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Synthesis and Structure of Cluster Monomer $Fe_2(CO)_6(\mu\text{-}SCH_2CH{=}CH_2)(\mu_3\text{-}S)Fe(CO)_2(\eta^5\text{-}C_5H_5)$

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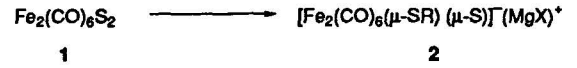
The reaction of complex $Fe_2(CO)_6S_2$ **1** with allylmagnesium chloride in tetrahydrofuran yields the compound $Fe_2(CO)_6(\mu\text{-}SCH_2CH{=}CH_2)(\mu\text{-}SMgCl)$ **2a**, whose treatment with $CpFe(CO)_2X$ (X = I, Cl; Cp = η^5-C_5H_5) leads to the title compound **3**, the structure of which has been determined by X-ray diffraction analysis.

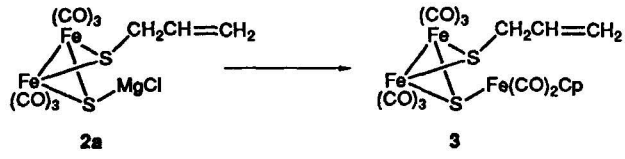
Perhaps the most promising ways of obtaining metal-filled polymers are polymerization and copolymerization of metal-containing monomers. Great advances have been achieved in this field,[1] with the exception of cluster monomers, because very few approaches have been developed for the direct synthesis of clusters containing ligands with a multiple carbon—carbon bond available for polymerization. Recently, the possibility of copolymerization of such monomers with, for example, styrene was shown for trinuclear osmium clusters.[2]

One general approach to the synthesis of the parent cluster monomer series is to build them using lower nuclearity fragments, starting with a common 'building block', for example, the well-known binuclear complex $Fe_2(CO)_6S_2$ **1**.[3]

The great success achieved in the study of the chemistry of compound **1** and of its mono- and di-anionic derivatives $[Fe_2(CO)_6S_2]^{2-}$ and $[Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}S)]^-$ **2**[3,4] allows us to suggest a possible route to the direct synthesis of potentially a great number of iron-containing homo- and hetero-metallic



Scheme 1 *Reagents and conditions*: RMgX, THF, −78°C



Scheme 2 *Reagents and conditions*: $CpFe(CO)_2X$, THF, −70°C

cluster monomers, based on the utilization of unsaturated Grignard reagents to obtain monoanion **2** (Scheme 1), followed by treatment of monoanion **2** with electrophiles containing a transition metal atom.

This communication presents the first example of such a synthetic route.

Treatment of a solution of **1** in tetrahydrofuran (THF) at −70°C with a stoichiometric amount of a solution of allylmagnesium chloride in diethyl ether or in THF results in the formation of compound **2a** as a green solution. Then $CpFe(CO)_2X$ (X = I, Cl; Cp = η^5-C_5H_5) was added to obtain cluster **3** (Scheme 2).† The yield of **3** after recrystallization from hexane was 60%.‡ Single crystals were grown from a solution held at −8°C for several days.

The structure of **3** was determined by a single crystal X-ray diffraction study.§ The molecule is shown in Fig. 1. The bridging ligands $SCH_2CH{=}CH_2$ and S are coordinated to the binuclear $[Fe_2(CO)_6]$ fragment, in which the Fe—Fe distance corresponds to a shortened metal—metal bond and differs only slightly from that in $Fe_2(CO)_6(\mu\text{-}SCH_2Me)_2$ [2.537(10) Å].[3] In addition, the (μ_3-S) ligand is bonded to the $[CpFe(CO)_2]$ group.

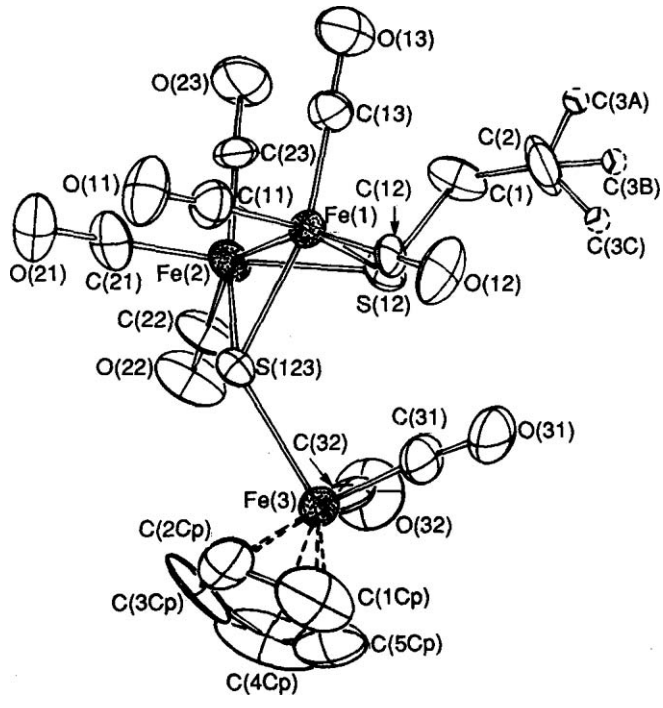


Fig. 1 Molecular structure of **3** (35%-probability ellipsoids). The hydrogen atoms are omitted for clarity. Main bond lengths (Å): Fe(1)—Fe(2) 2.510(5), Fe(1)—S(12) 2.245(6), Fe(2)—S(12) 2.253(6), Fe(1)—S(123) 2.280(6), Fe(2)—S(123) 2.267(7), Fe(3)—S(123) 2.301(7), S(12)—C(1) 1.85(2), C(1)—C(2) 1.52(3), C(2)—C(3A) 1.15(7), C(2)—C(3B) 1.05(7), C(2)—C(3C) 1.33(9), Fe(3)—C(Cp) 2.02–2.13(2) [mean 2.08(2)], Fe–C(CO) 1.71–1.80(3) [mean 1.75(3)], C–O(CO) 1.41–1.18(2) [mean 1.16(2)], C–C(Cp) 1.34–1.43(5) [mean 1.37(5)]

The Fe(1)···Fe(3) [4.011(5) Å] and Fe(2)···Fe(3) [3.998(6) Å] distances suggest an absence of metal—metal bonds between these atoms, corresponding to the presence of 52 valence electrons. The sulfur atoms in the molecule lie on different sides of the Fe_3 plane and the angles between the latter and planes Fe(1)Fe(2)S(12) and Fe(1)Fe(2)S(123) are 71° and 28°, respectively.

† Cluster **3** has been used successfully to obtain a metal-containing copolymer with styrene by Professor A. D. Pomogailo and his colleagues at the Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, Russian Federation.

‡ The product is dark brown, crystalline and stable in air, melting at 95–96°C without decomposition. Analytical and spectroscopic data of cluster **3** correspond to the determined structure. ^{1}H NMR, IR and mass spectra were recorded on a Bruker SXP 4-100, Specord IR75 and MX-1310, respectively.

IR (hexane) ν/cm^{-1} 2062(m), 2034(vs), 2025(s), 1995(m), 1990(s), 1977(s), 1970(m), 1959(w) (CO); ^{1}H NMR ($CDCl_3$) δ 3.02 (d, —CH_2—), 4.75–5.33 (m, CH_2=), 5.74–6.11 (m, —CH=), 4.95 (s, C_5H_5); *m/z* 562 (M^+).

§ *Crystal data* for **3**: $C_{16}H_{10}Fe_3O_8S_2$, M = 561.92, monoclinic, space group $P2_1/n$, a = 7.844(5), b = 23.045(22), c = 11.862(6) Å, β = 94.90(5)°, U = 2132(2) Å^3, D_c = 1.747 g cm^{-3}, Z = 4. The intensities of 2487 reflections (1130 observed) I_{hkl} were measured on a Syntex $P2_1$ diffractometer [graphite monochromated Cu-Kα radiation (λ = 1.54178 Å)] for a dark-brown prismatic crystal with dimensions 0.18 × 15 × 0.50 mm using the θ–2θ scan technique (2θ ≤ 100°). The structure was solved by direct methods and refined by the full-matrix least-squares method, anisotropically for the non-hydrogen atoms (except the statistically disordered terminal carbon atom in the $SCH_2CH{=}CH_2$ group, for which three positions were included in the refinement isotropically with occupancy factors = 1/3). The final R_F was 0.050 for 902 $F_{hkl} \geq 6\sigma$. The absorption correction was made using the 'DIFABS' program (μ = 185.04 cm^{-1}). The hydrogen atoms were fixed in their geometrical positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1992, Issue No. 1.

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