Complexes with a Trifluorophosphine Ligand Bridging a Tripalladium Triangle. Structure of $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-bis(diphenylphosphino)methane})_3]I$

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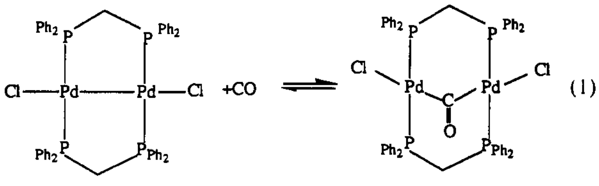
Received April 2, 1993

Synthetic and structural work describe the first examples of bridging monophosphine ligands. Treatment of $Pd_2(\mu\text{-dpm})_2X_2$ (**1**; dpm is bis(diphenylphosphino)methane; X is Cl or I) with excess trifluorophosphine yields brown $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}X)(\mu\text{-dpm})_3]X$ and yellow $Pd(dpm)X_2$. Metathesis of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]Cl$ with sodium iodide yields red-brown $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I$. $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I\cdot 3CH_2Cl_2$ crystallizes in the monoclinic space group Pn with $a = 11.149(2)$ Å, $b = 15.635(3)$ Å, $c = 22.857(5)$ Å, and $\beta = 90.17(2)°$ at 130 K with $Z = 2$. Refinement of 8454 reflections with ($F > 4.0\sigma(F)$) and 500 parameters yielded $R = 0.063$ and $R_w = 0.071$. The structure of the cation consists of a nearly equilateral triangle of palladium atoms bridged at the edges by dpm ligands and capped by the triply bridging phosphorus atom of the trifluorophosphine. An iodide ligand is almost symmetrically situated on the opposite face. Studies of the $Pd_2(\mu\text{-dpm})_2Cl_2/PF_3$ reaction by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy show that a variety of species are formed in the complex reaction that leads to the eventual formation of $[Pd_3(\mu\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]Cl$.

Introduction

In 1990 we reported the first characterization of a transition metal complex, namely $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)$, in which a monophosphine, in this case trifluorophosphine, acted as a bridging ligand.[1] Since the early work of Chatt and Wilkinson,[2] it has been widely recognized that there are considerable similarities between trifluorophosphine and carbon monoxide.[2–4] Consequently, since carbon monoxide readily and reversibly reacts with $Pd_2(\mu\text{-dpm})_2Cl_2$, **1** (dpm is bis(diphenylphosphino)methane), via eq 1 to form a complex, **2**, with a bridging carbon monoxide,[5] the reaction of trifluorophosphine with $Pd_2(\mu\text{-dpm})_2Cl_2$ was examined with the anticipation that a bridging trifluorophosphine complex might result. The reaction that ensues, which is shown in eq 2, is more complex than expected, but it does produce a complex with a bridging trifluorophosphine ligand. However, the trifluorophosphine bridges three, rather than two metal centers, and considerable reorganization of the palladium complex takes place to produce the trinuclear product.



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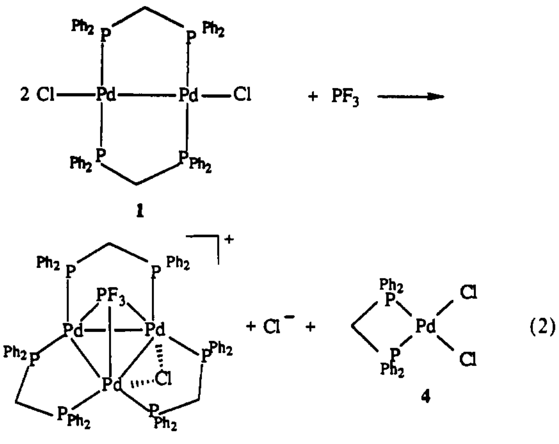

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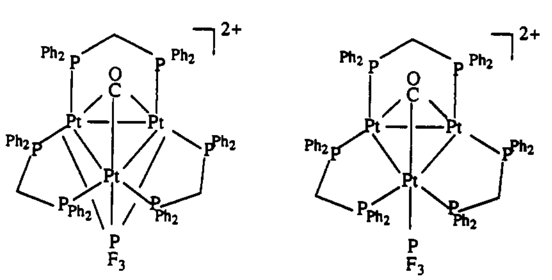
There are only a few reports of bridging behavior of phosphorus(III) ligands that are relevant in relation to this work. A $\mu_3\text{-}PF_3$ structure had been considered for the trifluorophosphine adduct of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dpm})_3]^{2+}$, but the available data did not allow differentiation between a bridged structure (**A**) and a fluctional, monodentate one (**B**).[6] Since our initial results were published, an additional example of a phosphine acting as a bridging ligand has been reported.[7] One phosphorus atom of each bidentate phosphine ligand in $[(dppp)_2Pd_2](SO_3CF_3)_2$, **5** (dppp is 1,3-bis(diphenylphosphino)propane), has been shown to asymmetrically bridge the palladium centers. Ab initio calculations by the authors predict the semibridging nature of these two phosphorus atoms, even in the absence of the supporting Pd–phenyl interactions.



A **B**

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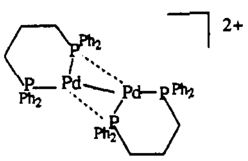

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Also relevant, but less directly related to this work, are the examples of phosphido groups that bridge three, rather than the usual two, transition metal centers. These include $Cu_8(Pr^iPCH_2PPr^i)_2Cl_4(py)_5$[8] and $Cu_4(Pr^iPCH_2PPr_2^i)Cl_3(py)_2$,[9] which contain phosphido groups that span three copper(I) centers, and $[Au_2Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_4](PF_6)_2$, which has diphenylphosphido groups that bridge two platinum centers and form a longer connection to the adjacent gold center.[10]

Here we present details of the preparation and characterization of **3** and of its iodide analog and ^{31}P NMR studies that give some insight into the reactions that are involved in the formation of these novel trinuclear complexes.

Results and Discussion

The reactions of trifluorophosphine with $Pd_2(\mu\text{-dpm})_2X_2$ with X = Cl, Br, I, SCN, N_3, or NO_2 have been examined. For the three halide ligands, the reaction proceeds analogously to that seen in reaction 2. However, for the pseudohalides, thiocyanate, azide, or nitrite, a complex mixture of products was found when the reaction was monitored by ^{31}P NMR spectroscopy. Moreover, it was not possible to isolate pure products from these reactions.

The introduction of dichloromethane to a flask containing the orange solid **1** and 1 atm of trifluorophosphine produces an orange solution, which darkens noticeably after 10 min and appears as a rich maroon color after 1 h. After the solution is stirred for 15 h, the gradual addition of diethyl ether leads to the isolation of a maroon crystalline mixture that contains both major products: $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]Cl$, **3** (and its hexafluorophosphate salt), and $Pd(dpm)Cl_2$, **4**. The latter, $Pd(dpm)Cl_2$, has been thoroughly characterized previously and is readily identified.[11,12] The separation of **3** and **4** by fractional crystallization, as originally reported, is inefficient. A more effective separation utilizes the higher solubility of the salt **3** in chloroform to achieve a crude separation from **4**. This is then followed by chromatography on basic alumina to further purify the maroon product.

The $^{31}P\{^1H\}$ NMR spectrum of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)$ in deuterated dichloromethane, which is shown in Figure 1, consists of a quartet centered at 101.6 ppm ($J(P,F)$ = 1296 Hz) that is split into heptets due to coupling to the six equivalent phosphorus atoms of the dpm ligands ($^2J(P,P)$ = 60 Hz). In the dpm region of the spectrum, there is a doublet centered at −12.6 ppm that is due to the phosphorus atoms of the dpm ligands. These phosphorus atoms are spin coupled to a unique phosphorus atom ($^2J(P,P)$ = 60 Hz) and are also coupled to three equivalent fluorines ($^3J(P,F)$ = 6 Hz). The integration of the two signals at 101.6 ppm and at −12.6 ppm gives a ratio of 1:6. This spectrum indicates that the six phosphorus atoms of the dpm ligands are equivalent. Hence, since the structure in the solid state shows that the chloride ligand is asymmetrically placed so that it bridges only two palladium centers; the structure in solution must be more symmetrical or the chloride ligand is freely moving around the tripalladium unit. The far upfield region of the spectrum contains the multiplet that arises from the hexafluorophosphate anion. A weak singlet at −9.4 ppm results from a ubiquitous, unidentified impurity.

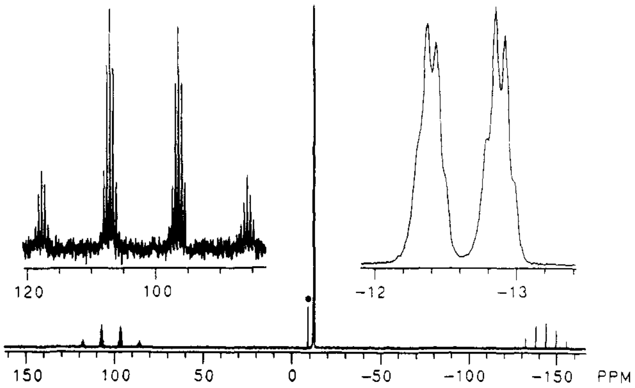

Figure 1. 121-MHz $^{31}P\{^1H\}$ NMR spectrum obtained from a dichloromethane solution of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_2](PF_6)$ at 23 °C.

The formation of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]Cl$ via eq 2 was initially reported to be reversible.[1] However, further work with purified samples reveals that the reaction is *not* reversible. A mixture of carefully purified $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]Cl$ and $Pd(dpm)Cl_2$ in dichloromethane shows no change in the ^{31}P NMR spectrum after storing the mixture for 22 h at 23 °C.

Treatment of $Pd_2(\mu\text{-dpm})_2I_2$ with trifluorophosphine yields $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I$, **6**, and $Pd(dpm)I_2$. The $^{31}P\{^1H\}$ NMR spectrum of $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I$ in dichloromethane-d_2 is similar to that of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)$. The downfield portion of the spectrum of $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3](PF_6)$ consists of a quartet of heptets that is centered at 106.4 ppm ($J(P,F)$ = 1302 Hz; $^2J(P,P)$ = 45 Hz). This is 4.8 ppm further downfield than that of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)$ (δ = 101.6 ppm). Both $J(P,F)$ and $^2J(P,P)$ are also significantly different from the comparable values seen in the $^{31}P\{^1H\}$ NMR spectrum of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)$: $J(P,F)$ is 6 Hz larger; $^2J(P,P)$ is 15 Hz smaller. The dpm portion of the $^{31}P\{^1H\}$ NMR spectrum of $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I$ contains a resonance at −12.8 ppm ($^2J(P,P)$ = 45 Hz; $^3J(P,F)$ = 7 Hz). This part of the spectrum differs less significantly from that of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)$ (δ = −12.6 ppm ($^2J(P,P)$ = 60 Hz; $^3J(P,F)$ = 6 Hz)), with the exception of the two-bond coupling constant $^2J(P,P)$, which, as mentioned above, is 15 Hz smaller.

The complexes $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}X)(\mu\text{-dpm})_3]^+$ (X = Cl, I) are remarkably stable, in contrast to the trifluorophosphine adduct of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dpm})_3]^{2+}$, which cannot be isolated due to the partial loss of trifluorophosphine and can only be characterized in solution in the presence of free trifluorophosphine.[6] The solid **3** when placed under vacuum for 62 h is unaffected, as shown by the $^{31}P\{^1H\}$ NMR spectrum that is obtained after the sample is dissolved in dichloromethane. In addition, the bound trifluorophosphine does not exchange with free trifluorophosphine in solution, again, as shown by the $^{31}P\{^1H\}$ NMR spectrum. Treatment of **3** with free carbon monoxide in dichloromethane solution does not give the known compound $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}Cl)(\mu\text{-dpm})_3]^+$.[13] The complex remains intact; however, the intensity of the impurity peak at −9.4 ppm modestly increases. Solutions of complex **3** are also stable to moderate heating. The stability of $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}X)(\mu\text{-dpm})_3]^+$ (X = Cl, I) toward hydroxylic solvents is also remarkable, since trifluorophosphine itself is readily hydrolyzed. The stability of these cations is probably due to the six-coordinate nature of the phosphorus atom and the steric protection offered by the phenyl groups of the dpm ligands that surround the bridging trifluorophosphine ligand.

The reaction of **1** with the less π acidic, but still highly polar

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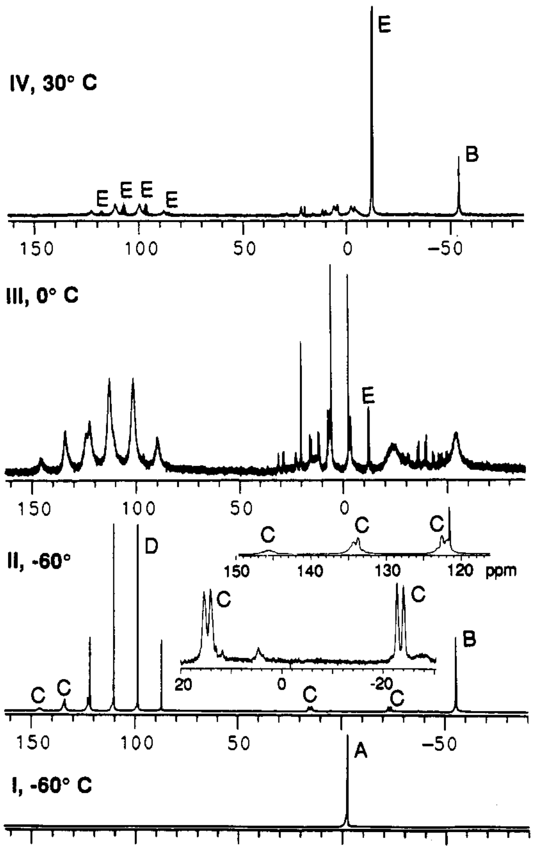


Figure 2. 121-MHz $^{31}P\{^1H\}$ NMR spectra of the reaction between $Pd_2(\mu\text{-dpm})_2Cl_2$ and PF_3 in dichloromethane: I, $Pd_2(\mu\text{-dpm})_2Cl_2$ alone at -60 °C; II, $Pd_2(\mu\text{-dpm})_2Cl_2$ and PF_3 at -60 °C; III, the sample from II warmed to 0 °C; IV, the sample from II and III warmed to 30 °C. Resonances are labeled as follows: A, $Pd_2(\mu\text{-dpm})_2Cl_2$; B, $Pd(dpm)Cl_2$; C, $Pd_2(\mu\text{-dpm})_2(PF_3)_y$; D, PF_3; E, $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]^+$.

fluorophosphine, tris(pentafluorophenyl)phosphine,[14] under conditions that are similar to those used to produce **3**, results only in the recovery of starting material.

In addition, the reaction of **1** with carbon monoxide (eq 1) was reinvestigated to determine if conditions (specifically solvent polarity) had been overlooked under which this reaction would produce a carbon monoxide-capped tripalladium species in an analogous manner to the reaction described by eq 2. However, when the reaction of **1** with carbon monoxide was repeated in a 10/1, 10/3, or 10/7 mixture of dichloromethane/methanol, no evidence was observed to support the formation of a $(OC)Pd_3$ species. As shown by $^{31}P\{^1H\}$ NMR, the reaction proceeds according to eq 1 and is unaffected by solvent polarity. The only product seen is the dipalladium μ-CO adduct, $Pd_2(\mu\text{-CO})Cl_2(\mu\text{-dpm})_2$. However, it should be noted that $Pd_2(\mu\text{-dpm})_2(O_2CCF_3)_2$, with a less strongly coordinating anionic ligands, does react with carbon monoxide to form $[Pd_3(\mu_3\text{-CO})(\mu\text{-dpm})_3]^{2+}$.[15]

Variable-Temperature ^{31}P NMR Studies of the Reaction between $Pd_2(\mu\text{-dpm})_2Cl_2$ and Trifluorophosphine. In order to obtain further insight into the processes leading to the formation of $[Pd_3(\mu\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]^+$, the reaction between **1** and PF_3 was monitored by ^{31}P NMR spectroscopy. The process was begun at low temperature in order to slow the kinetics of the reaction so that intermediates might be directly detected.

The results are presented as a series of spectra that are shown in Figure 2. Trace I shows the spectrum of a dichloromethane solution of **1**, $Pd_2(\mu\text{-dpm})_2Cl_2$, at -60°. Only the single (A) due to **1** is present. Upon addition of PF_3 at -60 °C, the spectrum shown in trace II was obtained. No signal due to **1** is present. A sharp singlet (B) at -55 ppm is present and corresponds to the resonance previously independently observed for $Pd(dpm)Cl_2$.[12] Two doublets (C) of equal integrated intensity are present at 23.5 ppm with $J = 156$ Hz and 14.6 ppm with $J = 156$ Hz. The narrow quartet (D) at 104 ppm results from free PF_3. Downfield of that quartet are a series of lines (C) which must represent coordinated forms of PF_3. Those features along with the doublets at -23.5 and 14.6 ppm appear to arise from a single species since all these resonances appear with a constant set of relative intensities. The insets to trace II show expanded sections of the spectrum where the resonances C appear.

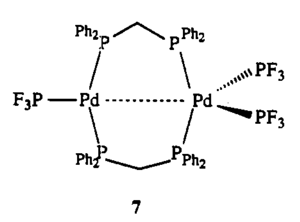
On warming of the sample to 0 °C, the spectrum shown in trace III is obtained. Numerous changes have occurred and are occurring at this point. A multiplicity of new sharp lines (at least 28) are seen in the 30 to -50 ppm region where resonances of coordinated dpm are expected to be found. Among these peaks, the doublet (E) at 12 ppm can be confidently identified as arising from the final product, $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]^+$. Additionally, other broad resonances are indicative of the presence of species that are undergoing dynamic exchange. Thus in the far downfield region, at least two broad quartets are present, one of which corresponds to uncoordinated PF_3, which must be undergoing exchange with some coordinated form(s). The breadth of the resonance of -55 ppm suggests that $Pd(dpm)Cl_2$ is involved in a dynamic process. An unidentified broad feature is present at 22 ppm.

Further warming of the sample to 30 °C produces the much simpler spectrum shown in trace IV. Narrow resonances (B and E) due to known products, $Pd(dpm)Cl_2$ and $[Pd_3(\mu\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]^+$, are present, as are broadened resonances of uncoordinated trifluorophosphine. In the region 30 to -20 ppm a number of additional resonances that must arise from other coordinated forms of dpm are present.

Similar data have been collected for the reaction between trifluorophosphine and $Pd_2(\mu\text{-dpm})_2Br_2$ or $Pd_2(\mu\text{-dpm})_2I_2$. The spectra collected at -60 °C showed that the singlets due to the initial dimers were no longer present once the trifluorophosphine had been added. In both cases, the spectra were very similar to that in trace II of Figure 2. In each case a sharp singlet due to either $Pd(dpm)Br_2$ or $Pd(dpm)I_2$ was present at low field. The chemical shift for this singlet varies with halide ligand and corresponds to the known chemical shifts for $Pd(dpm)Br_2$ or $Pd(dpm)I_2$.[12] On the other hand, for all three halides, an identical set of resonances C are present (as shown in trace II of Figure 2). We conclude that a common intermediate is present in all cases. To explain this result, we propose that the initial reaction between $Pd_2(\mu\text{-dpm})_2X_2$ and PF_3 is the disproportionation reaction that is shown in eq 3. The new set of resonances C are due to

$$2Pd_2(\mu\text{-dpm})_2X_2 + yPF_3 \rightarrow 2Pd(dpm)X_2 + Pd_2(\mu\text{-dpm})_2(PF_3)_y \qquad (3)$$

the formation of a new, Pd(0) complex for which we tentatively propose structure **7**. This asymmetric structure, with dissimilar



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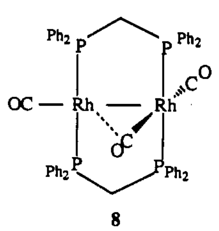

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coordination at the two palladium centers, would render the two phosphorus atoms of each dpm ligand inequivalent, and this would lead to the two distinct dpm chemical shifts shown in Figure 2. Since the phosphorus atoms are not trans to one another in the

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[14] Marriot, J. C.; Salthouse, J. A.; Ware, M. J.; Freeman, J. M. *J. Chem. Soc., Chem. Commun.* **1970**, 595.

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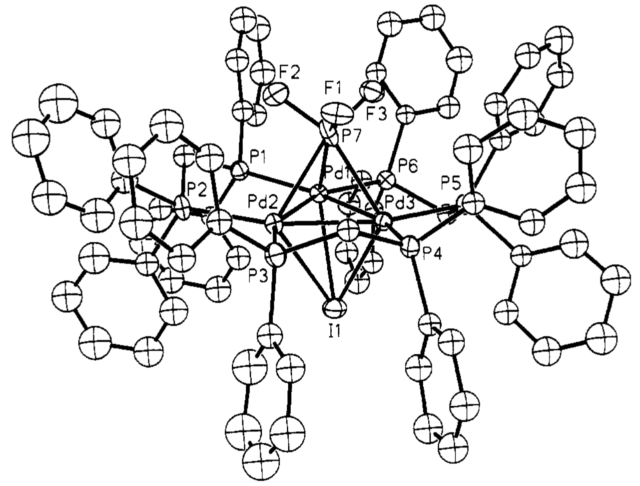

Figure 3. Perspective view of $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]^+$ with 50% thermal contours for all atoms.

proposed structure 7, strong P–Pd–P coupling would be absent and this could explain why the ^{31}P resonances of the dpm ligands appear as a pair of doublets. Precendent for such an asymmetric structure for a complex with the $M_2(dpm)_2$ core is seen in the structure of $Rh_2(\mu\text{-dpm})_2(CO)_3$, **8**.[16] Structure 7 requires that two distinct phosphorus resonances for the trifluorophosphine ligands should been seen. Careful examination of the 150–120 ppm region of the ^{31}P NMR spectrum (top inset of trace II of Figure 2) shows that each ^{31}P resonance of the trifluorophosphine ligands is broad, and those at ca. 134 and 122 ppm are asymmetric. We suggest that the asymmetric features result from the two trifluorophosphine environments which produce two overlapping quartets. Because of the line widths, we propose that exchange between the two sites is occuring.

As the temperature is raised, the reaction of $Pd(dpm)X_2$ with 7 proceeds through a complex series of intermediates to produce the trinuclear product 3. Thus, warming samples of $Pd(\mu\text{-dpm})_2Br_2$ and $Pd(\mu\text{-dpm})_2I_2$ that had been treated with excess PF_3 at −60 °C leads to a series of intermediates and then eventually to a mixture that consists primarily of $[Pd_3(\mu\text{-}PF_3)(\mu\text{-}X)(\mu\text{-dpm})_3]^+$ and $Pd(dpm)X_2$. In general, the spectra obtained from the bromo and iodo complexes are less complex than those shown in Figure 2, and the samples need to be warmed to higher temperatures before significant amounts of the final trinuclear product are detectable.

Crystal and Molecular Structure of $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I\cdot 3CH_2Cl_2$, 6. Because poor crystal quality led to a rather high *R* factor and large esd's for the bonding parameters in the previous structure determination for $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)\cdot 0.5CH_2Cl_2$,[1] a structure determination for a derivative that produced better crystals was deemed necessary. $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I\cdot 3CH_2Cl_2$ crystallizes with one complex cation, one iodide ion, and three dichloromethane molecules within the asymmetric unit. The dichloromethane molecules do not participate in bonding interactions with the complex. A view of the cation is shown in Figure 3. Figure 4 shows a view of the inner core of the cation with the phenyl groups removed. Selected atomic positional parameters are given in Table I. Table II lists relevant bond distances and angles.

The structure of 6 consists of an equilateral triangle of palladium ions that is capped by the triply bridging phosphorus atom. Three dpm ligands act as bridges around the periphery of the triangle of palladium centers in a structural motif that has been seen in a number of other palladium and platinum complexes.[17] The phosphorus atom is located 2.00 Å above the Pd_3 plane. The fluorine atoms of the trifluorophosphine group are symmetrically positioned over the triangular edges. An iodide ligand is very nearly symmetrically placed on the opposite face, 2.54 Å below the Pd_3 plane.

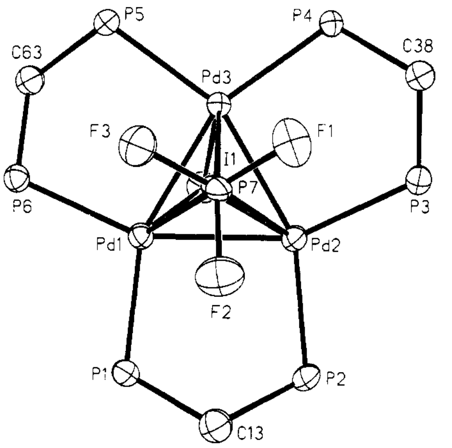

Figure 4. Perspective view of the core of $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]^+$ with all phenyl groups removed and 50% thermal contours.

Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I\cdot 3CH_2Cl_2$

	x	*y*	*z*	*U*(eq)[a]
Pd(1)	5598(1)	2241(1)	6373(1)	20(1)
Pd(2)	4685(1)	3024(1)	7266(1)	21(1)
Pd(3)	4587(1)	1368(1)	7199(1)	19(1)
I(1)	3023(1)	2147(1)	6343(1)	32(1)
P(1)	6424(3)	3450(2)	5959(1)	23(1)
P(2)	5286(3)	4391(2)	6975(1)	27(1)
P(3)	3752(3)	3082(2)	8170(1)	25(1)
P(4)	3729(3)	1150(2)	8113(1)	21(1)
P(5)	4964(3)	26(2)	6785(1)	22(1)
P(6)	6019(3)	1065(2)	5776(1)	22(1)
P(7)	6530(3)	2099(2)	7363(2)	31(1)
F(1)	6621(8)	2017(6)	8036(3)	39(3)
F(2)	7472(8)	2838(5)	7326(4)	42(3)
F(3)	7439(7)	1368(5)	7224(3)	34(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. Coordinates for carbon atoms, iodide counterion, and dichloromethane atoms are not given. See supplementary material.

In contrast to the chloride ligand in $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)\cdot 0.5CH_2Cl_2$, which bridges only two palladium ions, the iodide ligand in 6 bridges all three palladium centers. The iodide ligand is not, however, symmetrically placed; the distances to two of the palladium ions are slightly shorter (2.875(1) and 2.885(2) Å) than the distance to the third (3.120(2) Å). In the μ_3-CO bridged complex $[Pd_3(\mu_3\text{-}CO)(\mu_3\text{-}I)(\mu\text{-dpm})_3]^+$, **9**, the μ_3-I ligand is more nearly symmetrically placed (Pd–I distances: 2.951(1), 3.031(1), and 3.083(1) Å).[13] The Pd–I distances in both of these compounds are longer than those of known Pd–I single bonds (approximately 2.6 Å).[18] Consequently, the bonding

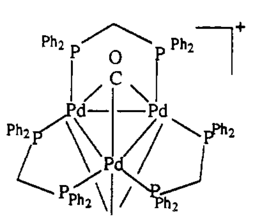

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Table II. Bond Lengths and Angles for $[Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]I\cdot 3CH_2Cl_2$

	Bond Lengths (Å)		
Pd(1)–Pd(2)	2.590(1)	Pd(1)–P(7)	2.498(4)
Pd(2)–Pd(3)	2.596(1)	Pd(2)–P(7)	2.524(4)
Pd(1)–Pd(3)	2.591(1)	Pd(3)–P(7)	2.476(4)
Pd(1)–I(1)	2.875(1)	P(7)–F(1)	1.547(9)
Pd(2)–I(1)	3.120(2)	P(7)–F(2)	1.565(9)
Pd(3)–I(1)	2.885(2)	P(7)–F(3)	1.561(9)
Pd(1)–P(6)	2.338(3)	Pd(1)–P(1)	2.308(3)
Pd(2)–P(2)	2.338(3)	Pd(2)–P(3)	2.319(3)
Pd(3)–P(4)	2.325(3)	Pd(3)–P(5)	2.341(3)
	Bond Angles (deg)		
Pd(2)–Pd(1)–Pd(3)	60.1(1)	Pd(2)–Pd(1)–I(1)	69.4(1)
Pd(3)–Pd(1)–I(1)	63.5(1)	Pd(2)–Pd(1)–P(1)	95.4(1)
Pd(3)–Pd(1)–P(1)	155.0(1)	I(1)–Pd(1)–P(1)	115.6(1)
I(1)–Pd(2)–Pd(1)	59.6(1)	I(1)–Pd(2)–Pd(3)	59.8(1)
Pd(2)–I(1)–Pd(1)	51.0(1)	Pd(2)–I(1)–Pd(3)	51.0(1)
Pd(2)–Pd(1)–P(6)	155.7(1)	Pd(3)–Pd(1)–P(6)	95.7(1)
I(1)–Pd(1)–P(6)	98.5(1)	P(1)–Pd(1)–P(6)	108.9(1)
Pd(2)–Pd(1)–P(7)	59.5(1)	P(2)–Pd(2)–I(1)	112.4(1)
P(3)–Pd(2)–I(1)	110.7(1)	P(7)–Pd(2)–I(1)	106.8(1)
Pd(3)–Pd(1)–P(7)	58.2(1)	I(1)–Pd(1)–P(7)	115.4(1)
P(1)–Pd(1)–P(7)	106.2(1)	P(6)–Pd(1)–P(7)	112.0(1)
Pd(1)–Pd(2)–Pd(3)	59.9(1)	Pd(1)–Pd(2)–P(2)	95.4(1)
Pd(3)–Pd(2)–P(2)	155.2(1)	Pd(1)–Pd(2)–P(3)	154.0(1)
Pd(3)–Pd(2)–P(3)	94.2(1)	P(2)–Pd(2)–P(3)	110.3(1)
Pd(1)–Pd(2)–P(7)	58.4(1)	Pd(3)–Pd(2)–P(7)	57.8(1)
P(2)–Pd(2)–P(7)	108.4(1)	P(3)–Pd(2)–P(7)	108.1(1)
Pd(1)–Pd(3)–Pd(2)	59.9(1)	Pd(1)–Pd(3)–I(1)	63.1(1)
Pd(2)–Pd(3)–I(1)	69.2(1)	Pd(1)–Pd(3)–P(4)	155.9(1)
Pd(2)–Pd(3)–P(4)	96.4(1)	I(1)–Pd(3)–P(4)	115.0(1)
Pd(1)–Pd(3)–P(5)	95.7(1)	Pd(2)–Pd(3)–P(5)	155.6(1)
I(1)–Pd(3)–P(5)	102.3(1)	P(4)–Pd(3)–P(5)	107.8(1)
Pd(1)–Pd(3)–P(7)	59.0(1)	Pd(2)–Pd(3)–P(7)	59.6(1)
I(1)–Pd(3)–P(7)	115.8(1)	P(4)–Pd(3)–P(7)	107.0(1)
P(5)–Pd(3)–P(7)	108.5(1)	Pd(1)–I(1)–Pd(3)	53.5(1)
P(5)–C(63)–P(6)	111.6(6)		
Pd(1)–P(7)–Pd(2)	62.1(1)	Pd(1)–P(7)–Pd(3)	62.8(1)
Pd(2)–P(7)–Pd(3)	62.5(1)	Pd(1)–P(7)–F(1)	159.2(4)
Pd(2)–P(7)–F(1)	100.7(4)	Pd(3)–P(7)–F(1)	99.7(4)
Pd(1)–P(7)–F(2)	99.3(4)	Pd(2)–P(7)–F(2)	96.8(4)
Pd(3)–P(7)–F(2)	156.9(4)	F(1)–P(7)–F(2)	94.2(5)
Pd(1)–P(7)–F(3)	98.6(3)	Pd(2)–P(7)–F(3)	158.6(4)
Pd(3)–P(7)–F(3)	101.5(3)	F(1)–P(7)–F(3)	95.8(5)
F(2)–P(7)–F(3)	95.3(5)	P(1)–C(13)–P(2)	110.8(7)
P(3)–C(38)–P(4)	109.7(6)		

of the iodide to the triangle of palladium centers may have considerable electrostatic or multicenter character.

The Pd–Pd distances in **6**, as in **3**, fall within a narrow range (2.590(1)–2.596(1) Å) and are typical for Pd–Pd single bonds.[5,17] The Pd–P distances in **6** that are associated with the triply bridging phosphorus also fall within a narrow range (2.476(4)–2.524(4) Å), and are longer than those seen in either independent cation of **3** (which span the range 2.376(12)–2.471(12) Å). This may reflect the increased softness of the halide in **6**, which makes σ-donation from the phosphorus in the PF_3 group to the cluster in **6**, relative to **3**, less important. The range of Pd–P distances associated with the dpm ligands in **6** (2.308(3)–2.341(3) Å) are similar to those of **3** (2.280(11)–2.349(12) Å).

The phosphorus atom of the bridging trifluorophosphine group has pseudo-octahedral coordination. The F–P–F angles, which span the range 94.2(5)–95.8(5)°, are wider than the Pd–P–Pd angles, which cover the range 62.1(1)–62.8(1)°. The Pd–P–F angles that involve groups in trans-like orientations fall in the range 156.9(4)–159.2(4)°. Thus, the triangular array of the three palladium centers, with the strong Pd–Pd bonding, constricts one side of the coordination sphere of the Pd_3PF_3 group.

Within the $Pd_3(\mu\text{-dpm})_3$ fragment, the methylene flaps of the three, envelope-shaped Pd_2P_2C rings are arranged so that two flaps lie on one side of the Pd_3 triangle and one flap lies on the opposite side, the side that also houses the iodide ligand. Puddephatt, Manojlovic-Muir, and Muir have suggested that, in this arrangement, the phenyl substituents make the face with the two methylene flaps up less sterically crowded than the face with only one methylene flap up.[17] This makes the steric crowding in the vicinity of the trifluorophosphine ligand less than it is in the vicinity of the iodide ligand. The asymmetric arrangement of the dpm ligands appears to be related to the asymmetric location of the iodide ligand. The Pd(2)–I(1) bond is longer than the Pd(1)–I(1) and Pd(3)–I(1) bonds. The environment around Pd(2) is the more crowded than those at Pd(1) or Pd(3) because of the orientations of the dpm ligands. These orientations place four phenyl rings in axial positions where they impinge most severely on Pd(2).

Conclusion

It is now clear that phosphines have joined the ranks of ligands that engage in the formation of electron-deficient bridging groups. Nevertheless, it remains to be seen how widespread the ability of phosphines to participate in such bridging will be. The recent discovery of the semibridging arrangement in **5**[7] indicates that bridging behavior is not confined to highly electronegatively substituted phosphines like trifluorophosphine. The nature of the bonding in both $[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3]^+$ and $Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3]^+$ can readily be accommodated by the molecular orbital scheme previously devised to account for the bonding in $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dpm})_3]^{2+}$ and related triangular complexes.[19] For the complexes **3** and **6** with PF_3 bridges, the empty phosphorus d orbitals simply substitute for the empty π^* orbitals of carbon monoxide.[20]

It has been widely assumed that trifluorophosphine binds to metal surfaces through a direct bond of the phosphorus lone pair to a single metal atom, and there have been a number of studies that have explored the nature of trifluorophosphine binding to clean metal surfaces.[21–25] One of the interesting features of such studies is the ability to probe the orientation of the trifluorophosphine unit relative to the surface and the barrier to rotation about the surface–PF_3 bond.[23] In light of the present work, it is also reasonable to anticipate that trifluorophosphine may associate with triangular M_3 units on such surfaces. Figure 4 shows an informative view of what might be expected for a trifluorophosphine bound to a triangular array of metal atoms. Notice that the trifluorophosphine group is staggered with respect to the triangle of metal atoms in this model.

Experimental Section

Preparation of Compounds. Trifluorophosphine was purchased from ATO North American and used without further purification. The compounds $Pd_2(\mu\text{-dpm})_2X_2$ (X = Cl, Br, I) were prepared by established routes.[5,26] The exposure of these compounds to trifluorophosphine was performed using dried, dioxygen-free dichloromethane. All subsequent manipulations were carried out in air.

$[Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3](PF_6)$. In a 50-mL Schlenk flask that was equipped with a ballast balloon and connected to a small tank of trifluorophosphine was placed 504.5 mg (0.479 mmol) of orange $Pd_2(\mu\text{-dpm})_2Cl_2$. This apparatus was degassed and 1 atm of trifluorophosphine introduced. No color change of the solid material was evident. The introduction of 30 mL of dichloromethane produced a maroon solution within 10 min, which deepened in color over the course of 1 h.

After being stirred for 15 h under an atmosphere of trifluorophosphine, the solution was filtered through Celite and concentrated using an N_2 stream and a warm water bath (40 °C) until the solution volume had been reduced to approximately 1 mL. The slow addition of diethyl ether,

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with scratching, precipitated 497 mg of a dark crystalline material. The crude material was collected by filtration on a glass frit. Chloroform was then used to wash the crude material until the material remaining on the funnel no longer appeared red but rather yellow. This took four 0.25-mL portions of chloroform. This procedure leaves the majority of the light yellow complex Pd(dpm)Cl_2 on the frit, since its solubility in chloroform is much less than that of the desired product.

The maroon chloroform solution was then placed on an 18-cm column of basic alumina. A yellow band of the remaining Pd(dpm)Cl_2 was eluted first with chloroform. The diffuse maroon product band, which follows, was eluted using an approximately 50:1 (v/v) mixture of chloroform/*n*-propyl alcohol, in which the concentration of *n*-propyl alcohol was gradually increased as the band moved down the column. As shown by the $^{31}P\{^1H\}$ NMR spectrum, the leading portion of this band is composed of the chloride salt of the complex, while the trailing portion is predominantly composed of the hexafluorophosphate salt. Longer reaction times increase the amount of hexafluorophosphate formed and, hence, the amount of the hexafluorophosphate salt of the complex, relative to that of the chloride salt of the complex, in the band.

A methanol suspension of 170.0 mg (0.924 mmol) of KPF_6 was added to the eluted product band solution and the resulting mixture evaporated to dryness using an N_2 stream and a warm water bath (60 °C). The resulting residue was taken up in a minimum of dichloromethane and the product precipitated by the slow addition, with scratching, of diethyl ether. Two additional recrystallizations using dichloromethane/diethyl ether and filtration through a small amount of carbon black yielded dark maroon crystals (100.8 mg, 24%). The $^{31}P\{^1H\}$ NMR spectrum is shown in Figure 1. UV/vis (dichloromethane) [λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})]: 278 (41 800), 298 (46 200), 378 (5200), 462 (25 300).

[$Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3$]I. This complex may be prepared by using 581.3 mg (0.471 mmol) of $Pd_2I_2(\mu\text{-dpm})_2$ and stirring under 1 atm of PF_3 for 67 h instead of 15 h but otherwise following the procedure outlined for the preparation of [$Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3$]($PF_6$). The crude product, 550 mg, when placed on the column, separates into four bands. Using chloroform, a diffuse tan band elutes first; a thin red band followed by a diffuse bright pink band separate behind it but do not come off. The gradual addition of *n*-propyl alcohol moves both these bands off the column but markedly diminishes the intensity of the pink band. The brown product band is the next to elute. After isolation and recrystallization, red-brown microcrystals were collected (102.6 mg, 24%).

Alternatively, the complex may be prepared by metathesis of a 1:1 (v/v) dichloromethane/methanol solution of [$Pd_3(\mu_3\text{-}PF_3)(\mu\text{-}Cl)(\mu\text{-dpm})_3$]($PF_6$) using a methanolic solution of NaI. UV/vis (dichloromethane): 270 (46 200), 292 (49 500), 380 (5100), 460 (31 700).

Physical Measurements. The $^{31}P\{^1H\}$ NMR spectra were recorded on a General Electric QE-300 NMR spectrometer operating at 121.7 MHz using an external 85% phosphoric acid standard and the high-field positive convention for reporting chemical shifts. Electronic spectra were recorded using a Hewlet-Packard 8452A spectrometer.

X-ray Data Collection. Deep red crystals were obtained by diffusion of diethyl ether into a dichloromethane solution of [$Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu_3\text{-dpm})_3$]I. Crystals were removed from the mother liquor and immediately coated with a protective coating of a hydrocarbon oil. The crystal selected for data collection was mounted in the cold stream of a Siemens R3m/V diffractometer equipped with a locally-modified Enraf-Nonius low-temperature apparatus. A mean fluctuation of 0.3% in the intensities of two standard reflections was observed during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table III.

Table III. Crystal Structure Data for [$Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3$]I·3$CH_2Cl_2$

a = 11.149(2) Å	fw = 2068.8
b = 15.635(3) Å	*Pn*, monoclinic
c = 22.857(5) Å	T = 130 K
β = 90.17(2)°	λ(Mo Kα) = 0.710 73 Å
Z = 2	μ = 1.836 mm^{-1}
R^a = 0.063	d_{calc} = 1.724 Mg/m^3
$R_w{}^b$ = 0.071	transm factors = 0.60–0.80

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \sum||F_o| - |F_c||w^{1/2}/|F_o|w^{1/2}$; $w^{-1} = \sigma^2|F| +).0027F^2$.

Solution and Refinement of the Structure of [$Pd_3(\mu_3\text{-}PF_3)(\mu_3\text{-}I)(\mu\text{-dpm})_3$]I·3$CH_2Cl_2$. Calculations were performed on a Micro VAX 3200 computing system with the Siemens SHELXTL PLUS software package. The space group was determined to be *Pn* (No. 13) or *P*2/*n* (No. 7) by the observation of systematic absences. Only *Pn* is a reasonable choice since the molecule possesses neither 2-fold nor inversion symmetry. Accordingly, the structure was solved by direct methods in *Pn*. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[27] Hydrogen atoms were located in a difference map and refined using a riding model, with C–H of 0.96 Å, and isotropic U of 0.04 $Å^2$ for nonsolvent hydrogens. For the molecules of dichloromethane, hydrogen atoms were assigned isotropic U values somewhat greater than those of the bonded carbons. The handedness of the structure was determined by a SHELXTL PLUS routine. An absorption correction was applied with program XABS that provides an empirical correction for absorption based on F_o and F_c differences.[28] Refinement was by block-diagonal least-squares methods, with anisotropic thermal parameters for I, Pd, Cl, and P atoms.

The largest residual feature on a final difference map was 3.33 e $Å^{-3}$ in height and located near the PF_3 ligand. This feature most likely represents electron density from a small amount of disorder in which the positions of the triply bridging iodide and trifluorophosphine groups are interchanged. A disordered model was examined in which the occupancies of the I and P atoms were tied together and allowed to refine. This indicated a disorder of 4%, and the R value changed by ca. 0.1%. The disordered fluorine atoms did not appear in a difference map. Since the disordered model did not appear to make a significant difference in the description of the structure, it was not included in the final refinement.

Acknowledgment. We thank the National Science Foundation (Grant CHE9022909) for support.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, hydrogen atom coordinates, anisotropic thermal parameters, and crystal structure refinement data and a fully labeled drawing of **6** (16 pages). Ordering information is given on any current masthead page.

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