

Preliminary Communication

Unexpected reactions of anionic intermediates $[(\mu\text{-RS})(\mu\text{-Se})\text{Fe}_2(\text{CO})_6]^-$ with SO_2Cl_2 . Synthesis of $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-Se})$ ($\text{R} = \text{Ph}, \text{Et}, {}^n\text{Pr}, {}^t\text{Bu}$) and crystal structure of $[(\mu\text{-PhS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-Se})$

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Abstract

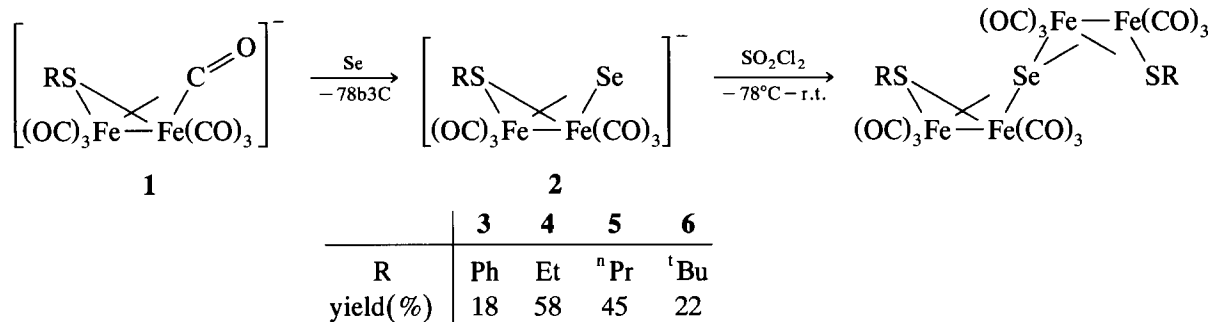
The addition of elemental selenium to CO-bridged anions $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ gave new selenido-bridged intermediates $[(\mu\text{-RS})(\mu\text{-Se})\text{Fe}_2(\text{CO})_6]^-$. Treatment of the intermediates in situ with SO_2Cl_2 , afforded unexpected products $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-Se})$ ($\text{R} = \text{Ph}, \text{Et}, {}^n\text{Pr}, {}^t\text{Bu}$), among which the structure of the product with $\text{R} = \text{Ph}$ was confirmed by X-ray crystallography. It crystallized in the monoclinic space group $\text{P}2_1/\text{n}(\#14)$ with the lattice constants $a = 8.971(3)$, $b = 12.891(8)$, $c = 26.955(7)$ Å, $\beta = 98.03(2)^\circ$ and $Z = 4$. The structure was refined to an R value of 0.069.

Keywords: Selenium; Iron; CO-bridged anion; Sulfuryl chloride; X-ray structure; Cluster

The CO-bridged anions $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ (**1**), derived from RSH , $\text{Fe}_3(\text{CO})_{12}$ and Et_3N , are of great interest and have become very useful in synthesizing a variety of novel bridged iron carbonyl complexes [1–7]. During the course of our study of the chemistry of these anions [5–7], we have recently found the

following interesting reactions starting from **1** ($\text{R} = \text{Ph}, \text{Et}, {}^n\text{Pr}, {}^t\text{Bu}$).

In a typical experiment, a selenido-bridged analog $[(\mu\text{-RS})(\mu\text{-Se})\text{Fe}_2(\text{CO})_6]^-$ (**2**, $\text{R} = \text{Ph}$) could be formed by a similar method to that for $[(\mu\text{-EtS})(\mu\text{-S})\text{Fe}_2(\text{CO})_6]^-$ [2], by adding selenium powder (0.474 g,



Scheme 1.

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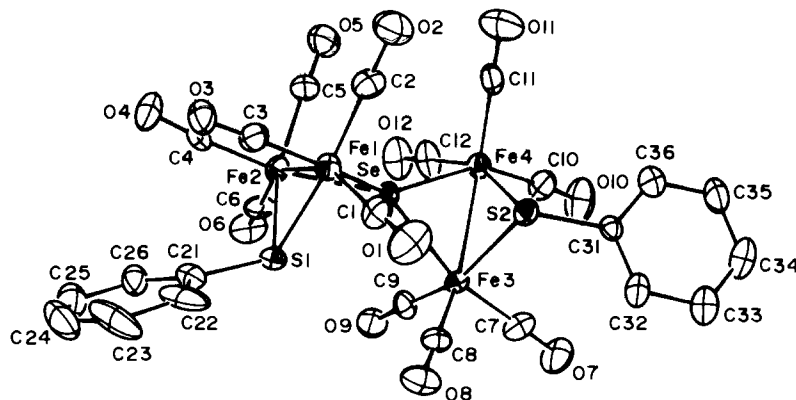


Fig. 1. ORTEP diagram of **3** with numbering scheme, selected interatomic distances (Å) and angles(°). Fe(1)–Fe(2) 2.553(3), Fe(3)–Fe(4) 2.553(3), Se–Fe(2) 2.340(3), Se–Fe(4) 2.344(3), Se–Fe(3) 2.348(3), Se–Fe(1) 2.355(3), Fe(1)–S(1) 2.275(4), Fe(2)–S(1) 2.266(4), Fe(3)–S(2) 2.274(5), Fe(4)–S(2) 2.264(4), Fe(2)–Se–Fe(4) 133.1(1), Fe(2)–Se–Fe(3) 136.5(1), Fe(2)–Se–Fe(1) 65.87(9), Fe(4)–Se–Fe(3) 65.93(9), Fe(4)–Se–Fe(1) 141.8(1), Fe(3)–Se–Fe(1) 127.9(1), S(1)–Fe(1)–Se 76.2(1), S(1)–Fe(2)–Se 76.6(1), S(2)–Fe(3)–Se 77.6(1), S(2)–Fe(4)–Se 77.9(1).

6.0 mmol) to the solution of **1** (R = Ph) prepared from $\text{Fe}_3(\text{CO})_{12}$ (1.50 g, 2.98 mmol), PhSH (0.32 ml, 3.03 mmol), Et_3N (0.50 ml, 3.03 mmol) and 40 ml THF, at -78°C for ca. 40 min. This selenido-bridged anion **2** (R = Ph) reacted further in situ with SO_2Cl_2 (0.16 ml, 2 mmol) from -78°C to room temperature for 2 h, unlike its sulfur analogs $[(\mu\text{-RS})(\mu\text{-S})\text{Fe}_2(\text{CO})_6]^-$ giving rise to the oxidative coupling products $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2$ – $(\mu\text{-S-S-}\mu)$ [8], afforded, after column chromatography, thin-layer chromatography and recrystallization from 10% CH_2Cl_2 /hexane, an unexpected cluster compound **3** (m.p. 146°C dec.) in 18% yield. Similarly, cluster compounds **4** (m.p. $129\text{--}130^\circ\text{C}$), **5** (m.p. $103\text{--}104^\circ\text{C}$) and **6** (m.p. $116\text{--}117^\circ\text{C}$) were also prepared as air-stable red solids in 22%–58% yield (Scheme 1). All these compounds are new and characterized by elemental analysis, IR, ^1H NMR and MS spectroscopies ¹.

Compounds **3**–**6** all contain a pseudo-tetrahedral selenium atom coordinated to four iron atoms of the two $\text{RSFe}_2(\text{CO})_6$ moieties. So far, to our knowledge, any cluster of this type and such kind of reactions have not yet been described in literature, although numerous corresponding sulfur analogs were prepared by different methods [9–15].

The structure of **3** was confirmed by X-ray diffrac-

tion ². The ORTEP diagram for **3** is shown in Fig. 1. The molecule consists of two identical $[(\mu\text{-PhS})(\text{Fe}_2(\text{CO})_6)]$ moieties joined to a unique selenium atom, which is situated at the center of a distorted tetrahedron made up of four iron atoms. The bond lengths between this selenium atom and the four iron atoms are almost the same (average, 2.347 Å), which is slightly shorter than the Fe–Se bond length (average, 2.364 Å) in $(\mu\text{-Se})_2\text{Fe}_2(\text{CO})_6$ [16]. The two equal Fe–Fe bond distances (2.553 Å) are close to the average Fe–Fe bond distance (2.540 Å) in $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ [10], but much longer than the average Fe–Fe distance (2.523 Å) both in $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6][\mu_4\text{-S}][(\mu\text{-PhS})\text{Fe}_2(\text{CO})_6]$ [11] and in $[(\mu\text{-}^i\text{BuS})\text{Fe}_2(\text{CO})_6][\mu_4\text{-S}][(\mu\text{-PhS})\text{Fe}_2(\text{CO})_6]$ [12]. However, the bond lengths between the four iron atoms and two sulfur atoms are very close to each other [Fe(1)–S(1) 2.275(4), Fe(2)–S(1) 2.266(4), Fe(3)–S(2) 2.274(5), Fe(4)–S(2) 2.264(4) Å]. The dihe-

¹ For example: Compound **3** (R = Ph), air stable, dark-red crystals, m.p. 146°C (dec.). ^1H NMR (CDCl_3 , TMS): 7.32 (s, $2\text{C}_6\text{H}_5$) ppm, IR(KBr): 2081.6(m), 2057.0(s), 2032.4(vs), 1991.4(vs), 1975.0(s, C=O) cm^{-1} . EI MS m/z : 802($\text{M}^+ - 2\text{CO}$, 0.9%). Anal. Found: C, 33.69; H, 1.30. Calc. for $\text{C}_{24}\text{H}_{10}\text{Fe}_4\text{O}_{12}\text{S}_2\text{Se}$: C, 33.64; H, 1.18%. Compound **6** (R = ^iBu), air-stable, dark-red crystals, m.p. $116\text{--}117^\circ\text{C}$. ^1H NMR (CDCl_3 , TMS): 1.46 [s, $2\text{C}(\text{CH}_3)_3$] ppm, IR(KBr): 2081.6(m), 2051.4(s), 2032.4(vs), 1991.4(vs), 1972.2(s, C=O) cm^{-1} . EI MS m/z : 762($\text{M}^+ - 2\text{CO}$, 0.7%). Anal. Found: C, 29.53; H, 2.17. Calc. for $\text{C}_{20}\text{H}_{18}\text{Fe}_4\text{O}_{12}\text{S}_2\text{Se}$: C, 29.41; H, 2.22%.

² Crystal data for **3** (R = Ph): $\text{C}_{24}\text{H}_{10}\text{Fe}_4\text{O}_{16}\text{S}_2\text{Se}$, $M = 856.80$, Monoclinic, $P2_1/n$ (#14), $a = 8.971(3)$, $b = 12.891(8)$, $c = 26.955(7)$ Å, $\beta = 98.03(2)^\circ$. $V = 3087(2)$ Å³, $Z = 4$, $D_c = 1.84$ g cm^{-3} . Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $F(000) = 1680$, $T = 296$ K. The structure was solved by direct methods (MITHRIL) using Enraf-nonius CAD4 diffractometer. All nonhydrogen atoms were refined using anisotropic thermal parameters. A total of 5916 independent reflections were collected, of which 2870 reflections with $I > 3\sigma(I)$ were considered to be observed and used to structural refinements. Data were corrected for Lp and absorption, $\omega/2\theta$ scans (minimum and maximum transmission factors: 0.5858 and 1.000, respectively). Final $R = 0.069$ and $R_w = 0.073$ [where $W = 1/\sigma^2(F)$]. $(\Delta/\sigma)_{\text{max}} = 0.01$. The largest peak in final difference map was $1.07e$ Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

dral angle between two Fe_2Se trigonal planes is 100.34° , which represents a distorted tetrahedron geometry around the Se atom, the two dihedral angles between Fe_2S and Fe_2Se trigonal planes are 95.81° and 97.76° , respectively. In addition, it can be seen intuitively from Fig. 1 that the two phenyl groups attached to the cluster core Fe_4SeS_2 are both bonded to $\mu\text{-S}(1)$ and $\mu\text{-S}(2)$ by an e-type of bond [17]. Work is continuing to investigate the mechanism of this novel kind of reaction and the reaction with similar selenium-centered anions $[(\mu\text{-RSe})(\mu\text{-Se})\text{Fe}_2(\text{CO})_6]^-$ in our laboratory.

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