Organometallics 1994, 13, 2910–2912

Synthesis and Structural Characterization of the μ_4-S Heterometallic Cluster $(\eta^5\text{-}C_5H_4CH_3)Fe_3Co(\mu_4\text{-}S)(CO)_{11}$

Wen-Hua Sun,* Han-Qing Wang, Quan-Fu Zhou, and Shi-Yan Yang

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

Kai-Bei Yu

Chengdu Center of Analysis and Measurement, Chinese Academy of Sciences, Chengdu 610041, China

Received April 8, 1994[●]

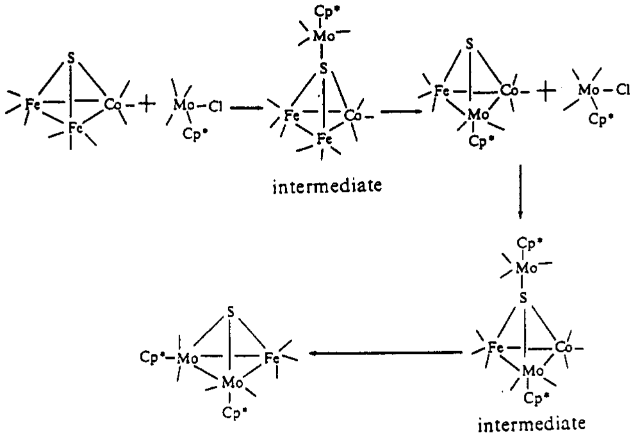
Summary: The new μ_4-S heterometallic cluster $(\eta^5\text{-}C_5H_4CH_3)Fe_3Co(\mu_4\text{-}S)(CO)_{11}$ was synthesized in high yield by the addition of $(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2$ (derived from $(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2Cl$) to $HFe_2Co(\mu_3\text{-}S)(CO)_9$ at room temperature. The cluster was characterized by elemental analyses, IR, and NMR as well as X-ray diffraction analysis. It crystallizes in the monoclinic space group $P112_1/n$, $a = 8.259(1)$ Å, $b = 12.832(2)$ Å, $c = 21.408(3)$ Å, $\gamma = 90.81(1)°$, $V = 2268.4(6)$ Å^3, $Z = 4$, and $D_c = 1.89$ g·cm^{-3}. Structure solution and refinement were based on 2367 independent reflections with $I \geq 3.0\sigma(I)$ (Mo Kα, λ = 0.710 73 Å) and converged at $R = 0.0447$ ($R_w = 0.0399$). The μ_4-S cluster is proposed as an example of intermediates in electrophilic addition–substituent elimination, and the existence of its isoelectronic analogues $(\eta^5\text{-}C_5H_5)MoFe_2Co(\mu_4\text{-}S)(CO)_{12}$ and $(\eta^5\text{-}C_5H_4CH_3)MoFe_2Co(\mu_4\text{-}S)(CO)_{12}$ also is proposed.

Introduction

With the development of transition-metal cluster chemistry, attempts to synthesize heterometallic clusters have received much attention.[1,2] The sulfido ligand has been found to promote such metal cluster formation by expanding its coordination number and stabilizing the resulting transition-metal clusters.[2-8] In our previous work,[9,10] heterometallic sulfido clusters, $Cp^*MoFeCo(\mu_3\text{-}S)(CO)_8$ and $Cp^*_2Mo_2Fe(CO)_7(\mu_3\text{-}S)$ ($Cp^* = \eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5H_4CH_3$), were formed in the reaction of $Cp^*Mo(CO)_3Cl$ with $HFe_2Co(CO)_9(\mu_3\text{-}S)$. It was proposed that an electrophilic addition–substituent elimination reaction sequence (Scheme 1) was involved, but attempts to isolate the intermediate $Cp^*MoFe_2Co(\mu_4\text{-}S)(CO)_{12}$ failed.

However, a new μ_4-S cluster, $(\eta^5\text{-}C_5H_4CH_3)Fe_3Co(\mu_4\text{-}S)(CO)_{11}$, could be synthesized by the reaction of $(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2Cl$ with $HFe_2Co(CO)_9(\mu_3\text{-}S)$. The synthesis and characterization of the title cluster is reported herein as well as an X-ray crystal structure determination.

Scheme 1



Results and Discussion

Synthesis. Treatment of $(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2Cl$ with $HFe_2Co(CO)_9(\mu_3\text{-}S)$ in tetrahydrofuran (THF) at room temperature gave a new μ_4-S cluster, $(\eta^5\text{-}C_5H_4CH_3)Fe_3Co(\mu_4\text{-}S)(CO)_{11}$. The μ_4-S cluster was formed by adding the $(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2$ fragment to the μ_3-S ligand of $HFe_2Co(CO)_9(\mu_3\text{-}S)$ while the hydride of the latter was lost;[11] i.e., nucleophilic attack at the metal chloride by the sulfido anion[5] was involved in the reaction to form the title cluster. Related additions have been carried out to form clusters of higher nuclearity.[3-8,12]

According to the theory of isolobal relationships,[13] the fragment $(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2$ is an isolobal analogue of $Cp^*Mo(CO)_3$. That means that the cluster $(\eta^5\text{-}C_5H_4CH_3)Fe_3Co(\mu_4\text{-}S)(CO)_{11}$ is an isoelectronic analogue of $Cp^*MoFe_2Co(\mu_4\text{-}S)(CO)_{12}$. Although μ_4-S clusters of the latter type have not been synthesized, their existence was implied by the isolation of the title cluster in terms of the isolobal relationships theory. Therefore, the electrophilic addition–substituent elimination process proposed for the reaction of $Cp^*Mo(CO)_3Cl$ with $HFe_2Co(CO)_9(\mu_3\text{-}S)$ (Scheme 1) is reasonable. The intermediates with a $MoFe_2Co(\mu_4\text{-}S)$ core are currently being sought.

Characterization of $(\eta^5\text{-}C_5H_4CH_3)Fe_3Co(\mu_4\text{-}S)(CO)_{11}$. The elemental analysis corresponded to the given formula. The presence of the terminal carbonyl ligands is confirmed by the IR absorptions in the range 1936–2075 cm^{-1}. In the

---

[●] Abstract published in *Advance ACS Abstracts,* June 1, 1994.

(1) Vahrenkamp, H. In *Transition Metal Chemistry*; Müller, A., Diemann, E., Eds.; Verlag Chemie: Weinheim: 1981, p 35.

(2) Whitmire, K. H. *J. Coord. Chem. B* **1988**, *17*, 95.

(3) Adams, R. D.; Horvath, I. T.; Wang, S. *Inorg. Chem.* **1985**, *24*, 1728.

(4) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1987**, *26*, 2807.

(5) Seyferth, D.; Henderson, R. S.; Gallagher, M. K. *J. Organomet. Chem.* **1980**, *193*, C75.

(6) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1988**, *7*, 503.

(7) Adams, R. D.; Babin, J. E.; Wang, J.-G.; Wu, W. *Inorg. Chem.* **1989**, *28*, 703.

(8) Adams, R. D. *J. Cluster Sci.* **1992**, *3*, 263.

(9) Sun, W.-H.; Wang, H.-Q.; Yang, S.-Y.; Zhou, Q.-F.; Yu, K.-B. *Polyhedron* **1994**, *13*, 389.

(10) Sun, W.-H.; Yang, S.-Y.; Wang, H.-Q.; Zhou, Q.-F.; Yu, K.-B. *J. Organomet. Chem.* **1994**, *465*, 263.

(11) Marko, L. *J. Organomet. Chem.* **1991**, *213*, 271.

(12) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 444.

(13) Hoffmann, R. *Science* **1982**, *211*, 995. Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

0276-7333/94/2313-2910$04.50/0

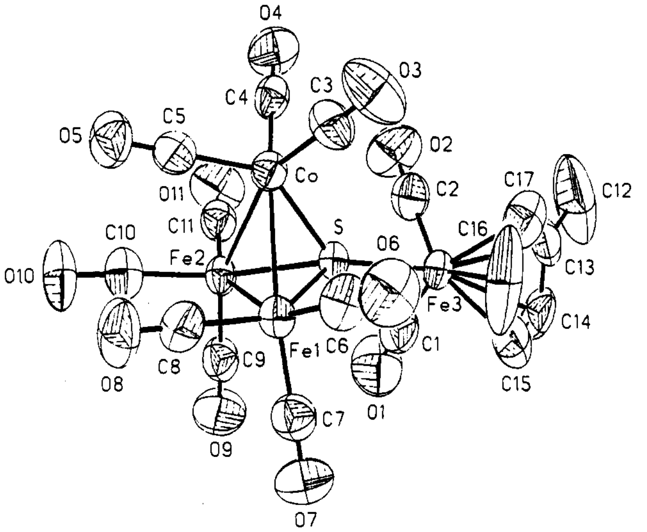


Figure 1. ORTEP drawing of (η^5-$C_5H_4CH_3$)Fe_3Co(μ_4-S)-$(CO)_{11}$.

NMR spectra observed, characteristic resonances are consistent with the structure of the title cluster. In the group of ^{13}C NMR signals at 96.1, 87.5, 87.6, and 112.6 ppm for C_5H_4, the small signal at 112.6 ppm is due to the tertiary carbon (C(13) in Figure 1). The three resonances in the ^{13}C NMR spectrum at 209.5, 210.5, and 213.7 ppm correspond to the carbonyl ligands coordinated to one cobalt and two types of iron.

Crystal Structure of (η^5-$C_5H_4CH_3$)Fe_3Co(μ_4-S)-$(CO)_{11}$. Suitable crystals of (η^5-$C_5H_4CH_3$)Fe_3Co(μ_4-S)-$(CO)_{11}$ were obtained by slowly lowering the temperature of its hexane/THF (4/1) solution. The molecular structure is illustrated in Figure 1. Final fractional atomic coordinates are listed in Table 1, while selected bond lengths and angles with estimated standard deviations are collected in Table 2.

The molecule consists of an equilateral triangle of two iron atoms and one cobalt atom with a mean M–M bond length of 2.60 Å and a mean M–M–M angle of 60°. A six-electron-donating sulfur atom bridges the three metals with a mean M–S bond length of 2.15 Å and is also attached to a terminal (η^5-$C_5H_4CH_3$)$Fe(CO)_2$ group with an Fe(3)–S bond length of 2.25 Å. The mean M–S bond length of 2.15 Å is significantly shorter than the sum of the single bond covalent radii for Fe(3) and S, 2.25 Å. The relative shortness of the bonds suggests that there is effective orbital overlap between the sulfur and the Fe(1), Fe(2), and Co atoms.

While the μ_4-S ligand acts as a six-electron donor, the terminal carbonyls act as two-electron donors and the methylcyclopentadienyl ring contributes five electrons. Thus the cluster reaches a "closed shell" electronic configuration.

Experimental Section

All operations were carried out under an atmosphere of dinitrogen on a standard Schlenk line. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. NMR spectra were obtained with a Bruker AM 400 NMR spectrometer. The peak positions are reported downfield of TMS. The IR spectrum was recorded on a Nicolet 10 DX FT-IR spectrometer. The C and H analyses were carried out with a Carlo-Erba 1106 microanalyzer. (η^5-$C_5H_4CH_3$)$Fe(CO)_2Cl$[14] and HFe_2Co(μ_3-S)$(CO)_9$[11] were prepared as described in the literature.

Table 1. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

	x	*y*	*z*	U^a
Co	9720(1)	2265(1)	479(1)	47(1)
Fe(1)	7468(1)	3564(1)	795(1)	46(1)
Fe(2)	6924(1)	1563(1)	855(1)	43(1)
Fe(3)	9482(1)	2349(1)	2393(1)	46(1)
S	8657(2)	2458(1)	1391(1)	39(1)
O(1)	6444(8)	1414(7)	2811(3)	126(3)
O(2)	10915(9)	317(5)	2145(3)	105(3)
O(3)	12505(7)	3684(5)	407(4)	110(3)
O(4)	11573(7)	340(4)	556(3)	87(2)
O(5)	8812(6)	2193(5)	−843(2)	81(2)
O(6)	9613(8)	5404(4)	807(3)	96(2)
O(7)	4816(8)	4314(5)	1567(3)	102(3)
O(8)	5983(8)	3857(5)	−433(3)	96(2)
O(9)	3968(7)	1534(6)	1590(3)	114(3)
O(10)	5296(7)	1248(5)	−344(2)	95(2)
O(11)	7949(7)	−574(4)	1076(3)	93(2)
C(1)	7622(10)	1789(7)	2640(3)	78(3)
C(2)	10343(10)	1115(7)	2240(3)	67(3)
C(3)	11411(8)	3142(6)	440(4)	66(3)
C(4)	10842(8)	1090(5)	530(3)	52(2)
C(5)	9155(8)	2218(5)	−322(3)	56(2)
C(6)	8790(10)	4690(6)	801(4)	66(3)
C(7)	5853(10)	4023(6)	1264(4)	66(3)
C(8)	6553(10)	3737(5)	46(3)	66(3)
C(9)	5135(8)	1543(6)	1307(4)	66(3)
C(10)	5984(9)	1376(5)	112(3)	61(3)
C(11)	7528(8)	256(5)	993(3)	59(3)
C(12)	12311(19)	1990(9)	3396(8)	199(9)
C(13)	11289(9)	2726(6)	3040(4)	70(3)
C(14)	9860(12)	3056(10)	3245(4)	102(4)
C(15)	9267(17)	3766(12)	2821(12)	177(9)
C(16)	10405(30)	3859(8)	2362(7)	167(9)
C(17)	11596(13)	3214(8)	2487(4)	93(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

Co–Fe(1)	2.604(1)	Co–Fe(2)	2.594(1)
Co–S	2.158(2)	Co–C(3)	1.783(7)
Co–C(4)	1.784(6)	Co–C(5)	1.777(7)
Fe(1)–Fe(2)	2.603(1)	Fe(1)–S	2.155(2)
Fe(1)–C(6)	1.799(8)	Fe(1)–C(7)	1.777(8)
Fe(1)–C(8)	1.789(7)	Fe(2)–S	2.153(2)
Fe(2)–C(9)	1.766(7)	Fe(2)–C(10)	1.786(7)
Fe(2)–C(11)	1.781(7)	Fe(3)–S	2.256(2)
Fe(3)–C(1)	1.767(8)	Fe(3)–C(2)	1.776(9)
Fe(1)–Co–Fe(2)	60.1(1)	Fe(1)–Co–S	52.8(1)
Fe(2)–Co–S	52.9(1)	Fe(1)–Co–C(3)	99.7(2)
Fe(2)–Co–C(3)	156.7(2)	S–Co–C(3)	106.6(3)
Fe(1)–Co–C(4)	155.4(2)	Fe(2)–Co–C(4)	99.1(2)
Fe(1)–Co–C(5)	94.8(2)	Fe(2)–Co–C(5)	93.2(2)
Co–Fe(1)–Fe(2)	59.8(1)	Co–Fe(1)–S	52.9(1)
Fe(2)–Fe(1)–S	52.8(1)	Co–Fe(1)–C(6)	94.9(3)
Fe(2)–Fe(1)–C(6)	152.4(3)	Co–Fe(1)–C(7)	154.9(3)
Fe(2)–Fe(1)–C(7)	100.3(2)	Co–Fe(1)–C(8)	98.8(2)
Fe(2)–Fe(1)–C(8)	95.7(2)	Co–Fe(2)–Fe(1)	60.1(1)
Co–Fe(2)–S	53.1(1)	Fe(1)–Fe(2)–S	52.9(1)
Co–Fe(2)–C(9)	156.3(2)	Fe(1)–Fe(2)–C(9)	100.0(2)
Co–Fe(2)–C(10)	98.8(2)	Fe(1)–Fe(2)–C(10)	99.1(2)
Co–Fe(2)–C(11)	96.8(2)	Fe(1)–Fe(2)–C(11)	152.9(2)
Co–S–Fe(1)	74.3(1)	Co–S–Fe(2)	74.0(1)
Fe(1)–S–Fe(2)	74.3(1)	Co–S–Fe(3)	136.9(1)
Fe(1)–S–Fe(3)	138.2(1)	Fe(2)–S–Fe(3)	132.3(1)

Preparation of (η^5-$C_5H_4CH_3$)Fe_3Co(μ_4-S)$(CO)_{11}$. A solution of η^5-$C_5H_4CH_3$)$Fe(CO)_2Cl$ (1.1 g, 5 mmol) and HFe_2Co(μ_3-S)-$(CO)_9$ (2.7 g, 6 mmol) in 70 mL of THF was stirred for 6 h at room temperature. The solvent then was removed under reduced pressure. The residue was chromatographed on neutral aluminum oxide (200–300 mesh). Eluting with petroleum ether (30–60 °C) removed unreacted HFe_2Co(μ_3-S)$(CO)_9$ (0.04 g) and

---

[14] Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

$Fe_3(CO)_9(\mu_3\text{-}S)_2$ (~0.5 g),[15] which was a coproduct of $HFe_2Co(\mu_3\text{-}S)(CO)_9$ (purified by extraction with hexane). Further elution with petroleum ether/THF (3/1) gave a fraction from which the black cluster $(\eta^5\text{-}C_5H_4CH_3)FeCo(\mu_4\text{-}S)(CO)_{11}$ (2.0 g, 72%) was obtained. The cluster was not changed when heated in refluxing THF for 4 h.

The title cluster was purified by column chromatography. Anal. Calcd for $C_{17}H_7CoFe_3O_{11}S$: C, 31.58; H, 1.08. Found: C, 31.23; H, 1.06. IR (KBr pellet): 2075.5 (s), 2048.5 (vs), 2004.2 (vs), 1959.8 (s), 1936.7 (s) cm^{-1}. NMR ($CDCl_3$, $SiMe_4$ as an internal standard, ppm): ^1H 2.19 (s, C*H*$_3$), 4.99, 5.25 (d, br, C_5*H*$_4$); ^{13}C 13.4 (s, *C*H$_3$), 87.5–112.6 (m, *C*$_5$H$_4$), 209.5, 210.5, 213.7 (T, *C*O).

Single-Crystal X-ray Diffraction Analysis. A black crystal of the title cluster having approximate dimensions of 0.18 × 0.20 × 0.52 mm was mounted on a R3M/e four-circle diffractometer. Graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) and a $\theta/2\theta$ scan type was used to measure the intensity data in the range $2° \leqslant 2\theta \leqslant 45°$. The unit cell was determined and refined with 24 reflections in 2θ range from 6.12 to 24.17°. Crystal data for $(\eta^5\text{-}C_5H_4CH_3)Fe_3Co(\mu_4\text{-}S)(CO)_{11}$: $C_{17}H_7CoFe_3O_{11}S_7$, monoclinic space group $P112_1/n$, $a = 8.259(1)$ Å, $b = 12.832(2)$ Å, $c = 21.408(3)$ Å, $\gamma = 90.81(1)°$, $V = 2268.4(6)$ Å^3, $Z = 4$, $D_c = 1.89$ g·cm^{-3}, μ(Mo Kα) = 27.42 cm^{-1}, $F(000) = 1271.76$. The 2367 independent reflections with $I \geqslant 3.0\sigma(I)$ of 3328 measured were corrected for Lorentz and polarization effects.

The structure was solved by the heavy-atom and refined by full-matrix least squares method. Refinement converged at a final R of 0.0447 ($R_w = 0.0399$, largest shift/esd −0.209), with allowance for the thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from the program package SHELXTL,[16] as implemented on an Eclipse S 140 computer, which was used for structure solution and refinement. A weighting scheme $\omega = \{1 - \exp[-5((\sin\theta)/\lambda)^2]\}/[\sigma^2(F) + 0.0001F^2]$ was used in the latter stages of refinement. Table 1 lists atomic positional parameters with estimated standard deviations.

Supplementary Material Available: For $(\eta^5\text{-}C_5H_4CH_3)Fe_3Co(\mu_4\text{-}S)(CO)_{11}$, tables of crystallographic data, complete bond lengths and angles, atomic parameters and anisotropic thermal parameters (*U* values) and structures of the complex (6 pages). Ordering information is given on any current masthead page.

OM940266C

---

(15) Bard, A. J.; Cowley, A. H.; Leland, J. K.; Thomas, J. N.; Norman, N. C.; Jutzi, P.; Morley, C. P.; Schlueter, E. *J. Chem. Soc., Dalton Trans.* 1985, 1303.

(16) Sheldrick, G. M. SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data (Revision 5.1). University of Gottingen, Germany, 1985.