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Iron Carbide–Sulfide Carbonyl Clusters

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Abstract

Described is the preparation of the first iron carbide–sulfides. The cluster $[\text{Fe}_6\text{C}(\text{CO})_{15}(\text{SO}_2)]^{2-}$ (**[2]**^{2−}), which is generated quantitatively from $[\text{Fe}_6\text{C}-(\text{CO})_{16}]^{2-}$ (**[1]**^{2−}), was O-methylated to give the sulfinite **[2Me]**[−]. Demethoxylation of **[2Me]**[−] with BF_3 gave the face-capped octahedral cluster $\text{Fe}_6\text{C}(\text{CO})_{15}(\text{SO})$ (**3**). In solution, **3** spontaneously converted to the sulfide $\text{Fe}_6\text{C}(\text{CO})_{16}(\text{S})$ (**4**), an edge-fused double cluster with Fe_5C and Fe_3S subunits. Although **4** undergoes $1e^-$ reduction reversibly, $2e^-$ reduction (or base hydrolysis) of **4** gives *closo*- $[\text{Fe}_6\text{C}(\text{CO})_{14}(\text{S})]^{2-}$ (**[5]**^{2−}). The synthetic entries into the Fe_6CS_x manifold may underpin the preparation of active-site analogues of the FeMoco and FeVco cofactors.

Synthetic analogues of biological FeS clusters are attractive as potential catalysts for small-molecule transformations.¹ While good progress is being made on hydrogenases,² active-site models for many other FeS-based biocatalysts remain elusive, e.g., CO dehydrogenase, radical SAMs, and, of course, the FeMoco cofactor in nitrogenase (Figure 1).^{3,4}

Efforts to prepare synthetic analogues of FeMoco have been a scientific roller coaster since the first serious efforts were reported in the 1970s.^{5,6} Initial experiments, guided by the stoichiometry of the extractable active site (FeMoco), focused on the preparation of FeMoS clusters by self-assembly.^{6,7} Synthetic strategies were dramatically redirected with the announcement that FeMoco features a prismatic Fe_6S_3 core.⁸ The stunning discovery of an interstitial atom “X” at the center of the cluster meant that the metals in the 6Fe core occupy conventional tetrahedral coordination sites.⁹ The subsequent identification of X as C^{10} essentially stopped efforts to synthetically replicate the structure and stoichiometry of FeMoco. Carbide is the least synthetically tractable of the N/O/C options. Subsequent work demonstrated the presence of a sulfided Fe_6C core at the active site of the V-based nitrogenase.^{11,12} In the case of FeMoco, the carbide is biosynthesized from a FeCH_3 center.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01231. Spectroscopic data, selected reaction schemes, selected procedures, and crystallography (PDF)

Accession Codes

CCDC 1912301–1912305 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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¹³ The near impossibility of incorporating carbide—the “carbide problem”—into FeS ensembles has forced chemists to model inorganic carbide with alkyl and arene ligands.^{14,15}

One solution to the carbide problem would be to start with preformed iron carbido clusters. The anion $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$ ($[\mathbf{1}]^{2-}$; Scheme 1) has been known for more than 40 years^{16,17} but has not been formally investigated as a precursor to models for FeMoco. In terms of its structure, $[\mathbf{1}]^{2-}$ shares the Fe_6C stoichiometry at the core of FeMoco and FeVco, although the 6Fe cluster in $[\mathbf{1}]^{2-}$ is octahedral, not trigonal-prismatic. Whereas sulfide derivatives have not been reported, $[\mathbf{1}]^{2-}$ has been the subject of some derivatizations, e.g., aured, nitrosylated, and reduced clusters.¹⁸ 5FeMoC clusters catalyze the hydrogenation of alkynes.¹⁹

Our initial efforts toward connecting $[\mathbf{1}]^{2-}$ to 6FeCS clusters tested obvious reagents for installing inorganic S ligands. Oxidizing S sources failed to react with $[\mathbf{1}]^{2-}$, including ethylene sulfide, elemental S, $(\text{MeC}_5\text{H}_4)_2\text{TiS}_5$, Ph_2S_2 , $(\text{Et}_2\text{NCS}_2)_2$, and $\text{Fe}_2\text{S}_2(\text{CO})_6$. Forcing conditions gave low yields of $\text{Fe}_5\text{C}(\text{CO})_{15}$, a known product of oxidative degradation.²⁰ Nucleophilic sulfiding agents ($[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$, $[\text{MoS}_4]^{2-}$, and SH^-) also failed to react.

The intermediate value of ν_{CO} for $[\mathbf{1}]^{2-}$ (1965 cm^{-1}) indicates that the cluster is neither particularly electrophilic nor readily oxidized.² Although $[\mathbf{1}]^{2-}$ reacts with SO_2 (Scheme 1), it appears inert toward other S-containing cumulenes, e.g., CS_2 , PhNSO , and $[\text{MeOC}_6\text{H}_4\text{PS}_2]_2$ (a source of $\text{MeOC}_6\text{H}_4\text{PS}_2$). The failure of conventional sulfiding reactions led us to investigate routes to iron carbide–sulfides starting from $[\text{Fe}_6\text{C}(\text{CO})_{15}\text{SO}_2]^{2-}$ ($[\mathbf{2}]^{2-}$). The initial phases of our approach followed protocols developed by Chihara et al. for the conversion of $[\text{Ru}_6\text{C}(\text{CO})_{15}\text{SO}_2]^{2-}$ into the double cluster $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{S}]$.²¹ Chihara et al.’s work was conducted well before the identification of carbide in FeMoco. The initial question was the extent that methods developed for Ru could be applied to Fe, which typically forms less robust clusters. Having confirmed the utility of Chihara et al.’s sulfiding protocol, the next challenge was the generation of a closed 6FeCS cluster.

The salt $(\text{NBu}_4)_2[\mathbf{2}]^{2-}$ is an attractive starting material because it can be produced quantitatively on a ~40-g scale, has a good shelf-life, and shows no tendency to revert to $(\text{NBu}_4)_2[\mathbf{1}]$ under ambient conditions. O-methylation of $[\mathbf{2}]^{2-}$ with MeOTf gave $[\mathbf{2}\text{Me}]^-$, isolated as the black salt $(\text{NBu}_4)[\mathbf{2}\text{Me}]$ in 82% yield. Crystallographic analysis confirmed that in $[\mathbf{2}\text{Me}]^-$ the 6FeC core is retained. The otherwise rare sulfinito ligand^{21,23,24} is doubly bridging via two Fe–S bonds. A CH_2Cl_2 solution of $\text{NBu}_4[\mathbf{2}\text{Me}]$ was found to react with $\text{BF}_3\cdot\text{Et}_2\text{O}$ to give the charge-neutral sulfur monoxide cluster $\text{Fe}_6\text{C}(\text{CO})_{15}(\text{SO})$ (**3**) in 76% yield. Excess MeOTf will also convert $[\mathbf{2}]^{2-}$ into **3**, although yields have not been optimized. Unlike other cluster derivatives described in this paper, **3** was relatively unstable. It degrades to oily products upon contact with polar solvents. Despite its poor handling properties, single crystals of **3** were obtained and characterized by X-ray crystallography. These results confirmed the octahedral 6FeC core, with one face capped with $\mu_3\text{-SO}$ ($d_{\text{Fe-S}} = 2.0910(10)$, $2.1049(10)$, and $2.1151(10)\text{ \AA}$). With no $\mu\text{-CO}$ ligands, **3** is structurally distinct vs $[\mathbf{1}]^{2-}$.

A range of reagents were investigated for transformations of **3**. We initially assumed that its reactivity would be akin to that of a sulfoxide.²⁵ Nucleophiles and reductants (PPh₃, Bu₄NI, Bu₄NSH, [MoS₄]²⁻, and Cp₂Co) gave intractable oils. Weak electrophiles, oxidants, and silanes (AcCl, FeBF₄, AgBF₄, and HSiCl₃/Et₃N) appeared unreactive toward **3** or gave intractable products.

Fortunately, and still mysteriously, **3** was found to spontaneously convert in a CH₂Cl₂ solution (25 °C, 12 h, 60%) to Fe₆C(CO)₁₆(S) (**4**). Overall, the conversion of **3** to **4** entails the addition of one CO ligand to the 6FeC(S) core, concomitant with deoxygenation of the SO ligand. The conversion of Ru₆C(CO)₁₅(SO) into Ru₆C(CO)₁₆(S) is induced by CO and by H₂ at elevated temperatures,²⁶ but the **3** → **4** conversion does not benefit from these reagents. Crystallographic analysis of **4** confirmed that the addition of CO induced partial disconnection of the 6FeC framework. Thus, **4** is the edge-shared fusion of 5FeC and 3FeS subclusters. With one additional CO ligand than in **3**, **4** features fewer Fe–Fe bonds, consistent with its 88-e⁻ configuration. Despite its noncloso structure, **4** is a particularly robust compound. Samples can be stored at room temperature in air.

The sulfide **4** exhibits rich redox behavior at moderate potentials. Its cyclic voltammogram (CV) features reversible reductions at $E_{1/2} = -0.48$, -1.70 , and -1.96 V versus Fc^{+/0}. Qualitative tests verify that a wave at -1.13 V exhibits a catalytic current in the presence of added CF₃CO₂H, indicative of hydrogen evolution catalysis (H₂ was detected by gas chromatography). This result suggests the possibility of obtaining hydride derivatives.²⁷ The reduction of **4** can be effected chemically with a variety of reagents (Cp₂Co, Cp*₂Co, and KC₈). Using cobaltocene as the reductant, we obtained the 1:1 salt Cp₂Co[**4**]. In addition to exhibiting a strong electron paramagnetic resonance spectrum ($g_{\text{iso}} = 2.009$), Cp₂Co[**4**] was characterized by single-crystal X-ray crystallography, which confirmed that clusters **4** and [**4**]⁻ are virtually isostructural (Figure 2). The ν_{CO} bands shift by about 30 cm⁻¹ to lower energy for the anion.

Hints of labile CO ligands in the anionic 6FeC sulfido clusters come from the electrospray ionization mass spectrometry (ESI-MS) results of Cp₂Co[**4**]. The spectrum showed an intense base peak at m/z 771, corresponding to [Fe₆C-(CO)₁₄(S)]⁻ as well as daughter peaks corresponding to [Fe₆C(CO)_{14-x}(S)]⁻ for $1 \leq x \leq 4$. The CV of **4** also revealed a partially reversible couple at $E_{1/2} = -1.13$ V. We propose that the irreversibility arises from the dissociation of CO concomitant with the re-formation of Fe–Fe bonds. The reductive decarbonylation was tested by the chemical reduction of **4** with 2 equiv of Cp₂Co. This reaction efficiently afforded the CH₂Cl₂-insoluble salt (Cp₂Co)₂[Fe₆C-(CO)₁₄(S)]. The reduction of **4** with 2 equiv of NaC₁₀H₈, followed by cation exchange with Bu₄NCl, gave (Bu₄N)₂[Fe₆C(CO)₁₄(S)].

The ESI-MS results of this material indicated the decarbonylated cluster dianion [Fe₆C(CO)₁₄(S)]²⁻ (**5**)²⁻. The cluster of **4** can also be directly converted into (NBu₄)₂[**5**] by treatment with NBu₄OH. Although X-ray crystallographic analysis of (NBu₄)₂[**5**] suffered from some disorder in the cations, the corresponding salt (PPh₄)₂[**5**] was well-behaved crystallographically (Figure 3). The dianionic 6FeC(S) core has idealized C_{3v}

symmetry. Its ^{13}C NMR spectrum exhibits three CO signals, which is consistent with the cluster's 3-fold symmetry, assuming rapid exchange of CO between bridge terminal sites.

Two further results demonstrate that the chemistry reported above can be improved and extended. First, $[\mathbf{2Me}]^-$ can be directly converted into $[\mathbf{5}]^{2-}$ using $\text{NaC}_{10}\text{H}_8$. The streamlined conversion entails reductive scission of the S–OMe bond and deoxygenation. Second, $(\text{NBu}_4)_2[\mathbf{5}]$ reacts with SO_2 , as indicated by a shift in ν_{CO} of 14 cm^{-1} , very similar to ν_{CO} for $[\mathbf{1}]^{2-}$ versus $[\mathbf{2}]^{2-}$, and the intense peak at m/z 1049.8 in the ESI-MS spectrum. The existence of $[\text{Fe}_6\text{C}(\text{CO})_{13}(\text{S})-(\text{SO}_2)]^{2-}$ ($[\mathbf{6}]^{2-}$) points toward the probable stability of 6FeCS_x clusters ($x > 1$).

In summary, this paper describes the first iron carbide–sulfides. By making an otherwise unlikely connection between classical metal carbonyl cluster chemistry and biological cofactors, the work may offer a new approach to the synthesis of the most synthetically challenging biological cofactors, FeMoco and FeVco. The overall methodology is appealing because the starting $(\text{NBu}_4)_2[\text{Fe}_6\text{C}(\text{CO})_{16}]$ can be produced on scale from iron pentacarbonyl.²⁰ With respect to bioinorganic modeling, major challenges lay ahead: replacing CO ligands with additional sulfides and capping the 6FeCS_x core to give the octametallic clusters.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 2.
Structure of the anion $[4]^-$ with thermal ellipsoids set at 50%.

Figure 3. Structure of the dianion $[5]^{2-}$ with thermal ellipsoids set at 50%. Selected Fe–C1 distances in ranked order (Å): Fe6–C1, 1.8761(16); Fe4–C1, 1.8847(16); Fe5–C1, 1.8895(16); Fe1–C1, 1.8958 (11); Fe3–C1, 1.9012(16); Fe2–C1, 1.9061(16).

Scheme 1.

Synthesis of $(\text{PPh}_4)_2[\text{Fe}_6\text{C}(\text{CO})_{14}(\text{S})]^a$

^aFor anionic clusters, the quat cations are described in the text. δ_{C} is the ^{13}C NMR chemical shift of the carbide.