the legend, that **2** is near square pyramidal. The four oxygen atoms, which form the base of the square pyramid, are coplanar to within ±0.05 Å, with the Ge atom displaced by 0.40 Å out of this plane toward the Cl atom. Based on the dihedral angle method, as applied to cyclic phosphoranes,[6,7] the geometry about the Ge atom is displaced by 84% (91% using unit vectors) from the trigonal bipyramid toward the square-pyramidal configuration. As is often the case for species which follow the local C_{2v} constraint of the coordinate connecting the trigonal bipyramid to the rectangular pyramid, the molecule has approximate 2-fold symmetry. In this case, the pseudo-2-fold axis is coincident with the Ge–Cl bond. Following the trend observed for cyclic phosphoranes,[6,7] the $Ge-O_{ax}$ bonds are, on the average, 0.03 Å longer than the $Ge-O_{eq}$ bonds.

On the basis of spectroscopic data, the water molecules in **1** are assigned to be coordinated to germanium through oxygen, making germanium hexacoordinated.[2] If this is the case, the formation of **2** from **1** in methyl cyanide and reversing **3** to **1** in aqueous medium[3] reflects the closeness of stabilization energy between a five- and a six-coordinated Ge(IV) species. The recent discovery of the rectangular pyramidal geometry for a pentacoordinated Sn(IV) species[8] and the present square-pyramidal structure for **2** strongly suggest the existence of similar structures for spirocyclic pentacoordinated compounds of silicon(IV).

Acknowledgment. The support of this research by the National Science Foundation is greatly appreciated as is the generous allocation of computing time by the University of Massachusetts Computing Center.

Supplementary Material Available: Atomic coordinates (Table I) and anisotropic thermal parameters (Table II) (4 pages). Ordering information is given on any current masthead page.

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(6) R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977).
(7) R. R. Holmes, *Acc. Chem. Res.*, **12**, 257 (1979).
(8) A. C. Sau, R. O. Day, and R. R. Holmes, submitted for publication.

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Synthesis and Structural Characterization of Bimetallic Fe-Pt Carbonyl Clusters: Their Relationship with Bimetallic Fe-Pd Carbonyl Clusters

Sir:

Recently we have reported the synthesis and structural characterization of $[Fe_4Pd(CO)_{16}]^{2-}$, $[Fe_4Pt(CO)_{16}]^{2-}$, and $[Fe_6Pd_6(CO)_{24}H]^{3-}$.[1] The dodecanuclear compound has been obtained in very low yields despite efforts to improve its synthesis. Subsequent work on the bimetallic Fe–Pt carbonyl clusters has resulted in the isolation and characterization of new mixed Fe–Pt carbonyl cluster anions, viz., $[Fe_3Pt_3(CO)_{15}]^{2-}$, $[Fe_3Pt_3(CO)_{15}]^{-}$, and $[Fe_4Pt_6(CO)_{22}]^{2-}$, and has suggested a reasonable mechanism of formation for the dodecanuclear Fe–Pd carbonyl clusters previously reported.[1]

The green $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion (ν_{CO} in CH_3CN at 1995 (s), 1960 (ms), 1930 (sh), and 1905 (m) cm^{-1}) has been obtained both by redox condensation between $[Pt_3(CO)_6]^{2-}$[2] and $Fe(CO)_5$ and by reaction under nitrogen of $[Fe_3(CO)_{11}]^{2-}$[3] with K_2PtCl_4 in a 1:1.5 molar ratio. In acetonitrile at 70 °C the reaction is complete in 3–4 h and follows the apparent stoichiometry in eq 1.

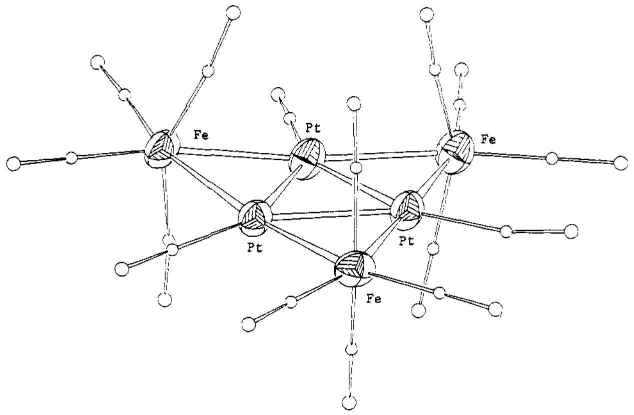

Figure 1. ORTEP view of one of the two independent monoanions found in the unit cell of $[N(CH_3)_3CH_2Ph][Fe_3Pt_3(CO)_{15}]$.

Table I. Average Bond Distances (Å) and Angles (Deg) in the Fe–Pt Bimetallic Carbonyl Clusters[a]

	$[Fe_3Pt_3(CO)_{15}]^{2-}$	$[Fe_3Pt_3(CO)_{15}]^{-}$	$[Fe_4Pt_6(CO)_{22}]^{2-}$
Pt-Pt	2.750	2.656	2.677[b] 2.790[c]
Fe-Pt	2.596	2.587	2.597[d] 2.540[e]
Pt–C	1.73	1.80	1.78
C–O	1.21	1.19	1.22
Pt–C–O	175.3	173.3	173.9
Fe–C	1.72	1.76	1.72
C–O	1.17	1.16	1.18
Fe–C–O	175.4	173.8	173.1

[a] Typical esd's on single distances follow: Pt-Pt, 0.001; Pt-Fe, 0.004; Pt–C and Fe–C, 0.03; C–O, 0.04 Å. [b] Pt-Pt distances within the two Fe_2Pt_3 units (average of six). [c] Pt-Pt distances between the two Fe_2Pt_3 units (average of four). [d] Fe-Pt distances involving the two outer Pt atoms (average of four). [e] Fe-Pt distances involving the four inner Pt atoms (average of four).

$$2[Fe_3(CO)_{11}]^{2-} + 3Pt^{2+} \rightarrow [Fe_3Pt_3(CO)_{15}]^{2-} + Fe(CO)_5 + 2Fe^{2+} + 2CO \quad (1)$$

Monitoring by IR shows the intermediate formation of $[Fe_4Pt(CO)_{16}]^{2-}$. The $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion may also be obtained by reaction of preformed $[Fe_4Pt(CO)_{16}]^{2-}$ and K_2PtCl_4 in a ca. 1:1 molar ratio.

In the presence of an excess of Pt(II) salts, reaction 1 easily results in the formation of variable amounts of the brown paramagnetic $[Fe_3Pt_3(CO)_{15}]^{-}$ anion (ν_{CO} in CH_3CN at 2015 (s), 2000 (sh), and 1950 (ms) cm^{-1}; $\mu = 1.6\ \mu_B$[4]).

This last compound has been obtained in almost quantitative yields from preformed $[Fe_3Pt_3(CO)_{15}]^{2-}$ salts by controlled oxidation in dichloromethane or tetrahydrofuran solution with iodine, acids (H_3PO_4 or H_2SO_4), or Cu^+ or Ag^+ salts. The dianion may be reversibly regenerated from the paramagnetic anion by reduction with alkali hydroxides in methanol. As a result, both the $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Fe_3Pt_3(CO)_{15}]^{-}$ derivatives may be obtained from reaction 1 in very good yields (ca. 70%).

The green $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion is stable in solution under an inert atmosphere, while the paramagnetic $[Fe_3Pt_3(CO)_{15}]^{-}$ anion slowly decomposes; the decomposition of the latter is greatly accelerated by heating the solution at ca. 80–90 °C for a few hours and affords the decanuclear brown $[Fe_4Pt_6(CO)_{22}]^{2-}$ dianion (ν_{CO} in CH_3CN at 2020 (s), 2010 (s), 1990 (sh), and 1930 (ms) cm^{-1}).

All of these Fe–Pt mixed-metal carbonyl clusters have been isolated in the solid state as trimethylbenzyl- or tetrabutylammonium salts, and their structures have been ascertained by X-ray diffraction.[5,6] The two hexanuclear $[Fe_3Pt_3(CO)_{15}]^{2-}$ and

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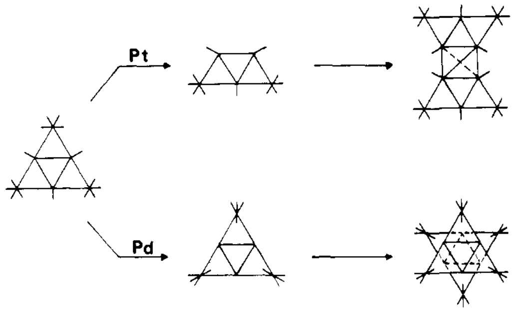
(1) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 3242–4.
(2) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225–31 and references therein.
(3) Yip-Kwai, Lo F.; Longoni, G.; Chini, P.; Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 7691.
(4) By the Gouy method.

0002-7863/80/1502-7973$01.00/0

Scheme I



$[Fe_3Pt_3(CO)_{15}]^-$ clusters have been found to be isostructural, and an ORTEP view of the latter is shown in Figure 1. In both cases the structure is based on an equilateral triangle of platinum atoms which is bridged on each edge by an $Fe(CO)_4$ group. The overall idealized symmetry may be assumed to be D_{3h}. However, in both compounds the six metal atoms are not exactly coplanar, owing to a tilting of the $Fe(CO)_4$ groups above or below the triplatinum plane, with out-of-plane displacements ranging from 0.1 to 0.6 Å.[7]

A comparison among the individual molecular parameters of $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Fe_3Pt_3(CO)_{15}]^-$ (Table I) shows in the latter a significant shortening (0.1 Å) of the average Pt–Pt bond, which suggests that the highest occupied molecular orbital involves primarily platinum atomic orbitals and is antibonding with respect to the Pt_3 triangle.[8] This unprecedented metallic array may seem unexpected for an 86 valence electron cluster such as $[Fe_3Pt_3(CO)_{15}]^{2-}$[9] and probably results from the tendency to planar coordination of platinum and the higher ligand requirement of iron. When considering the $Fe(CO)_4$ group as a bulky analogue of an edge-bridging carbonyl group, the $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion may be reformulated as $\{Pt_3(CO)_3[\mu\text{-}Fe(CO)_4]_3\}^{2-}$ and viewed as a stabilized analogue of $[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$.[2] The existence of a paramagnetic species such as $\{Pt_3(CO)_3[\mu\text{-}Fe(CO)_4]_3\}^-$ may be then ascribed to the presence of axial carbonyls, which hinders dimerization along the pseudo-C_3 axis to give a species formally corresponding to $[Pt_6(CO)_{12}]^{2-}$.[2]

The decanuclear $[Fe_4Pt_6(CO)_{22}]^{2-}$ dianion presents a structure of overall idealized D_{2d} symmetry (Figure 2), which is strictly related to that of $[Fe_3Pt_3(CO)_{15}]^-$ and $[Fe_3Pt_3(CO)_{15}]^{2-}$ and may be thought to derive from the former by loss of an $Fe(CO)_4$ group and orthogonal condensation along the pseudo-C_2 axis of two resulting trapezoidal $[Fe_2Pt_3(CO)_{11}]^-$ units to give rise to a tetrahedral core of platinum atoms,[11] such as indicated in Scheme I.

Scheme I suggests also a possible mechanism of formation for the previously reported $[Fe_6Pd_6(CO)_{24}]^{4-}$ and $[Fe_6Pd_6(CO)_{24}H]^{3-}$[1] and accounts for the nonexistence of Fe–Pd species analogous to the Fe–Pt clusters reported here. Thus, a hypothetical $[Fe_3Pd_3(CO)_{15}]^{2-}$ species, analogous to $[Fe_3Pt_3(CO)_{15}]^{2-}$, would loose easily the three terminal carbonyl groups bonded to the palladium atoms, owing to the well-known reluctance of palladium to bind carbon monoxide.[2,12] Once the steric limit has been removed, two of the resulting unsaturated $[Fe_3Pd_3(CO)_{12}]^{2-}$ units may condense along the C_3 axis in a staggered conformation to give the structure found in the $[Fe_6Pd_6(CO)_{24}H]^{3-}$ trianion.[13]

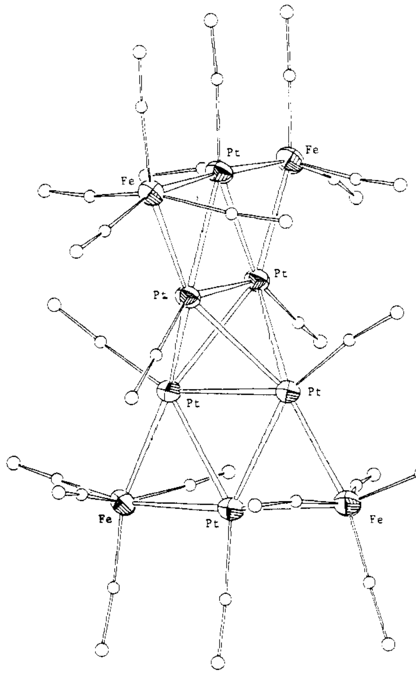


Figure 2. ORTEP view of the $[Fe_4Pt_6(CO)_{22}]^{2-}$ dianion.

Acknowledgment. We acknowledge the late Professor P. Chini, whose interest and helpful suggestions have been a continuous stimulus for carrying out this work.

Supplementary Material Available: Listings of the thermal and positional parameters of $[N(C_4H_9)_4]_2[Fe_3Pt_3(CO)_{15}]$ (Table II), $[N(CH_3)_3CH_2Ph][Fe_3Pt_3(CO)_{15}]$ (Table III), and $[N(CH_3)_3CH_2Ph]_2[Fe_4Pt_6(CO)_{22}]$ (Table IV) (6 pages). Ordering information is given on any current masthead page.

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(5) Crystal data follow. $[N(C_4H_9)_4]_2[Fe_3Pt_3(CO)_{15}]$: M_r = 1657.9; monoclinic; space group $P2_1/c$; a = 14.24 (1), b = 19.18 (2), c = 22.41 (2) Å; β = 96.4 (1)°; V = 6082 Å^3; D_c = 1.81 g/cm^3 for Z = 4. The current R for 3042 independent reflections having $I \geq 3\sigma(I)$ is 0.052. $[N(CH_3)_3CH_2Ph][Fe_3Pt_3(CO)_{15}]$: M_r = 1323.1; triclinic; space group $P\bar{1}$ (after refinement); a = 17.327 (6), b = 10.722 (4), c = 18.854 (6) Å; α = 96.25 (3), β = 90.37 (3), γ = 93.99 (4)°; V = 3473 Å^3; D_c = 2.53 g/cm^3 for Z = 4. The current R for 4614 independent reflections having $\sigma(I) \leq 0.30I$ is 0.046. $[N(CH_3)_3CH_2Ph]_2[Fe_4Pt_6(CO)_{22}]$: M_r = 2310.6; monoclinic; space group C_c (after refinement); a = 13.228 (4), b = 42.022 (13), c = 12.896 (6) Å; β = 124.68 (3)°; V = 5895 Å^3; D_c = 2.60 g/cm^3 for Z = 4. The current R for 3394 independent reflections having $I \geq 3\sigma(I)$ is 0.046. Intensity data were collected on a BASIC diffractometer with graphite-monochromatized Mo Kα radiation up to 2θ = 50° and corrected for absorption by the numerical integration method. The structures have been solved by standard Patterson and Fourier methods and refined by block-matrix least squares to the current R's.

(6) For distances and bond angles see supplementary material.

(7) The freedom of the $Fe(CO)_4$ groups is well documented by the two independent molecules found in the unit cell of $[N(CH_3)_3CH_2Ph][Fe_3Pt_3(CO)_{15}]$, which show different out-of-plane displacements of the iron atoms, although all the other individual molecular parameters are strictly equivalent.

(8) Strouse, C. E.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6032–41.

(9) With the exception of $[Pt_6(CO)_{12}]^{2-}$, all the other 86 valence electron hexanuclear carbonyl clusters present an octahedral metal skeleton.[10]

(10) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285–344.

(11) The idealized symmetry of the Pt_4 core is D_{2d} (see Table I).

(12) Nyholm, R. S. *Proc. Chem. Soc. London* **1961**, 273.

(13) In Scheme I the carbonyl groups bridging the Fe–Pd interlayer bonds and the $FePd_2$ triangular faces found in $[Fe_6Pd_6(CO)_{12}(\mu\text{-}CO)_6(\mu_3\text{-}CO)_6H]^{3-}$ are arbitrarily assigned only to the iron atoms for the sake of clarity.

Evidence against Phosphacylium Cation Participation in Nucleophilic Displacement at Tetracoordinated Phosphorus

Sir:

Information concerning the mechanistic aspects of organophosphorus chemistry has during its development been subject to interpretation based on analogy to hydrocarbon mechanisms. This can be especially noted in the chemistry of carboxylic acid esters and phosphoric acid esters. That carboxylates can undergo nucleophilic displacement via a tetrahedral intermediate was supported by the synthesis of orthoformates and orthocarbonates.[1]