

**Preliminary communication**

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**FROM AN  $\{\text{Fe}_4\text{S}_4\}$ -CLUSTER TO  $\{\text{Fe}_2\text{S}_2\}$ - AND  $\{\text{Fe}_3\text{S}\}$ -CARBONYLS.  
 CRYSTAL STRUCTURE OF  $[\text{Fe}_3\text{S}(\text{CO})_9]^{2-}$**

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**Summary**

We report the electrochemical and chemical synthesis of the first isolable iron carbonyls obtained directly from an  $\{\text{Fe}_4\text{S}_4\}$ -cluster and carbon monoxide: the structure of one product of chemical reduction,  $[\text{Fe}_3\text{S}(\text{CO})_9]^{2-}$ , has been determined by X-ray crystallography.

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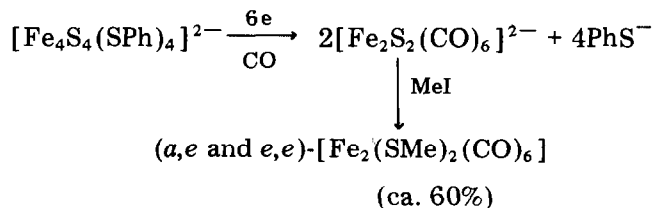
Carbon monoxide is a non-competitive inhibitor of enzymatic nitrogen fixation: the inhibition is a consequence of the binding of CO to a site (or sites) at which  $\text{N}_2$  does not bind [1]. Dinitrogen binding and reduction takes place on the MoFe-protein component of nitrogenase which possesses some sort of  $\{\text{Mo-Fe-S}\}$ -assembly as well as discrete  $\{\text{Fe-S}\}$ -assemblies, the so-called P-centres [2]. Whilst  $\text{N}_2$  binding and reduction probably occur at the  $\{\text{Mo-Fe-S}\}$ -assembly, it is possible that the inhibition by CO is a result of its binding during turnover at reduced  $\{\text{Fe-S}\}$ -centres. We were therefore curious to know how CO interacts with synthetic  $\{\text{Fe-S}\}$ -assemblies under reducing conditions.

We report the unique reductive cleavage of an  $\{\text{Fe}_4\text{S}_4\}$ -core in the presence of CO to  $\{\text{Fe}_2\text{S}_2\}$ - and  $\{\text{Fe}_3\text{S}\}$ -units bearing ligating CO. The reactions we describe provide the first examples of the direct formation of isolable  $\{\text{Fe-S}\}$ -carbonyls from CO and an  $\{\text{Fe}_4\text{S}_4\}$ -cluster.

Controlled potential electrolysis of  $[\text{NBu}_4]_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$  at a Hg-pool cathode ( $-2.1$  V versus the saturated calomel electrode;  $6\text{F}(\text{mole cluster})^{-1}$ ) in tetrahydrofuran (THF)  $-0.2$  M  $[\text{NBu}_4][\text{BF}_4]$  saturated with CO at 1 atmosphere, produces a dark green-brown solution which contains the dianion  $[\text{Fe}_2\text{S}_2(\text{CO})_6]^{2-}$ . The dianion was not isolated, its formation was established by trapping it with MeI following the method of Seyferth et al. [3]. After electrolysis the catholyte was quenched with MeI and the resulting dark-red solution was evaporated to dryness. The residue was extracted with  $\text{Et}_2\text{O}$  and the

extract chromatographed (silicic acid/Et<sub>2</sub>O eluent). This gives [Fe<sub>2</sub>(SMe)<sub>2</sub>(CO)<sub>6</sub>] in ca. 60% yield as a mixture of its axial/equatorial (*a,e*) and equatorial/equatorial (*e,e*) isomers. The red (*a,e*) and orange (*e,e*) isomers were separated by further column chromatography (silicic acid/pentane eluent). <sup>1</sup>H NMR (CH<sub>3</sub>) and IR (ν(C≡O)) data for the separated isomers were essentially identical to those given by Seyferth et al. [3]. These results are summarised in Scheme 1.

## SCHEME 1



Orme-Johnson and co-workers have briefly reported that CO reacts with [Fe<sub>4</sub>S<sub>4</sub>(SPh)<sub>4</sub>]<sup>3-</sup> to produce carbonyl species, but none were identified or isolated [4]. We find that on the time-scale of cyclic voltammetry (seconds) CO at one atmosphere does not interact with [Fe<sub>4</sub>S<sub>4</sub>(SPh)<sub>4</sub>]<sup>3-</sup> to a measurable extent, but that the reaction of CO with the unstable (4-) cluster is rapid.

The chemical reduction of [NBu<sub>4</sub>]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(SPh)<sub>4</sub>] by LiBu<sup>t</sup> (6 equivalents) in THF saturated with CO at 1 atmosphere gave a mixture of products, one of which, [Fe<sub>3</sub>S(CO)<sub>9</sub>]<sup>2-</sup>, we have isolated in the form of its [PPh<sub>4</sub>]<sup>+</sup> salt, as dark red needles, reaction 1. This product was identified by X-ray crystallography; the structure of the dianion is illustrated in Fig. 1.

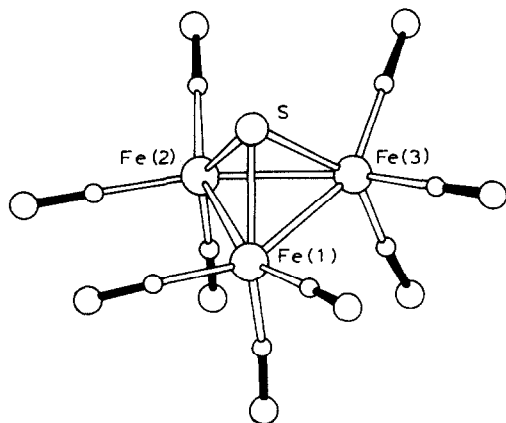
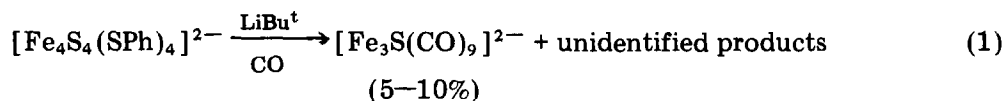


Fig. 1. View of the [Fe<sub>3</sub>(CO)<sub>9</sub>S]<sup>2-</sup> ion. Ranges of dimensions in the regular Fe<sub>3</sub>S centre: Fe—Fe 2.574(1)—2.595(1), Fe—S 2.184(1)—2.198(1) Å. Fe—Fe—Fe 59.6(1)—60.4(1), Fe—Fe—S 53.5(1)—54.3(1), Fe—S—Fe 72.0(1)—72.4(1)°.

The core of the anion is an almost perfect Fe<sub>3</sub>S trigonal pyramid. Each iron completes its six-fold coordination with three terminal carbonyl ligands. The ion has virtual 3*m* symmetry and is isostructural with the (disordered) neutral complex [Co<sub>2</sub>Fe(CO)<sub>4</sub>S] with which it is isoelectronic [5]. The two [PPh<sub>4</sub>]<sup>+</sup> cations are quite separate, contacted by normal van der Waals' interactions. The

IR data for the salt are identical with those reported for  $[\text{Et}_4\text{N}]_2[\text{Fe}_3\text{S}(\text{CO})_9]$  prepared earlier by Markó et al. from  $[\text{Fe}(\text{CO})_5]$  [6].



Finally, we note that Holm and co-workers [7] have shown that the oxidation of  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  by PhSSPh in the presence of  $\text{PhS}^-$  gives  $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ , thus the results reported here suggest that CO-dependent interconversion of  $\{\text{Fe}_4\text{S}_4\}$ - and  $\{\text{Fe}_2\text{S}_2\}$ -assemblies can be viewed as a chemically reversible process [8].

#### *X-ray analysis of $[\text{PPh}_4]_2[\text{Fe}_3(\text{CO})_9\text{S}]$*

*Crystal data.*  $\text{C}_{57}\text{H}_{40}\text{Fe}_3\text{O}_9\text{P}_2\text{S}$ ,  $M = 1130.5$ . Monoclinic,  $a$  10.483(3),  $b$  21.159(8),  $c$  23.670(8) Å,  $\beta$  93.70(3)°,  $V$  5239 Å<sup>3</sup> (from refinement of 25 reflections,  $\theta$  10–11°, automatically centred on diffractometer), space group  $P2_1/n$  (equiv. to no. 14),  $Z = 4$ ,  $D_c$  1.433 g cm<sup>-3</sup>. Crystals are ruby-red, air-stable, pointed prisms, dimensions 0.25 × 0.15 × 0.40 mm,  $\lambda(\text{Mo-K}\alpha)$  0.71069 Å,  $\mu(\text{Mo-K}\alpha)$  9.7 cm<sup>-1</sup>.

*Data collection and processing.* Preliminary photographic examination; intensity data measured on an Enraf–Nonius CAD4 diffractometer, monochromated radiation, with  $\omega - \frac{4}{3}\theta$  scan mode,  $\omega$ -scan width =  $0.5 + 0.35 \tan \theta$ ,  $\omega$ -scan speed range 0.9–6.7 deg min<sup>-1</sup>. 6837 unique reflections ( $\theta$  1.2–22.5°), 4405 having  $I > 2\sigma(I)$ ; empirical absorption correction applied: Bayesian methods applied to ensure no negative net intensities; no significant deterioration of crystal.

*Structure analysis and refinement.* Direct methods gave orientation of  $\text{Fe}_3\text{S}$  tetrahedron; Fourier syntheses located this fragment in the correct position in the cell and generated the remaining non-hydrogen atoms; H-atoms included in calculated sites. One phenyl ring disordered over two orientations. All non-hydrogen atoms (except those of the lesser occupied phenyl ring) refined anisotropically, H-atoms riding on C-atoms. After block-diagonal least-squares refinement, with reflections weighted  $W = \sigma_F^{-2}$ , final  $R = 0.062$   $R_w = 0.050$  for 5766 reflections having  $I > \sigma(I)$ .

The major computer programs, run on a VAX-750 computer, are listed in ref. 9\*.

## References

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- 3 D. Seyferth, R.S. Henderson, and Li Cheng Song, *Organometallics*, 1 (1982) 125.
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\*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

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- 8 We find the two electron reduction of  $[\text{Fe}_2\text{S}_2(\text{CO})_6]$  to the dianion to be a chemically reversible process.
- 9 As listed in refs. 14–20 of H. Dackhah, J.R. Dilworth, K. Fairman, C.T. Kan, R.L. Richards and D.L. Hughes, *J. Chem. Soc. Dalton*, (1985) 1523; also program BLOKLS, for block-diagonal least-squares refinement, adapted by J.D. Owen, Rothamsted Experimental Station, Harpenden, Herts., 1983.