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Hydridocopper Complexes Embedded in Iron Carbido-carbonyl Clusters: Synthesis, Reactivity, and Structure of $[\text{Fe}_4\text{C}(\text{CO})_{12}\text{CuCl}]^{2-}$, $[\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}(\eta^2\text{-BH}_4)]^{2-}$, $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-H})\}_2]^{2-}$, and $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-OiPr})\}_2]^{2-}$

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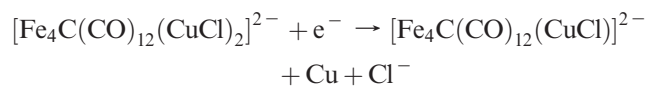
The reaction of $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]^{2-}$ with NaBH_4 yields sequentially $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})]^{2-}$ (**1**) and $[\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}(\eta^2\text{-BH}_4)]^{2-}$ (**2**), depending on the $\text{Fe}_4\text{Cu}_2\text{:NaBH}_4$ ratio. The reaction of $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuNCMe})_2]$ with NaBH_4 yields $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-H})\}_2]^{2-}$ (**3**), which, upon precipitation with 2-propanol, forms $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-OiPr})\}_2]^{2-}$ (**4**). **1** and **2** are isostructural, with a CuX linearly bonded to the exposed carbide ligand of a butterfly $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$ unit. **3** and **4** are also very similar, with the four copper atoms of two Fe_4Cu_2 octahedra connected by bridging hydrides (in **3**) and bridging alkoxides (in **4**). However, **3** and **4** are not isoelectronic, and in agreement with the unsaturation of **3**, its $\text{Cu}\text{--}\text{Cu}$ distance is much shorter.

In a recent paper we have described the synthesis, structure, and reactivity of $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuL})_2]$ and $[\text{Fe}_5\text{C}(\text{CO})_{14}(\text{CuL})]^-$ clusters (where $\text{L} = \text{Cl}^-$ or NCMe).¹ The cyclic voltammetry of the two halide-substituted $\text{Fe}\text{--}\text{Cu}$ clusters showed that their reductions follow different paths. In particular, the electrochemical reduction of $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]^{2-}$ is localized at the $\text{Cu}(\text{I})$ center, since elemental copper is deposited. To confirm this finding, we tested the chemical reduction of $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]^{2-}$ with NaBH_4 . However, besides the expected fragmentation, we could rapidly identify and isolate several other products, obtained by substitution at the copper center, but also by copper addition, with reconstruction of the original octahedron. In this paper we describe the rich chemistry of this $\text{Fe}\text{--}\text{Cu}$ system, which allowed us to isolate hybrid complexes containing metallic centers in both high and low oxidation state and the corresponding ligands (such as BH_4^-)

that are familiar in the coordination chemistry of copper but are quite unusual for carbonyl species. Hydrido^{2,3} or borohydrido^{4–10} complexes of copper can reduce carbon dioxide to formate^{2,11} and are relevant for stoichiometric organic synthesis.¹²

Results

Synthesis and Reactivity. Electrochemical experiments suggested that the reduction of $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]^{2-}$ causes deposition of elemental copper, which is stripped in the return oxidation. Therefore, the following fragmentation was suggested:¹



This hypothesis was verified when we carried out the reaction with NaBH_4 in THF at room temperature. The product formed in the initial steps of the reaction, $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})]^{2-}$ (**1**), was isolated and identified by X-ray analysis.

However, in keeping with the lability of the halide ligands, the unique remaining chloride can be substituted by a large

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excess of BH_4^- , after prolonged reaction times, to yield $[\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}(\eta^2\text{-BH}_4)]^{2-}$ (**2**).

The conversions of $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]^{2-}$ into **1** or **2** are poorly reproducible, owing to variable reaction times and because it is difficult to dose tiny amounts of NaBH_4 . In agreement, we obtained repeatedly a mixed salt of formula $(\text{NEt}_4)_6[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2][\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$, which was partially characterized by X-ray analysis.¹³ Moreover, **1** and **2** are both pentanuclear clusters containing an anionic ligand, and their infrared spectra are virtually superimposable. Therefore we devised a more rational route for the synthesis of **1** and **2**, that is, the assembling of $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$, $[\text{Cu}(\text{NCMe})_4]^+$, and the anionic ligand (either Cl^- or BH_4^-). The reaction is fast, selective, and complete, but the apparent simplicity is counterbalanced by the tedious preparation of $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$.¹⁴

At the same time, we tested the reaction between NaBH_4 and $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuNCMe})_2]$. In this case, we were able to observe an intermediate species, less reduced than **2**, which was isolated by precipitation with NEt_4BF_4 . The salt was crystallized and was found to contain a dioctahedral anion of formula $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-H})\}_2]^{2-}$ (**3**). The same anion was also obtained by cluster reconstruction, which is done by adding Cu(I) ions (in the form of the acetonitrile complex) to **2**. By attempting the precipitation of **3** with 2-propanol, we obtained instead the dimer $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-O}i\text{Pr})\}_2]^{2-}$ (**4**). This unexpected result suggests that the H atoms in **3** maintain some hydride reactivity. More rationally, **4** can be synthesized by titrating a THF solution of $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuNCMe})_2]$ with a solution of $\text{NaO}i\text{Pr}$ in 2-propanol, until the infrared shows complete formation of the desired product.

No NMR signals attributable to the hydridic ligands of **2** and **3** could be detected in the temperature range -70 to $+25$ °C. This result could be largely anticipated, owing to the quadrupolar nature of the ^{63}Cu and ^{65}Cu nuclei.^{15,16}

Solid-State Structures. The solid-state structures of **1** and **2** are very similar, consisting of a distorted trigonal bipyramid of metal atoms, with an isosceles Fe_2Cu triangle in the equatorial plane. The structure of **2** is shown in Figure 1; the structure of **1** is deposited in the Supporting Information. The Fe–Fe edge is short (2.517(1) and 2.507(1) Å, respectively), and the two Fe–Cu edges are very long (> 3.5 Å), so that Fe–Cu interactions in this plane can be excluded. Thus, in the equatorial plane there is a cavity large enough to lodge the carbide. This arrangement of metal atoms was found in other pentanuclear carbide clusters and was referred to as an *arachno*-pentagonal bipyramid, since the known compounds are formed by addition of one ligand to square-pyramidal carbido clusters.¹⁷ As predicted by the

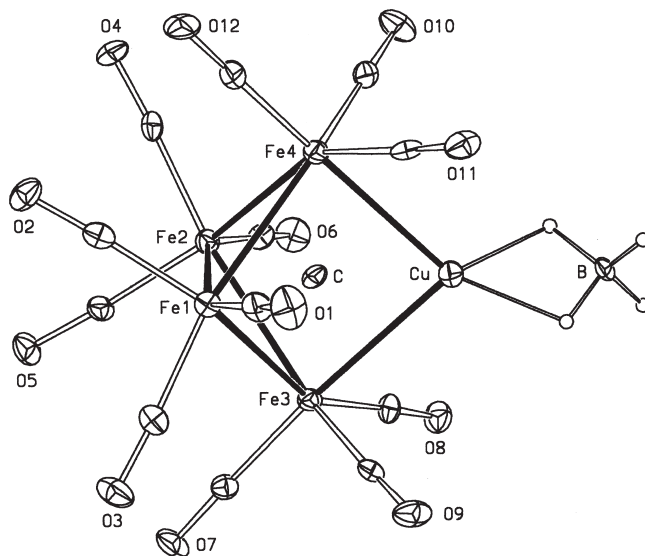


Figure 1. Solid-state structure of anion **2**, $[\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}(\eta^2\text{-BH}_4)]^{2-}$.

Wade rules for *arachno* structures,¹⁸ they possess 76 cluster valence electrons (two more than the square pyramids).

Conversely, **1** and **2** are short of electrons (74 CVE) and isoelectronic with other $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuL})]^-$ -substituted clusters (L = pyridine, pyrazine, or dppe), which adopt other isomeric structures including the almost regular square pyramidal.¹⁹ The complete series of pentanuclear clusters, with structural parameters of the $\text{Fe}_4\text{C}(\text{CO})_{12}$ moiety that remain remarkably constant, and the Fe–Cu separation of increasing length (from 2.7 up to 3.5 Å) reinforce the idea that these clusters are actually the adducts between the carbide atom of $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$ (the electron donor) and a linear $\text{Cu(I)}\text{-L}$ fragment (the acceptor) and that Fe–Cu bonding is substantially absent.²¹ Developing a similar approach, Scheer and co-workers exploited metal clusters containing exposed atoms of p-block elements to connect CuX units into polymeric structures, without M–Cu interactions.²²

The tetrahydroborato ligand is connected to Cu with two bridging hydrides. In agreements with the three-center–two-electron nature of these bonds, they should be longer than the terminal B–H lengths (the average values are indeed 0.87 and 1.07 Å), but the individual values are scattered and affected by high experimental uncertainty (± 0.05 Å). Tetrahydroborate is a well-known ligand in copper coordination chemistry and is typically accompanied by phosphine^{4,5} or phenanthroline.⁶ Among these, the complexes with bidentate tetrahydroborate are prevalent, but there are several examples with monodentate ligands.⁶ Tridentate coordination of BH_4 , common in lanthanide chemistry,²³ is unknown for copper; however a tetradentate, bridging ligand was structurally determined.¹⁰ The Cu–B and the corresponding

(13) Cell parameters: monoclinic $P2(1)/m$; $a = 11.1106(10)$ Å, $b = 43.6707(40)$ Å, $c = 12.9684(12)$ Å, $\beta = 115.108(1)^\circ$, $V = 5697.7(8)$; $Z = 2$; the refinement of the structure was abandoned because of severe disorder.

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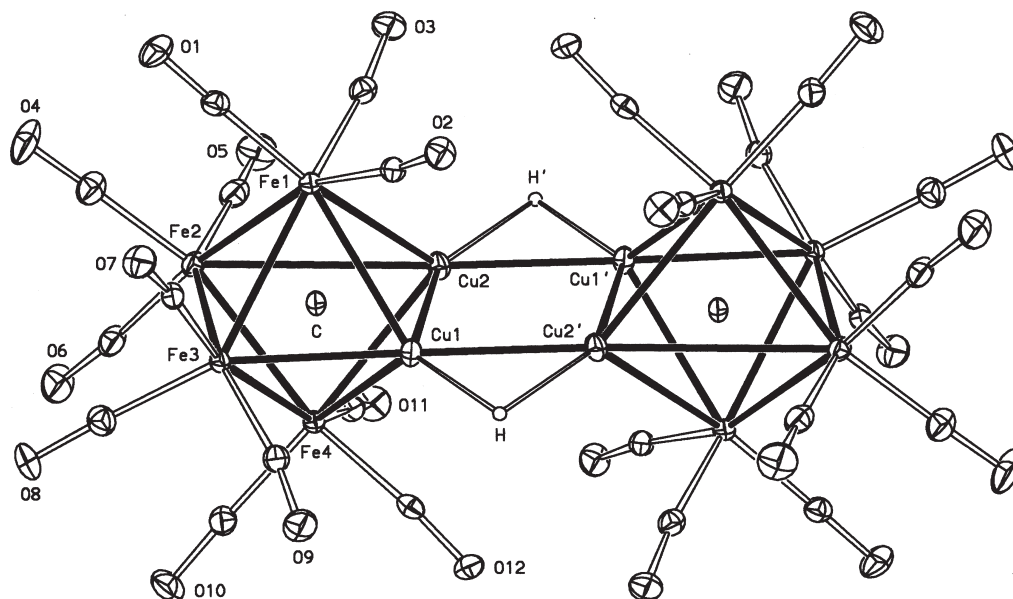


Figure 2. Solid-state structure of anion **3**, $[\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-H})]^{2-}$.

Cu–H bond lengths in **2** [2.139(7) and 1.74 (average) Å, respectively] are longer than those reported for the dimethyl-diphenylphenanthroline complex (2.115(1) and (average) 1.66 Å),⁸ but shorter than those observed by Lippard in the prototypical complex $(\text{PPh}_3)_2\text{CuBH}_4$ [2.184(9) and 2.02(5) Å]. It should be mentioned, however, that the Cu–H distance established by Moncol at low temperature [Cu–H 1.79(2) Å]⁹ is smaller and (within experimental uncertainty) similar to the Cu–H bond length observed in **2**.

The two octahedral dimers **3** and **4** are also very similar and comparable with the known $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-Cl})\}]^{2-}$.¹ Both anions sit on crystallographic inversion centers, so that all individual structural parameters can be compared. They are shown in Figures 2 and 3, respectively.

As already observed in the halide-bridged anion, in the equatorial plane one of the Fe–Cu separations (Fe2–Cu2, 3.258(1) and 3.113(1) Å, respectively) is much longer than the other (Fe3–Cu1, 2.545(1) and 2.505(1) Å). The observation that the Fe–Cu bond lengths can be easily accommodated reinforces the idea that their bond energy must be weak. However, **3**, **4**, and $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-Cl})\}]^{2-}$ are not isoelectronic. Bridging halides and alkoxides are three-electron donors, and therefore in **4** the two octahedra possess 86 CVE each, as expected. On the contrary $\mu\text{-H}$'s are necessarily one-electron donors, and the dimer $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-H})\}]^{2-}$ is short of four valence electrons. In agreement with its unsaturated nature, the interoctahedral Cu–Cu separations (Cu1–Cu2' 2.475(1) Å) are even shorter than the intraoctahedral edge (Cu1–Cu2 2.555(1) Å). The former value is significant if compared with the corresponding separation in **4** (3.022(1) Å) or the Cu–Cu distance found in elemental copper (2.56 Å), but should not be considered

exceptional since a few shorter Cu–Cu distances (down to 2.35 Å) are reported.^{24,25}

Experimental Section

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under an oxygen-free nitrogen atmosphere using Schlenk-tube techniques.²⁶ $(\text{NEt}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$ and $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ were prepared by literature methods. Infrared spectra in solution were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer, using calcium fluoride cells previously purged with N_2 . Elemental analyses were carried out by the staff of Laboratorio di Analisi of the Dipartimento di Chimica Inorganica, Metallorganica e Analitica.

1a. Synthesis of $(\text{NEt}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$ ($[\text{NEt}_4]_2\textbf{1}$). In 20 mL of THF were suspended $(\text{NEt}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$ (0.12 g; 0.116 mmol) and finely ground NaBH_4 (0.030 g). The mixture was stirred for 1 h at room temperature and filtered. The filtrate was dried under vacuum; the residue was suspended in MeOH and precipitated by addition of water. The solid was recovered by filtration, dissolved in THF, and layered with hexane. Yield: 0.042 g, 39%.

Owing to contamination by $(\text{NEt}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$ or $[\text{NEt}_4]_2\textbf{2}$ (see Results), the elemental analyses are only satisfactory and the infrared bands are less sharp and less resolved than in **1b**. Typical values are as follows: Anal. Calcd for $\text{C}_{29}\text{H}_{40}\text{ClCuFe}_4\text{N}_2\text{O}_{12}$: C 37.41; H 4.33; N 3.01. Found: C 38.40; H 4.24; N 2.57. IR $\nu(\text{CO})$ in THF: 1984 s, 1959 s cm^{-1} .

1b. Synthesis of $(\text{PPh}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$ ($[\text{PPh}_4]_2\textbf{1}$). In 10 mL of THF were suspended $(\text{PPh}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$ (0.12 g; 0.10 mmol), $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ (0.036 g; 0.10 mmol), and PPh_4Cl (0.036 g; 0.10 mmol). The mixture was treated as for **2b**. Yield: 0.094 g (72%). Anal. Calcd for $\text{C}_{61}\text{H}_{40}\text{ClCuFe}_4\text{O}_{12}\text{P}_2$: C 54.30; H 2.99. Found: C 54.13; H 3.03; N 0.0. IR $\nu(\text{CO})$ in THF: 2032 w, 1979 s, 1956 vs, 1930 mw, 1907 w cm^{-1} .

2a. Synthesis of $(\text{PPh}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuBH}_4)]$ ($[\text{PPh}_4]_2\textbf{2}$) from $[\text{PPh}_4]_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$. $(\text{PPh}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuCl})_2]$ (0.18 g; 0.12 mmol) was dissolved in 20 mL of THF. Finely

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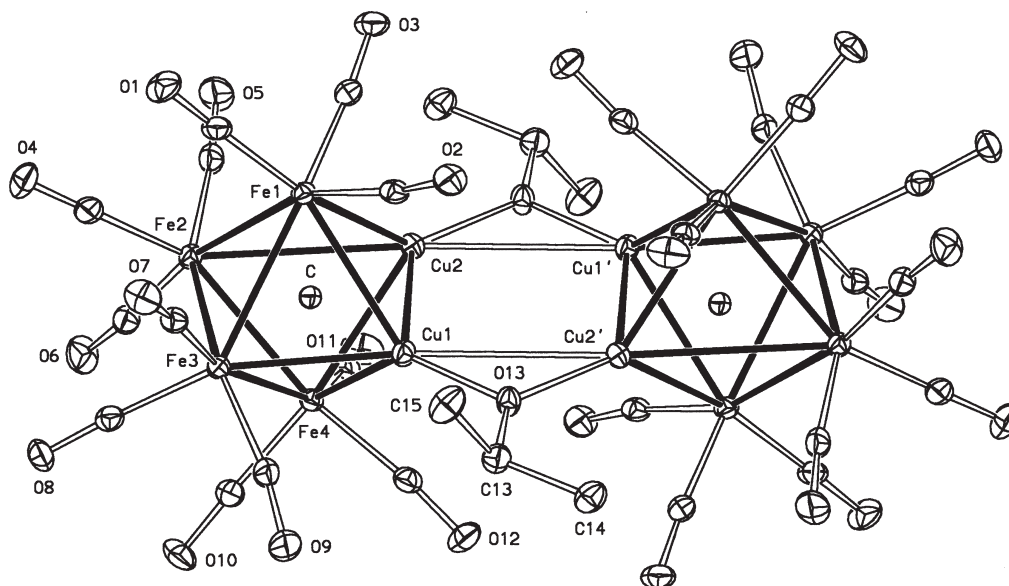


Figure 3. Solid-state structure of anion **4**, $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-O-}i\text{Pr})\}_2]^{2-}$.

ground NaBH_4 (0.040 g) was added in four small portions, every 12 h, continuously with stirring at room temperature. The reaction mixture was filtered and dried under vacuum. The residue was suspended in 2-propanol, dissolved in the minimum amount of THF (ca. 10 mL), and layered with 2-propanol. Yield: 0.100 g, 63%.

2b. Synthesis of $(\text{PPh}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuBH}_4)]$ ($[\text{PPh}_4]_2\mathbf{2}$) from $[\text{PPh}_4]_2[\text{Fe}_4\text{C}(\text{CO})_{12}]$. $(\text{PPh}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}]$ (0.10 g; 0.084 mmol) was dissolved in 10 mL of THF followed by the addition of $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ (0.03 g; 0.084 mmol) and NaBH_4 (0.005 g, 0.08 mmol). The mixture was stirred for 5 h and filtered. The liquid was transferred into a small Schlenk tube and layered with *i*PrOH. Yield: 0.018 g, 15%. Anal. Calcd for $\text{C}_{61}\text{H}_{44}\text{BCu-Fe}_4\text{O}_{12}\text{P}_2$: C 55.14; H 3.34. Found: C 54.9; H 3.7. IR $\nu(\text{CO})$ in THF: 1980 s, 1956 cm^{-1} .

3a. Synthesis of $(\text{NEt}_4)_2[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-H})\}_2]$ ($[\text{NEt}_4]_2\mathbf{3}$) from $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuNCMe})_2]$. $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuNCMe})_2]$ (0.065 g; 0.08 mmol) was dissolved in 20 mL of THF. NaBH_4 (0.005 g; 0.08 mmol) was added and the reaction mixture stirred at room temperature for 10 h. The completeness of the reaction was checked by IR, and excess NEt_4BF_4 (0.10 g) was added. The solution was filtered and concentrated under vacuum, and heptane (20 mL) was added. The precipitate was filtered and dried under vacuum. The residue was dissolved in the minimum amount of THF (ca. 10 mL) and layered with cyclohexane. Yield: 8 mg; 12%. Anal. Calcd for $\text{C}_{42}\text{H}_{42}\text{Cu}_4\text{Fe}_8\text{N}_2\text{O}_{24}$: C 30.55; H 3.13; N 1.96. Found: C 30.4; H 2.7; N 1.7. IR $\nu(\text{CO})$ in THF: 2042 w, 2010 s, 1979 vs, 1960 cm^{-1} .

3b. Synthesis of $(\text{NEt}_4)_2[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-H})\}_2]$ ($[\text{NEt}_4]_2\mathbf{3}$) from $[\text{NEt}_4]_2\mathbf{2}$. $(\text{NEt}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuBH}_4)]$ (0.063 g; 0.071 mmol) prepared as described above was dissolved in 20 mL of THF. $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ (0.011 g; 0.10 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and was treated as above. Yield: 30 mg; 52%.

4a. Synthesis of $(\text{PPh}_4)_2[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-O-}i\text{Pr})\}_2]$ ($[\text{PPh}_4]_2\mathbf{4}$) from $[\text{PPh}_4]_2\mathbf{2}$. $(\text{PPh}_4)_2[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuBH}_4)]$ (0.050 g; 0.036 mmol) was dissolved in 20 mL of THF. $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ (0.011 g; 0.035 mmol) was added and the reaction mixture stirred at room temperature for 2 h. The reaction mixture was filtered and dried under vacuum. The product was suspended in 2-propanol and filtered again. The residue was dissolved in the minimum amount of THF (ca. 10 mL) and layered with 2-propanol. Yield: 0.015 g; 36%. Anal. Calcd for $\text{C}_{80}\text{H}_{54}\text{Cu}_4\text{Fe}_8\text{O}_{26}\text{P}_2$: C 43.76; H 2.46. Found: C 43.72; H 2.82. IR $\nu(\text{CO})$ in THF: 2039 w, 2003 s, 1973 cm^{-1} . ^1H NMR (THF- d_8): δ 1.40 (d, 6H, CH_3); 4.97 (sept, 1H, CHMe_2) ppm.

4b. Synthesis of $(\text{PPh}_4)_2[\{\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2(\mu\text{-O-}i\text{Pr})\}_2]$ ($[\text{PPh}_4]_2\mathbf{4}$) from $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuNCMe})_2]$ and $\text{NaO-}i\text{Pr}$. $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuNCMe})_2]$ (0.050 g; 0.036 mmol) was dissolved in 20 mL of THF. A solution of ca. 0.5 M $\text{NaO-}i\text{Pr}$ was prepared by adding a small piece of Na (0.06 g) in 5 mL of anhydrous 2-propanol. Then 80 μL of this second solution was added to the first, and the reaction product was checked by IR. Solid PPh_4BF_4 was added and allowed to dissolve for 1 h. The product was precipitated by adding hexane and treated as above. Yield: 12 mg; 27%.

X-ray Data Collections and Structure Determinations. Crystal data are summarized in Table S1. The diffraction experiments were carried out on a Bruker APEX II CCD area-detector diffractometer at 150 K. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,²⁸ and an empirical absorption correction was applied (SADABS)²⁹ to the collected reflections. The calculations were performed using the Personal Structure Determination Package³⁰ and the physical constants tabulated therein.³¹ The structures were solved by direct methods (SHELXS)³² and refined by full-matrix least-squares using all reflections and minimizing the function $\sum w(F_o^2 - kF_c^2)^2$ (refinement on F^2). In $(\text{NEt}_4)_2\mathbf{1}$ both crystallographically independent cations are disordered in their carbon atoms, but the disorder has been rationalized. Thus, while atom N1 has an occupancy factor of 1.00, its ethyl groups are split into two sets, one having an occupancy factor of 0.70 and the other of 0.30. The occupancy factors of the single atoms have all been refined, and the average values for the two sets (0.70 and 0.30, respectively) have been kept fixed in the final refinements. The disorder of this first cation is complicated by the fact that atom C111, bonded to N1, belongs to both sets, so that its total occupancy factor is $0.70 + 0.30 = 1.00$. Besides being bonded to atom N1, it is bonded both to atom C112, which has an occupancy factor of 0.70, and to atom C126, which has an occupancy factor of 0.30. Because of the disorder, bond lengths and angles involving this cation, while not all being ideal, can all

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be considered acceptable. The disorder of the second cation is different. Here, besides atom N2, also the methylic carbon atoms are ordered (occupancy factors of 1.00), whereas the methylenic carbon atoms, bonded to N2, are split into two groups having occupancy factors of 0.65 and 0.35 (refined as above), respectively. In this second cation bond parameters are less satisfactory than in the first one. Atoms having occupancy factors in the range 0.65–1.00 have been refined with anisotropic thermal parameters, and those having occupancies of 0.30 and 0.35 have been refined isotropically. All the other non-hydrogen atoms of all complexes have been refined with anisotropic thermal factors. Hydrogen atoms of the two disordered cations in $(\text{NEt}_4)_2\mathbf{1}$ have been ignored. In $(\text{PPh}_4)_2\mathbf{2}$ hydrogen atoms H1–H4, belonging to the BH_4^- ligand, have been detected in the final Fourier maps and refined with a fixed isotropic thermal parameter, 1.10 times that of the B atom. As expected, atoms H1 and H2, bonded also to Cu, are more distant from B than H3 and H4 (see text, Solid State Structures). In $(\text{NEt}_4)_2\mathbf{3}$ the hydrido hydrogen atom H was detected in the final Fourier maps and refined with an isotropic thermal parameter. All the other hydrogen atoms were placed in their ideal positions ($\text{C}-\text{H} = 0.97 \text{ \AA}$), with the thermal parameter U 1.10 times that of the carbon atom to which they are attached, and not refined. In the final Fourier maps the maximum residuals were $1.29(65) \text{ e} \cdot \text{\AA}^{-3}$ at 0.08 \AA from Fe2, $1.86(40) \text{ e} \cdot \text{\AA}^{-3}$ at 0.33 \AA from Cu, $0.80(26) \text{ e} \cdot \text{\AA}^{-3}$ at 0.93 \AA from Fe3, and $1.07(30) \text{ e} \cdot \text{\AA}^{-3}$ at 0.83 \AA from Cu2 for $(\text{NEt}_4)_2\mathbf{1}$, $(\text{PPh}_4)_2\mathbf{2}$, $(\text{NEt}_4)_2\mathbf{3}$, and $(\text{PPh}_4)_2\mathbf{4}$, respectively. Minimum peaks (holes), in the same order, were $-0.77(65)$, $-1.28(40)$, $-0.70(26)$, and $-0.77(30) \text{ e} \cdot \text{\AA}^{-3}$.

Conclusions

The cluster anions $\mathbf{1}$ – $\mathbf{4}$ can be conceived as linear complexes of Cu(I) with one coordination site occupied by the carbide atom of the iron cluster $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$. $\mathbf{1}$ and $\mathbf{2}$ belong to the family of isoelectronic substituted $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{CuL})]^-$ ($\text{L} = \text{pyz}$, py , dppe , Cl^- , BH_4^-) clusters;

in the whole series the metallic framework gradually changes from almost regular square pyramidal (of C_s idealized symmetry $\text{L} = \text{Pyz}$) to trigonal bipyramidal (of C_{2v} symmetry, $\text{L} = \text{Cl}^-$, BH_4^-). The reasons for these variations do not seem related to electronic or sterical effects of the ligand and support the idea that Fe–Cu interactions must be very weak. $\mathbf{2}$ is the first borohydrido copper complex that does not contain, as ancillary ligands, substituted phenanthroline or phosphine. Additionally, $\mathbf{3}$ and $\mathbf{4}$ represent other examples of $\text{Cu}_4(\mu\text{-L})_4$ units;^{25,33–37} in all these polycopper aggregates³⁸ the nature of the Cu–Cu bond is questionable.^{24,38,39} The matter is still more intriguing since the bridging ligands can be both one- ($\text{L} = \text{hydride}$, alkyl ,²⁵ aryl ³³) or three-electron donors ($\text{L} = \text{alkoxide}$,³⁴ silyloxide ,³⁵ amide ,³⁶ imine ³⁷).

The whole metallic framework of $\mathbf{3}$ shows a direct (without bridging metal ions⁴⁰) edge-to-edge connection between two octahedra, to our knowledge unprecedented. Alternative ways to dimerize octahedra are exemplified by $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ (vertex-to-vertex)⁴¹ and $[\text{Ir}_{12}(\text{CO})_{26}]^{2-}$ (face-to-face).⁴² The $\mu\text{-H}$ ligands in $\mathbf{3}$ retain enough hydridic nature to react with alcohols, but neither $\mathbf{2}$ nor $\mathbf{3}$ can reduce carbon dioxide.

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Supporting Information Available: Crystallographic information files (CIF), Figure S1 (solid-state structure of $\mathbf{1}$), and Tables S1, S2, and S3 (crystallographic data and selected distances and angles). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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