JOM 23940

Heterometallic sulfido clusters by metal exchange: syntheses and X-ray crystal structures of $(\eta^5\text{-}C_5H_4CH_3)MoFeCo(CO)_8(\mu_3\text{-}S)$ and $(\eta^5\text{-}C_5H_4CH_3)_2Mo_2Fe(CO)_7(\mu_3\text{-}S)$

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

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000 (China); and State Key Laboratory of Structural Chemistry, Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, Fuzhou 35002 (China)

Kai-Bei Yu

Chengdu Centre of Analysis and Measurement, Chinese Academy of Sciences, Chengdu 610041 (China)

(Received April 3, 1993; in revised form June 16, 1993)

Abstract

Heterometallic sulfido clusters $(\eta^5\text{-}C_5H_4CH_3)MoFeCo(CO)_8(\mu_3\text{-}S)$ and $(\eta^5\text{-}C_5H_4CH_3)_2Mo_2Fe(CO)_7(\mu_3\text{-}S)$ were obtained through metal exchange with electrophilic addition-elimination via substitution from the reaction of $HFe_2Co(CO)_9(\mu_3\text{-}S)$ with $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3Cl$ in THF. The title clusters were characterized by elemental analyses, and IR and NMR spectroscopies. The X-ray crystal structures of the title clusters are reported here as well.

Key words: Heterometallics; Sulfido; Iron; Molybdenum; Cobalt; Crystal structure

Syntheses of heterometallic clusters by metal exchange following the addition-elimination sequence have boundless prospects [1]. The electrophilic relationship of metals towards sulphur has been used in syntheses of sulfido clusters [2]. The synthesis of heterometallic sulfido clusters by metal exchange with electrophilic addition and substitutional elimination might be a versatile and readily available method; the electrophilic addition reaction of $Co_2Fe(CO)_9(\mu_3\text{-}S)$ with $Cr(CO)_5$ derived from $Cr(CO)_6$ was previously carried out to form $(CO)_5Cr(\mu_4\text{-}S)Co_2Fe(CO)_9$ [3]. However, its isoelectronic analogous cluster $(\eta^5\text{-}C_5H_4CH_3)(CO)_2Mo(\mu_4\text{-}S)Fe_2Co(CO)_9$ was not separated from the reaction of $HFe_2Co(CO)_9(\mu_3\text{-}S)$ with $CpMo(CO)_3Cl$. The fact that $(\eta^5\text{-}C_5H_4CH_3)MoFeCo(CO)_8(\mu_3\text{-}S)$ [4] and $(\eta^5\text{-}C_5H_4CH_3)_2Mo_2Fe(CO)_7(\mu_3\text{-}S)$ were produced reveals that electrophilic addition-elimination via substitution might take place in the reaction. The syntheses and characterizations of the title clusters are reported here along with their crystal structures.

Under N_2 atmosphere, a mixture of $HFe_2Co(CO)_9(\mu_3\text{-}S)$ [5] (2.3 g, 5.0 mmol) and $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3Cl$ [6] (1.5 g, 5.1 mmol) was refluxed for 6 h in 60 ml tetrahydrofuran. The solvent was then removed on a vacuum line to afford a black residue. The residue was chromatographed to give tiny crystals of $HFe_2Co(CO)_9(\mu_3\text{-}S)$ (black), $[(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3]_2$ (violet) (0.1 g, 3.7%), $(\eta^5\text{-}C_5H_4CH_3)MoFeCo(CO)_8(\mu_3\text{-}S)$ (black) (0.8 g, 29%) and $(\eta^5\text{-}C_5H_4CH_3)_2Mo_2Fe(CO)_7(\mu_3\text{-}S)$ (brown) (0.4 g, 13%). Spectroscopic and analytical data of the resulting clusters were consistent with their formulae.

$(\eta^5\text{-}C_5H_4CH_3)MoFeCo(CO)_8(\mu_3\text{-}S)$. Anal. $C_{14}H_7CoFeMoO_8S$ calc.: C, 30.65; H, 1.277; Co, 10.79; Fe, 10.23; Mo, 17.57. Found: C, 30.86; H, 1.19; Co, 11.00; Fe, 10.36; Mo, 17.44%. $\nu(CO)$(KBr pellet): 2071s,

---

Correspondence to: Dr. W.-H. Sun.

0022-328X/94/$7.00
SSDI 0022-328X(93)23940-Y

2027vs, 2006vs, 1965vs, 1961s cm^{-1}. ^{1}H NMR (CD_3COCD_3, TMS): 2.24 (s, CH_3), 5.57–5.74 (m, C_5H_4) ppm. ^{13}C NMR (CD_3COCD_3, TMS): 14.35 (s, CH_3), 90.43–112.18 (m, C_5H_4), 211.83 (br, CO) ppm.

(η^5-$C_5H_4CH_3)_2Mo_2Fe(CO)_7(\mu_3$-S): Anal. $C_{19}H_{14}FeMo_2O_7S$ calc.: C, 35.99; H, 2.23. Found: C, 36.02; H, 2.44%. ν(CO)(KBr pellet): 2038vs, 1979vs, 1925s, 1894s, 1847vs cm^{-1}. ^{1}H NMR (CD_3COCD_3, TMS): 2.06 (s, CH_3), 5.33–5.53 (m, C_5H_4) ppm. ^{13}C NMR (CD_3COCD_3, TMS): 14.67 (S, CH_3), 89.80–112.27 (m, C_5H_4), 214.50–230.86 (T, CO) ppm.

Confirmation of the structure comes from single crystal X-ray crystallographic studies on the title clusters. Their molecular structures are shown in Figs. 1 and 2. The structure of (η^5-$C_5H_4CH_3$)MoFeCo-$(CO)_8(\mu_3$-S) is a triangle of one atom each of molybdenum, iron and cobalt with the Mo–Co bond length of 2.765(1) Å, the Mo–Fe distance of 2.797(1) Å and the Co–Fe bond length of 2.577(1) Å; these bond lengths are indicative of a single bond in each metal–metal interaction. A four electron-donating sulphur atom, which acts as a one-electron donor to each of the Co and Mo and as a two-electron donor to the Fe, caps the three metals. Each terminal carbonyl acts as a two-electron donor to give the metals the '18 electron configuration', while the π-bound methylcyclopentadienyl contributes five electrons to molybdenum. The broad absorption at 212.83 ppm in ^{13}C NMR is due to the fluxionality of all carbonyls over the whole cluster in its solution at room temperature [7].

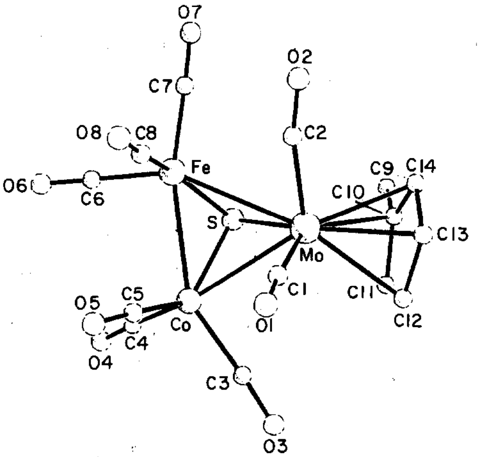

Fig. 1. Molecular structure of $C_{14}H_7CoFeMoO_8S$. Selected interatomic distances (Å) and angles (°): Mo–Co 2.765(1) Mo–Fe 2.797(1) Mo–S 2.357(1), Co–Fe 2.577(1) Co–S 2.195(1) Fe–S 2.181(1) Co–Mo–Fe 55.2(1) Co–Mo–S 50.0(1) Fe–Mo–S 49.2(1) Mo–Co–Fe 63.0(1) Mo–Co–S 55.3(1) Fe–Co–S 53.7(1) Mo–Fe–Co 61.8(1) Mo–Fe–S 54.8(1) Co–Fe–S 54.2(1) Mo–S–Co 74.7(1) Mo–S–Fe 76.0(1) Co–S–Fe 72.1(1)

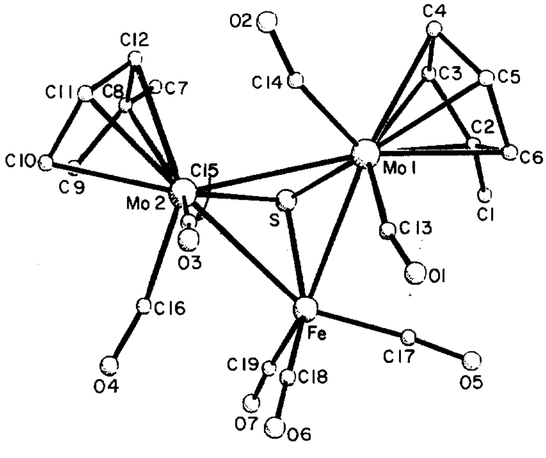

Fig. 2. Molecular structure of $C_{19}H_{14}FeMo_2O_7S$. Selected interatomic distances (Å) and angles (°): Mo(1)–Mo(2) 3.063(1) Mo(1)–Fe 2.806(1) Mo(1)–S 2.374(1) Mo(2)–Fe 2.823(1) Mo(2)–S 2.378(1) Fe–S 2.201(1) Mo(2)–Mo(1)–Fe 57.3(1) Mo(2)–Mo(1)–S 49.9(1) Fe–Mo(1)–S 49.4(1) Mo(1)–Mo(2)–S 49.8(1) Fe–Mo(2)–S 49.2(1) Mo(1)–Fe–Mo(2) 65.8(1) Mo(1)–Fe–S 55.0(1) Mo(2)–Fe–S 54.8(1) Mo(1)–S–Mo(2) 80.3(1) Mo(1)–S–Fe 75.5(1) Mo(2)–S–Fe 76.0(1)

The Mo_2Fe core in (η^5-$C_5H_4CH_3)_2Mo_2Fe(CO)_7$-$(\mu_3$-S) displays an isosceles triangle with one long (Mo(1)–Mo(2) 3.063 Å) and two short (mean Mo–Fe 2.815 Å) edges. The iron atom is bound to three terminal carbonyls and the two molybdenum atoms are each bound to two terminal carbonyls and a methylcyclopentadienyl ring (see Fig. 2). The sulfido ligand sits above the Mo_2Fe triangle coordinates to all three metals in a μ_3-fashion. The longer bond length of 3.063 Å indicates that the Mo–Mo interaction is weak. The cluster reaches a 'closed shell' electronic configuration while each of the carbonyl ligands contributes two electrons to the cluster and the methylcyclopentadienyl rings act as five-electron donors along with the four-electron donor of μ_3-S ligand. By comparison with the ^{13}C NMR spectrum of (η^5-$C_5H_4CH_3$)MoFe-$Co(CO)_8(\mu_3$-S), the triplet of carbonyl ligands at 214.50, 229.76, 230.86 ppm shows that the stereo-resistance of two methylcyclopentadienyl rings increases the rigidity of the cluster framework.

Both crystal structure determinations were carried out using a R3M/e CAD4 diffractometer with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by heavy atom methods and refined by full matrix least squares.

(η^5-$C_5H_4CH_3$)$MoFeCo(CO)_8(\mu_3$-S): Crystal data: orthorhombic, space group *Pcab* with cell dimensions of $a = 12.658(2)$, $b = 16.907(3)$, $c = 17.002(3)$ Å, $V = 3639$ Å^3, $Z = 8$, $D_c = 1.99$ g cm^{-3}, $F(000) = 2127.35$. $R = 0.0279$ ($R_w = 0.0260$) for 2029 unique reflections with $I \geqslant 3\sigma(I)$.

(η^5-$C_5H_4CH_3$)$_2$Mo$_2$Fe(CO)$_7$(μ_3-S): Crystal data: orthorhombic, space group *Pbca* with cell dimensions of $a = 13.337(3)$, $b = 16.770(5)$, $c = 18.398(4)$ Å, $V = 4115(2)$ Å^3, $Z = 8$, $D_c = 2.05$ g cm^{-3}, $F(000) = 2479.06$. $R = 0.0311$ ($R_w = 0.0287$) for 2335 unique reflections with $I \geqslant 3\sigma(I)$.

The cluster (η^5-$C_5H_4CH_3$)MoFeCo(CO)$_8$(μ_3-S) [4] where X-ray crystal structure has not been determined previously, was synthesized by metal exchange with addition-elimination of HFe$_2$Co(CO)$_9$(μ_3-S) with (η^5-$C_5H_4CH_3$)Mo(CO)$_3$As(CH$_3$)$_2$. In the reaction of HFe$_2$Co(CO)$_9$(μ_3-S) with (η^5-$C_5H_4CH_3$)Mo(CO)$_3$Cl, both the known cluster (η^5-$C_5H_4CH_3$)MoFeCo-(CO)$_8$(μ_3-S) and (η^5-$C_5H_4CH_3$)$_2$Mo$_2$Fe(CO)$_7$(μ_3-S) were synthesized along with the by-product [(η^5-$C_5H_4CH_3$)Mo(CO)$_3$]$_2$. The by-product was formed in our experiment involving the reflux of a THF solution of (η^5-$C_5H_4CH_3$)Mo(CO)$_3$Cl. The electrophilic addition-elimination via substitution might take place in the reaction to form the title clusters. As proposed, the (η^5-$C_5H_4CH_3$)Mo(CO)$_3$ initiated an electrophilic addition at μ_3-S of HFe$_2$Co(CO)$_9$(μ_3-S) to form an unstable intermediate (η^5-$C_5H_4CH_3$)(CO)$_3$Mo(μ_4-S)-Fe$_2$Co(CO)$_9$, then substitutional elimination was carried out in the intermediate to yield (η^5-$C_5H_4CH_3$)MoFe$_2$Co(CO)$_8$(μ_3-S). Similar to this process, the cluster (η^5-$C_5H_4CH_3$)$_2$Mo$_2$Fe(CO)$_7$(μ_3-S) was formed from the electrophilic addition and substitutional elimination reaction of (η^5-C_5H_4-CH$_3$)Mo(CO)$_3$Cl with (η^5-$C_5H_4CH_3$)MoFe$_2$Co(CO)$_8$-(μ_3-S). Although the intermediates were not separated in the reaction, one of their analogues (η^5-C_5H_4-CH$_3$)(CO)$_2$Fe(μ_4-S)Fe$_2$Co(CO)$_9$ [8*] was synthesized by the reaction of HFe$_2$Co(CO)$_9$(μ_3-S) with (η^5-$C_5H_4CH_3$)Fe(CO)$_2$Cl. The title cluster analogues Cp*MoFeCo(CO)$_8$(μ_3-S) and Cp*Mo$_2$Fe(CO)$_7$(μ_3-S) (Cp* = η^5-C_5H_5 or η^5-$C_5H_4CH_3$; M = Mo or W) have also been synthesized and confirmed by their IR spectra.

The metal exchange reaction with electrophilic addition-elimination via substitution may be useful in the syntheses of heterometallic sulfido clusters. More conclusive evidence for the reaction mechanism is currently being sought and efforts to achieve this objective are now being made.

Supplementary material available

Tables of crystallographic data and listings of observed and calculated structure factors for the work are available from the authors.

References and notes

1 H. Vahrenkamp in A. Muller and E. Diemann (eds.), *Transition Metal Chemistry*, Verlag Chemie, 1981, p. 35.
2 P.A. Eldredge, K.S. Bose, D.E. Barker, R.F. Bryan, E. Sinn, A. Rheingold and B.A. Averill, *Inorg. Chem., 30* (1991) 2365 and references cited therein.
3 F. Richter and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl., 17* (1978) 444.
4 F. Richter and H. Vahrenkamp, *Organometallics, 1* (1982) 756.
5 L. Marko, *J. Organomet. Chem., 213* (1981) 271.
6 T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem., 3* (1956) 104.
7 S. Aime, L. Milone, R. Rossetti and P.L. Stanghellini, *Inorg. Chim. Acta, 25* (1977) 103.
8 (η^5-$C_5H_4CH_3$)(CO)$_2$Fe(μ_4-S)Fe$_2$Co(CO)$_9$: monoclinic, space group $P112_1/n$, $a = 8.259(1)$, $b = 12.832(2)$, $c = 21.408(3)$ Å, $\gamma = 90.81(1)°$, $V = 2268.4(6)$ Å^3, $Z = 4$, $D_c = 1.89$ g·cm^{-3}, $F(000) = 1271.76$.

---

* Reference number with asterisk indicates a note in the list of references