

Synthesis and characterization of the cluster complexes containing tetrahedral FeCrCo(μ_3 -S) cluster cores generated by isolobal displacement reactions. Crystal structures of $(\eta^5\text{-RC}_5\text{H}_4)\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8$ (R = H, CO₂Et) and FeCo₂(μ_3 -S)₂(CO)₉

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Abstract

The monoanions $(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_3\text{Cr}^-$ (**1**, R = H; **2**, R = Me; **3**, R = CO₂Et) reacted with tetrahedral cluster FeCo₂(μ_3 -S)(CO)₉ to give single isolobal displacement products $(\eta^5\text{-RC}_5\text{H}_4)\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8$ (**4**, R = H; **5**, R = Me; **6**, R = CO₂Et) in 86–89% yields, whereas monoanion $(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_3\text{Cr}^-$ (**7**, R = C(O)Me) reacted with FeCo₂(μ_3 -S)(CO)₉ to afford the expected single isolobal displacement product $(\eta^5\text{-RC}_5\text{H}_4)\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8$ (**8**, R = C(O)Me) in 5% yield and an unexpected square pyramidal cluster FeCo₂(μ_3 -S)₂(CO)₉ (**9**) in 45% yield. Similarly, the dianions $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5][(\text{CO})_3\text{Cr}^-]_2$ (**10**, $n = 1$; **11**, $n = 2$; **12**, $n = 3$) reacted with two molecules of FeCo₂(μ_3 -S)(CO)₉ to produce double isolobal displacement products $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5][\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8]_2$ (**13**, $n = 1$; **14**, $n = 2$; **15**, $n = 3$) in 32–36% yields, while treatment of dianion $[\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2]_2[(\text{CO})_3\text{Cr}^-]_2$ (**16**) with two molecules of FeCo₂(μ_3 -S)(CO)₉ gave the unexpected square pyramidal cluster FeCo₂(μ_3 -S)₂(CO)₉ (**9**) in 42% yield and the corresponding double isolobal displacement product $[\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2]_2[\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8]_2$ (**17**) in 8% yield. Products **4–6**, **8**, **9**, **13–15** and **17** were characterized by elemental analyses, IR and ¹H NMR spectroscopy, as well as for **4**, **6** and **9** by X-ray diffraction techniques.
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Keywords: Chromium; Iron; Cobalt; Substituted cyclopentadienyl ligands; Cluster complexes; Isolobal displacement; X-ray structures

1. Introduction

During recent years transition metal cluster complexes have received considerable attention, largely due to their potential applications in catalysis and the novelty and diversity of their reactions and structures [1–5]. Previously, we reported the synthesis and characterization of the cluster complexes containing tetrahedral FeMCo(μ_3 -S)(CO)₈ (M = Mo, W) cores produced by isolobal displacement reactions [6,7]. Recently, as part of this project, we studied the isolobal displacement reactions of monoanions $(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_3\text{Cr}^-$ (R = H,

Me, CO₂Et, C(O)Me) and dianions $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5][(\text{CO})_3\text{Cr}^-]_2$ ($n = 1–3$) or $[\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2]_2[(\text{CO})_3\text{Cr}^-]_2$ with tetrahedral cluster FeCo₂(μ_3 -S)(CO)₉. Interestingly, these reactions have allowed us to obtain the corresponding single and double isolobal displacement products $(\eta^5\text{-RC}_5\text{H}_4)\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8$ (R = H, Me, CO₂Et, C(O)Me), $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5][\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8]_2$ ($n = 1–3$) and $[\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2]_2[\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8]_2$. In addition, a square pyramidal cluster FeCo₂(μ_3 -S)₂(CO)₉ has been also obtained unexpectedly from both the reactions of monoanion $(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_3\text{Cr}^-$ (R = C(O)Me) and dianion $[\eta^5\text{-RC}_5\text{H}_4\text{C(O)CH}_2]_2[(\text{CO})_3\text{Cr}^-]_2$ with tetrahedral cluster FeCo₂(μ_3 -S)(CO)₉. Now we report these interesting results obtained from this study.

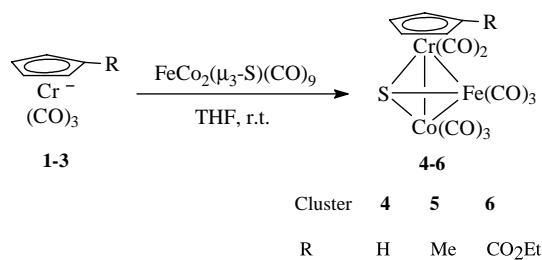
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2. Results and discussion

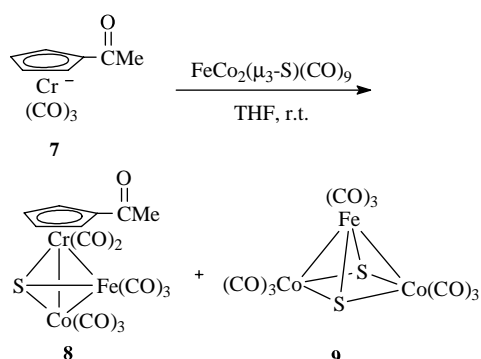
2.1. Synthesis and characterization of 4–6, 8, 9, 13–15 and 17

We found that the sodium salts of the chromium monoanions ($\eta^5\text{-RC}_5\text{H}_4$)(CO)₃Cr[−] (**1–3**, R = H, Me, CO₂Et) generated from Cr(CO)₆ and ($\eta^5\text{-RC}_5\text{H}_4$)Na reacted in situ with tetrahedral cluster FeCo₂(μ₃-S)(CO)₉ in THF at room temperature for 3 h to give single clusters **4–6** in 86–89% yields (Scheme 1), whereas the sodium salt of monoanion [$\eta^5\text{-MeC(O)C}_5\text{H}_4$](CO)₃Cr[−] (**7**), generated from Cr(CO)₆ and [$\eta^5\text{-MeC(O)C}_5\text{H}_4$]Na reacted in situ with FeCo₂(μ₃-S)(CO)₉ under similar conditions to produce 5% yield of single cluster **8** and 45% yield of square pyramidal cluster **9** (Scheme 2).

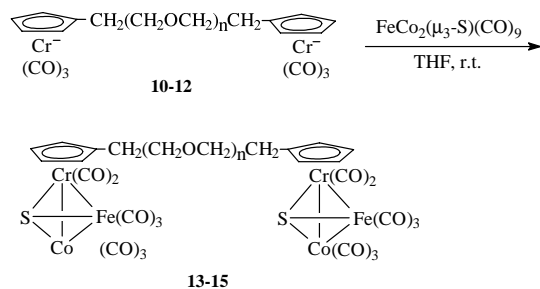
Similarly, we further found that the sodium salts of the dichromium dianions [$\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5$][(CO)₃Cr[−]]₂ (**10–12**, *n* = 1–3) formed from [$\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5$]Na₂ (*n* = 1–3) and Cr(CO)₆ reacted in situ with two molecules of FeCo₂(μ₃-S)(CO)₉ in THF at room temperature to afford the ether chain-bridged double clusters **13–15** in 32–36% yields (Scheme 3), whereas the sodium salt of the dichromium dianion [$\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2$]₂ [(CO)₃Cr[−]]₂ (**16**) generated from [$\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2$]₂Na₂ and Cr(CO)₆ reacted in situ with two molecules of FeCo₂(μ₃-S)(CO)₉ under similar conditions to give the



Scheme 1.



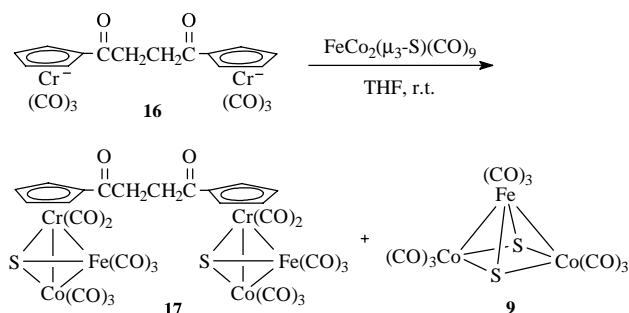
Scheme 2.



13–15

Cluster	13	14	15
<i>n</i>	1	2	3

Scheme 3.



Scheme 4.

succinyl bridged double cluster **17** in 8% yield and the square pyramidal cluster **9** in 42% yield (Scheme 4).

At the present stage we are not clear about the reaction mechanism for formation of the single and double-tetrahedral clusters **4–6**, **8**, **13–15** and **17**, and particularly the square pyramidal cluster **9**. However, it is apparent that the single-tetrahedral clusters **4–6** and **8** may be simply regarded as the products of the single isolobal displacements of the Co(CO)₃ (d⁹ML₃) structural unit in the starting cluster FeCo₂(μ₃-S)(CO)₉ by ($\eta^5\text{-RC}_5\text{H}_4$)Cr(CO)₂ (d⁵ML₅) fragments formed in situ from the sodium salts of the monoanions **1–3** and **7** [6,8], whereas the double-tetrahedral clusters **13–15** and **17** can be regarded as derived from the double isolobal displacements of the two Co(CO)₃ (d⁹ML₃) structural units in two molecules of the starting cluster FeCo₂(μ₃-S)(CO)₉ by the bridging double d⁵ML₅ isolobal fragments [$\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5$][Cr(CO)₂]₂ (*n* = 1–3) and [$\eta^5\text{-C}_5\text{H}_4\text{C(O)CH}_2$]₂[Cr(CO)₂]₂ generated in situ from the corresponding Cr/Na salts of dianions **10–12** and **16** [6,8]. Although we do not know the mechanism by which the square pyramidal cluster **9** was formed in the reaction of monoanion **7** or dianion **16** with cluster FeCo₂(μ₃-S)(CO)₉, the ketonic carbonyl groups in the substituted cyclopentadienyl rings of anions **7** and **16** may possibly play a key role in the formation of the unexpected product **9**.

All the products are new, except that **4** was previously prepared by another method [9]. The elemental analyt-

ical data for all the products are consistent with their compositions and the IR spectra display several absorption bands in the range 2105–1847 cm^{-1} for their metal-carbonyls. In addition, the IR spectra of **6**, **8** and **17** show one absorption band in the region 1718–1667 cm^{-1} for their ketonic and ester's carbonyls and those of **13–15** exhibit one absorption band in the range 1112–1104 cm^{-1} for their C–O–C functionalities. It is known that ^1H NMR spectra of a monosubstituted cyclopentadienyl ring in transition metal complexes vary greatly in complexity, such as a single resonance, an A_2B_2 or A_2BB' pattern or a multiplet pattern, mainly depending on the nature of the substituent and the transition metal moieties [6,10]. For example, the ^1H NMR spectrum of **5** displays two singlets at 4.85 and 4.93 ppm, the upfield singlet being assigned to H^2 and H^5 protons close to the electron-donating methyl substituent and the downfield one to H^3 and H^4 remote from the substituent, whereas the ^1H NMR spectrum of **8** shows two doublets at 5.05 and 5.60 ppm, the upfield doublet being attributed to H^3 and H^4 protons and the downfield one to H^2 and H^5 , since the acetyl substituent is electron-withdrawing. In addition, the ^1H NMR spectra for the four protons of the substituted Cp rings in **14**, **15** and **17** exhibit three singlets. Finally, it should be noted that products **5**, **6**, **8**, **13–15** and **17** also display the ^1H NMR signals for the substituted groups attached to their cyclopentadienyl rings.

2.2. Crystal structures of **4**, **6** and **9**

The molecular structures of **4**, **6** and **9** have been confirmed by X-ray diffraction analyses. The molecular structures of **4**, **6** and **9** are shown in Figs. 1, 2 and 3, respectively. The bond lengths and angles of **4**, **6** and **9** are listed in Tables 1, 2 and 3, respectively.

As can be seen in Figs. 1 and 2, products **4** and **6** each consist of a distorted tetrahedral $\text{FeCrCo}(\mu_3\text{-S})$ cluster core, which carries one parent or substituted cyclopentadienyl ligand coordinated to Cr atom, one set of two CO ligands attached to Cr atom and two sets of three CO ligands attached to Co and Fe atoms, respectively. According to our knowledge, these are the first compounds containing the tetrahedral $\text{FeCrCo}(\mu_3\text{-S})$ cluster core which have been characterized crystallographically. In **4** and **6**, the bond lengths $\text{Cr}(1)\text{--S}(1)$ (2.243(2), 2.2433(18) Å), $\text{Cr}(1)\text{--Fe}(1)$ (2.7289(16), 2.7342(14) Å) and $\text{Cr}(1)\text{--Co}(1)$ (2.7391(16), 2.7419(13) Å) are very close to the corresponding those reported in literatures [11,12], whereas the bond lengths $\text{Co}(1)\text{--S}(1)$ (2.158(2), 2.1461(19) Å), $\text{Co}(1)\text{--Fe}(1)$ (2.5797(17), 2.5530(13) Å) and $\text{Fe}(1)\text{--S}(1)$ (2.190(2), 2.1775(18) Å) are very similar to the corresponding those of $[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2[\text{MFeCo}(\mu_3\text{-S})(\text{CO})_8]_2$ (M = Mo, W) [6]. It is worthy of note that the π -system of the substituent ethoxycarbonyl group $\text{EtOC}=\text{O}$ in **6** seems to be conjugated to a certain

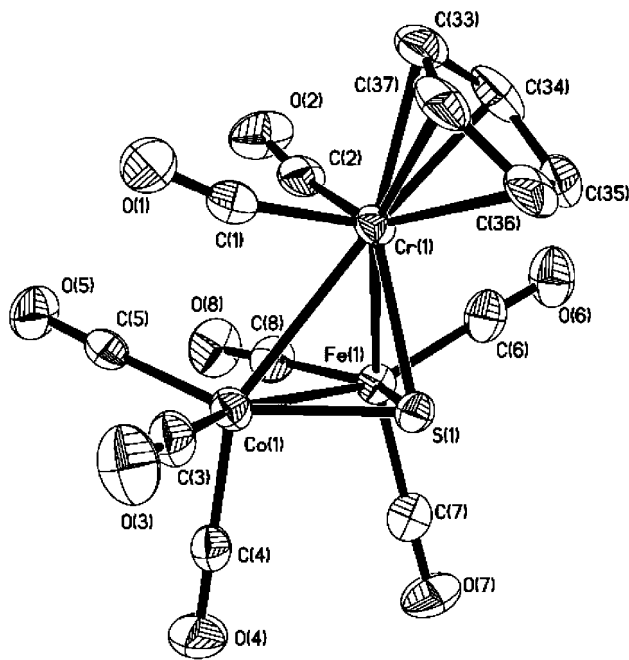


Fig. 1. ORTEP drawing of **4** with the atom labeling scheme.

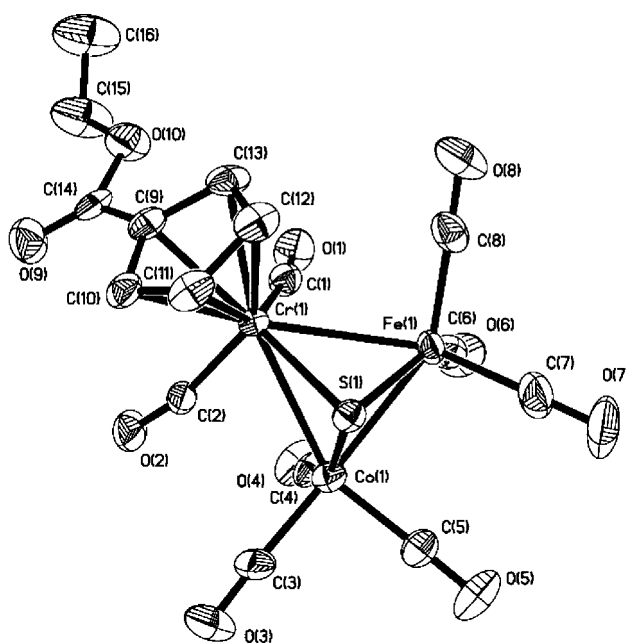


Fig. 2. ORTEP drawing of **6** with the atom labeling scheme.

degree with that of the cyclopentadienyl ring, since the dihedral angle between the Cp ring and the plane of $\text{C}(9)\text{--C}(14)\text{--O}(9)$ is only 2.2° and the bond length of $\text{C}(9)\text{--C}(14)$ (1.482(10) Å) is obviously shorter than that of a normal C–C single bond.

Interestingly, as can be seen in Fig. 3, the molecule of **9**, in contrast to **4** and **6** each containing a tetrahedral $\text{FeCrCo}(\mu_3\text{-S})$ cluster core, comprises a square pyramidal $\text{FeCo}_2(\mu_3\text{-S})_2$ cluster core, in which the Fe atom

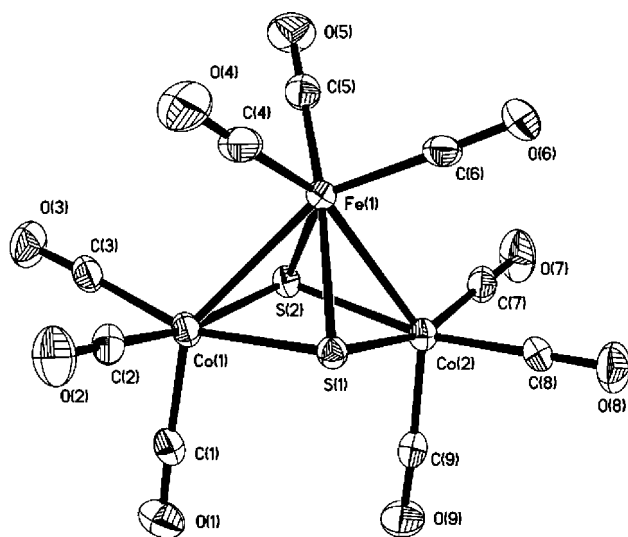


Fig. 3. ORTEP drawing of **9** with the atom labeling scheme.

occupies the vertex of the pyramid with three carbonyls, and the two Co atoms carry two sets of three carbonyls. In fact, the four atoms Co(1), S(1), S(2) and Co(2), which constitutes the base of the pyramid, are not completely coplanar and the dihedral angle between Co(1)–S(1)–S(2) and S(1)–S(2)–Co(2) is 17.1°. All the bond lengths and angles of **9** are very close to the corresponding those of $\text{FeCo}_2(\mu_3\text{-S})(\text{CO})_9$ [13].

Finally, it should be pointed out that while in **9** all the carbonyls are terminal, in **4** or **6** the six carbonyls attached to Fe and Co are terminal and the two carbonyls attached to Cr are semibridging. This is because, as shown in Table 4, the asymmetry parameters α for the two carbonyls attached to Cr in **4** and **6** fall within the range $0.1 \leq \alpha \leq 0.6$ [14].

3. Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. THF and diglyme were distilled from Na-benzophenone ketyl under nitrogen. $\eta^5\text{-RC}_5\text{H}_4\text{Na}$ (R = H [15], Me[16], C(O)Me [17], CO_2Et [18]), $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5]\text{Na}_2$ ($n = 1\text{--}3$) [7], $[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2\text{Na}_2$ [19], $\text{FeCo}_2(\mu_3\text{-S})(\text{CO})_9$ [20] were prepared according to the reported procedures. Products were isolated by preparative TLC and further recrystallized from the CH_2Cl_2 /hexane mixed solvent. IR spectra were recorded on a Nicolet Magna 560 FTIR infrared spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC-P200 NMR spectrometer. C/H analyses were performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Table 1
Selected bond lengths (Å) and bond angles (°) for **4**

Cr(1)–S(1)	2.243(2)	Fe(1)–S(1)	2.190(2)
Cr(1)–Fe(1)	2.7289(16)	Cr(1)–C(1)	1.879(10)
Cr(1)–Co(1)	2.7391(16)	Fe(1)–C(6)	1.804(11)
Co(1)–S(1)	2.158(2)	C(1)–O(1)	1.141(10)
Co(1)–Fe(1)	2.5797(17)	Co(1)–C(4)	1.774(9)
S(1)–Co(1)–Cr(1)	52.91(6)	Co(1)–Fe(1)–Cr(1)	62.05(4)
S(1)–Co(1)–Fe(1)	54.18(6)	Co(1)–S(1)–Fe(1)	72.77(7)
S(1)–Cr(1)–Fe(1)	51.14(6)	Co(1)–S(1)–Cr(1)	76.95(7)
S(1)–Cr(1)–Co(1)	50.14(6)	Fe(1)–Co(1)–Cr(1)	61.65(4)
S(1)–Fe(1)–Co(1)	53.05(6)	Fe(1)–Cr(1)–Co(1)	56.30(4)
S(1)–Fe(1)–Cr(1)	52.88(6)	Fe(1)–S(1)–Cr(1)	75.98(7)

Table 2
Selected bond lengths (Å) and bond angles (°) for **6**

Cr(1)–S(1)	2.2433(18)	Fe(1)–S(1)	2.1775(18)
Cr(1)–Fe(1)	2.7342(14)	Co(1)–C(3)	1.780(8)
Cr(1)–Co(1)	2.7419(13)	Cr(1)–C(1)	1.865(7)
Co(1)–S(1)	2.1461(19)	Fe(1)–C(6)	1.785(9)
Co(1)–Fe(1)	2.5530(13)	C(9)–C(14)	1.482(10)
S(1)–Co(1)–Cr(1)	52.95(5)	Co(1)–Fe(1)–Cr(1)	62.36(3)
S(1)–Co(1)–Fe(1)	54.38(5)	Co(1)–S(1)–Fe(1)	72.38(6)
S(1)–Cr(1)–Fe(1)	50.72(5)	Co(1)–S(1)–Cr(1)	77.28(6)
S(1)–Cr(1)–Co(1)	49.77(5)	Fe(1)–Co(1)–Cr(1)	62.06(4)
S(1)–Fe(1)–Co(1)	53.24(5)	Fe(1)–Cr(1)–Co(1)	55.58(3)
S(1)–Fe(1)–Cr(1)	52.89(5)	Fe(1)–S(1)–Cr(1)	76.39(6)

Table 3
Selected bond lengths (Å) and bond angles (°) for **9**

Co(1)–S(2)	2.2380(17)	Co(2)–S(2)	2.2368(17)
Co(1)–S(1)	2.2495(17)	Co(2)–S(1)	2.2499(16)
Co(1)–Fe(1)	2.6118(13)	Co(2)–Fe(1)	2.6047(14)
Fe(1)–S(1)	2.2685(16)	Fe(1)–S(2)	2.2486(17)
Co(1)–Fe(1)	2.5530(13)	C(8)–O(8)	1.129(6)
Co(1)–S(1)–Co(2)	97.56(6)	Co(2)–S(2)–Co(1)	98.28(6)
S(2)–Co(1)–S(1)	80.59(6)	S(2)–Fe(1)–S(1)	79.95(6)
S(2)–Co(2)–S(1)	80.60(6)	Co(2)–Fe(1)–Co(1)	80.90(4)
Co(2)–S(2)–Fe(1)	71.00(5)	Co(1)–S(1)–Fe(1)	70.63(5)
Co(1)–S(2)–Fe(1)	71.20(5)	Co(2)–S(1)–Fe(1)	70.40(5)
S(2)–Co(1)–Fe(1)	54.59(5)	S(2)–Fe(1)–Co(1)	54.21(4)
S(1)–Co(1)–Fe(1)	55.02(4)	S(1)–Fe(1)–Co(1)	54.35(4)

Table 4
Semibrddging CO's for **4** and **6**^a

	d_1 (Å)	d_2 (Å)	α
4			
C(1)O(1)	Cr(1)–C(1) 1.878	Co(1)···C(1) 2.575	0.37
C(2)O(2)	Cr(1)–C(2) 1.841	Fe(1)···C(2) 2.788	0.51
6			
C(1)O(1)	Cr(1)–C(1) 1.865	Fe(1)···C(1) 2.790	0.50
C(2)O(2)	Cr(1)–C(2) 1.858	Co(1)···C(2) 2.581	0.39

^a An asymmetric parameter α is defined as $\alpha = (d_2 - d_1)/d_1$, where d_1 and d_2 are the short and long distances of M–(CO), respectively [14].

3.1. Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8$ (**4**)

A 100 ml three-necked flask equipped with a stir-bar, a serum cap and a reflux condenser topped with a nitrogen inlet tube was charged with 0.220 g (1.0 mmol) of $\text{Cr}(\text{CO})_6$, 1.0 mmol of $\eta^5\text{-C}_5\text{H}_5\text{Na}$ and 15 ml of diglyme. The reaction mixture was stirred at reflux for 5 h. After evaporation of diglyme under vacuum, 0.458 g (1.00 mmol) of $\text{FeCo}_2(\mu_3\text{-S})(\text{CO})_9$ and 20 ml of THF were added, the mixture was stirred at room temperature for 3 h. Solvent was removed under reduced pressure. The residue was subjected to preparative TLC separation using a mixed solvent of CH_2Cl_2 /light petroleum ether ($v/v = 1/4$) as eluent. The main brown green band afforded 0.429 g (88%) of **4** as a black crystal, m.p. 98–99 °C. *Anal. Calc.* for $\text{C}_{13}\text{H}_5\text{CoCrFeO}_8\text{S}$: C, 32.00; H, 1.03. Found: C, 31.82; H, 1.13%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2074vs, 2032vs, 2003vs, 1971vs; 1931vs; 1882s, 1852s cm^{-1} . ^1H NMR (200 MHz, CDCl_3): δ 5.08 (s, 5H, C_5H_5) ppm.

3.2. Preparation of $(\eta^5\text{-MeC}_5\text{H}_4)\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8$ (**5**)

The same procedure as that for **4** was followed, but 1.0 mmol of $\eta^5\text{-MeC}_5\text{H}_4\text{Na}$ was used in place of $\eta^5\text{-C}_5\text{H}_5\text{Na}$. The main brown green band afforded 0.458 g (86%) of **5** as a black crystal, m.p. 75–76 °C. *Anal. Calc.* for $\text{C}_{14}\text{H}_7\text{CoCrFeO}_8\text{S}$: C, 33.49; H, 1.41. Found: C, 33.69; H, 1.54%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2071vs, 2029vs, 2010vs, 1973vs, 1930vs, 1897s, 1874s, 1847s cm^{-1} . ^1H

NMR (CDCl_3): δ 2.07 (s, 3H, CH_3), 4.85 (s, 2H, $\text{H}^{2,5}$), 4.93 (s, 2H, $\text{H}^{3,4}$) ppm.

3.3. Preparation of $(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8$ (**6**)

The same procedure as that for **4** was followed, but 1.0 mmol of $\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Na}$ was used instead of $\eta^5\text{-C}_5\text{H}_5\text{Na}$. The main brown green band afforded 0.498 g (89%) of **6** as a black crystal, m.p. 70–71 °C. *Anal. Calc.* for $\text{C}_{16}\text{H}_9\text{CoCrFeO}_{10}\text{S}$: C, 34.31; H, 1.62. Found: C, 34.37; H, 1.69%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2082vs, 2044vs, 2017vs, 1975s, 1940s, 1877s; $\nu_{\text{C}=\text{O}}$ 1718s cm^{-1} . ^1H NMR (CDCl_3): δ 1.29 (t, $J = 7.0$ Hz, 3H, CH_3), 4.26 (q, $J = 7.0$ Hz, 2H, CH_2), 4.98 (d, 2H, $\text{H}^{3,4}$), 5.62 (d, 2H, $\text{H}^{2,5}$) ppm.

3.4. Preparation of $(\eta^5\text{-MeC}(\text{O})\text{C}_5\text{H}_4)\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8$ (**8**) and $\text{FeCo}_2(\mu_3\text{-S})_2(\text{CO})_9$ (**9**)

The same procedure as that for **4** was followed, but 1.0 mmol of $\eta^5\text{-MeC}(\text{O})\text{C}_5\text{H}_4\text{Na}$ was used instead of $\eta^5\text{-C}_5\text{H}_5\text{Na}$. A brown green band afforded 0.027 g (5%) of **8** as a black solid, m.p. 74–75 °C. *Anal. Calc.* for $\text{C}_{15}\text{H}_7\text{CoCrFeO}_9\text{S}$: C, 33.99; H, 1.33. Found: C, 34.10; H, 1.42%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2082s, 2040vs, 1988s, 1866m; $\nu_{\text{C}=\text{O}}$ 1667s cm^{-1} . ^1H NMR (CDCl_3): δ 2.31 (s, 3H, CH_3), 5.05 (d, 2H, $\text{H}^{3,4}$), 5.60 (d, 2H, $\text{H}^{2,5}$) ppm.

Further separation with 1:1 (v/v) of acetone/light petroleum ether as eluent gave a main brown red band, from which 0.217 g (45%) of **9** was obtained as a brown red solid, m.p. 107–108 °C. *Anal. Calc.* for $\text{C}_9\text{Co}_2\text{FeO}_9\text{S}_2$: C, 22.06. Found: C, 22.42%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2066vs, 2043vs, 2020vs, 1998vs cm^{-1} .

3.5. Preparation of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5)[\text{FeCrCo}(\mu_3\text{-S})(\text{CO})_8]_2$ (**13**)

The same equipped flask as above was charged with 0.440 g (2.0 mmol) of $\text{Cr}(\text{CO})_6$, 1.0 mmol of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5)\text{Na}_2$ and 20 ml of diglyme. The reaction mixture was stirred at reflux for 6 h.

Table 5
Crystal data and structural refinements details for **4**, **6** and **9**

	4	6	9
Empirical formula	C ₁₃ H ₅ CoCrFeO ₈ S	C ₁₆ H ₈ CoCrFeO ₁₀ S	C ₉ Co ₂ FeO ₉ S ₂
Formula weight	488.01	559.06	489.92
Crystal size (mm)	0.24 × 0.22 × 0.18	0.24 × 0.20 × 0.14	0.36 × 0.30 × 0.08
Crystal system	triclinic	tetragonal	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 4(3)2(1)2	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.554(3)	9.9056(16)	6.834(3)
<i>b</i> (Å)	19.072(6)	9.9056(16)	9.161(4)
<i>c</i> (Å)	20.818(6)	41.688(13)	13.197(5)
α (°)	63.938 (5)	90	93.844(7)
β (°)	88.914(5)	90	94.262(6)
γ (°)	88.701(6)	90	110.938(6)
<i>V</i> (Å ³)	3406.4(16)	4090.5(16)	765.6(5)
<i>Z</i>	8	8	2
<i>D</i> _{calc} (g cm ⁻³)	1.903	1.816	2.125
<i>F</i> (000)	1920	2216	476
μ (Mo K α) (mm ⁻¹)	2.589	2.176	3.388
Temperature (K)	293(2)	293(2)	293(2)
Scan type	ω -2 θ	ω -2 θ	ω -2 θ
2 θ _{max} (°)	50.00	52.80	52.92
Reflections collected	17 656	19 444	4470
Independent reflections	11 879	4199	3134
<i>R</i> _{int}	0.0366	0.0733	0.0292
Data/restraints/parameters	11 879/0/901	4199/0/273	3134/0/208
<i>R</i>	0.0585	0.0574	0.0453
<i>R</i> _w	0.1253	0.1053	0.0946
Goodness-of-fit	0.994	1.135	1.008
Largest difference peak and hole (eÅ ⁻³)	2.165, -0.800	0.433, -0.485	0.570, -0.464

After removal of diglyme under vacuum, 0.916 g (2.00 mmol) of FeCo₂(μ_3 -S)(CO)₉ and 30 ml of THF were added, the mixture was stirred at room temperature for 3 h. The resulting mixture was condensed to a suitable volume under reduced pressure, which was subjected to TLC separation using acetone/light petroleum ether (*v/v* = 1/4) as eluent. From the major brown green band was obtained 0.376 g (36%) of **13** as a brown black solid, m.p. 61–62 °C. *Anal.* Calc. for C₃₀H₁₆Co₂Cr₂Fe₂O₁₇S₂: C, 34.44; H, 1.54. Found: C, 34.59; H, 1.59%. IR (KBr disk): $\nu_{C=O}$ 2075s, 2032vs, 1974s, 1868m; ν_{C-O-C} 1104s cm⁻¹. ¹H NMR (CDCl₃): δ 2.63 (s, 4H, 2CH₂Cp), 3.59 (s, 4H, 2CH₂O), 4.97 (s, 8H, 2C₅H₄) ppm.

3.6. Preparation of [η^5 -C₅H₄CH₂(CH₂OCH₂)₂CH₂C₅H₄- η^5][FeCrCo(μ_3 -S)(CO)₈]₂ (**14**)

The same procedure as that for **13** was followed, but 1.0 mmol of [η^5 -C₅H₄CH₂(CH₂OCH₂)₂CH₂C₅H₄- η^5]₂Na₂ was used in place of (η^5 -C₅H₄CH₂CH₂OCH₂CH₂C₅H₄- η^5)₂Na₂. The main brown green band afforded 0.371 g (34%) of **14** as a brown black solid, m.p. 66–67 °C. *Anal.* Calc. for C₃₂H₂₀Co₂Cr₂Fe₂O₁₈S₂: C, 35.26; H, 1.85. Found: C, 35.20; H, 1.94%. IR (KBr disk): $\nu_{C=O}$ 2075s, 2032vs, 1974s, 1933 m, 1858m; ν_{C-O-C} 1106s cm⁻¹. ¹H NMR (CDCl₃): δ 2.63 (t, *J* = 5.7 Hz, 4H, 2CH₂Cp), 3.58 (s, 8H, 4CH₂O), 4.88, 4.95, 5.02 (s, s, s, 8H, 2C₅H₄) ppm.

3.7. Preparation of [η^5 -C₅H₄CH₂(CH₂OCH₂)₃CH₂C₅H₄- η^5][FeCrCo(μ_3 -S)(CO)₈]₂ (**15**)

The same procedure as that for **13** was followed, but 1.0 mmol of [η^5 -C₅H₄CH₂(CH₂OCH₂)₃CH₂C₅H₄- η^5]₂Na₂ was used in stead of (η^5 -C₅H₄CH₂CH₂OCH₂CH₂C₅H₄- η^5)₂Na₂. The main brown green band afforded 0.363 g (32%) of **15** as a brown black solid, m.p. 69–70 °C. *Anal.* Calc. for C₃₄H₂₄Co₂Cr₂Fe₂O₁₉S₂: C, 36.00; H, 2.13. Found: C, 36.16; H, 2.27%. IR (KBr disk): $\nu_{C=O}$ 2076s, 2032vs, 1975s, 1940m, 1867m; ν_{C-O-C} 1112s cm⁻¹. ¹H NMR (CDCl₃): δ 2.63 (t, *J* = 5.7 Hz, 4H, 2CH₂Cp), 3.59 (s, 12H, 6CH₂O), 4.89, 4.95, 5.02 (s, s, s, 8H, 2C₅H₄) ppm.

3.8. Preparation of [η^5 -C₅H₄C(O)CH₂]₂[FeCrCo(μ_3 -S)(CO)₈]₂ (**17**) and FeCo₂(μ_3 -S)₂(CO)₉ (**9**)

The same procedure as that for **13** was followed, but 0.220 g (1.00 mmol) of Cr(CO)₆, 0.50 mmol of [η^5 -C₅H₄C(O)CH₂]₂Na₂, and 0.458 g (1.00 mmol) of FeCo₂(μ_3 -S)(CO)₉ were used. A brown black solid afforded 0.042 g (8%) of **17** as a brown black solid, m.p. 75–76 °C. *Anal.* Calc. for C₃₀H₁₂Co₂Cr₂Fe₂O₁₈S₂: C, 34.05; H, 1.14. Found: C, 34.21; H, 1.19%. IR (KBr disk): $\nu_{C=O}$ 2105s, 2056vs, 2004vs, 1962vs, 1894s, 1868s; $\nu_{C=O}$ 1682s cm⁻¹. ¹H NMR (CDCl₃): δ 2.32 (t, *J* = 6.0 Hz, 4H, 2CH₂), 5.08, 5.15, 5.22 (s, s, s, 8H, 2C₅H₄) ppm.

Further separation with 1:1 (v/v) of acetone/light petroleum ether as eluent gave a main brown red band, from which 0.203 g (42%) of **9** was obtained.

3.9. X-ray structure determinations of **4**, **6** and **9**

Single-crystals of **4** and **6** suitable for X-ray diffraction analyses were grown by slow evaporation of their n-hexane solutions at about 4 °C, whereas the suitable crystal of **9** was grown from PhBr/*n*-pentane at room temperature. Each crystal was mounted on a Bruker Smart 1000 diffractometer with a graphite monochromator with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Details of the crystal data, data collections and structure refinements are summarized in Table 5. The structures were solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. The calculations for **4**, **6** and **9** were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 218488, 218489 and 218490. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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