

of 4 and 5, as well as the two Me carbons of the COOEt groups in 5, are distinguished by the lone asymmetric center. The  $^1\text{H}$  NMR spectra of 4-6 show the presence of a trisubstituted alkene (5.2-5.35 ppm) and a 1,1-disubstituted alkene (two broad singlets in the 4.88-4.96 ppm region). In addition to the signals for the two Et groups, a Me group is clearly seen. The UV spectra of 4-6 indicate the presence of either a conjugated diene or triene. These spectral data, together with the correct elemental analyses and the consistent  $^1\text{H}$  2D NOESY and COSY NMR spectra, as well as  $^1\text{H}$ - $^{13}\text{C}$  HETCOR spectra for 6, firmly identify 4-6.<sup>9</sup>

**Acknowledgment.** We thank the National Institutes of Health (GM 36792) for support. We also thank Johnson Matthey for a loan of  $\text{PdCl}_2$ .

**Supplementary Material Available:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR data for 1-5 (1 page). Ordering information is given on any current masthead page.

(9) Several attempts to convert 6 into crystalline derivatives for X-ray analysis have failed. Further attempts to obtain X-ray data are in progress.

### Tripily Bridging Trifluorophosphine. Formation of $[(\mu_3\text{-F}_3\text{P})\text{Pd}_3(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_3(\mu\text{-Cl})]^+$ by Disproportionation of $\text{Pd}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Cl}_2$

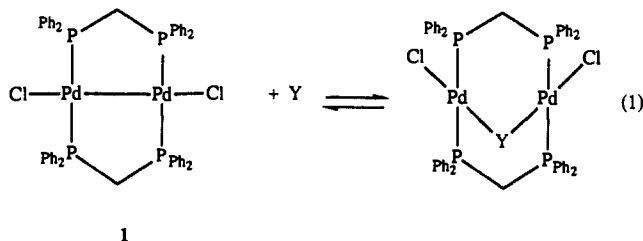
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The analogy between trifluorophosphine and carbon monoxide as ligands was first made by Chatt in 1950,<sup>1</sup> and since then a variety of complexes have been obtained in which the fluorophosphine acts as a terminal ligand.<sup>2</sup> Pursuing this analogy, we considered the possibility that trifluorophosphine might also be capable of acting as a bridging ligand. Bridging monophosphine ligands have not previously been observed,<sup>3</sup> but numerous forms of bridging carbon monoxide are known.<sup>4</sup>

To this end we examined the reaction of trifluorophosphine with  $\text{Pd}_2(\mu\text{-dpm})_2\text{Cl}_2$  (dpm is bis(diphenylphosphino)methane) (1), which is known to undergo ready, and frequently reversible, insertion of a variety of ligands, Y, including inter alia carbon monoxide via eq 1.<sup>5</sup> However, the reaction does not follow eq



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(3) A  $\mu\text{-PF}_3$  structure has been considered for the  $\text{PF}_3$  adduct of  $[\text{Pt}_3(\mu_3\text{-CO})(\mu\text{-dpm})_3]^{2+}$ , but the available data did not allow differentiation between a bridged structure and a fluxional monodentate one. Bradford, A. M.; Douglas, G.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* 1990, 9, 409.

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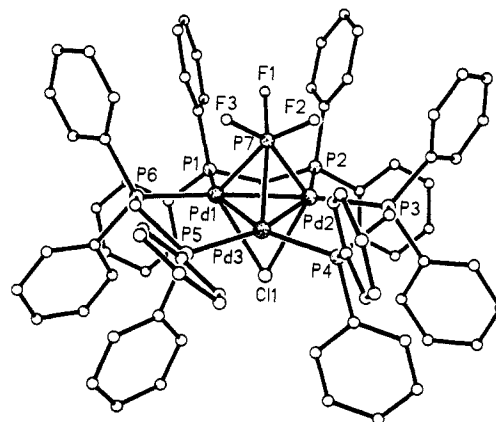
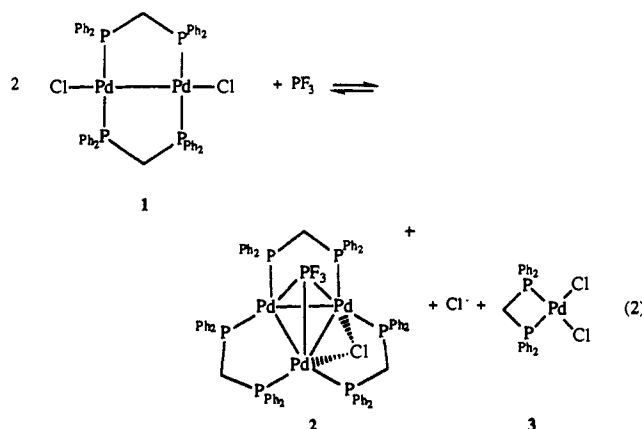


Figure 1. A perspective view of the cation in  $[(\mu\text{-F}_3\text{P})\text{Pd}_3(\mu\text{-dpm})_3(\mu\text{-Cl})][\text{PF}_6]\cdot 0.5\text{CH}_2\text{Cl}_2$ .

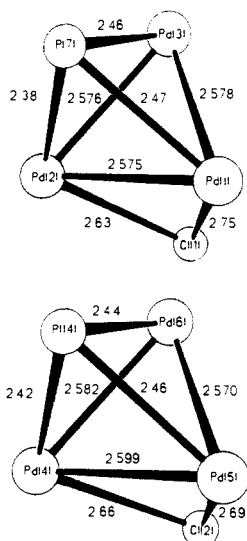
1. Rather, the novel disproportionation reaction shown in eq 2 occurs.



Exposure of an orange dichloromethane solution of 1 to 1 atm of phosphorus trifluoride results in a darkening to produce a rich red-brown solution after 1 h. Gradual addition of ethyl ether produces a light yellow precipitate of  $\text{Pd}(\text{dpm})\text{Cl}_2$  (3), which was identified by comparison with an authentic sample.<sup>6</sup> Further addition of ethyl ether yields a deep red-brown powder of  $[(\mu_3\text{-F}_3\text{P})\text{Pd}_3(\mu\text{-dpm})_3(\mu\text{-Cl})]\text{Cl}$ , which may be converted into the corresponding hexafluorophosphate salt by metathesis. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum consists of a resonance centered at -12.3 ppm due to the dpm phosphorus that consists of a doublet due to coupling to a unique phosphorus ( $^2J(\text{P},\text{P}) = 60$  Hz) that is further split into a quartet due to coupling to three equivalent fluorines ( $^3J(\text{P},\text{F}) = 8.6$  Hz) and a resonance centered at 101.5 ppm due to the coordinated trifluorophosphine which consists of a quartet due to coupling to three fluorine atoms ( $^1J(\text{P},\text{F}) = 1295$  Hz) that is further split into a heptet because of coupling to six equivalent phosphorus atoms ( $^2J(\text{P},\text{P}) = 60$  Hz). Cooling the sample to -70 °C produces broadening of the resonance at -12.3. This may result from localization of the halide ligand (as seen in the crystallographic study, vide infra), which is otherwise free to move between the three palladium atoms. The electronic spectrum shows a broad peak in the visible range with  $\lambda_{\text{max}} = 458$  nm. Reaction 2 is

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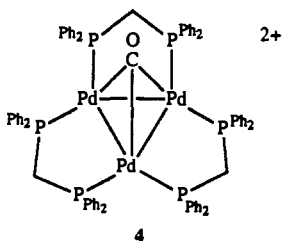
(7) Deep red-brown crystals were obtained by diffusion of ethyl ether into a dichloromethane solution of the complex.  $[(\mu\text{-F}_3\text{P})\text{Pd}_3(\mu\text{-dpm})_3(\mu\text{-Cl})]\text{-PF}_6\cdot 0.5\text{CH}_2\text{Cl}_2$  crystallizes in the monoclinic space group  $P2_1/c$  with cell dimensions  $a = 26.725$  (11) Å,  $b = 27.101$  (12) Å,  $c = 21.304$  (9) Å, and  $\beta = 110.70$  (2)° at 130 K with  $Z = 8$ . Refinement of 6509 reflections with  $F > 4.0 \sigma(F)$  and 546 parameters yielded  $R = 0.109$ ,  $R_w = 0.123$ . The asymmetric unit contains two independent cations, two hexafluorophosphate ions, and 1.5 dichloromethane molecules with disorder in one of the hexafluorophosphate ions and one of the dichloromethane molecules. The disordered dichloromethane site was refined with 50% occupancy. See the supplementary material for details.



**Figure 2.** Dimensions within the cores of the two independent cations of  $[(\mu\text{-F}_3\text{P})\text{Pd}_3(\mu\text{-dpm})_3(\mu\text{-Cl})][\text{PF}_6]\cdot 0.5\text{CH}_2\text{Cl}_2$ . In cation A (top) the Pd(3)---Cl(1) distance is 3.13 (1) Å, the P(4)---F distances (Å) are 1.59 (2) (F(1)), 1.60 (2) (F(2)), and 1.61 (3) (F(3)), and the Pd-P(dpm) distances range from 2.31 (1) to 2.35 (1) Å. In cation B (bottom) the Pd(6)---Cl(2) distance is 2.96 (1) Å, the P(14)---F distances (Å) are 1.57 (3) (F(4)), 1.56 (2) (F(5)), and 1.64 (2) (F(6)), and the Pd-P(dpm) distances range from 2.28 (1) to 2.34 (1) Å. The Pd-P-Pd angles at the bridging PF<sub>3</sub> group are in the 63.0 (3)–64.4 (3)° range while the F-P-F angles span the range 91 (1)–93 (1)°. The esd's on the Pd-Pd distances are 0.004 Å, on the Pd-P distances 0.01 Å, and on the Pd-Cl distances 0.01 Å.

partially reversible. Removal of phosphorus trifluoride from a reaction solution in which only **2** and **3** are present allows **1** to reform as shown by <sup>31</sup>P NMR experiments.

The structure of the brown cluster has been determined by X-ray crystallography. There are two independent cationic clusters within the asymmetric unit; both have very similar dimensions. The structure of one is shown in Figure 1. Figure 2 shows some important dimensions within the PPd<sub>3</sub>Cl core of both cations. The structure of each consists of a nearly equilateral triangle of palladium ions capped by the triply bridging phosphorus atom. The phosphorus atom is 1.93 Å out of the Pd<sub>3</sub> plane in both cations. A chloride ligand is unsymmetrically placed on the opposite face with relatively long Pd-Cl distances. This asymmetry is much greater in cation A than in cation B. While the position of this chloride bridge lowers the symmetry of the cluster, the F<sub>3</sub>PPd<sub>3</sub> core very nearly has C<sub>3v</sub> symmetry with a very narrow range of Pd-Pd distances (2.576–2.599 Å) and Pd-P distances (2.38–2.47 Å). The fluorine atoms of the PF<sub>3</sub> group are staggered over the Pd<sub>3</sub> plane. The structure is closely related to those of two palladium clusters with a triply bridging carbon monoxide,  $[(\mu_3\text{-OC})\text{Pd}_3(\mu\text{-dpm})_3]^{2+}$  (**4**), and its halide ion adduct,  $[(\mu_3\text{-OC})\text{Pd}_3(\mu\text{-dpm})_3(\mu\text{-Cl})]^+$  (**5**).<sup>8</sup> The Pd-Pd distances in **2** fall



in the range seen for the typical single bonds in **4** (2.576 (1)–2.610 (1) Å),<sup>9</sup> **5** (2.584 (1)–2.603 (1) Å),<sup>8</sup> and Pd<sub>2</sub>(μ-dpm)<sub>2</sub>Br<sub>2</sub> (2.699 (1) Å).<sup>10</sup> As might be expected, the Pd-P distances to the triply

bridging trifluorophosphine are slightly longer (by approximately 0.1 Å) than the Pd-P distances that are involved in bonding to the dpm ligands (which fall in the 2.28 (1)–2.35 (1) Å range). The Pd-P distances are also longer than the M-P distances in comparable terminal trifluorophosphine complexes (2.23 (1) Å for Pt-P in Pt(PF<sub>3</sub>)<sub>4</sub>,<sup>11</sup> 2.141 (2) Å for Pt-P in PtCl<sub>2</sub>(PEt<sub>3</sub>)(PF<sub>3</sub>)<sub>2</sub>).<sup>12</sup>

This observation of bridging by a simple phosphine introduces a new structural element into the chemistry of phosphorus(III) ligands and suggests that studies, such as those of phosphorus trifluoride binding to metal surfaces,<sup>13</sup> may need reevaluation since a basic assumption, that phosphorus trifluoride will confine itself to terminal coordination sites, is no longer valid. Further studies of bridging by group 15 ligands are in progress; doubly bridged complexes are a clear target.

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**Supplementary Material Available:** Views of the two cations and tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for  $[(\mu_3\text{-F}_3\text{P})\text{Pd}_3(\mu\text{-dpm})_3(\mu\text{-Cl})][\text{PF}_6]\cdot 0.5\text{CH}_2\text{Cl}_2$  (17 pages); listing of observed and calculated structure factors for  $[(\mu_3\text{-PF}_3)\text{Pd}_3(\text{dpm})_3\text{Cl}][\text{PF}_6$  (56 pages). Ordering information is given on any current masthead page.

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### C-O Bond Scission in Heterometallic Alkoxides: Formation and Structure of K<sub>4</sub>Zr<sub>2</sub>O(O<sup>i</sup>Pr)<sub>10</sub>

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Efforts<sup>1-3</sup> to produce solid materials M<sub>a</sub>M'<sub>b</sub>Y<sub>c</sub> and M<sub>a</sub>M'<sub>b</sub>M''<sub>c</sub>Y<sub>x</sub> from "molecular precursors" (M<sub>a</sub>M'<sub>b</sub>X<sub>m</sub> and M<sub>a</sub>M'<sub>b</sub>M''<sub>c</sub>X<sub>n</sub>, respectively, where X = R, OR, NR, NR<sub>2</sub>, etc.) must focus on the *mechanism* of the transformation from molecule to infinite solid lattice if the performance of the resulting solid material is to be optimized. Such transformations could be envisioned to occur by low-energy hydrolysis (if Y = O), ammonolysis (if Y = N), but also higher energy bond scission processes due to pyrolysis, photolysis, or electrolysis. Scission of O-C bonds in particular (e.g., M(OR)<sub>n</sub> → OM(OR)<sub>n-2</sub> + ...) is a procedure that is not yet under rational control, in part for lack of mechanistically detailed examples. We report here a contribution to this problem: the observation of C-O bond cleavage under very mild conditions, as well as the production of some new heterometallic alkoxides with noteworthy structures and solubility properties.

Reaction of equimolar Zr<sub>2</sub>(O<sup>i</sup>Pr)<sub>8</sub>(<sup>i</sup>PrOH)<sub>2</sub> with KH in THF (or pentane) yields KZr<sub>2</sub>(O<sup>i</sup>Pr)<sub>9</sub> (with release of 1 mol of <sup>i</sup>PrOH and 1 mol of H<sub>2</sub>) as an extremely pentane soluble product.<sup>4</sup> The

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