	P(1)···P(2)	3.039(3)
P–CH_2	1.823(8)–1.848(8), mean 1.836(4)	P(3)···P(4)	3.015(3)
		P(5)···P(6)	3.029(3)
P–C(phenyl)	1.809(8)–1.828(10), mean 1.819(2)		

Pd(2)–Pd(1)–Pd(3)	59.8(1)	Pd(2)–Pd(1)–I	67.2(1)
Pd(2)–Pd(1)–P(1)	95.8(1)	Pd(2)–Pd(1)–P(6)	153.3(1)
Pd(2)–Pd(1)–C(CO)	54.1(2)	Pd(3)–Pd(1)–I	65.9(1)
Pd(3)–Pd(1)–P(1)	155.3(1)	Pd(3)–Pd(1)–P(6)	93.5(1)
Pd(3)–Pd(1)–C(CO)	53.2(2)	I–Pd(1)–P(1)	102.6(1)
I–Pd(1)–P(6)	105.2(1)	I–Pd(1)–C(CO)	109.4(2)
P(1)–Pd(1)–P(6)	110.9(1)	P(1)–Pd(1)–C(CO)	117.6(3)
P(6)–Pd(1)–C(CO)	110.1(3)	Pd(1)–Pd(2)–Pd(3)	60.1(1)
Pd(1)–Pd(2)–I	61.9(1)	Pd(1)–Pd(2)–P(2)	95.0(1)
Pd(1)–Pd(2)–P(3)	154.7(1)	Pd(1)–Pd(2)–C(CO)	52.1(2)
Pd(3)–Pd(2)–I	63.9(1)	Pd(3)–Pd(2)–P(2)	154.8(1)
Pd(3)–Pd(2)–P(3)	95.4(1)	Pd(3)–Pd(2)–C(CO)	52.9(2)
I–Pd(2)–P(2)	102.1(1)	I–Pd(2)–P(3)	115.5(1)
I–Pd(2)–C(CO)	103.5(2)	P(2)–Pd(2)–P(3)	109.8(1)
P(2)–Pd(2)–C(CO)	116.7(2)	P(3)–Pd(2)–C(CO)	109.2(2)
Pd(1)–Pd(3)–Pd(2)	60.1(1)	Pd(1)–Pd(3)–I	62.7(1)
Pd(1)–Pd(3)–P(4)	153.8(1)	Pd(1)–Pd(3)–P(5)	96.3(1)
Pd(1)–Pd(3)–C(CO)	52.4(2)	Pd(2)–Pd(3)–I	66.0(1)
Pd(2)–Pd(3)–P(4)	95.1(1)	Pd(2)–Pd(3)–P(5)	154.9(1)
Pd(2)–Pd(3)–C(CO)	54.0(2)	I–Pd(3)–P(4)	117.7(1)
I–Pd(3)–P(5)	96.7(1)	I–Pd(3)–C(CO)	106.0(2)
P(4)–Pd(3)–P(5)	109.3(1)	P(4)–Pd(3)–C(CO)	107.3(3)
P(5)–Pd(3)–C(CO)	120.1(3)	Pd(1)–I–Pd(2)	51.0(1)
Pd(1)–I–Pd(3)	51.5(1)	Pd(2)–I–Pd(3)	50.1(1)
Pd(1)–P(1)–C(1)	108.4(3)	Pd(2)–P(2)–C(1)	109.3(3)
Pd(2)–P(3)–C(2)	107.7(3)	Pd(3)–P(4)–C(2)	109.3(3)
Pd(3)–P(5)–C(3)	110.1(3)	Pd(1)–P(6)–C(3)	109.3(3)
Pd(1)–C(CO)–Pd(2)	73.8(3)	Pd(1)–C(CO)–Pd(3)	74.4(3)
Pd(1)–C(CO)–O(CO)	143.4(6)	Pd(2)–C(CO)–Pd(3)	73.1(3)
Pd(2)–C(CO)–O(CO)	131.9(6)	Pd(3)–C(CO)–O(CO)	132.3(6)
P(1)–C(1)–P(2)	111.7(4)	P(3)–C(2)–P(4)	110.1(4)
P(5)–C(3)–P(6)	111.4(4)	O(S)–C(1S)–C(2S)	121.8(12)
O(S)–C(1S)–C(3S)	115.0(11)	C(2S)–C(1S)–C(3S)	123.2(12)
O(1A)–C(1A)–O(2A)	129.8(13)	O(1A)–C(1A)–C(2A)	105.0(10)
O(2A)–C(1A)–C(2A)	120.5(9)	F(1A)–C(2A)–F(2A)	107.7(13)
F(1A)–C(2A)–F(3A)	102.6(10)	F(1A)–C(2A)–C(1A)	112.4(10)
F(2A)–C(2A)–F(3A)	107.9(12)	F(2A)–C(2A)–C(1A)	116.0(10)
F(3A)–C(2A)–C(1A)	109.3(8)	Pd–P–C(phenyl)	115.0(3)–122.2(3)
		C–P–C	99.4(4)–105.8(4)

each oxidation state, it seems that thermodynamic factors may be important in determining the observed products. Nevertheless, this work establishes the overall route to cluster formation.

Coordination Chemistry of the Pd_3 Cluster, 1. The cluster complex $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, **1**, has 42 electrons in the valence shells of palladium, and each palladium has a 16-electron configuration. It is therefore coordinatively unsaturated and is expected to form coordination complexes. Complex **1**, as the $[PF_6]^-$ salt, has $\delta(^{31}P) = -6.9$ ppm in acetone solution, but this resonance moves to the region $\delta = -11.8$ to -12.8 on addition of NaX, where X = CF_3CO_2, Cl, Br, or I, as the clusters $[Pd_3(\mu_3\text{-}X)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$, **2a**, X = CF_3CO_2; **2b**, X = Cl; **2c**, X = Br; **2d**, X = I, are formed. There is also a significant color change on addition of these salts, though the colors of all of the palladium cluster solutions are different shades of purple.

The structures of the clusters $[Pd_3(\mu_3\text{-}O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]\cdot 3Me_2CO$ and $[Pd_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]\cdot H_2O$ have been reported earlier.[2,4] It was noted that the Pd–X bond lengths of the $Pd_3(\mu_3\text{-}X)$ groups were long, and it was not clear if there was any significant covalent bonding involved or if the bonds were essentially ionic in character. A more detailed study of the complexation was therefore made. Reaction of **2a**$[CF_3CO_2]$ with 1 equiv of a halide salt, followed by crystallization, gave the corresponding cluster $[Pd_3(\mu_3\text{-}X)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]$, showing that halides would displace trifluoroacetate from the coordination sphere of palladium, while reaction with $NH_4[PF_6]$ in acetone gave **2a**$[PF_6]$ and in methanol gave **1**$[PF_6]_2$. The molar conductivities ($ohm^{-1}\ cm^2\ mol^{-1}$) of these complexes as 2×10^{-4} M solutions in methanol were **1**$[PF_6]_2$, 328; **2a**$[PF_6]$, 133; **2a**$[CF_3CO_2]$, 127; **2b**$[CF_3CO_2]$, 83; **2c** and **2d**$[CF_3CO_2]$, 81. Clearly, **1**$[PF_6]_2$ is a 2:1 conductor while the salts of **2** are 1:1 conductors, showing that the $Pd_3(\mu_3\text{-}X)$ groups in **2** remain intact even in dilute solution in methanol.

The halide adducts were studied further by using UV-visible spectroscopy. Spectral titration of **2a** with each halide confirmed the 1:1 stoichiometry required for formation of **2b**–**d**. A typical spectral titration is illustrated in Figure 2. In addition, titration of **2b** with bromide gave **2c**, and titration of **2c** with iodide gave **2d** quantitatively, showing that one halide can easily displace another and that the order of complexing ability is $I^- > Br^- > Cl^- > CF_3CO_2^-$. This is the order expected for coordination to a soft metal acceptor and suggests that there is some covalency in the PdX bonds.

The structure of complex **2d** was further characterized by X-ray analysis of its trifluoroacetate salt, crystals of which proved to contain one molecule of acetone and one of water per cation/anion pair. The structure of the cation (Figure 3 and Table I) is strikingly similar to those of **2a** and **2b** determined previously.[2,4] It is based on a nearly equilateral triangle of metal atoms [Pd–Pd 2.591(1)–2.599(1) Å], and the variation in Pd–P bond lengths, 2.301(2)–2.325(2) Å, is slight. Two of the dppm methylenic carbon atoms, C(1) and C(3), are displaced toward the carbonyl-capped side of the metal triangle, whereas the displacement of C(2) is in the opposite direction; consequently, the inner $Pd_3(\mu_3\text{-}I)(\mu_3\text{-}I)(PCH_2P)_3$ core of the cation approximates to C_s symmetry, the mirror plane passing through the Pd(1), I, and C(2) atoms and through the midpoint of the Pd(2)–Pd(3) bond.

The $Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)$ unit (Figure 4) is the most interesting structural feature of **2d**, especially since there is no evidence of the halide/carbonyl disorder which precluded accurate determination of the geometry of **2b**.[4] The Pd_3 triangle is triply-bridged by both the iodo and carbonyl ligands. Both ligands show *small* but apparently correlated deviations from an exactly symmetrical bridging arrangement; both interact most strongly with Pd(1) and least strongly with Pd(2). Thus, the Pd(1)–C(CO) distance [2.14(1) Å] is very slightly shorter and the Pd(1)–C(CO)–O(CO) angle [143(1)°] more obtuse than the corresponding distances [2.19(1) and 2.16(1) Å] and angles [132(1) and 132(1)°] involving Pd(2) and Pd(3). Similarly, the Pd(1)–I distance of 2.951(1) Å is shorter than those involving Pd(2)

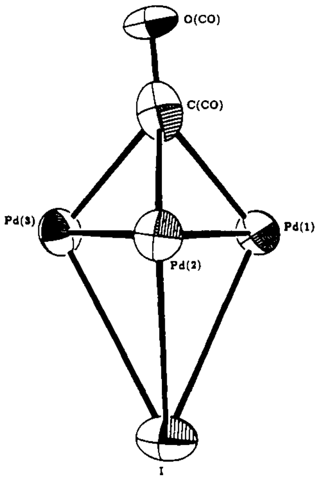

Figure 4. A view of the $Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)$ unit in **2d**; 50% vibrational ellipsoids are displayed.

and Pd(3) [3.083(1) and 3.031(1) Å]. In the pseudohalide analog $[Pt_3(SCN)(CO)(\mu\text{-dppm})_3]^+$ the carbonyl group is displaced from the symmetrical μ_3 position toward the atom which interacts most strongly with the SCN^- ligand; this effect, which is believed to be electronic in origin, is much greater [Pt–CO 2.04(1)–2.18(1) Å] than that found in the μ_3-I complex, as is expected since the variation in Pt–S(SCN) distances is much greater than that shown by the Pd–I distances in **2d**.[13]

As far as we are aware, complex **2d** contains the longest Pd–I bonds so far reported [2.95(1)–3.083(1) Å]. In *fac*-$[PdIMe_3(2,2'\text{-bipyridyl})]$, the terminal Pd–I bond length is 2.834(1) Å;[14] other terminal Pd–I distances, occurring mainly in Pd(II) species, lie in the range 2.55–2.71 Å, with a mean of 2.63 Å for 44 such bonds.[15] For $Pd_2(\mu_2\text{-}I)$ systems, the longest Pd–I distance reported[16] is 2.740(5) Å, and in general, the bridging distances are not much greater than for terminal Pd–I bonds.[15] Relatively few systems containing $M_3(\mu_3\text{-}I)$ units, where M is a platinum group metal, have been reported, and none involves palladium. Two $Rh_3(\mu_3\text{-}I)$ complexes, each with only two Rh–Rh bonds, have been described; the Rh–I distances are 2.706(2)–2.812(2) Å and 2.801(2)–3.149(2) Å.[17] In $[Ni_3(\mu_3\text{-}I)(\mu_3\text{-}CNMe)(CNMe)_2(\mu\text{-dppm})_2]^+$, the Ni–I distances are 2.730(2)–2.783(2) Å,[18] and in $[Pt(\mu_3\text{-}I)Me_3]_4$, where there is no direct Pt–Pt bonding, the Pt–I bond lengths are 2.806(2)–2.825(2) Å.[19] Finally, in $[Au_3(\mu_3\text{-}I)(\mu_3\text{-}AuI)(\mu\text{-dppm})_3]$ there are very long triply-bridging Au–I distances of 3.13–3.67 Å.[20]

Experimental Section

General methods have been reported elsewhere.[13]

$[Pd(O_2CCF_3)_2(dppm)]$. A mixture of $Pd(OAc)_2$ (1.17 mmol) and dppm (1.19 mmol) was stirred in acetone (20 mL) and CF_3CO_2H (5 mL) for 3 h. The solvent was evaporated under vacuum, and the residue was crystallized from acetone/pentane to give colorless crystals. Yield 73%. Anal. Calcd for $C_{29}H_{22}F_6O_4P_2Pd$: C, 48.6; H, 3.1. Found: C, 48.7; H, 3.1. NMR: $\delta(^1H) = 4.69$ [t, $^2J(PH) = 11$, CH_2P_2]; $\delta(^{31}P) = -48.2$ [s, P]. IR: $\nu(C{=}O) = 1660\ cm^{-1}$.

$[Pd_2(CF_3CO_2)_2(\mu\text{-dppm})_2]$. CO was bubbled through a mixture of $Pd(OAc)_2$ (5.68 mmol) and dppm (5.85 mmol) in acetone (50 mL), trifluoroacetic acid (10 mL), and H_2O (3 mL), and the reaction was allowed to proceed for 3 h. The solvent was then removed under vacuum, and the resultant red oil was crystallized from cold acetone solution. Yield ~39%. Anal. Calcd for $C_{54}H_{44}F_6O_4P_4Pd_2$: C, 53.7; H, 3.7. Found: C, 54.1; H, 3.7. NMR: $\delta(^1H) = 4.35$ [quint, $^2J(PH) + {}^4J(PH) = 4$, CH_2P_2]; $\delta(^{31}P) = -9.4$ [s, P]. IR: $\nu(C{=}O) = 1660\ cm^{-1}$.

$[Pd_2(CF_3CO_2)_2(\mu\text{-}CO)(\mu\text{-dppm})_2]$. A sample of $[Pd_2(CF_3CO_2)_2(\mu\text{-dppm})_2]$ (0.04 mmol) was dissolved in benzene (~20 mL) under $N_2(g)$. The $^{31}P\{^1H\}$ NMR and IR spectra were recorded. CO(g) was then purged through the solution, and the $^{31}P\{^1H\}$ NMR and IR spectra were recorded. $[Pd_2(CF_3CO_2)_2(\mu\text{-}CO)(\mu\text{-dppm})_2]$ gave $\delta(P) = +18$ ppm and $\nu(CO) = 1712\ cm^{-1}$. The product was isolated by precipitation with pentane while maintaining the CO atmosphere. Anal. Calcd for $C_{55}H_{44}F_6O_5P_4Pd_2$: C, 53.3; H, 3.75. Found: C, 53.6; H, 3.5. NMR: $\delta(^1H) = 3.11$ and 3.68 [m, each $^2J(H^aH^b) = 14.5$, $CH^aH^bP_2$]; $\delta(^{13}C) = 230.0$ [quint, $^2J(PC) = 6$, μ-CO].

$[Pd_3(O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]$. CO was bubbled through a mixture of $Pd(OAc)_2$ (0.472 mmol) and dppm (0.486 mmol) in acetone (20 mL), trifluoroacetic acid (5 mL), and H_2O (2 mL). The mixture was allowed to react under the static CO atmosphere for 16 h. The solvent was removed under vacuum, and the resultant dark red oil was crystallized by slow diffusion of hexane into a solution in acetone/toluene. Yield 90%.

One sample crystallized in this manner was characterized by X-ray crystallography as $[Pd_3(O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]\cdot 3(Me_2CO)$. Anal. Calcd for $C_{89}H_{84}O_8F_6P_6Pd_3$: C, 56.2; H, 4.45; F, 6.0. Found: C, 56.95; H, 4.3; F, 5.4. NMR: $\delta(^1H) = 4.75$ and 5.00 [m, $^2J(H^aH^b) = 14$, $CH^aH^bP_2$]; $\delta(^{31}P) = -12.7$ [s, P]. IR: $\nu(CO) = 1820\ cm^{-1}$.

The cluster was also prepared by using $[Pd(CF_3CO_2)_2(dppm)]$ or $[Pd_2(CF_3CO_2)_2(\mu\text{-dppm})_2]$ as precursors. These reactions were carried out in acetone–H_2O mixtures similar to that of the previous synthesis without the addition of any excess dppm ligand or the presence of trifluoroacetic acid. Product isolation and characterization were also conducted as above.

Observation of Cluster Formation by $^{31}P\{^1H\}$ NMR. Reaction of $[Pd(CF_3CO_2)_2(dppm)]$. $[Pd(CF_3CO_2)_2(dppm)]$ (0.103 mmol) was dissolved in acetone (3 mL), trifluoroacetic acid (0.5 mL), and H_2O (0.5 mL) under N_2 in a 10-mm tube sealed with a rubber septum. The $^{31}P\{^1H\}$ NMR spectrum was recorded. CO was then purged through this system via a syringe needle, and the $^{31}P\{^1H\}$ NMR spectrum was recorded at various time intervals over a 15-h period. The CO atmosphere was maintained by bubbling CO through the solution prior to each $^{31}P\{^1H\}$ NMR spectral run.

Reaction of $[Pd_2(CF_3CO_2)_2(\mu\text{-dppm})_2]$. Three experiments were carried out with $[Pd_2(CF_3CO_2)_2(\mu\text{-dppm})_2]$ (0.1 mmol) dissolved in: (1) acetone (3 mL), CF_3COOH (1.5 mL); (2) acetone (3 mL), CF_3COOH (0.5 mL); and (3) acetone (3 mL), CF_3COOH (0.5 mL), H_2O (0.2 mL) in a 10-mm NMR tube. The reactions with CO were monitored as above.

Reaction of $[Pd_2(\mu\text{-dppm})_3]$ and $[Pd(CF_3CO_2)_2(dppm)]$. $[Pd_2(\mu\text{-dppm})_3]$ (0.070 mmol) was dissolved in acetone (2 mL) under N_2 in a 10-mm NMR tube, and the $^{31}P\{^1H\}$ NMR spectrum was recorded. $[Pd(CF_3CO_2)_2dppm]$ (0.035 mmol) was then dissolved in acetone (2 mL) under N_2 and added to the tube by syringe, followed immediately by a CO purge. The $^{31}P\{^1H\}$ NMR spectrum was then recorded.

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Table II. Crystallographic Data for $[Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][O_2CCF_3]\cdot(CH_3)_2CO\cdot H_2O$ (2d)

empirical formula	$C_{81}H_{74}F_3IO_5P_6Pd_3$
formula weight	1816.5
space group	$P2_1/n$
a, Å	15.009(2)
b, Å	26.851(4)
c, Å	18.911(2)
β, deg	94.22(1)
V, Å^3	7601(2)
molecules in unit cell	4
D_{calc}, g cm^{-3}	1.587
crystal dimensions, mm	0.51 × 0.43 × 0.35
temperature, °C	22
radiation	Mo Kα
wavelength, Å	0.71069
μ(Mo Kα), cm^{-1}	12.8
data collection range, θ (deg)	2–25
absorption factors (on F)	0.91–1.18
unique reflections with $I > 3\sigma(I)$	10,018
parameters refined	877
discrepancy factor, R	0.043
R_w	0.066
largest shift/esd ratio	0.44
range of values in final difference synthesis, e Å^{-3}	0.90 to –0.75

Reaction of $[Pd_2(\mu\text{-dppm})_2]$ and $[Pd_2(CF_3CO_2)_2(\mu\text{-dppm})_2]$. This reaction was monitored in a similar way using $[Pd_2(CF_3CO_2)_2(\mu\text{-dppm})_2]$ (0.118 mmol) and $[Pd_2(\mu\text{-dppm})_3]$ (0.061 mmol).

Reaction of $[Pd_2(\mu\text{-dppm})_3]$. $[Pd_2(\mu\text{-dppm})_3]$ (~0.06 mmol) was dissolved in acetone (3 mL), trifluoroacetic acid (0.5 mL), and H_2O (0.5 mL) under N_2 in a 10-mm NMR tube fitted with a rubber septum, and the $^{31}P\{^1H\}$ NMR spectrum was recorded. CO was then added, and the $^{31}P\{^1H\}$ NMR spectrum was recorded.

Observation of CO_2 Production by Gas Chromatography. $[Pd(CF_3CO_2)_2dppm]$ (0.756 mmol) was dissolved in acetone (54 mL), trifluoroacetic acid (1 mL), and H_2O (10 mL) under N_2 in a Parr pressure reactor (300-mL capacity). The solution was then purged three times with CO, and the mixture was left to react at 3.5 atm of pressure and room temperature. CO_2 production was observed to be completed after 24 h by using GC. Calibration for the analysis was carried out using known volumes of CO_2.

Reaction of $[Pt_2(\mu\text{-dppm})_3]$ and $[Pd(CF_3CO_2)_2(dppm)]$. $[Pt_2(\mu\text{-dppm})_3]$ (0.070 mmol) was allowed to react with $[Pd(CF_3CO_2)_2(dppm)]$ (0.073 mmol) in acetone (50 mL) under CO for 24 h. A minor product was identified as $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ by its $^{31}P\{^1H\}$ NMR spectrum, but several other unidentified species were present.

Reaction of $[Pd_2(\mu\text{-dppm})_3]$ and $[Pt(CF_3CO_2)_2(dppm)]$. This reaction was carried out similarly using $[Pd_2(\mu\text{-dppm})_3]$ (0.118 mmol) and $[Pt(CF_3CO_2)_2(dppm)]$ (0.118 mmol). The only species identified in the complex product mixture was $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$.

Reaction of $[Pt(CF_3CO_2)_2(dppm)]$ and $[Pd(CF_3CO_2)_2(dppm)]$. $[Pt(CF_3CO_2)_2(dppm)]$ (0.293 mmol) and $[Pd(CF_3CO_2)_2(dppm)]$ (0.286 mmol) were reached under CO (4.3 atm) at 100 °C in methanol (50 mL) and H_2O (4 mL) for 24 h. The pressure was released, the mixture was filtered to remove a black precipitate, the solvent was removed from the filtrate under vacuum, and the resultant crude solid was characterized by $^{31}P\{^1H\}$ NMR. A mixture of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, major, and $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, minor, were the only products identified.

$[Pd_3(\mu_3\text{-}O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]$. $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]_2$ (0.067 mmol) was dissolved in acetone (10 mL) containing excess NH_4PF_6. Benzene was added dropwise until a white precipitate formed. This precipitate was removed by filtration, and the volume of acetone in the filtrate was reduced under vacuum, yielding dark red crystals. Yield 91.5%. Anal. Calcd for $C_{78}H_{66}F_9O_3P_7Pd_3$: C, 53.3; H, 3.8. Found: C, 53.6; H, 3.8. NMR identical with the $CF_3CO_2^-$ salt.

$[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$. $[Pd_3(O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]$ (0.248 mmol) was dissolved in methanol (10 mL), and a methanolic solution (10 mL) containing excess NH_4PF_6 was added. A dark red precipitate was observed to form upon cooling and was isolated by filtration. Yield 70%. Anal. Calcd for $C_{76}H_{66}OF_{12}P_8Pd_3$: C, 51.0; H, 3.7. Found: C, 49.6; H, 3.7. NMR: $\delta(^1H) = 5.22$ [s, CH_2P_2]; $\delta(^{31}P) = -6.9$ [s, P].

$[Pd_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]$. $[Pd_3(O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]$ (0.129 mmol) was dissolved in acetone (20 mL) under N_2, and excess KCl (1.23 mmol) was added. After 24 h, the solvent was removed under vacuum. The resultant oil was dissolved in a benzene–acetone mixture (10 mL) followed by precipitation of the product, as a dark red solid, by slow diffusion of pentane (40 mL). One sample was recrystallized from a methanol–H_2O solvent system via slow evaporation and characterized as $[Pd_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]\cdot H_2O$. Anal. Calcd for $C_{78}H_{66}ClF_3O_3P_6Pd_3$: C, 56.8; H, 4.0. Found: C, 57.3; H, 3.9. NMR: $\delta(^1H) = 4.72$ and 4.89 [m, $^2J(H^aH^b) = 14$, $CH^aH^bP_2$]; $\delta(^{31}P) = -12.1$ [s, P]. IR: $\nu(CO) = 1820$ cm^{-1}.

$[Pd_3(\mu_3\text{-}Br)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]$. This was prepared similarly from $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]_2$ (0.113 mmol) and KBr (0.378 mmol) in acetone (20 mL). Yield 98%. Anal. Calcd for $C_{78}H_{66}BrF_3O_3P_6Pd_3$: C, 55.3; H, 3.9. Found: C, 55.85; H, 4.4 NMR: $\delta(^1H) = 4.77$ and 4.88 [m, each $^2J(H^aH^b) = 14$, $CH^aH^bP_2$]; $\delta(^{31}P) = -11.8$ [s, P]. IR: $\nu(CO) = 1820$ cm^{-1}.

$[Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]$. This was prepared similarly from $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]_2$ (0.083 mmol) and KI (0.277 mmol) in acetone (20 mL). Yield 96%. Anal. Calcd for $C_{78}H_{66}F_3IO_3P_6Pd_3$: C, 53.8; H, 3.8. Found: C, 53.8; H, 4.0. NMR: $\delta(^1H) = 4.84$ and 4.93 [m, each $^2J(H^aH^b) = 14$, $CH^aH^bP_2$]; $\delta(^{31}P) = -12.0$ [s, P]. IR: $\nu(CO) = 1815$ cm^{-1}.

The same complex cation, as the iodide salt, was prepared by reaction of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]_2$ (0.026 mmol) with MeI (2 mL) in benzene (20 mL) under N_2 for 3 h. A black precipitate of the product was removed by filtration. Further product was precipitated from the filtrate by slow diffusion of pentane into the benzene solution. Yield 98%. Anal. Calcd for $C_{76}H_{66}I_2OP_6Pd_3$: C, 52.0; H, 3.8. Found: C, 52.3; H, 4.1. NMR and IR data as for the trifluoroacetate salt.

UV–Visible Spectral Titrations. Halide Reactions with $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]_2$. Stock solutions of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]_2$ and potassium halide in methanol were mixed and the volume made up to 10 mL, such that the concentration of Pd_3 cluster was constant at 4.9×10^{-5} M and the mol ratio of KX/cluster = 0.25, 0.5, 0.75, 1.0, and 2.0. UV–visible spectra from 700 to 300 nm were recorded for each solution. Reactions of KBr and KI with $[Pd_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$ and of KI with $[Pd_3(\mu_3\text{-}Br)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$ were carried out in a similar way. There were no spectral changes when KCl was added to $[Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$ in methanol solution.

X-ray Analysis of $[Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)(\mu\text{-dppm})_3][O_2CCF_3]\cdot(CH_3)_2CO\cdot H_2O$ (2d). All X-ray measurements were made at 22 °C with graphite-monochromated Mo radiation on an Enraf-Nonius CAD4 diffractometer, using a crystal grown from aqueous acetone. Experimental details are summarized in Table II.

The unit cell constants were determined by the least-squares treatment of 25 reflections with Bragg angles in the range $15 < \theta < 18°$. Intensities for 14 290 reflections were measured from continuous $\omega/2\theta$ scans. The scan speeds were adjusted to give $\sigma(I)/I$, 0.02 subject to a time limit of 100 s. Two reflections, (0 6 0) and (2 4 2), were used to monitor the stability of the crystal and the diffractometer. Their mean intensity showed random variations of +1% over the period of data collection. Lorentz and polarization factors were applied to the intensities. Empirical absorption corrections were made by the method of Stuart and Walker[21] at the end of the isotropic refinement. The internal agreement factor, R_{int}, for merging 584 duplicate intensities was 0.053 before and 0.045 after correction for absorption. Of 13 705

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[21] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2)

atom	x/a	y/b	z/c	U^a	atom	x/a	y/b	z/c	U^a
Pd(1)	0.20811(3)	0.33244(2)	0.29576(3)	0.033	C(F6)	0.0266(6)	0.0786(3)	0.3010(4)	0.057
Pd(2)	0.10414(3)	0.25509(2)	0.28199(3)	0.034	C(G1)	0.2874(5)	0.1129(3)	0.3104(4)	0.051
Pd(3)	0.27539(3)	0.24437(2)	0.27929(3)	0.035	C(G2)	0.3257(5)	0.1262(3)	0.3778(4)	0.057
I	0.21485(4)	0.26990(2)	0.42434(2)	0.050	C(G3)	0.3441(6)	0.0895(4)	0.4276(5)	0.077
P(1)	0.09591(12)	0.38901(7)	0.31585(10)	0.039	C(G4)	0.3261(7)	0.0403(4)	0.4108(5)	0.083
P(2)	−0.02555(12)	0.29853(7)	0.30026(9)	0.036	C(G5)	0.2875(7)	0.0285(3)	0.3473(6)	0.078
P(3)	0.06980(13)	0.17352(7)	0.25246(9)	0.039	C(G6)	0.2686(6)	0.0648(3)	0.2936(4)	0.062
P(4)	0.26871(14)	0.16223(7)	0.24461(10)	0.044	C(H1)	0.3429(6)	0.1443(3)	0.1765(5)	0.063
P(5)	0.42396(12)	0.26752(7)	0.30238(10)	0.041	C(H2)	0.3242(8)	0.1612(4)	0.1069(5)	0.093
P(6)	0.34585(12)	0.37159(7)	0.29856(9)	0.037	C(H3)	0.3880(10)	0.1530(5)	0.0586(6)	0.126
O(CO)	0.1832(3)	0.2867(2)	0.1449(2)	0.042	C(H4)	0.4635(10)	0.1275(5)	0.0777(7)	0.131
C(CO)	0.1898(5)	0.2861(3)	0.2039(4)	0.047	C(H5)	0.4830(8)	0.1093(5)	0.1469(7)	0.118
C(1)	0.0028(5)	0.3551(3)	0.3515(4)	0.042	C(H6)	0.4219(6)	0.1180(4)	0.1963(5)	0.078
C(2)	0.1591(5)	0.1495(3)	0.1994(4)	0.050	C(I1)	0.4874(5)	0.2296(3)	0.3681(4)	0.051
C(3)	0.4308(5)	0.3306(3)	0.3408(4)	0.048	C(I2)	0.5255(6)	0.1855(4)	0.3445(5)	0.076
C(A1)	0.1198(5)	0.4366(3)	0.3824(4)	0.054	C(I3)	0.5688(7)	0.1544(4)	0.3915(7)	0.109
C(A2)	0.1537(7)	0.4837(4)	0.3641(5)	0.079	C(I4)	0.5742(6)	0.1656(5)	0.4617(7)	0.117
C(A3)	0.1748(7)	0.5175(3)	0.4132(7)	0.092	C(I5)	0.5412(8)	0.2091(6)	0.4867(6)	0.122
C(A4)	0.1600(9)	0.5088(5)	0.4835(7)	0.113	C(I6)	0.4940(7)	0.2409(4)	0.4403(5)	0.084
C(A5)	0.1319(13)	0.4639(6)	0.5010(7)	0.185	C(J1)	0.4962(5)	0.2685(3)	0.2300(4)	0.048
C(A6)	0.1103(12)	0.4296(5)	0.4487(6)	0.162	C(J2)	0.4640(6)	0.2604(3)	0.1604(5)	0.064
C(B1)	0.0461(4)	0.4230(3)	0.2402(4)	0.046	C(J3)	0.5201(7)	0.2579(4)	0.1071(5)	0.077
C(B2)	0.0607(5)	0.4078(3)	0.1724(4)	0.056	C(J4)	0.6083(7)	0.2641(4)	0.1192(5)	0.081
C(B3)	0.0208(7)	0.4331(4)	0.1145(5)	0.072	C(J5)	0.6418(6)	0.2763(5)	0.1873(6)	0.095
C(B4)	−0.0307(7)	0.4731(4)	0.1207(5)	0.074	C(J6)	0.5872(5)	0.2768(4)	0.2433(5)	0.067
C(B5)	−0.0446(7)	0.4885(4)	−0.1867(7)	0.094	C(K1)	0.3858(5)	0.3862(3)	0.2122(4)	0.043
C(B6)	−0.0098(6)	0.4636(3)	0.2466(5)	0.069	C(K2)	0.4748(6)	0.3906(3)	0.2004(4)	0.057
C(C1)	−0.0948(5)	0.3199(3)	0.2235(4)	0.042	C(K3)	0.5001(6)	0.4004(3)	0.1354(5)	0.074
C(C2)	−0.0894(5)	0.2932(3)	0.1587(4)	0.052	C(K4)	0.4374(7)	0.4059(4)	0.0800(4)	0.074
C(C3)	−0.1421(6)	0.3058(4)	0.1005(4)	0.070	C(K5)	0.3502(7)	0.4030(4)	0.0896(4)	0.074
C(C4)	−0.1979(6)	0.3455(4)	0.1026(5)	0.088	C(K6)	0.3231(6)	0.3921(3)	0.1567(4)	0.056
C(C5)	−0.2030(6)	0.3723(4)	0.1657(5)	0.068	C(L1)	0.3672(5)	0.4273(3)	0.3520(4)	0.044
C(C6)	−0.1510(5)	0.3591(3)	0.2244(4)	0.055	C(L2)	0.3492(7)	0.4248(4)	0.4229(4)	0.068
C(D1)	−0.1004(5)	0.2677(3)	0.3579(4)	0.045	C(L3)	0.3689(8)	0.4640(4)	0.4679(5)	0.081
C(D2)	−0.0652(6)	0.2329(3)	0.4043(5)	0.062	C(L4)	0.4050(8)	0.5055(4)	0.4449(5)	0.084
C(D3)	−0.1167(7)	0.2103(4)	0.4525(5)	0.083	C(L5)	0.4209(8)	0.5100(3)	0.3765(7)	0.090
C(D4)	−0.2043(7)	0.2205(5)	0.4537(5)	0.095	C(L6)	0.4040(6)	0.4699(3)	0.3296(5)	0.067
C(D5)	−0.2401(7)	0.2540(6)	0.4069(7)	0.127	O(S)	0.1960(6)	0.4451(3)	0.9466(5)	0.115
C(D6)	−0.1895(6)	0.2792(5)	0.3595(5)	0.086	C(1S)	0.2582(7)	0.4524(4)	0.9071(6)	0.095
C(E1)	−0.0313(5)	0.1643(3)	0.1952(4)	0.051	C(2S)	0.2869(11)	0.4134(6)	0.8571(10)	0.168
C(E2)	−0.1134(6)	0.1664(3)	0.2276(4)	0.059	C(3S)	0.3005(10)	0.5027(5)	0.9137(7)	0.123
C(E3)	−0.1945(7)	0.1648(4)	0.1844(6)	0.085	O(W)	0.6276(11)	0.3575(7)	0.4938(8)	0.267
C(E4)	−0.1922(8)	0.1614(4)	0.1137(6)	0.106	O(1A)^b	0.7673(5)	0.4063(7)	0.3903(10)	0.263
C(E5)	−0.1138(8)	0.1599(5)	0.0857(5)	0.102	O(2A)	0.6389(9)	0.3866(4)	0.3510(3)	0.350
C(E6)	−0.0334(7)	0.1603(4)	0.1237(5)	0.076	F(1A)	0.6484(9)	0.4665(6)	0.2603(7)	0.260
C(F1)	0.0625(5)	0.1250(3)	0.3194(4)	0.041	F(2A)	0.6673(12)	0.5025(3)	0.3517(8)	0.279
C(F2)	0.0989(5)	0.1321(3)	0.3883(4)	0.049	F(3A)	0.7717(5)	0.4767(4)	0.3054(6)	0.364
C(F3)	0.0983(6)	0.0940(4)	0.4368(4)	0.062	C(1A)	0.6896(5)	0.4128(3)	0.3645(4)	0.279
C(F4)	0.0650(7)	0.0479(3)	0.4178(5)	0.068	C(2A)	0.6921(5)	0.4679(3)	0.3213(5)	0.266
C(F5)	0.0290(6)	0.0404(3)	0.3506(5)	0.070					

^{a} U is one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. ^{b} Atoms O(1A)–C(2A) were refined as a rigid group (see text).

unique reflections measured, 10 018 for which $I > 3\sigma(I)$ were used in the structure analysis.

The positions of the non-hydrogen atoms were obtained using Patterson and difference Fourier methods. Hydrogen atoms of the dppm ligands were included in calculated positions with C–H = 0.96 Å and U(isotropic) fixed at 0.070 Å^2. No allowance was made for the scattering of water and acetone hydrogen atoms. The structure was refined by block-diagonal least-squares minimization of the function $\sum\omega(|F_o| - |F_c|)^2$ were $\omega = \sigma(|F_o|)^{-2}$. Anisotropic displacement parameters were refined for all non-hydrogen atoms. These parameters (see Table III) are large for the water oxygen atom and for the atoms of the trifluoroacetate anion and suggest positional disorder of these residues, although alternative atomic sites were not obvious from difference maps. The relative positions of the atoms of the anion were determined from a difference map at $R = 0.06$, and the anion was subsequently refined as a rigid group with individual anisotropic displacement parameters. The GX program package^{22} was used for all calculations; atomic scattering factors and anomalous dispersion corrections were taken from ref 23.

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Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic displacement parameters of non-hydrogen atoms, and bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

OM920608J

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