Organometallics 1984, 3, 1128–1129

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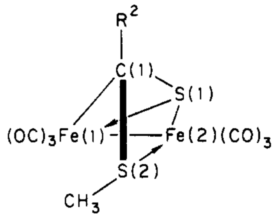
Summary: The new complex RO-C(S)SMe$[Fe_2(CO)_6]$, obtained without fragmentation of the organic ligand, by reacting $Fe_2(CO)_9$ with *S*-methyl *O*-adamantylmethane dithiocarbonate, is shown to be the precursor of the previously described $(\mu^2\text{-}RO\text{-}C\text{-}S)(\mu^2\text{-}SMe)Fe_2(CO)_6$.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

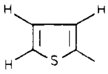
Interconversions between isomers, commonly observed in mononuclear complexes, are often achieved thermally, although cases are known of photochemical transformations and of isomerizations induced by oxidation or reduction.[1] In polynuclear complexes more complicated modifications of coordinated organic 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 ($\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$).[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, R² =


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

[†] Laboratoire de Chimie des Organometalliques.

[‡] Laboratoire d'Electrochimie.

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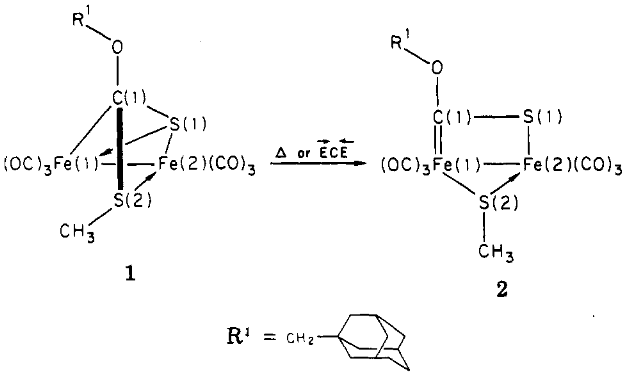
Scheme I



perature, we have found that the major red complex **2** is accompanied by a new yellow, slightly more polar, complex, **1**.[14] Structure **1** is readily identified by the usual techniques; particularly relevant are the ^{13}C NMR data for the resonance of C(1): 109 and 85 ppm, respectively, for compounds **1** and **3b** vs. 296 ppm for complex **2**. The ^1H NMR spectrum of **1** shows for the methylene protons an AB quartet characteristic of nonequivalent hydrogen atoms; similarly, for compound **3b** the methyl groups were found to be diastereotopic, in agreement with the proximity of a chiral carbon atom. In refluxing acetone complex **1** is progressively transformed into **2**;[15] these findings are consistent with complex **1** being the precursor of **2** and with the fact that **1** can only be isolated when complexation of the ligand **4** is performed at room temperature.

Electrochemical studies of **2** and **3** have been performed,[16,17] and we have shown that they behave differently. The voltammetric study of **1** in acetone solution shows a behavior typical of complex **3**: two one-electron quasi-reversible reductions are observed during the first sweep at 1 V·s⁻¹ ($E_{p_{c1}} = -1.20$, $E_{p_{a1}} = -0.68$ and $E_{p_{c2}} = -1.60$, $E_{p_{a2}} = -1.37$ V vs. SCE). However, the rearrangement being fast under electrochemical activation, it occurs during the voltammetric time scale and new peaks characteristic of **2** appear at $E_{p_c} = -1.30$ and $E_{p_a} = 1.00$ V vs. SCE during the following sweeps (Figure 1). The transformation **1** → **2** is shown by the decreasing intensities of the peaks corresponding to compound **1**.[18] The electron-transfer catalysis of the rearrangement is confirmed by bulk electrolysis at a controlled potential[19] affording **2** with low consumption of electricity. These results show for the first time that a complicated ligand rearrangement in a binuclear complex can be carried out by thermal activation or considerably more rapidly by electron-transfer catalysis. In both cases the same complex **2** is obtained.

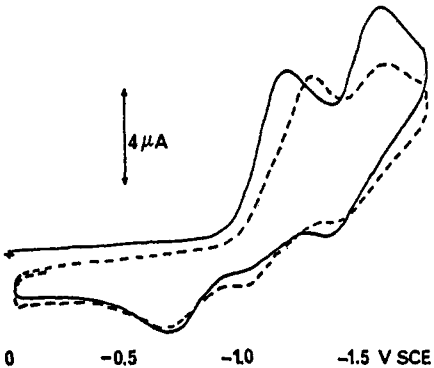


Figure 1. Cyclic voltammetry of complex **1** (2 × 10⁻³ M) in n-$Bu_4N^+BF_4^-$ (0.1 M acetone) at platinum electrode (scan rate = 1 V·s⁻¹): —, first scan; ---, second scan.

Thus, reaction **4** with $Fe_2(CO)_9$ affords primarily complex **1** in which no fragmentation has occurred and it is of interest to compare compounds **1** and **3** in which the main difference is the presence of an oxygen atom linked to C(1) in complex **1**. Although complexes **3** appear to be under strong geometrical constraint shown by the distortion in the X-ray structure,[13] it is noteworthy that they never rearrange. On the contrary, compound **1** of analogous structure, in which the carbon–metal σ-bond may be less stable but can lead to a carbene stabilized by the oxygen atom, is readily transformed into complex **2**, the X-ray structure of which does not show any geometrical constraint.[12]

Complex **2** appears to be thermodynamically more stable than complex **1**; the driving force for the rearrangement **1** → **2** may be found in the steric decompression that accompanies the transformation of the tetragonal carbon atom C(1) into a trigonal-planar state. This rearrangement is only possible when the carbene is stabilized by an external heteroatom.[20] The observed rearrangement may be described schematically by C(1)–S(2) and S(1)–Fe(1) bond cleavages followed by coordination of S(2) on Fe(1) and electronic redistribution. In the absence of conclusive arguments, a mechanistic description remains speculative; labeling experiments,[21] for instance, on one iron atom by a phosphorus ligand may shed light on the behavior of the metallic framework during this rearrangement.

Registry No. **1**, 90507-74-7; **2**, 90530-56-6; **3b**, 80148-59-0; **4**, 90507-75-8; **5**, 5874-02-2; $Fe_2(CO)_9$, 15321-51-4.

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(14) To a solution of **4** (1.6 × 10⁻² mol) in 200 mL of dry acetone was added $Fe_2(CO)_9$ (2.2 × 10⁻² mol) in one portion. The mixture was stirred for 24 h at room temperature under N_2 and filtered on a short bed of silica gel and the solvent concentrated to approximately 20 mL. Chromatography on silica plates eluted with petroleum ether gave red strips of the known complex **2** (R_f 0.92) and yellow strips of compound **1** (R_f 0.73). The silica was washed by diethyl ether to afford 5.5 g (64%) of **2** (mp 130 °C (pentane)) and 0.6 g (7%) of **1** (mp 109–110 °C (pentane)). **1**: $C_{19}H_{20}O_7S_2Fe_2$, M⁺ 535.9349 (calcd), 535.9350 (found). Anal. Calcd: C, 42.54; H, 3.73; S, 11.94; Fe, 20.88. Found: C, 42.73; H, 3.68; S, 11.56; Fe, 20.57. ^{13}C NMR ($CDCl_3$, 36 °C): δ 211.4 and 210.2–209.1 (CO), 109.6 [C(1)], 79.2 (OCH_2), 30.8 (SCH_3). ^1H NMR ($CDCl_3$): δ 2.98 (q, 2 H, $^2J(H_AH_B) = 8.9$ Hz), 2.23 (3 H), 1.95, 1.68, 1.52 (15 H). IR (CH_2Cl_2): ν (CO) 2070, 2030, 1990, 1970 cm⁻¹.

(15) The transformation **1** → **2** can be monitored by TLC. A solution of **1** (100 mg) in 20 mL of acetone is refluxed for 4 h; the solvent is removed and the two products are separated.[14] A 42-mg sample of **1** and 47 mg of **2** are obtained; their characteristics are identical with those of authentic samples: IR ^1H NMR, melting point, and mixed melting point. When the ^{13}C NMR spectrum of **1** was recorded at 36 °C for 12 h, a small signal at 296 ppm, typical of the carbene C(1) in complex **2**, was observed.

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(17) Darchen, A.; Lhadi, E. K.; Patin, H. *J. Organomet. Chem.* **1983**, *259*, 189.

(18) A behavior typical of electron-transfer-catalyzed reactions is that the reaction occurs at the electrode surface, the starting material remaining intact in the bulk solution during the voltammetric study. This explains the aspect of the voltammogram where the peaks corresponding to compound **1** are still present although the first peak ($E_{p_{c1}}$) is not well resolved because the first reduction peaks of **1** and **2** are very closed. A better resolution is obtained when the voltammogram is recorded at a slower scan rate; in these conditions the reduction peak of **2** appears during the first sweep.

(19) Electrolysis of complex **1** (57 mg) in 20 mL of acetone containing $LiClO_4$ (0.1 M) was carried out at controlled potential (−1.1 V vs. SCE) in the dark and under nitrogen by using a mercury cathode (6 cm²). After 30 min the transformation was complete with a consumption of 0.3 electron·mol⁻¹. Chromatography on silica[14] afforded 43 mg (74%) of **2** whose characteristics are identical with those of an authentic sample: IR, ^1H NMR, melting point, and mixed melting point non depressed.

(20) Patin, H.; Mignani, G.; Mahe, C.; Le Marouille, J. Y.; Southern, T. G.; Benoit, A.; Grandjean D. *J. Organomet. Chem.* **1980**, *197*, 315.

(21) Work in progress.