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Preliminary communication

Formation of asymmetrical twin clusters $[(\mu\text{-RS})Fe_2(CO)_6](\mu_4\text{-S})[(\mu\text{-R'S})Fe_2(CO)_6]$ by reaction of $(\mu\text{-RS})(\mu\text{-XMgS})Fe_2(CO)_6$ with $(\mu\text{-R'S})[\mu\text{-PhC(O)S}]$-$Fe_2(CO)_6$—Crystal structure of $[(\mu\text{-EtS})Fe_2(CO)_6]$-$(\mu_4\text{-S})[(\mu\text{-PhS})Fe_2(CO)_6]$

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Abstract

Reaction of $(\mu\text{-RS})(\mu\text{-XMgS})Fe_2(CO)_6$ with $(\mu\text{-R'S})[\mu\text{-PhC(O)S}]Fe_2(CO)_6$ in THF affords asymmetrical twin clusters $[(\mu\text{-RS})Fe_2(CO)_6](\mu_4\text{-S})[(\mu\text{-R'S})Fe_2(CO)_6]$. An X-ray analysis of one of the clusters where R = Ph and R' = Et indicates that it consists of two different moieties, $PhSFe_2(CO)_6$ and $EtSFe_2(CO)_6$, joined together by a μ_4-S spiran sulfur atom.

The reactions of $(\mu\text{-RS})(\mu\text{-XMgS})Fe_2(CO)_6$ (I), derived from $\mu\text{-}S_2Fe_2(CO)_6$ and Grignard reagent, have been extensively studied. They were demonstrated to be very useful in synthesizing various classes of Fe–S cluster complexes, particularly the symmetrical twin clusters [1–15]. Recently, we have found that the reaction of $(\mu\text{-RS})(\mu\text{-XMgS})Fe_2(CO)_6$ (I) with $[\mu\text{-PhC(O)S}](\mu\text{-R'S})Fe_2(CO)_6$ (II) may produce asymmetrical twin clusters $[(\mu\text{-RS})Fe_2(CO)_6](\mu_4\text{-S})[(\mu\text{-R'S})Fe_2(CO)_6]$ (III) together with symmetrical twin clusters $[(\mu\text{-RS})Fe_2(CO)_6]_2(\mu_4\text{-S})$ (IV) and $[(\mu\text{-R'S})Fe_2(CO)_6]_2(\mu_4\text{-S})$ (V), which are shown in Scheme 1.

In a typical experiment, a 10 mL THF solution of 1.32 mmol of II (R' = $CH_2CH{=}CH_2$) [16] was added at −78 °C to a 40 mL THF solution of I (R = $PhCH_2$, X = Cl) prepared from 1.32 mmol of $\mu\text{-}S_2Fe_2(CO)_6$ and 1.32 mmol of $PhCH_2MgCl$, giving a brown-red mixture. The mixture was warmed to room temperature and stirred for about 4 h. Solvent was removed at reduced pressure and the residue was extracted by 10% CH_2Cl_2–petroleum ether. The extracts were first separated by column chromatography and then by TLC using 10% CH_2Cl_2–petroleum ether as eluant to give three products: III (R = $PhCH_2$, R' = $CH_2{=}CHCH_2$), red crystals, 22%, m.p. 107–108 °C; IV (R = $PhCH_2$), 13%; and V (R' = $CH_2{=}CHCH_2$), 11%.

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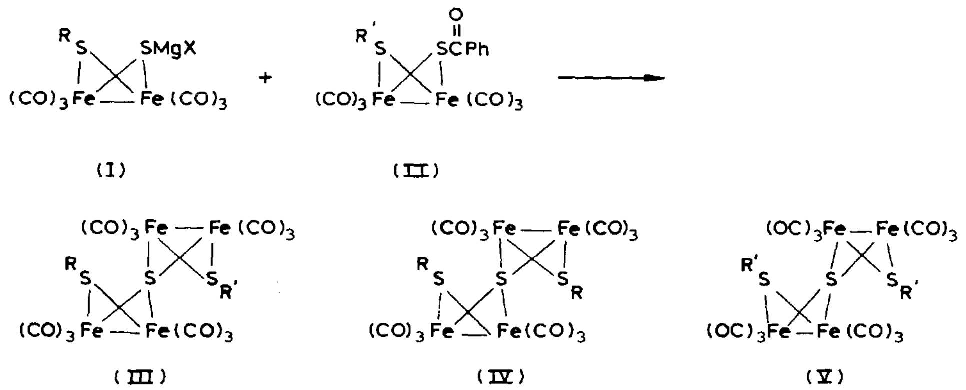

Scheme 1.

Similarly, the reaction of I (R = $PhCH_2$, X=Cl) with II (R′ = Ph) [8] gave III (R = $PhCH_2$, R′ = Ph), red crystals, 13%, m.p. 166–169 °C; IV (R = $PhCH_2$), 7%; and V (R′ = Ph), 5%.

Reaction of I (R = Ph, X = Br) with II (R′ = Me) [16] gave III (R = Ph, R′ = Me), red crystals, 19%, m.p. 134.5–135.5 °C; IV (R = Ph), 14%; and V (R′ = Me), 8%.

Reaction of I (R = Ph, X = Br) with II (R′ = Et) [16] gave III (R = Ph, R′ = Et), red crystals, 24%, m.p. 152–154 °C; IV (R = Ph), 13%; and V (R′ = Et), 13%.

Finally, reaction of I (R = Ph, X = Br) with II (R′ = CH_2=$CHCH_2$) gave III (R = Ph, R′ = CH_2=$CHCH_2$), red crystals, 20%, m.p. 150–152 °C; IV (R = Ph), 13%; and V (R′ = CH_2=$CHCH_2$), 11%.

As seen from the above, the reaction of I with II (R $\neq$ R′) always produces three twin clusters, the major one being asymmetrical, the other two symmetrical.

It is noteworthy that the yields of asymmetrical products are not high (about 20%). The low yields are mainly due to the formation of the two corresponding symmetrical cluster by-products (each in a yield of about 10%) and the difficulty of separating these three structurally similar clusters. However, the overall yields for the three twin clusters are moderate (in most cases about 50%).

The new twin cluster complexes described in this communication were characterized by elemental analysis, IR and ^1H NMR spectroscopy *. The analytical data for four already known symmetrical complexes (IV, R = Ph; IV, R = $PhCH_2$; V, R′ = Me; V, R′ = Et) coincide well with those reported in the literature [9].

The structure of III (R = Ph, R′ = Et) has been determined by X-ray crystallography ** and is shown in Fig. 1, together with selected bond lengths and angles. As seen from the figure, the twin cluster core of this complex is composed of two butterfly-shaped subclusters, S(1)Fe(1)S(2)Fe(2) and S(2)Fe(3)S(3)Fe(4), connected through a common spiran sulfur atom μ_4-S(2); the ethyl and phenyl group sub-

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* For example: For III (R = $PhCH_2$, R′ = CH_2=$CHCH_2$), IR (KBr) 2089(s), 2040(vs), 1998(vs), 1985(vs), 1974(vs, C≡O) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) 3.06 (d, J = 6.5 Hz, 2H, CH_2=$CHCH_2$), 3.64 (s, 2H, $SCH_2C_6H_5$), 5.13–5.40 (m, 3H, CH=CH_2), 7.37 (s, 5H, C_6H_5). Anal. Found: C, 34.02, H, 1.54; $C_{22}H_{12}Fe_4O_{12}S_3$ calc.: 33.54, H, 1.54%.
For III (R = $PhCH_2$, R′ = Ph), IR (KBr): 2082(s), 2030(vs), 1998(vs), 1983(vs), 1972(vs, C≡O) cm^{-1}; ^1H NMR ($CDCl_3$, TMS): 3.68 (s, 2H, SCH_2), 7.21–7.48 (broad, 10H, $2C_6H_5$). Anal., Found: C, 36.47, H, 1.42; $C_{25}H_{12}Fe_4O_{12}S_3$ calc.: C, 36.44, H, 1.47%.

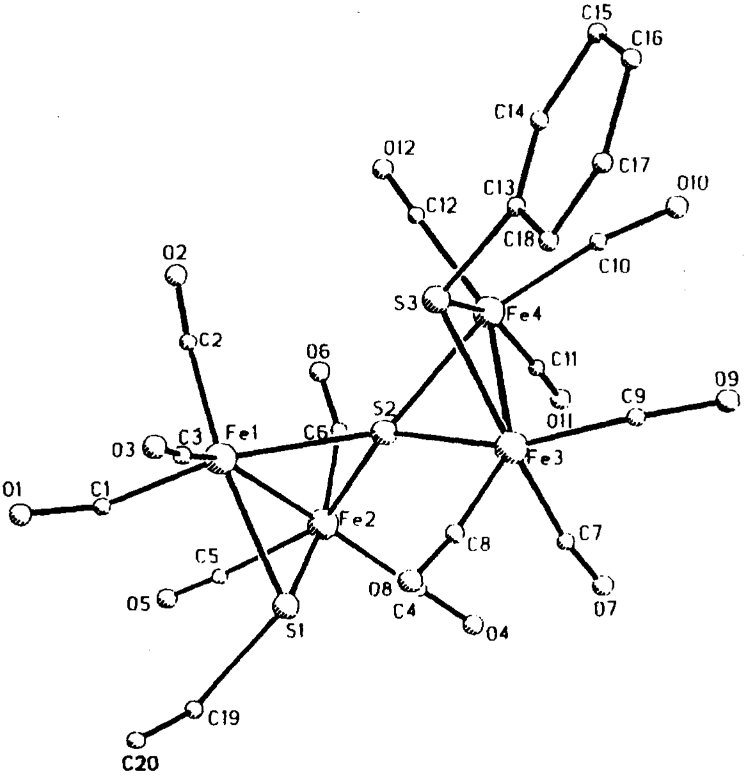

Fig. 1. Structure of III (R = Ph, R′ = Et). Selected bond lengths (Å) and angles (°) for one of two independent molecules: Fe(1)–S(1) 2.251(4), Fe(2)–S(2) 2.232(4), Fe(1)–Fe(2) 2.518(3), Fe(3)–Fe(4) 2.526(3); Fe(1)–S(2)–Fe(2) 68.4(1), S(1)–Fe(1)–S(2) 76.1(1), Fe(4)–Fe(3)–S(2) 55.0(1), Fe(1)–S(2)–Fe(3) 126.2(2).

stituents on the cluster core are both attached to μ_2-S(1) and μ_2-S(2) by an *e*-type bond [17]. Generally, the geometry of μ_4-S in this molecule coordinated to four iron atoms, is quite similar to that of μ_4-S in $[(\mu\text{-EtS})Fe_2(CO)_6]_2(\mu_4\text{-S})$ [9], μ_4-Sn in $[Fe_2(CO)_8(\mu_2\text{-SnMe}_2)]_2(\mu_4\text{-Sn})$ [18], and μ_4-As in $[Co_4(Cp)_4(CO)_4(\mu_4\text{-As})]$ [19], where we also find coordination to four corresponding metal atoms.

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** *Crystal data* for III (R = Ph, R′ = Et): $C_{20}H_{10}Fe_4O_{12}S_3$, $M = 761.86$, monoclinic, space group $P2_1$, a 9.111(2), b 12.130(2), c 25.886(5) Å, β 90.52(2)°, V 2860.57(1) Å^3, $Z = 4$, D_c 1.77 g cm^{-3}, λ 0.7107 Å, μ 22.5 cm^{-1}, $F(000) = 1512$, T 295 K. Data were collected on a R3M/E diffractometer for $3° \leq 2\theta \leq 45°$. The structure was solved by direct methods and refined by least-squares to R 0.031 for 3199 unique, observed $[(I \geq 3\sigma(I)]$ intensity data.

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