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COMMUNICATION

The first Fe_3 cluster complex containing (μ-HS)(μ_3-RS) ligands through an unexpected reaction of [(μ-RS)(μ-CO)$Fe_2(CO)_6$][Et_3NH]. Preparation and crystal structure of (μ-HS)(μ_3-t-BuS)$Fe_3(CO)_9$

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Abstract—The novel carbonyl cluster (μ-HS)(μ_3-t-BuS)$Fe_3(CO)_9$ was formed in the presence of $Zn(OAc)_2 \cdot H_2O$ from a complex salt [(μ-t-BuS)(μ-CO)$Fe_2(CO)_6$][Et_3NH], whose crystal structure has been unequivocally confirmed by X-ray diffraction techniques. © 1997 Elsevier Science Ltd

Keywords: Fe_3 cluster; μ-HS; μ_3-RS; synthesis; crystal structure; [(μ-RS)(μ-CO)$Fe_2(CO)_6$][Et_3NH].

The clusters containing both transition metals and main group elements, especially Fe–S cluster complexes, have long been an object of study, because they often exhibit unusual structural and reactivity patterns as well as some valuable catalytic properties [1–3]. Over the past decade one of our research interests has been focused on the reactivity of anionic Fe/S clusters [(μ-RS)(μ-CO)$Fe_2(CO)_6$][Et_3NH] (**1**). Up to now, we [4], the Seyferth group [5] and the others [6] have found that reactions of clusters **1** with most electrophiles can be rationalized in terms of their action as iron centered nucleophiles and the μ-CO ligands are either replaced or retained in the final products. However, the μ-CO-retained type of reactions is so far known for only one case in which reaction of **1** with Ph_3PAuCl to give (μ-RS)(μ-CO)(μ-Ph_3PAu)$Fe_2(CO)_6$ as the major compound [6]. Our initial purpose was to develop the μ-CO-retained type of reactions of cluster **1** and to synthesize Fe_4Zn clusters [(μ-RS)(μ-CO)$Fe_2(CO)_6$]$_2$(μ_4-Zn) (**2**) by reaction of **1** with $Zn(OAc)_2 \cdot H_2O$. However, the experiment with **1** (R = *t*-Bu) failed to give the expected cluster **2** (R = *t*-Bu); instead, it afforded a novel Fe–S cluster (μ-HS)(μ_3-*t*-BuS)$Fe_3(CO)_9$ (**3**) along with (μ-*t*-BuS)$_2$ $Fe_2(CO)_6$ [7].

To a solution of 1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$ in 30 cm^3 of THF was added 0.28 cm^3 (2.00 mmol) of triethylamine and 0.22 cm^3 (2.00 mmol) of *tert*-butyl mercaptan. The mixture was stirred under N_2 at room temperature for 30 min, followed by 0.219 g (1.00 mmol) of $Zn(OAc)_2 \cdot H_2O$ and the mixture was stirred for additional 24 h. After removal of the solvent in vacuo the dark-red residue was subjected to column chromatography. The first red band was eluted using petroleum ether to give 0.340 g (38%) of (μ-*t*-BuS)$_2$ $Fe_2(CO)_6$, which was identified by comparison with authentic sample [7]. Elution of the second red band yielded 0.83 g (17%) of cluster (μ-HS)(μ_3-*t*-BuS) $Fe_3(CO)_9$ (**3**), which has been fully characterized by

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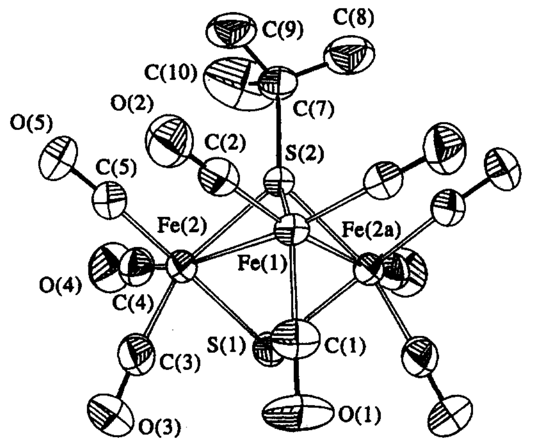

Fig. 1. ORTEP plot of 3. Selected bond distance (Å) and angles (°): Fe(1)—Fe(2), 2.679(1); Fe(1)—S(2), 2.129(1); Fe(2)—S(1), 2.338(1); Fe(2)—S(2), 2.225(1); S(2)—C(7), 1.882(5); Fe(2)—Fe(1)—Fe(2a), 76.6(1); Fe(2)—S(1)—Fe(2a), 90.5(1); Fe(2)—S(2)—Fe(2a), 96.5(1)

elemental-analysis, IR and ^1H NMR spectroscopy,* as well as by single crystal X-ray diffraction.†

A dark-red crystal of **3** suitable for X-ray diffraction was obtained from its solution at room temperature. The X-ray diffraction analysis revealed that **3** has the structure shown in Fig. 1.

Cluster **3** actually consists of one SH group, one *tert*-butylthio group and three $Fe(CO)_3$ units, of which three iron atoms are triangular and joined together through two Fe—Fe bonds. The bond angle of Fe(2)—Fe(1)—Fe(2a), the two Fe—Fe bonds [Fe(1)—Fe(2) and Fe(1)—Fe(2a)] and the non-bonded Fe(2) ··· Fe(2a) distance are equal to 76.6(1)°, 2.679(1), 2.679(1) and 3.322 Å, respectively. This molecule has a symmetric plane through Fe(1), S(1), and S(2) atoms. It is worth noting that the sulfur atom bearing a *tert*-butyl group i.e. S(2), as a 5e ligand, is coordinated to all three iron atoms, whereas the sulfur atom of SH group, i.e. S(1), as a 3e ligand, is coordinated only to two iron atoms Fe(2) and Fe(2a). The Fe/S clusters with simple sulfur atoms, which adopt μ_3- and μ_4- are quite common coordinated pattern, such as in the clusters $(\mu_3\text{-S})_2Fe_3(CO)_9$ [8], $(\mu_3\text{-S})FeCo_2(CO)_9$ [9], $(CO)_5Cr(\mu_4\text{-S})FeCo_2(CO)_9$ [10], and $[(\mu\text{-RS})Fe_2(CO)_6]_2$ (μ_4-S) [11]. However, the Fe/S clusters with a μ-SH ligand such as cluster **3** is quite few. In **3** the bond length of Fe(1)—S(2) [2.129(1) Å] is somewhat shorter than those of Fe(2)—S(2) or Fe(2a)—S(2) [2.225(1) Å] and Fe(2)—S(1) or Fe(2a)—S(1) [2.338(1) Å].

It follows that the structure of **3** is very similar to that of cluster $(\mu\text{-Cl})(\mu_3\text{-}t\text{-BuS})Fe_3(CO)_9$ [12]. For example, in the latter the corresponding two Fe—Fe bond lengths [2.681(4) Å], one non-bonded Fe—Fe distance [3.338(6) Å], and the bond angle formed by three Fe atoms [77.0(1)°] are almost the same with those of cluster **3**. In addition, **3** is isoelectronic with $(\mu\text{-Cl})(\mu_3\text{-}t\text{-BuS})Fe_3(CO)_9$ [12], which are both 50e clusters and antimagnetic. The proton of SH group in **3** is most likely abstracted from the Et_3NH cation of the complex salt $[(\mu\text{-}t\text{-BuS})(\mu\text{-CO})Fe_2(CO)_6][Et_3NH]$.

Finally, it should be pointed out that the complex salt $[(\mu\text{-}t\text{-BuS})(\mu\text{-CO})Fe_2(CO)_6][Et_3NH]$ alone, under similar conditions, could not give any amount of **3**. Therefore, the electrophile $Zn(OAc)_2 \cdot H_2O$ must be responsible for the formation of the novel cluster **3**. However, at the present stage we do not know how $Zn(OAc)_2 \cdot H_2O$ is mediated in this reaction. Studies on the mechanism and generality about this class of reactions will be soon carried out in this laboratory.

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* *Characterization data for* **3**: air-stable, dark-red solid, M. p. 145–147°C. IR (KBr disk): $\nu_{C\equiv O}$, 2082 s, 2057 s, 2008 vs, 1950 s (cm^{-1}). ^1H NMR [$CDCl_3$, TMS, δ (ppm)]: 1.72 (s, 9H, $3CH_3$). EIMS: m/z 369 [M^+-$SFe(CO)_3$, 0.14%], 257 ($BuSFe_3^+$, 0.21), 201 ($BuSFe_2^+$, 0.37), 145 ($BuSFe^+$, 0.16), 200 (SFe_3^+, 0.65), 144 (SFe_2^+, 0.69), 88 (SFe^+, 1.12), 112 [$Fe(CO)_2^+$, 0.52], 84 ($FeCO^+$, 8.27), 89 (BuS^+, 0.13), 57 (Bu^+, 1.21), 56 (Fe^+, 0.63).

† *Crystal data for* **3**: $C_{13}H_{10}Fe_3O_9S_2$: M = 541.9, Crystal dimensions 0.20 × 0.20 × 0.35 mm, monoclinic, space group $P2_{1/m}$ (No. 11), $a = 7.860(1)$, $b = 15.265(1)$, $c = 8.735(1)$ Å, $\beta = 108.11(1)°$. $V = 996.13$ Å^3, $Z = 2$, F(000) = 538, $D_c = 1.80$ g cm^{-3}, absorption coefficient 2.398 mm^{-1}. A total of 2536 reflections collected, 1759 observed reflections with $|F_0| \geq 4\sigma(|F_0|)$, empirical absorption correction (ω-scan), $R_f = 0.032$, $R_w = 0.046$. The raw intensities were collected on a Rigaku AFC 7R with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω-scan method in the range $2 < 2\theta < 55$. Patterson superposition yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinement. All hydrogens were generated geometrically (C—H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms; they were assigned the same isotropic temperature factors ($\mu = 0.05$ Å) and included in the structure factor calculations. Computations were performed using the SHELXTL PC program package on a PC 486 computer. Analytical expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated. Atomic coordinates, thermal parameters and structure factor tables have been deposited at the Cambridge Crystal Crystallographic Data Centre.

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