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does not permit a definite conclusion. While no other η^2-CH(SMe) complexes have been reported, the C–S distances in several η^2-CH_2SMe complexes are known; the examples closest to the present system are $Cp(CO)_2Mo(\eta^2\text{-}CH_2SMe)$[14] and $[Me_2Ga(N_2C_3H_3)[OCH_2CH_2NMe_2)]Mo(CO)_2(\eta^2\text{-}CH_2SMe)$[15] that have C–S distances of 1.78 (1) and 1.744 (3) Å, respectively. The dihedral angle between the C(3)–S(1)–C(4) and W–C(3)–S(1) planes is 103.8°.

The addition of bases, NaH in THF and K_2CO_3 or Et_3N in CH_2Cl_2, to **2** results in the regeneration of carbyne complex 1 (eq 1) in 10% yield. This deprotonation of **2** represents a new route to carbyne complexes. Other products of this reaction have not been identified.

Recently, Nicholas[16] argued for the likely involvement of hydroxycarbyne species $M{\equiv}COH$ as intermediates in catalytic hydrogenation reactions of CO. Using this species, he rationalizes the formation of alcohols and methyl formate in these processes. The studies reported in this communication suggest a mechanism (Scheme I) whereby the hydroxycarbyne intermediate may also account for the formation of hydrocarbons. Proton transfer to the carbyne C, as in eq 1, would give an η^2-CH(OH) group that could undergo C–OH bond cleavage to $(HO)M{\equiv}CH$. This latter species would be expected to react with hydrogen to give H_2O and CH_4, as well as higher hydrocarbons through carbene (CH_2) and methyl (CH_3) intermediates by mechanisms suggested previously.[17-19] Thus, $M{\equiv}COH$, $M[\eta^2\text{-}CH(OH)]$, and $(HO)M{\equiv}CH$ intermediates are reasonable alternatives to those commonly proposed[17-19] for catalytic reactions of CO and H_2.

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Supplementary Material Available: Tables of positional and thermal parameters, all bond distances and angles, and structure factors (8 pages). Ordering information is given on any current masthead page.

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Synthesis and X-ray Structure of the $[Fe_4S_4(CO)_{12}]^{2-}$ Ion: An Example of Intermolecular Disulfide Formation by the $(\mu\text{-}S)_2Fe_2(CO)_6$ Unit

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Summary: Reaction of $(\mu\text{-}S)_2Fe_2(CO)_6$ with 1 equiv of $LiEt_3BH$ in tetrahydrofuran produces the green complex anion $[Fe_4S_4(CO)_{12}]^{2-}$ (**1**). The crystal structure of the Ph_4As^+ salt of **1** shows that the anion contains two $[(\mu\text{-}S)_2Fe_2(CO)_6]^-$ units linked by an S–S bond.

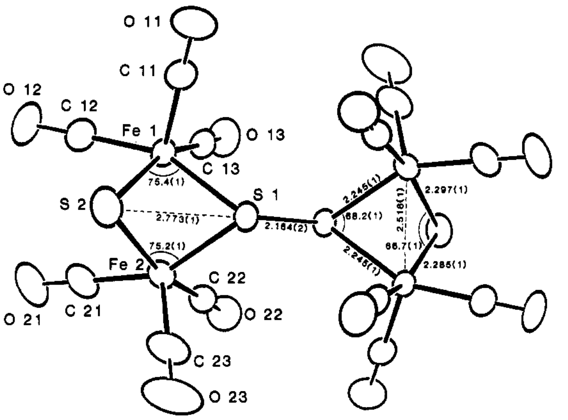

Figure 1. Structure of the $[Fe_4S_4(CO)_{12}]^{2-}$ ion, showing the atomic labeling scheme and selected distances and angles.

The chemistry of transition-metal carbonyl complexes containing heteroatoms is of substantial current interest.[2] One particularly well-characterized system is the complex (μ-dithio)bis(tricarbonyliron), originally reported by Brendel[3] and by Hieber and Gruber.[4] Seyferth et al.[5] have demonstrated that the S–S bond of the parent compound exhibits reactions typical of organic disulfides, the most notable being reduction to produce a dianion that undergoes reactions comparable to those of an organic dithiolate, e.g., alkylation,[5-7] protonation,[7,8] metalation,[5,7-10] and addition to olefins.[11] Oxidative addition of the S–S bond to low-valent metals has also been reported,[2b,12-14] providing a route to heterometallic clusters. We report herein the synthesis and structure of a new tetranuclear cluster, the $[Fe_4S_4(CO)_{12}]^{2-}$ ion, which demonstrates the ability of the $(\mu\text{-}S)_2Fe_2(CO)_6$ unit to form *intermolecular* disulfide bonds in addition to the known *intramolecular* disulfide of the parent compound.

Slow addition of $LiEt_3BH$ (1 equiv) in THF to a solution of $(\mu\text{-}S)_2Fe_2(CO)_6$ in THF at −78 °C produces a deep green solution; addition of $Ph_4As^+Cl^-$ (1 equiv) in a minimum volume of acetonitrile and slow warming to −20 °C results in the separation of deep green needles of the Ph_4As^+ salt of 1 in 75% yield.[15] The compound is stable to air in the solid state for brief periods but decomposes slowly in so-

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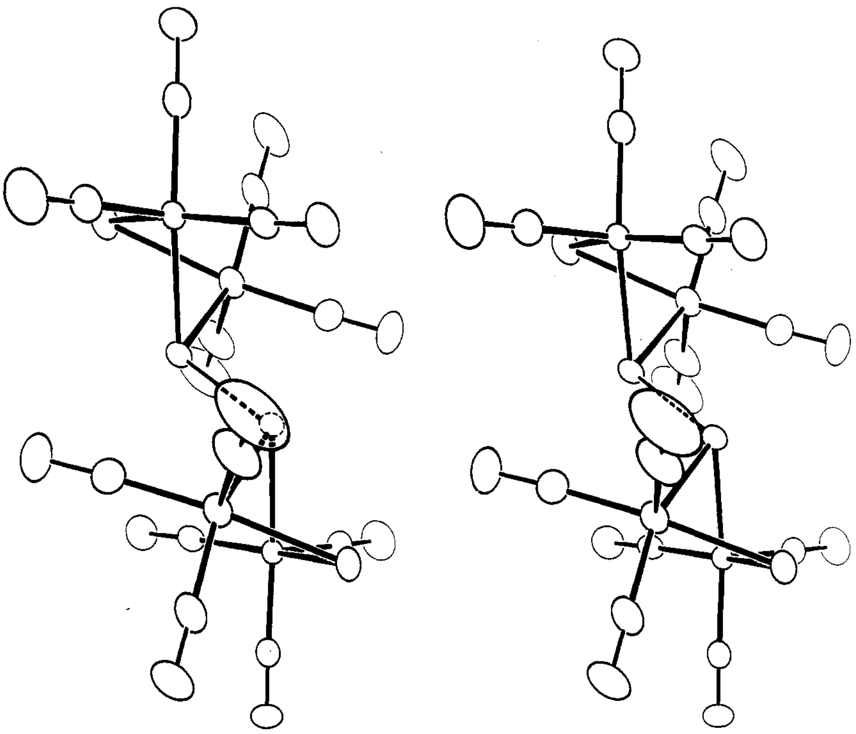

Figure 2. A stereoview of the $[Fe_4S_4(CO)_{12}]^{2-}$ ion.

lution at room temperature even in the absence of oxygen. Elemental analyses[16] are most consistent with the empirical formula $(Ph_4As)Fe_2S_2(CO)_6$, which could well be formulated as the dianion of the neutral cubane cluster $Fe_4S_4(CO)_{12}$, prepared and structurally characterized by Dahl and co-workers.[17]

The crystal structure of the Ph_4As^+ salt of 1[18] shows that the anion contains a "linear" Fe_4S_4 core, consisting of two $(\mu\text{-}S)_2Fe_2(CO)_6$ units linked by an S–S bond in a centrosymmetric butterfly structure (Figure 1), rather than the anticipated cubane structure. Selected distances and angles are shown in Figure 1, while a stereoview illustrating the puckered nature of the (e,e′)-linked[10,20] $(Fe_2S_2)_2$ unit is given in Figure 2. Each $(\mu\text{-}S)_2Fe_2(CO)_6$ unit has an overall conformation similar to that found in $(\mu\text{-}S_2)Fe_2(CO)_6$,[21] $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$,[22] and $(\mu\text{-RS})(\mu\text{-RHgS})Fe_2(CO)_6$ ($R = CH_3$, C_2H_5),[10] with a dihedral angle of 90.91° for the FeS_2 planes. Surprisingly, the presence of the S–S bond causes only a small (1.5°) increase in the corresponding Fe–S–Fe angle and actually results in a significant *decrease* (0.045 Å) in the corresponding Fe-S distance. Perhaps the most intriguing structural feature stems from a comparison of the bonded S1–S1′ and formally nonbonded S1...S2 distances (2.164 (2) and 2.773 (1) Å, respectively). The former is over 0.1 Å longer than normal values for S–S single bonds,[23] while the latter is 0.10–0.15 Å shorter than that found in $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$[22] and $(\mu\text{-RS})(\mu\text{-RHgS})Fe_2(CO)_6$[10] and is less than the expected van der Waals contact (3.4–3.7 Å[24]). The relatively short "nonbonded" distance of 2.773 (1) Å is well within the range reported for S···S bonding interactions (e.g., the 2.83 Å transannular interaction in S_8^{2+}[25] and the 2.76 Å interligand distance in $MoO_2[SC(CH_3)_2CH_2NH(CH_3)]_2$[26]). This suggests that a delocalized bonding description involving all four sulfur atoms may be appropriate, in which the short S1···S2 distance is due to partial disulfide character and compensates for the long S1–S1′ distance.

Seyferth et al. have proposed[5] that formation of the $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ ion (2) from $(\mu\text{-}S_2)Fe_2(CO)_6$ by reaction with metal hydrides involves initial nucleophilic attack of hydride on the S–S bond to form the green $[(\mu\text{-}S)(\mu\text{-}HS)Fe_2(CO)_6]^-$ (3) intermediate, which is then deprotonated by a second hydride to yield the dianion. The first step parallels the reaction of alkyllithium reagents, RLi, with $Fe_2S_2(CO)_6$ to produce the $[(\mu\text{-}S)(\mu\text{-RS})Fe_2(CO)_6]^-$ ions.[5] In order to determine how the unexpected product 1 is formed, we have performed the following experiments. (The requirement for low temperature in forming 2 makes this difficult to address by spectroscopic methods.) Reaction of 1[27] with 1 equiv of $LiEt_3BH$ in THF at −78 °C

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[16] Anal. Calcd for $C_{60}H_{40}As_2Fe_4O_{12}S_4$: C, 49.55; H, 2.77; As, 10.30; Fe, 15.35; S, 8.82. Found: C, 49.87; H, 3.05; As, 11.50; Fe, 14.46; S, 8.95.

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[18] Measurements were performed on an Enraf-Nonius CAD-4 diffractometer using graphite-filtered Mo Kα radiation. The θ–2θ scan technique was used as previously described[19] to record intensities for all nonequivalent reflections with 1.5° < 2θ < 58°. Intensities were corrected for Lorentz polarization effects and for absorption. A total of 3523 reflections with $F^2 > 3\sigma(F^2)$ were used in the refinement. The crystal used was an irregular prism with dimensions 0.38 mm × 0.31 mm × 0.17 mm × 0.08 mm. $(Ph_4As)_2$-1 crystallizes in space group $P2_1/n$ with $a = 10.662$ (3) Å, $b = 18.397$ (4) Å, $c = 16.245$ (7) Å, $\beta = 107.66$ (4)°, $V = 3036$ Å^3, and $Z = 2$. Heavy atoms were located by a three-dimensional Patterson synthesis, while remaining non-hydrogen atoms were located by Fourier syntheses. Full-matrix least-squares refinement[19] with anisotropic temperature factors for non-hydrogen atoms converged with $R = 3.2\%$ and $R_w = 3.4\%$. The computing programs used are described in ref 19.

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[27] A solution of 1 was prepared in situ by following the normal procedure except for addition of $Ph_4As^+Cl^-$; IR and optical spectra in THF were identical with those of the Ph_4As^+ salt.

followed by reaction with excess CH_3I and warming to room temperature produces $(\mu\text{-}CH_3)_2Fe_2(CO)_6$ in 70% yield, consistent with formation of 2 from 1.[28] On the other hand, if the synthesis of 1 is carried out as described above, but the reaction mixture is maintained at −78 °C after addition of $Ph_4As^+Cl^-$, no precipitate is observed. Since the Ph_4As^+ salt of 1 is insoluble under these conditions, this suggests strongly that 1 is not present in the initial mixture and that it forms only upon warming, presumably[29] via the reaction

$$2[(\mu\text{-}S)(\mu\text{-}HS)Fe_2(CO)_6]^- \rightarrow [Fe_4S_4(CO)_{12}]^{2-} + H_2$$

Because 1 forms readily at temperatures above −78 °C, it may well be a byproduct or reactant in some reactions involving 3. Most importantly, 1 is quite stable in the solid state at room temperature. It may therefore prove to be a convenient source of the dianion 2, as well as exhibiting interesting reaction chemistry of its own.

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Supplementary Material Available: Tables of atomic coordinates, interatomic distances and angles, thermal parameters, and observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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[28] Reaction of 1 with 2 equiv of CH_3I afforded a dark reddish oil that could not readily be purified. This product is most likely $(CH_3S)Fe_2(CO)_6S_2(CO)_6Fe_2(SCH_3)$, the methyl analogue of the novel $(C_6H_5S)Fe_2(CO)_6S_2(CO)_6Fe_2(SC_6H_5)$ molecule, recently prepared and structurally characterized by Seyferth et al. (Seyferth, D.; Kiwan, A. M.; Sinn, E., manuscript in preparation).

[29] An alternative reaction in which 3 reduces acetonitrile to produce 1 cannot be ruled out at this time; mechanistic studies are in progress.

Electron-Transfer Catalysis of a Ligand Rearrangement around a Fe–Fe Bond

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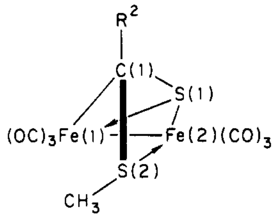
Summary: The new complex RO–C(S)SMe$[Fe_2(CO)_6]$, obtained without fragmentation of the organic ligand, by reacting $Fe_2(CO)_9$ with *S*-methyl *O*-adamantylmethane dithiocarbonate, is shown to be the precursor of the previously described $(\mu^2\text{-}RO\text{-}C\text{-}S)(\mu^2\text{-}SMe)Fe_2(CO)_6$. This transformation of the ligand in the coordination sphere of the bimetallic skeleton can be effected thermally or electrochemically by electron-transfer catalysis.

Interconversions between isomers, commonly observed in mononuclear complexes, are often achieved thermally, although cases are known of photochemical transformations and of isomerizations induced by oxidation or reduction.[1] In polynuclear complexes more complicated modifications of coordinated organic ligands can be expected and some examples of ligand site exchange induced by intrametallic rearrangements,[2] of interconversion of isomers,[3] of transformations of ligands on the edge of clusters,[4,5] and of bridging ligand rearrangement[6] have been reported to occur under thermal activation, sometimes under drastic conditions. More recently, Seyferth[7] has described the rearrangements of anions formed by the deprotonation of $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$. We speculated that transformation of ligands coordinated to polymetallic species could also be achieved by using electron-transfer catalysis, a versatile method which has proved useful to effect specific replacement of carbon monoxide by other ligands[8,9] and which was used once for the stereospecific preparation of isomeric dicobalt species.[10]

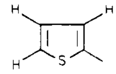
We describe in this paper the first example of a ligand rearrangement that can be achieved either thermally (Δ) or electrochemically by electron-transfer catalysis $(\bar{E}C\bar{E})$.[11] It concerns the transformation of the new complex 1 in which the carbon atom C(1) is σ-bonded to the metal, into the known complex 2 where C(1) becomes a carbene carbon atom (Scheme I). This rearrangement that implies two bond breaking steps and the formation of a new bond is accompanied by an important change in the geometry and electronic distribution.

We have recently published the synthesis and X-ray structure determinations of complexes 2 and 3a, obtained by reacting, respectively, *O*-alkyl *S*-alkyl dithiocarbonates 4 $[R^1OC(S)SCH_3]$ and dithioesters 5 $[R^2C(S)SCH_3]$ with $Fe_2(CO)_9$.[12,13] During large scale synthesis at room tem-



3

3a, R^2 =



b, $R^2 = -CH(CH_3)_2$

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[‡] Laboratoire d'Electrochimie.

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