

Mixed Copper/Iron Clusters. The Preparation and Structures of $[(\text{Ph}_3\text{P})_2\text{Cu}]_2\text{Fe}(\text{CO})_4$ and $[(\text{diphos})_2\text{Cu}]_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$

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Abstract: Depending on the nature of the ligands and the reaction conditions, phosphine substituted copper(I) halides (L_nCuX) can react with $\text{Fe}(\text{CO})_4^{2-}$ to form either trinuclear Cu_2Fe derivatives or the novel 10-atom $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ cluster anion. $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuCl}$ and $\text{Fe}(\text{CO})_4^{2-}$ react to form $\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}\}_2\text{Fe}(\text{CO})_4$, the structure of which was determined by X-ray methods. Crystals were monoclinic, space group $\text{P}2_1/c$ with $z = 4$ in a unit cell with dimensions $a = 10.723$ (3) Å, $b = 39.960$ (14) Å, $c = 15.283$ (6) Å, and $\beta = 99.31$ (3)°. The structure was solved by direct methods and refined by full-matrix least squares to $R = 0.105$, $R_w = 0.094$ for 2141 observed reflections. The structure consists of two $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}$ groups bridging opposite edges of a flattened $\text{Fe}(\text{CO})_4$ tetrahedron resulting in a nearly linear $\text{Cu}-\text{Fe}-\text{Cu}$ angle. All four carbonyl groups show a semibridging interaction with the copper atoms. The reaction of $(\text{diphos})\text{CuCl}$ ($\text{diphos} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) and $\text{Fe}(\text{CO})_4^{2-}$ results in the formation of the ionic complex $[(\text{diphos})_2\text{Cu}]_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$; its structure was also determined by X-ray methods. The complex crystallizes in the trigonal space group $\text{P}3$ with $a = 28.495$ (7) Å, $c = 12.471$ (2) Å, and $z = 3$. The metal atoms were located by direct methods and the remaining non-hydrogen atoms were located from a series of difference Fourier syntheses. Refinement of carbon atoms with isotropic and other non-hydrogen atoms with anisotropic temperature factors led to values of $R = 0.055$ and $R_w = 0.047$ for 5722 observed reflections. In the cation 4 phosphorus atoms are bound to the copper in a distorted tetrahedral arrangement. The anion consists of an octahedron of copper atoms capped on four faces by $\text{Fe}(\text{CO})_4$ groups forming a ν_2 -tetrahedron. Three carbonyl groups on each iron show some semibridging interaction with the copper atoms.

The interesting and somewhat unexpected structural variations observed in some recently characterized heteronuclear bimetallic copper-containing complexes¹⁻⁵ prompted us to attempt the synthesis of some analogous tri- and tetranuclear species. The binuclear complexes, which can generally be prepared by the simple reaction of a substituted copper(I) halide with a metal carbonyl monoanion, suggested that the reaction of dianions, such as $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Fe}_2(\text{CO})_8^{2-}$, might lead to the formation of complexes containing a Cu_2Fe or Cu_2Fe_2 core, respectively. At least two trinuclear Cu_2Fe complexes have been reported. The first, prepared by Hieber almost a half century ago, was characterized solely by elemental analysis and has the composition $[(\text{NH}_3)_2\text{Cu}]_2\text{Fe}(\text{CO})_4$.⁶ More recently, Nyholm and co-workers prepared a complex with the composition $[(o\text{-triars})\text{Cu}]_2\text{Fe}(\text{CO})_4$ ($o\text{-triars} = \text{bis}(o\text{-dimethylarsinophenyl})\text{methylarsine}$).⁷ This complex is believed to possess a C_{2v} geometry for the ligand arrangement about the iron atom based on its infrared spectrum, but its actual structure is not known.

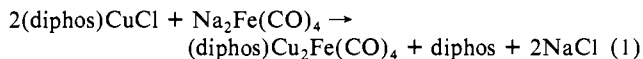
In the binuclear complexes which have been studied, a wide range of $\text{Cu}-\text{M}$ and $\text{Cu}-\text{CO}$ interactions is observed. At one end of the scale, $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{CuV}(\text{CO})_6$, there is no metal-metal bonding or any interaction between the Cu atom and the carbonyl ligands.⁵ At the other extreme, the $(\text{tmed})\text{CuCo}(\text{CO})_4$ complex ($\text{tmed} = N,N,N',N'$ -tetramethylethylenediamine) possesses a very short $\text{Cu}-\text{Co}$ bond (2.36 Å) and a semibridging carbonyl with a short $\text{Cu}-\text{C}$ distance (2.03 Å).⁴ Intermediate are the ($o\text{-triars}$) $\text{CuMn}(\text{CO})_5$ compound with a normal $\text{Cu}-\text{Mn}$ single bond and no apparent $\text{Cu}-\text{CO}$ bonding¹ and the $\text{Cu}-\text{Mo}^{3,5}$ and $\text{Cu}-\text{W}^2$ complexes, which also have a $\text{Cu}-\text{M}$ single bond but which also have two semibridging carbonyls with significantly longer $\text{Cu}-\text{C}$ distances than that observed in the $\text{Cu}-\text{Co}$ complex. There apparently have been no binuclear $\text{Cu}-\text{Fe}$ complexes reported which might serve as a source of information as to the types of bonding which could be expected in the higher nuclearity complexes.

Results and Discussion

Attempts to prepared 1:1 $\text{Cu}-\text{Fe}$ complexes by the reaction of substituted copper halides and the $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ anion were largely unsuccessful. The $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ anion is an effective reducing agent and will reduce most amine- and phosphine-substituted copper halides to copper metal with the concurrent for-

mation of $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$. Some success was achieved with chelating diphosphines, in particular 1,2-bis(dimethylphosphino)ethane (dmpe). The reaction of $(\text{dmpe})\text{CuCl}$ with $\text{Na}(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ leads to the formation of a complex with the composition $(\text{dmpe})\text{CuFe}(\text{CO})_2(\text{C}_5\text{H}_5)$. This material, which slowly decomposes at room temperature, has two CO stretching bands in the infrared at 1825 and 1890 cm^{-1} . These bands are at slightly higher frequencies than that of the sodium salt (1809 and 1880 cm^{-1}) and are typical of the shift observed for copper bonded to transition-metal carbonyl species compared to the free anions.¹⁻⁵ These data are, therefore, consistent with a $\text{Cu}-\text{Fe}$ bonded complex but are by no means proof. Crystals suitable for X-ray studies of this compound are not yet available, and the structural details are, therefore, not known.

The reaction of $\text{Na}_2\text{Fe}(\text{CO})_4$ with a number of phosphine-substituted copper halides was carried out in an attempt to prepare trinuclear Cu_2Fe complexes analogous to the $[(o\text{-triars})\text{Cu}]_2\text{Fe}(\text{CO})_4$ complex but where all the coordination sites on the copper are not occupied. It was found that $(\text{diphos})\text{CuCl}$ ($\text{diphos} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) reacts readily at room temperature to form a complex with the stoichiometry $(\text{diphos})\text{Cu}_2\text{Fe}(\text{CO})_4$ in quantitative yields (eq 1). $(\text{dmpe})\text{CuCl}$ reacts in



a similar manner. The liberation of the free chelating diphosphine ligand in the course of the reaction seemed quite unusual although not unprecedented.⁸ It was later found that one could carry out the same type of reaction by using $(\text{diphos})\text{Cu}_2\text{Cl}_2$ or (dmpe) -

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Table I. Average Bond Distances and Angles for $[(\text{diphos})_2\text{Cu}]_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^a$

Bond Distances							
anions				cations			
atom 1	atom 2	distance (Å)		atom 1	atom 2	distance (Å)	
Fe ₁	Cu ₁	2.463 (4, 4, 5, 3)		Cu	P	2.285 (5, 16, 30, 8)	
Fe ₂	Cu	2.469 (3, 8, 13, 9)					
Cu	Cu	2.616 (3, 8, 31, 12)					
Fe	C _{apical}	1.74 (3, 3, 5, 6)					
Fe	C _{equatorial}	1.76 (2, 2, 6, 12)					
O	C	1.17 (3, 3, 7, 18)					

Bond Angles							
anions				cations			
atom 1	atom 2	atoms	angle (deg)	atom 1	atom 2	atom 3	angle (deg)
Cu ₁	Fe ₁	Cu _{1'}	64.2 (1, 1, 1, 3)	P	Cu	P (bite)	89.6 (2, 4, 5, 4)
Cu	Fe ₂	Cu	64.0 (1, 3, 7, 9)	P ₁	Cu	P ₃	113.4 (2, 13, 13, 2)
Fe ₁	Cu ₁	Fe ₂	174.8 (1, 2, 3, 3)	P ₁	Cu	P ₄	131.0 (2, 10, 10, 2)
Fe ₂	Cu ₂	Fe _{2'}	175.3 (1, 3, 4, 3)	P ₂	Cu	P ₃	117.0 (2, 13, 13, 2)
Fe ₁	C ₁₁	O ₁₁	180.0 (-, 0, 0, 3) ^d	P ₂	Cu	P ₄	118.7 (2, 0, 0, 2)
Fe ₂	C	O _{apical}	177 (2, 1, 1, 3)				
Fe	C	O _{equatorial}	170 (2, 2, 4, 12)				
C _{apical}	Fe	C _{equatorial}	94.4 (8, 14, 53, 12)				

^a The first number in parentheses following an average value for a bond distance or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number is the number of individual values included in the average. ^b This is a symmetry-required value and is, therefore, listed without an estimated standard deviation.

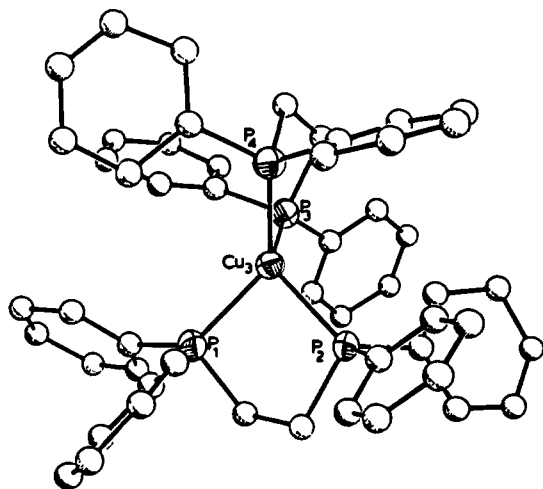


Figure 1. Perspective ORTEP drawing of one of the two crystallographically-independent $(\text{diphos})_2\text{Cu}^+$ cations present in $[(\text{diphos})_2\text{Cu}]_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$. Cu and P atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; carbon atoms are represented by arbitrary-sized spheres.

Cu_2Cl_2 which avoids the separation of the diphosphine from the product. The $(\text{diphos})\text{Cu}_2\text{Fe}(\text{CO})_4$ and $(\text{dmpe})\text{Cu}_2\text{Fe}(\text{CO})_4$ complexes, both in solution and in the solid state, have infrared spectra which resemble, but are not identical with, that reported for $[(o\text{-triars})\text{Cu}]_2\text{Fe}(\text{CO})_4$.⁷ The phosphine complexes have two carbonyl stretching bands at approximately 1970 and 1870 cm^{-1} , whereas the arsine derivative has two bands at 1942 and 1852 cm^{-1} . These differences seemed too large to be accounted for by the change in ligands and coordination number on copper. It also seemed that there were no compelling steric or electronic arguments for the loss of the diphosphine ligands if the resulting complexes were to have the same structure as the $[(o\text{-triars})\text{Cu}]_2\text{Fe}(\text{CO})_4$ complex. A single-crystal X-ray diffraction study of $(\text{diphos})\text{Cu}_2\text{Fe}(\text{CO})_4$ was undertaken. The results of this study revealed the complex to be a salt consisting of $(\text{diphos})_2\text{Cu}^+$ cations and $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ anions, the overall composition being $[(\text{diphos})_2\text{Cu}]_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$. The structure of the cations (an ORTEP diagram of one of the two crystallographically independent cations is shown in Figure 1) shows a distorted tetrahedral geometry for the four phosphorus atoms coordinated to the copper, similar to

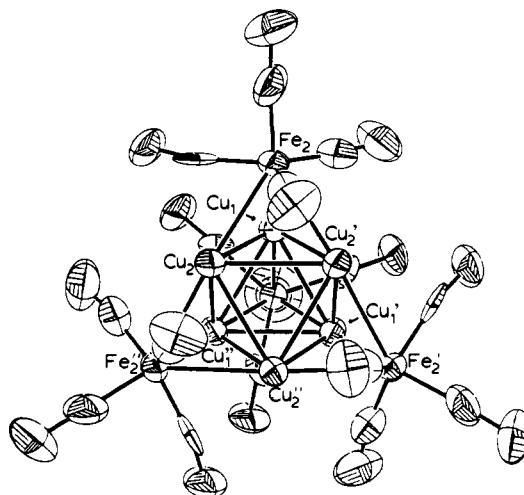


Figure 2. Perspective ORTEP drawing of one of the three crystallographically-independent $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ anions present in $[(\text{diphos})_2\text{Cu}]_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$ with thermal vibration ellipsoids drawn at the 50% probability level. This drawing shows anion I viewed down the crystallographic C_3 -axis located at $1/3, 2/3, z$ in the unit cell which passes through (unlabeled atoms) Fe₁, C₁₁, and O₁₁, and the center of the triangular face defined by atoms Cu₂, Cu_{2'}, and Cu_{2''}. Primed atoms (') are related to nonprimed atoms by the symmetry operation $-x + y, 1 - x, z$; doubly-primed atoms (') are related to nonprimed atoms by the symmetry operation $1 - y, 1 + x - y, z$ where the fractional atomic coordinates x, y, z are those given in Table IV.

that reported by Leoni and co-workers.⁹ All important bond angles and bond lengths seem ordinary for a cation of this type (Table I).

The structure of the anion is exceptionally interesting, consisting of an octahedron of copper atoms capped on four faces by $\text{Fe}(\text{CO})_4$ groups. (See Figure 2 for an ORTEP drawing of one of the three crystallographically independent $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ anions.) The structure can also be described as a ν_2 -tetrahedron, and the arrangement of the metal atoms (Figure 3) is similar to that reported for $\text{H}_4\text{Os}_{10}(\text{CO})_{24}^{2-10}$ and $\text{Os}_{10}\text{C}(\text{CO})_{24}^{2-11}$. The $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$

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Table II. Important Bond Distances and Angles for $[(\text{Ph}_3\text{P})_2\text{Cu}]_2\text{Fe}(\text{CO})_4^a$

Bond Distances in Angstroms											
atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Fe	Cu ₁	2.499 (4)	Cu ₁	P ₁	2.300 (7)	Cu ₂	C ₃	2.25 (2)			
Fe	Cu ₂	2.522 (4)	Cu ₁	P ₂	2.285 (7)	Cu ₂	C ₄	2.46 (1)			
Fe	C ₁	1.83 (2)	Cu ₁	C ₁	2.27 (2)	C ₁	O ₁	1.12 (3)			
Fe	C ₂	1.91 (2)	Cu ₁	C ₂	2.39 (2)	C ₂	O ₂	1.12 (2)			
Fe	C ₃	1.73 (1)	Cu ₂	P ₃	2.287 (6)	C ₃	O ₃	1.24 (2)			
Fe	C ₄	1.78 (2)	Cu ₂	P ₄	2.276 (7)	C ₄	O ₄	1.20 (2)			

Bond Angles in Degrees											
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cu ₁	Fe	Cu ₂	168.7 (2)	Fe	Cu ₁	P ₂	127.0 (2)	P ₄	Cu ₂	C ₃	120.0 (5)
Cu ₁	Fe	C ₁	60.8 (5)	Fe	Cu ₁	C ₁	44.8 (6)	P ₄	Cu ₂	C ₄	101.0 (4)
Cu ₁	Fe	C ₂	64.2 (5)	Fe	Cu ₁	C ₂	45.9 (4)	C ₃	Cu ₂	C ₄	83.2 (5)
Cu ₁	Fe	C ₃	111.3 (7)	P ₁	Cu ₁	P ₂	114.8 (3)	Fe	C ₁	Cu ₁	74.3 (7)
Cu ₁	Fe	C ₄	122.0 (5)	P ₁	Cu ₁	C ₁	116.3 (5)	Fe	C ₁	O ₁	175. (2)
Cu ₂	Fe	C ₁	127.5 (5)	P ₁	Cu ₁	C ₂	94.5 (4)	Cu ₁	C ₁	O ₁	107. (2)
Cu ₂	Fe	C ₂	108.8 (5)	P ₂	Cu ₁	C ₁	110.5 (5)	Fe	C ₂	Cu ₁	69.9 (5)
Cu ₂	Fe	C ₃	60.6 (7)	P ₂	Cu ₁	C ₂	128.7 (4)	Fe	C ₂	O ₂	171. (2)
Cu ₂	Fe	C ₄	67.1 (5)	C ₁	Cu ₁	C ₂	90.0 (6)	Cu ₁	C ₂	O ₂	118. (1)
C ₁	Fe	C ₂	123.6 (6)	Fe	Cu ₂	P ₃	115.2 (3)	Fe	C ₃	Cu ₂	77.4 (8)
C ₁	Fe	C ₃	105.9 (8)	Fe	Cu ₂	P ₄	122.6 (2)	Fe	C ₃	O ₃	171. (2)
C ₁	Fe	C ₄	96.6 (8)	Fe	Cu ₂	C ₃	42.0 (3)	Cu ₂	C ₃	O ₃	105. (2)
C ₂	Fe	C ₃	104.6 (9)	Fe	Cu ₂	C ₄	41.8 (4)	Fe	C ₄	Cu ₂	71.1 (5)
C ₂	Fe	C ₄	101.8 (7)	P ₃	Cu ₂	P ₄	121.4 (2)	Fe	C ₄	O ₄	178. (1)
C ₃	Fe	C ₄	126.5 (9)	P ₃	Cu ₂	C ₃	108.3 (6)	Cu ₂	C ₄	O ₄	111. (1)
Fe	Cu ₁	P ₁	118.2 (2)	P ₃	Cu ₂	C ₄	116.3 (4)				

^aNumbers in parentheses are estimated standard deviations in the last significant digit.

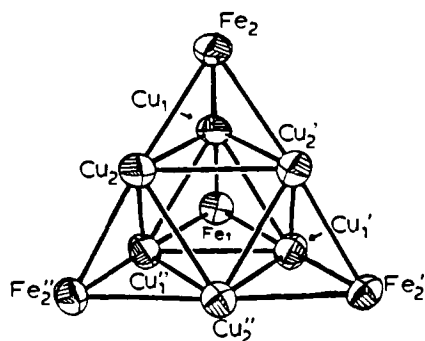


Figure 3. A perspective ORTEP drawing of the metal core of the $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ anion similar to Figure 2 but with the carbonyl groups removed for clarity.

cluster with an electron count of 132 is two electrons short of the 134 predicted by electron-counting schemes for 10 metal-atom clusters with this geometry.¹³ Metals, such as copper, that tend to form 16-electron configurations often form clusters with less than the required electron count, thus the low electron count for the Cu_6Fe_4 complex is not entirely unexpected. Although a number of octahedral copper clusters have previously been prepared,¹² this is the first in which the only bridging ligands are metal carbonyl groups and is the largest bimetallic carbonyl cluster containing copper which has been synthesized. The average Cu–Cu distance (Table I) is 2.64 Å which is about the same distance observed in other hexanuclear copper clusters and slightly longer than the Cu–Cu distance (2.55 Å) found in Cu metal.¹⁴ The average Cu–Fe distance of 2.46 Å is somewhat shorter than that predicted by summing the atomic radii (2.54 Å) but is in line with the Cu–M distances determined for other copper–metal complexes.^{1–5}

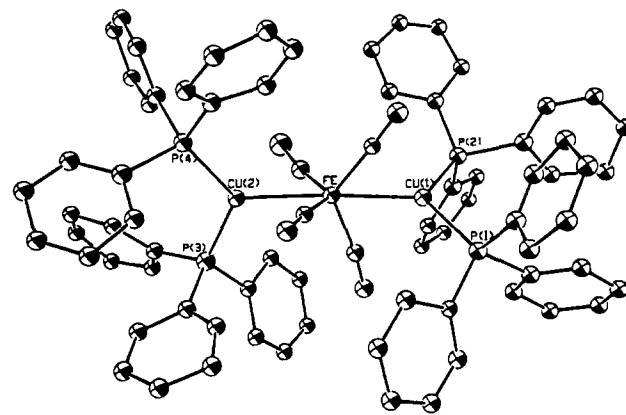


Figure 4. A perspective ORTEP drawing of the $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}_2\text{Fe}(\text{CO})_4$ molecule. Labeling of the carbon atoms has been omitted for clarity.

The arrangement of the carbonyl groups about the iron can best be described as trigonal bipyramidal with carbonyl groups occupying one of the apical and the three equatorial positions. The remaining apical position of the trigonal bipyramid is taken by a Cu_3 face of the Cu_6 octahedron. The apical CO is located on a threefold axis. The carbon atoms of the three equatorial carbonyls are located quite close to a copper atom (average Cu–C distance ~ 2.3 Å) indicating a weak semibridging interaction.

The ease of formation of the Cu_6Fe_4 cluster anion under such mild conditions seems remarkable since the reaction involves an extensive rearrangement of the ligands and copper atoms, yet proceeds in high yields. One is accustomed to thinking of cluster formation as requiring robust conditions and often yielding small amounts of products or, commonly, product mixtures requiring lengthy separations.

The reaction of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuCl}$ with $\text{Na}_2\text{Fe}(\text{CO})_4$ at first glance appears to proceed in the same manner as the analogous reaction with $(\text{diphos})\text{CuCl}$. A quantitative yield of NaCl is produced, and the IR spectrum of the reaction solution has two CO stretching bands at positions nearly identical with those of the diphos derivative (1970 and 1880 cm^{-1}). On evaporation of the solvent, the yellow crystals which form display an entirely different infrared spectrum with a weak band at 1965 cm^{-1} and three bands of approximately equal intensity at 1820, 1799, and

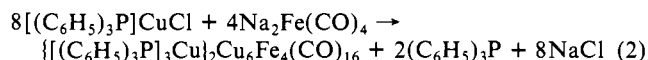
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(12) For typical examples, see: Bezman, S. A.; Churchill, M. R.; Osborne, J. A.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 2063. van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *102*, 551. ten Hoedt, R. W. M.; Noltes, J. G.; van Koten, G.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1979**, 1800.

(13) Teo, B. *Inorg. Chem.* **1984**, *23*, 1251.

(14) Wells, A. F. "Structural Inorganic Chemistry"; Oxford University Press: Oxford, England, 1962; p 985.

1780 cm^{-1} . No triphenylphosphine can be extracted from the solid by washing with pentane, indicating that all the phosphine is complexed to the copper, and elemental analyses confirmed the composition $[(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Cu}_2\text{Fe}(\text{CO})_4$. When redissolved in THF, the spectrum of the complex reverts to the two-band pattern typical of the $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ dianion. Crystals obtained by evaporation of the solvent and slow cooling were subjected to an X-ray diffraction study. An ORTEP representation of this complex is shown in Figure 4. This complex consists of a nearly linear (see Table II for a listing of important bond angles and bond lengths) three metal atom Cu–Fe–Cu grouping. The Cu–Fe distances are slightly longer but similar to those seen in the Cu_6Fe_4 dianion. The coordination of the carbonyl groups about the central iron atom is very nearly tetrahedral with the copper atoms bridging opposite edges of the tetrahedron. The four carbonyl groups are directed toward the copper atoms, and each copper atom appears to interact with two carbonyl groups. The Cu–C distances are approximately 2.25 and 2.4 Å. Disregarding the carbonyl groups, the other groups are arranged in a trigonal plane about the copper atoms. The nearly linear arrangement of the three metal atoms in this complex was somewhat unexpected since in $\text{H}_2\text{Fe}(\text{CO})_4$ and in the $[(\text{C}_6\text{H}_5)_3\text{PAu}]_2\text{Fe}(\text{CO})_4$ complex the H–Fe–H and the Au–Fe–Au angles are only 100° and 73°, respectively, with the overall structures approaching those of a bicapped tetrahedron.^{15,16} The reasons for this marked difference in structure may be either electronic or steric or a combination of both since the additional phosphine ligand on the copper should have an effect on both properties. The very bulky $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}$ groups could play a significant role in preventing the close Cu–Cu contact that would be required for a structure with a severely bent Cu–Fe–Cu angle in the Cu_2Fe complex. Such steric constraints should not exist for $(\text{C}_6\text{H}_5)_3\text{PCu}$ groups; however, attempts to prepare $[(\text{C}_6\text{H}_5)_3\text{PCu}]_2\text{Fe}(\text{CO})_4$ by the reaction of $[(\text{C}_6\text{H}_5)_3\text{P}]\text{CuCl}$ with $\text{Na}_2\text{Fe}(\text{CO})_4$ were not successful. The product obtained in these reactions was $\{[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cu}_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$ (eq 2), and no evidence of the formation of $[(\text{C}_6\text{H}_5)_3\text{PCu}]_2\text{Fe}(\text{CO})_4$ or $\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}_2\text{Fe}(\text{CO})_4$ was observed.



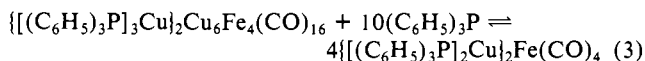
The ability to prepare such vastly different complexes as the Cu_6Fe_4 dianion and the Cu_2Fe compound by making minor adjustments in the ligands or reaction conditions, and the ease in which the two complexes can be interconverted, is interesting. On the basis of infrared data, it would appear that the Cu_6Fe_4 cluster is the dominant species in solutions resulting from the reaction of $\text{Fe}(\text{CO})_4^{2-}$ with any of the phosphine-substituted copper(I) halides. The Cu_6Fe_4 cluster is apparently in equilibrium with the Cu_2Fe species, and the particular complex isolated is dependent on the nature and concentration of the phosphine ligands. In the case where bidentate phosphines, such as diphos or dmpe, are used, only the Cu_6Fe_4 clusters were obtained. With $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuCl}$ as the starting material, either the Cu_6Fe_4 or the Cu_2Fe complexes can be isolated. Under conditions where there is a relatively high concentration of $(\text{C}_6\text{H}_5)_3\text{P}$ the equilibrium is driven in the direction of the formation of $\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}_2\text{Fe}(\text{CO})_4$ compound and it precipitates as the least soluble material. If, on the other hand, one prepares a solution of $\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}_2\text{Fe}(\text{CO})_4$ in a solvent such as THF or acetone, careful spectroscopic studies indicate the presence of only a single major species with properties consistent with those of a salt of the $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ anion. The infrared spectrum shows only two peaks in the CO stretching region at 1970 and 1867 cm^{-1} , and only a single resonance at 214.7 ppm is observed in the ^{13}C NMR spectrum. (The Na^+ and $(\text{diphos})_2\text{Cu}^+$ salts of the $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ anion have resonances at 214.1¹⁷ and 215.3 ppm, respectively, when observed under

Table III. Crystal Data and Summary of Data Collection and Structure Refinement

data	compound	
	$[(\text{diphos})_2\text{Cu}]_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$	$\{[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Cu}_2\text{Fe}(\text{CO})_4$
form wt	2773.6	1344.2
crystal system	trigonal	monoclinic
space group	$P_3-C_3^1$ (no. 143)	$P2_1/c$
cell constants		
<i>a</i> , Å	28.495 (7)	10.723 (3)
<i>b</i> , Å	28.495 (7)	39.960 (14)
<i>c</i> , Å	12.471 (2)	15.283 (6)
<i>α</i> , deg	90.00	90.00
<i>β</i> , deg	90.00	99.31 (3)
<i>γ</i> , deg	120.00	90.00
cell volume, Å ³	8767 (3)	6462.4
<i>z</i>	3	4
ρ (calcd) g/cm ³	1.576	1.38
crystal size, mm	$0.74 \times 0.62 \times 0.56$	$0.26 \times 0.28 \times 0.32$
radiation	$\text{Mo K}\alpha$	$\text{Mo K}\alpha$
scan technique	ω scan	$\omega - 2\theta$
scan range	0.90°	$1.00 + 0.35 \tan \theta$
2θ limits	$3.00\text{--}50.70^\circ$	$0\text{--}40^\circ$
independent reflections	11372	5388
collected		
no. of independent data	5722	2141
parameters refined	885	424
R^a	0.055	0.105
R_w^b	0.047	0.094
goodness of fit ^c	1.86	1.96
largest peak, e/Å ³	0.48	0.75

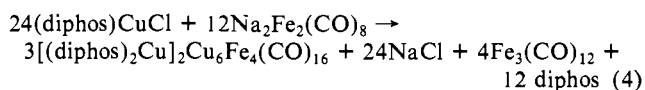
$$^a R = \sum (|F_o| - |F_c|) / \sum |F_o|, \quad ^b R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o| \}^{1/2}, \\ ^c \text{GOF} = \{ \sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV}) \}^{1/2}.$$

similar conditions.) Although complexes with nuclearities intermediate between Cu_2Fe and Cu_6Fe_4 do exist,¹⁸ neither these nor any other Cu–Fe species have been detected in the phosphine-containing solutions prepared from $\{[(\text{C}_6\text{H}_5)_3\text{P}]\text{Cu}_2\text{Fe}(\text{CO})_4$. This, of course, does not preclude such complexes as being intermediates in the interconversion of the Cu_2Fe and Cu_6Fe_4 species. The addition of an inert solvent such as hexane to such solutions precipitates the $\{[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cu}_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$ complex, the same product which is obtained from the reaction of $[(\text{C}_6\text{H}_5)_3\text{P}]\text{CuCl}$ with $\text{Na}_2\text{Fe}(\text{CO})_4$. The $\{[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cu}_2\text{Cu}_6\text{Fe}_4(\text{CO})_{16}$ compound can be converted to the $\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}_2\text{Fe}(\text{CO})_4$ complex by the addition of triphenylphosphine to a solution of the Cu_6Fe_4 derivative and allowing the solvent to slowly evaporate (eq 3). It is also interesting to note that if one adds



free diphos to a solution prepared by dissolving the Cu_2Fe complex, the product obtained on crystallization is the $(\text{diphos})_2\text{Cu}^+$ salt of the $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ dianion.

All attempts to prepare four-atom Cu_2Fe_2 complexes by the reaction of phosphine-substituted copper halides with $\text{Na}_2\text{Fe}_2(\text{CO})_8$ have failed thus far. In most cases the $\text{Fe}_2(\text{CO})_8^{2-}$ species undergoes a disproportionation reaction leading to $\text{Fe}_3(\text{CO})_{12}$ and a complex derived from $\text{Fe}(\text{CO})_4^{2-}$ such as the $\text{Cu}_6\text{Fe}_4(\text{CO})_{16}^{2-}$ dianion (eq 4).



The chemistry of the Cu–Fe bimetallic complexes is proving to be a rich synthetic area. The products obtained from seemingly simple metathesis reactions are often complex and largely unpredictable. The ease of interconversion of some of these complexes also lends interest and may provide clues to how the larger clusters are formed. The reactions of these materials are just now

(15) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243.

(16) Lauher, J.; Wald, K., unpublished results quoted in the following: Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237.

(17) Doyle, G.; Heaton, B. T.; Occhiello, E. *Organometallics* **1985**, *4*, 1224.

(18) Doyle, G.; Eriksen, K. A.; Van Engen, D., in press.

Table IV. Table of Positional Parameters and their Estimated Standard Deviations^a for [(diphos)₂Cu]₂Cu₆Fe₄(CO)₁₆

Anion I									
atom ^b	x	y	z	B (Å ²) ^c	atom ^b	x	y	z	B (Å ²) ^c
Fe ₁	0.3333 ^d	0.6667 ^d	-0.1010 (3)	3.5 (1)	O ₂₃	0.2562 (5)	0.6248 (4)	0.4397 (8)	6.4 (6)
Fe ₂	0.2213 (1)	0.5852 (1)	0.2218 (2)	3.7 (1)	O ₂₄	0.1741 (5)	0.6351 (5)	0.0881 (10)	8.3 (7)
Cu ₁	0.2740 (1)	0.6238 (1)	0.0546 (2)	3.4 (1)	C ₁₁	0.3333 ^d	0.6667 ^d	-0.2376 (31)	8.0 (13)
Cu ₂	0.3171 (1)	0.6072 (1)	0.2259 ^e	3.6 (1)	C ₁₂	0.3008 (6)	0.5947 (7)	-0.0889 (12)	3.7 (7)
O ₁₁	0.3333 ^d	0.6667 ^d	-0.3395 (20)	14.0 (13)	C ₂₁	0.1594 (9)	0.5386 (7)	0.2667 (16)	6.8 (10)
O ₁₂	0.2804 (5)	0.5478 (4)	-0.0993 (9)	6.6 (6)	C ₂₂	0.2334 (5)	0.5347 (6)	0.1715 (12)	4.8 (7)
O ₂₁	0.1149 (5)	0.5068 (5)	0.3052 (13)	11.2 (8)	C ₂₃	0.2461 (7)	0.6129 (6)	0.3493 (11)	4.5 (8)
O ₂₂	0.2333 (5)	0.4959 (5)	0.1347 (11)	6.9 (6)	C ₂₄	0.1968 (7)	0.6171 (7)	0.1415 (14)	6.1 (8)
Anion II									
atom ^b	x	y	z	B (Å ²) ^c	atom ^b	x	y	z	B (Å ²) ^c
Fe ₁	0.0000 ^d	0.0000 ^d	0.2661 (3)	4.0 (1)	O ₂₃	-0.0210 (5)	-0.0753 (6)	0.8096 (9)	7.7 (7)
Fe ₂	-0.0474 (1)	-0.1143 (1)	0.5890 (2)	4.1 (1)	O ₂₄	-0.1490 (5)	-0.1367 (4)	0.4939 (9)	7.3 (6)
Cu ₁	-0.0250 (1)	-0.0607 (1)	0.4220 (2)	4.1 (1)	C ₁₁	0.0000 ^d	0.0000 ^d	0.1264 (27)	7.3 (12)
Cu ₂	0.356 (1)	-0.0253 (1)	0.5936 (2)	3.8 (1)	C ₁₂	0.0469 (7)	-0.0212 (8)	0.2764 (14)	5.5 (9)
O ₁₁	0.0000 ^d	0.0000 ^d	0.0334 (15)	8.6 (9)	C ₂₁	-0.0778 (7)	-0.183 (8)	0.6424 (21)	9.9 (11)
O ₁₂	0.0779 (6)	-0.0381 (6)	0.2662 (10)	8.2 (8)	C ₂₂	0.0019 (8)	-0.1150 (7)	0.5123 (16)	6.2 (9)
O ₂₁	-0.0977 (5)	-0.2223 (5)	0.6774 (15)	12.4 (9)	C ₂₃	-0.0275 (8)	-0.0846 (7)	0.7205 (17)	6.0 (9)
O ₂₂	0.0328 (6)	-0.1261 (5)	0.4659 (11)	8.9 (7)	C ₂₄	-0.1069 (8)	-0.1220 (7)	0.5294 (14)	5.8 (9)
Anion III									
atom ^b	x	y	z	B (Å ²) ^c	atom ^b	x	y	z	B (Å ²) ^c
Fe ₁	0.6667 ^d	0.3333 ^d	1.1085 (3)	2.8 (1)	O ₂₃	0.6333 (6)	0.2557 (7)	0.5635 (11)	8.6 (8)
Fe ₂	0.6188 (1)	0.2186 (1)	0.7850 (2)	3.9 (1)	O ₂₄	0.7109 (6)	0.2147 (6)	0.8854 (10)	7.8 (8)
Cu ₁	0.6420 (1)	0.2723 (1)	0.9521 (2)	3.5 (1)	C ₁₁	0.6667 ^d	0.3333 ^d	1.2490 (19)	4.0 (9)
Cu ₂	0.6064 (1)	0.2980 (1)	0.7803 (2)	3.9 (1)	C ₁₂	0.5948 (5)	0.3004 (6)	1.1013 (12)	3.8 (6)
O ₁₁	0.6667 ^d	0.3333 ^d	1.3374 (17)	11.0 (12)	C ₂₁	0.5878 (8)	0.1495 (8)	0.7429 (16)	8.6 (12)
O ₁₂	0.5489 (4)	0.2751 (5)	1.1125 (9)	6.3 (6)	C ₂₂	0.5645 (8)	0.2090 (7)	0.8677 (15)	5.9 (9)
O ₂₁	0.5668 (6)	0.1058 (6)	0.7166 (15)	13.5 (9)	C ₂₃	0.6283 (8)	0.2448 (8)	0.6544 (16)	5.8 (10)
O ₂₂	0.5247 (5)	0.1941 (5)	0.9156 (11)	8.2 (7)	C ₂₄	0.6761 (8)	0.2190 (7)	0.8503 (13)	5.5 (10)
Cation I									
atom ^b	x	y	z	B (Å ²) ^c	atom ^b	x	y	z	B (Å ²) ^c
Cu ₃	0.9228 (1)	0.6378 (1)	0.2823 (1)	2.9 (1)	C _{B23}	0.8495 (9)	0.7685 (9)	0.3223 (17)	8.7 (6)
P ₁	0.9033 (2)	0.5751 (2)	0.1526 (3)	3.4 (2)	C _{B24}	0.8067 (8)	0.7593 (8)	0.2502 (16)	7.2 (5)
P ₂	0.8332 (2)	0.6154 (2)	0.2873 (4)	3.2 (2)	C _{B25}	0.7655 (8)	0.7141 (8)	0.2001 (15)	7.2 (5)
P ₃	0.9829 (2)	0.7247 (2)	0.2328 (4)	3.0 (2)	C _{B26}	0.7759 (7)	0.6664 (7)	0.2108 (14)	6.1 (5)
P ₄	0.9678 (2)	0.6509 (2)	0.4388 (4)	3.3 (2)	C _{A31}	0.9673 (6)	0.7692 (6)	0.1532 (11)	3.2 (3)
C ₁	0.8473 (6)	0.5796 (5)	0.0877 (11)	3.3 (3)	C _{A32}	0.9438 (6)	0.9490 (6)	0.0526 (12)	4.0 (3)
C ₂	0.8025 (6)	0.5696 (6)	0.1713 (11)	3.6 (3)	C _{A33}	0.9303 (7)	0.7830 (7)	-0.0109 (13)	5.1 (4)
C ₃	1.0082 (6)	0.7601 (6)	0.3661 (11)	3.6 (3)	C _{A34}	0.9386 (7)	0.8311 (7)	0.0269 (13)	4.8 (4)
C ₄	1.0204 (6)	0.7261 (6)	0.4427 (10)	3.3 (3)	C _{A35}	0.9606 (7)	0.8489 (7)	0.1270 (15)	6.1 (5)
C _{A11}	0.8729 (5)	0.5039 (6)	0.1934 (11)	3.2 (3)	C _{A36}	0.9760 (7)	0.8194 (7)	0.1949 (12)	4.9 (4)
C _{A12}	0.8625 (6)	0.4638 (6)	0.1140 (12)	4.1 (4)	C _{B31}	1.0453 (5)	0.7340 (6)	0.1715 (10)	3.0 (3)
C _{A13}	0.8358 (6)	0.4085 (7)	0.1488 (13)	4.5 (4)	C _{B32}	1.0736 (5)	0.7767 (6)	0.0930 (11)	3.8 (3)
C _{A14}	0.8211 (6)	0.3965 (6)	0.2509 (12)	3.9 (3)	C _{B33}	1.1212 (6)	0.7793 (6)	0.0486 (11)	3.6 (3)
C _{A15}	0.8292 (7)	0.4338 (7)	0.3314 (13)	5.3 (4)	C _{B34}	1.1387 (7)	0.7428 (7)	0.0802 (13)	5.1 (4)
C _{A16}	0.8579 (6)	0.4906 (6)	0.3009 (11)	3.4 (3)	C _{B35}	1.1069 (8)	0.7000 (7)	0.1565 (15)	6.6 (5)
C _{B11}	0.9503 (6)	0.5807 (6)	0.0443 (11)	3.6 (3)	C _{B36}	1.0626 (7)	0.6971 (7)	0.1951 (12)	4.6 (4)
C _{B12}	0.9933 (7)	0.5752 (7)	0.0729 (13)	5.2 (4)	C _{A41}	1.0073 (6)	0.6167 (6)	0.4602 (11)	3.2 (3)
C _{B13}	1.0305 (8)	0.5782 (8)	-0.0105 (17)	7.4 (5)	C _{A42}	1.0442 (7)	0.6371 (7)	0.5504 (14)	5.7 (4)
C _{B14}	1.0213 (9)	0.5883 (8)	-0.1154 (17)	8.0 (6)	C _{A43}	1.0794 (9)	0.6133 (10)	0.5663 (18)	9.4 (6)
C _{B15}	0.9763 (9)	0.5891 (8)	-0.1404 (16)	8.2 (6)	C _{A44}	1.0732 (8)	0.5733 (8)	0.4956 (17)	7.4 (5)
C _{B16}	0.9383 (7)	0.5895 (7)	-0.0628 (15)	6.3 (5)	C _{A45}	1.0370 (9)	0.5552 (8)	0.4080 (16)	7.7 (5)
C _{A21}	0.7849 (6)	0.5748 (6)	0.3971 (11)	3.6 (3)	C _{A46}	1.0045 (7)	0.5796 (7)	0.3949 (13)	5.1 (4)
C _{A22}	0.7597 (7)	0.5203 (7)	0.3932 (13)	5.2 (4)	C _{B41}	0.9290 (6)	0.6389 (6)	0.5574 (11)	3.8 (3)
C _{A23}	0.7241 (7)	0.4880 (7)	0.4777 (14)	5.8 (4)	C _{B42}	0.9204 (7)	0.6754 (6)	0.6165 (12)	4.4 (4)
C _{A24}	0.7194 (8)	0.5183 (9)	0.5615 (16)	7.4 (5)	C _{B43}	0.8845 (7)	0.6583 (7)	0.7061 (14)	6.1 (5)
C _{A25}	0.7481 (8)	0.5743 (9)	0.5740 (15)	7.1 (5)	C _{B44}	0.8557 (7)	0.6058 (8)	0.7296 (15)	6.5 (5)
C _{A26}	0.7828 (7)	0.6061 (8)	0.4838 (15)	6.3 (5)	C _{B45}	0.8595 (7)	0.5674 (7)	0.6780 (14)	6.1 (5)
C _{B21}	0.8203 (7)	0.6733 (7)	0.2688 (13)	4.9 (4)	C _{B46}	0.8980 (7)	0.5833 (7)	0.5905 (13)	5.3 (4)
C _{B22}	0.5870 (7)	0.7223 (7)	0.3281 (13)	5.3 (4)					
Cation II									
atom ^b	x	y	z	B (Å ²) ^c	atom ^b	x	y	z	B (Å ²) ^c
Cu ₃	0.0789 (1)	0.3542 (1)	0.7168 (1)	2.8 (1)	C _{B23}	0.1669 (8)	0.2350 (8)	0.7260 (15)	6.9 (5)
P ₁	0.0964 (2)	0.4205 (2)	0.8394 (3)	3.2 (2)	C _{B24}	0.2205 (9)	0.2528 (8)	0.7694 (15)	7.2 (5)
P ₂	0.1703 (2)	0.3814 (2)	0.7155 (4)	3.0 (2)	C _{B25}	0.2583 (8)	0.3085 (9)	0.7920 (15)	7.1 (5)
P ₃	0.0191 (2)	0.2693 (2)	0.7812 (4)	2.9 (2)	C _{B26}	0.2444 (7)	0.3493 (7)	0.7773 (14)	5.9 (4)
P ₄	0.0331 (2)	0.3317 (2)	0.5590 (4)	3.2 (2)	C _{A31}	0.0365 (6)	0.2289 (6)	0.8698 (11)	3.3 (3)
C ₁	0.1531 (6)	0.4218 (6)	0.9200 (11)	3.9 (3)	C _{A32}	0.0555 (6)	0.2501 (6)	0.9693 (13)	4.3 (4)
C ₂	0.1984 (6)	0.4306 (6)	0.8360 (11)	4.0 (3)	C _{A33}	0.0712 (7)	0.2233 (7)	1.0454 (14)	5.6 (4)
C ₃	-0.0060 (6)	0.2286 (6)	0.6575 (11)	3.4 (3)	C _{A34}	0.0657 (7)	0.1722 (7)	1.0121 (14)	5.3 (4)
C ₄	-0.0212 (6)	0.2591 (6)	0.5772 (11)	3.9 (3)	C _{A35}	0.0448 (7)	0.1495 (7)	0.9156 (14)	5.1 (4)

Table IV (Continued)

Cation II									
atom ^b	x	y	z	B (Å ²) ^c	atom ^b	x	y	z	B (Å ²) ^c
C _{A11}	0.1288 (6)	0.4916 (6)	0.7894 (11)	3.5 (3)	C _{A36}	0.0288 (6)	0.1784 (6)	0.8389 (11)	3.9 (3)
C _{A12}	0.1391 (6)	0.5331 (7)	0.8656 (12)	4.5 (4)	C _{B31}	-0.0433 (5)	0.2619 (6)	0.8411 (10)	2.8 (3)
C _{A13}	0.1676 (7)	0.5889 (7)	0.8253 (13)	5.3 (4)	C _{B32}	-0.0799 (7)	0.2147 (7)	0.8955 (12)	4.7 (4)
C _{A14}	0.1838 (7)	0.5988 (7)	0.7186 (13)	5.0 (4)	C _{B33}	-0.1292 (7)	0.2077 (7)	0.9297 (13)	5.2 (4)
C _{A15}	0.1713 (7)	0.5564 (7)	0.6497 (13)	5.0 (4)	C _{B34}	-0.1435 (7)	0.2484 (7)	0.9119 (12)	4.9 (4)
C _{A16}	0.1417 (6)	0.4987 (7)	0.6809 (13)	4.6 (4)	C _{B35}	-0.1082 (6)	0.2945 (6)	0.8575 (11)	3.6 (3)
C _{B11}	0.0510 (7)	0.4169 (7)	0.9449 (13)	5.0 (4)	C _{B36}	-0.0553 (6)	0.3031 (6)	0.8152 (11)	3.8 (3)
C _{B12}	0.0117 (8)	0.4320 (7)	0.9118 (15)	6.2 (5)	C _{A41}	-0.0061 (6)	0.3629 (5)	0.5128 (11)	3.1 (3)
C _{B13}	-0.0282 (9)	0.4290 (9)	0.9924 (18)	8.5 (6)	C _{A42}	-0.0413 (7)	0.3427 (7)	0.4218 (13)	5.2 (4)
C _{B14}	-0.0257 (9)	0.4107 (9)	1.0912 (18)	8.7 (6)	C _{A43}	-0.0724 (8)	0.3689 (8)	0.3992 (15)	6.9 (5)
C _{B15}	0.0128 (10)	0.3943 (9)	1.1271 (19)	9.6 (6)	C _{A44}	-0.0674 (8)	0.4081 (8)	0.4556 (15)	7.0 (5)
C _{B16}	0.0522 (8)	0.4004 (8)	1.0455 (16)	6.7 (5)	C _{A45}	-0.0333 (8)	0.4301 (8)	0.5456 (16)	7.6 (5)
C _{A21}	0.2131 (6)	0.4194 (6)	0.6022 (11)	3.7 (3)	C _{A46}	-0.0002 (7)	0.4080 (7)	0.5812 (13)	5.2 (4)
C _{A22}	0.2442 (8)	0.4786 (8)	0.6010 (15)	6.7 (5)	C _{B41}	0.0701 (6)	0.3316 (7)	0.4365 (12)	4.0 (3)
C _{A23}	0.2744 (8)	0.5059 (8)	0.5020 (16)	6.8 (5)	C _{B42}	0.0741 (7)	0.2866 (7)	0.4189 (13)	5.1 (4)
C _{A24}	0.2764 (7)	0.4757 (8)	0.4226 (15)	6.7 (5)	C _{B43}	0.1105 (8)	0.2922 (8)	0.3255 (16)	1.4 (5)
C _{A25}	0.2474 (7)	0.4188 (7)	0.4271 (14)	6.4 (5)	C _{B44}	0.1336 (9)	0.3374 (10)	0.2667 (18)	9.4 (7)
C _{A26}	0.2165 (6)	0.3926 (6)	0.5183 (12)	4.2 (4)	C _{B45}	0.1288 (9)	0.3810 (9)	0.2775 (17)	8.4 (6)
C _{B21}	0.1909 (6)	0.3312 (6)	0.7363 (11)	3.4 (3)	C _{B46}	0.0946 (7)	0.3789 (8)	0.3803 (15)	6.3 (5)
C _{B22}	0.1538 (7)	0.2799 (7)	0.7213 (13)	4.8 (4)					

^aThe numbers in parentheses are the estimated standard deviations in the last significant digit. ^bAtoms are labeled in agreement with figures 1 and 2. ^cFor atoms which were refined anisotropically (all anion atoms and the Cu and P atoms of the cation) this is the equivalent isotropic *B* which is defined as one-third of the trace of the orthogonalized *B_v* tensor. For all remaining (cation non-hydrogen) atoms this is the isotropic thermal parameter which was actually least-squares refined. ^dThis is a symmetry-required value and is, therefore, listed without an estimated standard deviation. ^eThis parameter was used to define the origin of the unit cell along the *c* axis and is, therefore, listed without an estimated standard deviation.

Table V. Table of Positional Parameters and Their Estimated Standard Deviations for [(Ph₃P)₂Cu]₂Fe(CO)₄

atom	x	y	z	B (Å ²)	atom	x	y	z	B (Å ²)
Fe	0.8063 (4)	0.8669 (1)	0.5601 (2)	2.8 (1)	C ₃₄	1.050 (3)	0.8859 (8)	0.965 (2)	5.4 (8)*
Cu ₁	0.9275 (3)	0.8969 (1)	0.6903 (2)	3.08 (9)	C ₃₅	1.099 (2)	0.8344 (8)	0.811 (2)	3.7 (7)*
Cu ₂	0.7259 (3)	0.83561 (9)	0.4190 (2)	2.97 (8)	C ₃₆	1.037 (3)	0.8119 (8)	0.752 (2)	4.5 (8)*
P ₁	0.8734 (7)	0.9514 (2)	0.7150 (5)	2.7 (2)	C ₃₇	1.038 (3)	0.7764 (9)	0.767 (2)	6.3 (9)*
P ₂	1.0945 (7)	0.8767 (2)	0.7879 (5)	3.0 (2)	C ₃₈	1.105 (3)	0.768 (1)	0.846 (2)	8 (1)*
P ₃	0.8071 (7)	0.8527 (2)	0.2969 (5)	3.5 (2)	C ₃₉	1.166 (3)	0.7836 (9)	0.905 (2)	5.5 (8)*
P ₄	0.5609 (7)	0.7992 (2)	0.4074 (5)	3.2 (2)	C ₄₀	1.169 (3)	0.8188 (8)	0.890 (2)	5.7 (9)*
C ₁	0.767 (2)	0.5893 (3)	0.671 (2)	2.0 (6)	C ₄₁	0.697 (3)	0.8812 (7)	0.235 (2)	4.3 (7)*
O ₁	0.746 (2)	0.8524 (4)	0.738 (1)	4.0 (5)	C ₄₂	0.651 (3)	0.9052 (8)	0.282 (2)	4.2 (7)*
C ₂	0.908 (2)	0.9035 (3)	0.533 (1)	1.4 (6)	C ₄₃	0.558 (3)	0.9315 (8)	0.250 (2)	5.1 (8)*
O ₂	0.958 (2)	0.9249 (4)	0.507 (1)	3.9 (5)	C ₄₄	0.497 (3)	0.9262 (9)	0.167 (2)	6.1 (9)*
C ₃	0.886 (2)	0.8316 (8)	0.534 (1)	3.2 (7)	C ₄₅	0.538 (3)	0.9027 (8)	0.112 (2)	4.6 (7)*
O ₃	0.935 (2)	0.8041 (5)	0.524 (1)	4.9 (6)	C ₄₆	0.637 (3)	0.8785 (8)	0.148 (2)	4.3 (7)*
C ₄	0.653 (2)	0.8800 (5)	0.510 (1)	1.3 (6)	C ₄₇	0.957 (2)	0.8748 (7)	0.317 (2)	3.1 (7)*
O ₄	0.549 (2)	0.8892 (5)	0.478 (1)	4.4 (5)	C ₄₈	1.055 (2)	0.8609 (7)	0.375 (2)	3.2 (7)*
C ₅	0.801 (2)	0.9746 (7)	0.623 (2)	2.7 (6)*	C ₄₉	1.169 (3)	0.8776 (8)	0.394 (2)	4.4 (8)*
C ₆	0.693 (3)	0.9596 (8)	0.572 (2)	4.4 (7)*	C ₅₀	1.187 (2)	0.9097 (7)	0.353 (2)	3.7 (7)*
C ₇	0.637 (3)	0.9771 (8)	0.492 (2)	4.8 (8)*	C ₅₁	1.085 (2)	0.9220 (7)	0.298 (1)	2.2 (6)*
C ₈	0.686 (2)	1.0058 (8)	0.463 (2)	4.2 (8)*	C ₅₂	0.971 (3)	0.9069 (8)	0.279 (2)	4.4 (7)*
C ₉	0.979 (3)	1.0192 (9)	0.509 (2)	5.9 (9)	C ₅₃	0.834 (2)	0.8220 (7)	0.215 (2)	3.9 (7)*
C ₁₀	0.855 (3)	1.0029 (8)	0.585 (2)	4.7 (8)*	C ₅₄	0.938 (3)	0.8214 (8)	0.175 (2)	4.5 (7)*
C ₁₁	1.002 (2)	0.9791 (7)	0.770 (1)	2.3 (6)*	C ₅₅	0.940 (3)	0.7957 (9)	0.105 (2)	5.8 (8)*
C ₁₂	1.004 (3)	0.9951 (8)	0.849 (2)	4.7 (8)*	C ₅₆	0.848 (3)	0.7721 (8)	0.093 (2)	5.6 (9)*
C ₁₃	1.107 (3)	1.0164 (8)	0.883 (2)	4.4 (7)*	C ₅₇	0.746 (3)	0.7691 (8)	0.130 (2)	5.6 (9)*
C ₁₄	1.211 (3)	1.0171 (8)	0.842 (2)	5.3 (8)*	C ₅₈	0.738 (3)	0.7980 (8)	0.190 (2)	4.8 (8)*
C ₁₅	1.211 (3)	1.0015 (9)	0.766 (2)	6.4 (9)*	C ₅₉	0.600 (3)	0.7545 (8)	0.404 (2)	4.2 (7)*
C ₁₆	1.108 (3)	0.9785 (7)	0.727 (2)	3.9 (7)*	C ₆₀	0.522 (3)	0.7294 (8)	0.429 (2)	5.9 (9)*
C ₁₇	0.757 (2)	0.9539 (7)	0.794 (2)	3.6 (7)*	C ₆₁	0.558 (3)	0.6988 (9)	0.432 (2)	7 (1)*
C ₁₈	0.769 (3)	0.9360 (8)	0.862 (2)	4.3 (8)*	C ₆₂	0.665 (3)	0.6892 (8)	0.367 (2)	5.7 (9)*
C ₁₉	0.691 (3)	0.9338 (9)	0.929 (2)	5.8 (9)*	C ₆₃	0.742 (3)	0.7131 (9)	0.370 (2)	6.1 (9)*
C ₂₀	0.600 (3)	0.9580 (8)	0.917 (2)	4.5 (8)*	C ₆₄	0.707 (3)	0.7451 (7)	0.373 (2)	3.7 (7)*
C ₂₁	0.578 (3)	0.9799 (9)	0.849 (2)	7 (1)*	C ₆₅	0.470 (2)	0.8004 (7)	0.495 (2)	3.0 (6)*
C ₂₂	0.662 (3)	0.9787 (9)	0.780 (2)	6.2 (9)*	C ₆₆	0.336 (3)	0.8009 (8)	0.482 (2)	4.3 (7)*
C ₂₃	1.241 (2)	0.8828 (6)	0.750 (1)	1.5 (5)*	C ₆₇	0.273 (3)	0.8026 (8)	0.555 (2)	4.9 (8)*
C ₂₄	1.361 (2)	0.8796 (6)	0.804 (1)	1.8 (6)*	C ₆₈	0.338 (2)	0.8020 (7)	0.638 (2)	3.6 (7)*
C ₂₅	1.469 (3)	0.8849 (8)	0.767 (2)	4.2 (7)*	C ₆₉	0.467 (2)	0.8051 (7)	0.654 (1)	2.5 (6)*
C ₂₆	1.463 (3)	0.8973 (8)	0.683 (2)	4.5 (7)*	C ₇₀	0.531 (2)	0.8063 (7)	0.584 (1)	2.7 (6)*
C ₂₇	1.352 (3)	0.9010 (8)	0.631 (2)	4.9 (8)*	C ₇₁	0.449 (2)	0.8051 (7)	0.309 (2)	3.0 (7)*
C ₂₈	1.238 (2)	0.8967 (8)	0.664 (2)	3.9 (7)*	C ₇₂	0.404 (3)	0.7820 (9)	0.247 (2)	6.7 (9)*
C ₂₉	1.111 (3)	0.8982 (8)	0.900 (2)	5.0 (8)*	C ₇₃	0.325 (3)	0.7880 (9)	0.171 (2)	5.2 (8)*
C ₃₀	1.195 (2)	0.9224 (7)	0.912 (2)	3.5 (7)*	C ₇₄	0.286 (3)	0.8213 (9)	0.152 (2)	5.8 (9)*
C ₃₁	1.198 (3)	0.9415 (9)	0.996 (2)	6.0 (9)*	C ₇₅	0.327 (2)	0.8467 (7)	0.210 (2)	3.5 (7)*
C ₃₂	1.136 (3)	0.9267 (8)	1.060 (2)	4.1 (7)*	C ₇₆	0.413 (2)	0.8365 (6)	0.289 (1)	1.8 (5)*
C ₃₃	1.053 (3)	0.9021 (8)	1.046 (2)	5.4 (8)*					

^aAsterisk values represent atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as the following: $(\frac{4}{3})[a^2B(1, 1) + b^2B(2, 2) + c^2B(3, 3) + ab(\cos \gamma)B(1, 2) + ac(\cos \beta)B(1, 3) + bc(\cos \alpha)B(2, 3)]$.

being exploited and hopefully will lead to some interesting new chemistry.

Experimental Section

All syntheses and manipulations were carried out under a nitrogen atmosphere unless specified. Solvents were dried prior to use by standard procedures. Reagents were obtained from commercial sources and were used without further purification. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Elemental analyses were carried out by the Analytical Division, Exxon Research and Engineering Company and Galbraith Microanalytical Laboratories.

(dmpe)CuFe(CO)₂(η^5 -C₅H₅). To a suspension of 0.27 g (2.7 mmol) of CuCl in 75 mL of THF was added 0.41 g (2.7 mmol) of dmpe. After having been stirred for 20 min, a solution containing 0.75 g (3.7 mmol) of NaFe(CO)₂(η^5 -C₅H₅), prepared by the Na amalgam reduction of [(η^5 -C₅H₅)Fe(CO)₂]₂, was slowly added over 30 min, and the resulting mixture was stirred for 3 h and then filtered. The filtrate was evaporated to near dryness, and the residue was washed several times with pentane yielding 0.90 g of orange-brown solids. ν_{CO} (Nujol) 1824, 1890 cm⁻¹. Anal. Calcd for C₁₃H₂₁CuFeP₂O₂: C, 39.97; H, 5.42; Cu, 16.26; Fe, 14.29; P, 15.86. Found: C, 39.23; H, 5.49; Cu, 16.2; Fe, 14.2; P, 15.4.

[(diphos)₂Cu]₂Cu₆Fe₄(CO)₁₆. To a suspension of 0.55 g (5.6 mmol) of CuCl in 75 mL of THF was added 1.12 g (2.8 mmol) of diphos. After 20 min of stirring, all the solid material had dissolved and 1.0 g (3.1 mmol) of Na₂Fe(CO)₄^{3/2}dioxane was added in small increments over a 20-min period. The resulting solution was stirred under CO for 16 h and then filtered, and the yellow filtrate was evaporated to dryness. The yellow solid was crystallized from methylene chloride-ether yielding 1.0 g yellow crystals. ν_{CO} (Nujol) 1970, 1873 cm⁻¹. Anal. Calcd for C₁₂₀H₉₆P₈Cu₈Fe₄O₁₆: C, 51.97; H, 3.49; Cu, 18.33; Fe, 8.05; P, 8.93. Found: C, 51.54; H, 3.54; Cu, 19.03; Fe, 8.51; P, 8.63.

[(dmpe)₂Cu]₂Cu₆Fe₄(CO)₁₆. This complex was prepared in the same manner as the diphos analogue from 1.12 g (11.3 mmol) of CuCl, 0.85 g (5.67 mmol) of dmpe, and 2.0 g (6.19 mmol) of Na₂Fe(CO)₄^{3/2}dioxane. A bright yellow solid (1.75 g) was obtained. ν_{CO} (Nujol) 1960, 1875 cm⁻¹. Anal. Calcd for C₄H₆₄Cu₈Fe₄P₈O₁₆: C, 26.98; H, 3.62; Cu, 28.55; Fe, 12.55; P, 13.92. Found: C, 26.23; H, 3.79; Cu, 28.33; Fe, 13.01; P, 13.50.

[(C₆H₅)₃P]₃Cu]₂Cu₆Fe₄(CO)₁₆. A solution of Na₂Fe(CO)₄ was prepared by the addition of 1.6 g (4.9 mmol) of Na₂Fe(CO)₄^{3/2}dioxane in 75 mL of THF and filtering off the insoluble residue. To this solution was added 3.34 g (9.3 mmol) of [(C₆H₅)₃P]CuCl in small increments over a 1-h period. The mixture was stirred under CO for an additional 16 h and then filtered. The filtrate was evaporated to approximately 15 mL, and then 200 mL of pentane was added precipitating a yellow solid. The yellow solid was collected on a filter and dried yielding 2.99 g of yellow product. ν_{CO} (Nujol) 1970, 1875 cm⁻¹. Anal. Calcd for C₁₂₄H₉₀Cu₈Fe₄P₆O₁₆: C, 54.08; H, 3.29; Cu, 18.46; Fe, 8.11; P, 6.75. Found: C, 54.03; H, 3.72; Cu, 18.30; Fe, 8.18; P, 6.75.

[(C₆H₅)₃P]₂Cu]₂Fe(CO)₄. A solution of [(C₆H₅)₃P]₂CuCl was prepared by the addition of 1.03 g (10.4 mmol) of CuCl followed by 5.46 g (20.8 mmol) of (C₆H₅)₃P to 125 mL of CH₂Cl₂. To the resulting pale yellow solution was added 2.26 g (7.0 mmol) of Na₂Fe(CO)₄^{3/2}dioxane in increments. The resulting mixture was stirred overnight and then filtered giving a clear red-brown filtrate. This was evaporated until solids just began to form and then was placed in a freezer at -25 °C for 3 days yielding a small quantity of yellow crystals. ν_{CO} (Nujol) 1780, 1799, 1820 cm⁻¹. Anal. Calcd for C₇₆H₆₀Cu₂FeP₄O₄: C, 67.91; H, 4.50; Cu, 9.45; Fe, 4.16; P, 9.22. Found: C, 67.51; H, 4.50; Cu, 9.81; Fe, 4.24; P, 9.17.

Reaction of (diphos)Cu₂Cl₂ with Na₂Fe₂(CO)₈. A solution of (diphos)Cu₂Cl₂ was prepared by the addition of 0.79 g (8.0 mmol) of CuCl and 1.60 g (4.0 mmol) of diphos to 75 mL of CH₂Cl₂. Na₂Fe₂(CO)₈ (2.50 g, 6.5 mmol, which was prepared from equimolar amounts of Fe(CO)₅ and Na₂Fe(CO)₄, was then added in small increments over a 45-min period. The mixture was then stirred under CO for 16 h. The mixture was filtered, and the filtrate was partially evaporated to ap-

proximately one-third the original volume. Pentane (70 mL) was then added precipitating 2.0 g of a bright yellow solid which was identified as [(diphos)₂Cu]₂Cu₆Fe₄(CO)₁₆. The green filtrate remaining was evaporated to dryness giving 0.30 g of dark green crystals which proved to be Fe₃(CO)₁₂ by comparison to a known sample.

X-ray Data for [(diphos)₂Cu]₂Cu₆Fe₄(CO)₁₆. The structure determination of this complex was carried out by Crystalitics Co. A single crystal was glued to the inside of a thin-walled glass capillary and sealed under N₂. Lattice parameters were determined by a least-squares refinement of 15 computer-centered reflections (2 θ < 25°) and are given in Table III. Data were collected on a computer-controlled four-circle Nicolet Autodiffractometer with graphite monochromated Mo K α radiation using the ω scan technique. A scan range of 0.90° with a ratio of background counting time to net scanning time of 0.50 was used. A total of 17 steps were taken, 13 of which were used in intensity calculations. Background counts were measured at ω settings 0.90° above and below the calculated value for each reflection. The intensities were corrected for Lorentz and polarization effects. The intensity data were also corrected empirically for absorption effects with ψ scans for five reflections having 2 θ between 8.55° and 23.25° and were then reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

The 14 metal atoms of the asymmetric unit were located with the SHELXT Direct Methods programs. The remaining non-hydrogen atoms were located from a series of difference Fourier syntheses. Refinement of cation carbon atoms with isotropic and the other non-hydrogen atoms with anisotropic temperature factors led to values of R and R_w of 0.055 and 0.047, respectively. A final Fourier map showed no peaks above the noise level of 0.48 e/Å³. The final values of the positional parameters are given in Table IV. Tables of thermal parameters, complete bond lengths and angles, and structure factors are given as supplementary material.

X-ray Data for [(C₆H₅)₃P]₂Cu]₂Fe(CO)₄. A single crystal measuring 0.26 × 0.28 × 0.32 mm was glued to the end of a glass fiber. Cell dimensions, determined by a least-squares fit of 25 accurately measured 2 θ values, are given in Table III. Data were collected on a Enraf-Nonius CAD 4 diffractometer with graphite monochromated Mo K α radiation with an ω -2 θ scan technique and a scan range of 1.00 + 0.35 tan θ . The scan was extended by 25% on either side for background measurement. Because of the generally poor scattering quality of the crystals, data were observed and collected only for 0° ≤ 2 θ ≤ 40°. Of the 5388 measured intensities, 2141 were considered observed [$|F_o|^2 \geq 2\sigma(F_o^2)$] after correction for Lorentz, polarization, and background effects. Standard intensities, measured after every 1 h of radiation time, showed no loss in intensity with time and ψ scan data indicated absorption effects to be negligible ($\mu = 10.23$ cm⁻¹). The structure was solved by using direct methods, followed by a series of difference Fourier syntheses and refined by full-matrix least-squares procedures. Because of the limited number of observed data, only the Cu, Fe, and P atoms and the carbonyl groups were refined anisotropically; the phenyl groups were refined with isotropic temperature factors. Hydrogen atoms were entered at their theoretically calculated positions and held fixed. The agreement factors were $R = 0.105$, $R_w = 0.094$. Final atomic coordinates are given in Table V. Tables of thermal parameters, complete bond lengths and bond angles, and structure factors amplitudes are given as supplementary material.

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Supplementary Material Available: Tables of thermal parameters, anion and cation bond lengths and angles, and structure factor amplitudes for [(diphos)₂Cu]₂Cu₆Fe₄(CO)₁₆ and temperature factors, bond distances and angles, and structure factor amplitudes for [(C₆H₅)₃P]₂Cu]₂Fe(CO)₄ (57 pages). Ordering information is given on any masthead page.