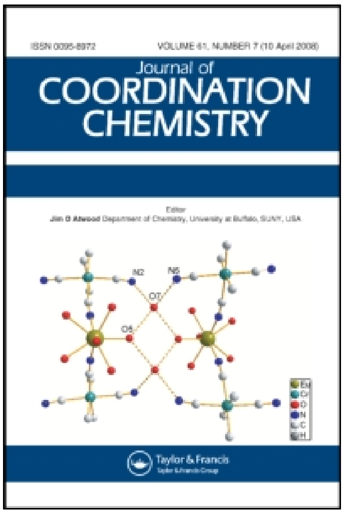

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SYNTHESIS, CHARACTERIZATION AND REACTIONS OF THE TETRAHEDRAL MCoFeS CLUSTERS CONTAINING A FORMYLCYCLOPENTADIENYL LIGAND η^5-CHOC$_5$H$_4$MCoFeS(CO)$_8$ (M = Mo, W). THE SINGLE CRYSTAL STRUCTURE OF η^5-CHOC$_5$H$_4$WCoFeS(CO)$_8$

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The tetrahedral formyl-substituted cyclopentadienyl clusters η^5-CHOC$_5$H$_4$MCoFeS(CO)$_8$ (**1a**, M = Mo, **1b**, M = W) were successfully prepared by isolobal displacement reactions of monoanions η^5-CHOC$_5$H$_4$(CO)$_3$M$^-$ with a tetrahedral cluster Co$_2$FeS(CO)$_9$. The formyl substituents of **1a** and **1b** could undergo interesting transformation reactions to give a series of cluster derivatives containing various functionally substituted cyclopentadienyl ligands. Clusters **1a** and **1b** reacted with NaBH$_4$ or with MeMgI followed by hydrolysis to give, respectively, primary alcohol clusters η^5-HOCH$_2$C$_5$H$_4$MCoFeS(CO)$_8$ (**2a**, M = Mo, **2b**, M = W) and secondary alcohol clusters η^5-HOCHMeC$_5$H$_4$MCoFeS(CO)$_8$ (**3a**, M = Mo, **3b**, M = W), whereas those with semicarbazide or with 2,4-dinitrophenylhydrazine afforded semicarbazone clusters η^5-NH$_2$C(O)NHNCHC$_5$H$_4$MCoFeS(CO)$_8$ (**4a**, M = Mo, **4b**, M = W) and phenylhydrazone clusters η^5-2,4-(NO$_2$)$_2$C$_6$H$_3$NHNCHC$_5$H$_4$MCoFeS(CO)$_8$ (**5a**, M = Mo, **5b**, M = W), respectively. Further treatment of **2a** and **2b** with Et$_3$OBF$_4$ produced single clusters η^5-C$_2$H$_5$OCH$_2$C$_5$H$_4$MCoFeS(CO)$_8$ (**6a**, M = Mo, **6b**, M = W) and double clusters [MCoFeS(CO)$_8$]$_2$[η^5-C$_5$H$_4$CH$_2$OCH$_2$C$_5$H$_4$-η^5] (**7a**, M = Mo, **7b**, M = W). All the new clusters have been characterized by elemental analysis and spectroscopic methods, as well as, for **1b**, by X-ray diffraction analysis.

Keywords: Formylcyclopentadienyl; MCoFeS (M = Mo, W); isolobal displacement; functional transformation; X-ray structure

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INTRODUCTION

Recently there has been growing interest in the subject of transition metal cluster complexes containing functionally substituted cyclopentadienyl ligands.[1–7] This is mainly owing to the fact they could be potentially used as homogeneous catalysts or as models for organic species adsorbed on the solid surface of heterogeneous catalysts and thus to facilitate understanding of heterogeneous catalytic processes.[8–11] Through functional transformation of organic functionality on the cyclopentadienyl rings numerous novel transition metal cluster derivatives may be obtained, and which would be difficult to prepare by other methods.[2–5] We now report the synthesis of two tetrahedral clusters containing a formylcyclopentadienyl ligand η^5-$CHOC_5H_4MCoFeS(CO)_8$ ($M = Mo, W$) and the functional transformation of their formyl substituents, as well as the single crystal molecular structure of η^5-$CHOC_5H_4WCoFeS(CO)_8$.

EXPERIMENTAL

All reactions were carried out under a dry nitrogen atmosphere. Diglyme, THF and diethylether were distilled from sodium benzophenone ketyl. Dichloromethane, petroleum ether, methanol, ethanol and distilled water were bubbled with nitrogen for 10 min prior to use. $Mo(CO)_6$ and $W(CO)_6$ were purchased from Strem Chemicals Inc. $CHOC_5H_4Na$,[12] $Co_2Fe(CO)_9(\mu_3\text{-}S)$,[13] Et_3OBF_4[14] and MeMgI[15] were prepared according to literature methods. $NaBH_4$, semicarbazide and 2,4-dinitrophenylhydrazine were C.P. grade reagents. Chromatographic separation was carried out on a silica gel (300–400 mesh) column under nitrogen. IR and ^1H NMR spectra were recorded on a Nicolet FT-IR 5DX spectrophotometer and a Jeol FX 90 Q spectrometer. C/H analysis, MS and melting points were obtained by using a 240 C model analyzer, an HP 5988 A spectrometer and a Yanako MP-500 instrument, respectively.

Preparation of 1a

A solution of 0.290 g (1.1 mmol) of $Mo(CO)_6$ and 0.162 g (1.4 mmol) of $CHOC_5H_4Na$ in 30 cm^3 of THF was stirred at reflux for 16 h. Upon cooling to room temperature, 0.458 g (1.0 mmol) of $Co_2Fe(CO)_9(\mu_3\text{-}S)$ was added and the reaction mixture was stirred for 30 min at 45–50°C. Solvent was removed at reduced pressure and the residue extracted with 4 : 1 (v/v) CH_2Cl_2/petroleum ether. The extracts were subjected to column chromatography.

A brown-red main band was eluted with 4 : 1 CH_2Cl_2/petroleum ether followed by evaporation of the solvents to give 0.349 g (62%) of **1a**, as a brown-black solid. M.p. 95–96°C; anal., calcd. for $C_{14}H_5CoFeMoO_9S$: C, 30.03; H, 0.90%; found: C, 30.45; H, 0.75%; IR (KBr disc): $\nu_{C\equiv O}$, 2082(s), 2032(vs), 1975(s), 1950(s), 1918(s), 1877(s) cm^{-1}; $\nu_{C=O}$, 1688(s) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 5.52–5.68, 5.72–5.84 (m, m, 2H, H^3, H^4), 5.96–6.12 (m, 2H, H^2, H^5), 9.80 (s, 1H, CHO) ppm; MS(EI), m/z (Mo^{98}, relative intensity): 450 (M^+-4CO, 0.25%), 247 ($SFeCoMo^+$, 0.27).

Preparation of 1b

A solution of 0.422 g (1.2 mmol) of $W(CO)_6$ and 0.162 g (1.4 mmol) of $CHOC_5H_4Na$ in 30 cm^3 of diglyme was stirred at reflux for 5 h. After diglyme had been removed, 30 cm^3 of THF and 0.458 g (1.0 mmol) of $Co_2Fe(CO)_9(\mu_3\text{-}S)$ were added and the reaction mixture was stirred for 15 min at 45–50°C. After the same workup as that for **1a**, 0.432 g (67%) of **1b** was obtained as a brown-red solid. M.p. 105–106°C; anal., calcd. for $C_{14}H_5CoFeO_9SW$: C, 25.95; H, 0.78%; found: C, 25.95; H, 0.69%; IR (KBr disc): $\nu_{C\equiv O}$, 2082(s), 2024(vs), 1975(s), 1942(s), 1901(s), 1877(s) cm^{-1}; $\nu_{C=O}$, 1688(s) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 5.56–5.70, 5.74–5.84 (m, m, 2H, H^3, H^4), 5.90–6.08 (m, 2H, H^2, H^5), 9.74 (s, 1H, CHO) ppm; MS(EI), m/z (W^{184}, relative intensity): 648 (M^+, 0.11%), 592 (M^+-2CO, 0.22), 331 ($SFeCoW^+$, 0.09).

Preparation of 2a

To a solution of 0.14 g (0.25 mmol) of **1a** dissolved in 10 cm^3 of MeOH was added 0.009 g (0.25 mmol) of $NaBH_4$ and the mixture was stirred for 40 min at room temperature. Solvent was removed at reduced pressure and the residue was extracted with CH_2Cl_2. The extracts were subjected to column chromatography. A brown-red main band was eluted with CH_2Cl_2 followed by evaporation of the solvent to give 0.039 g (28%) of **2a**, as a brown-red viscous oil; anal., calcd. for $C_{14}H_7CoFeMoO_9S$: C, 29.92; H, 1.25%; found: C, 29.77; H, 1.99%; IR (KBr disc): ν_{OH}, 3411(m) cm^{-1}; $\nu_{C\equiv O}$, 2073(s), 2024(vs), 1930(vs), 1893(s) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.84–2.16 (m, 1H, OH), 4.40–4.70 (m, 2H, CH_2), 5.20–5.68 (m, 4H, C_5H_4) ppm.

Preparation of 2b

The same procedure as that for **2a** was followed, but 0.162 g (0.25 mmol) of **1b** was used instead of **1a** to give 0.064 g (40%) of **2b**, as a brown-red viscous oil; anal., calcd. for $C_{14}H_7CoFeO_9SW$: C, 25.87; H, 1.09%; found: C, 26.24; H, 1.23%; IR (KBr disc): ν_{OH}, 3443(m) cm^{-1}; $\nu_{C\equiv O}$, 2073(s), 2024(vs), 1975(vs), 1885(m) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.88–2.24 (m, 1H, OH), 4.48–4.92 (m, 2H, CH_2), 5.28–5.78 (m, 4H, C_5H_4) ppm.

Preparation of 3a

To a stirred solution of 0.14 g (0.25 mmol) of **1a** in 10 cm^3 of diethylether was added 0.2 cm^3 (3.65 M, 0.73 mmol) of MeMgI/Et_2O solution at room temperature. After stirring for about 5 min, 10 cm^3 of distilled water and 1 cm^3 (1.5 M) of dilute HCl were added. The ether phase was separated and the aqueous phase was extracted with 10 cm^3 of diethylether. The extracts were combined with the ether phase. Ether was removed under reduced pressure and the residue was extracted with 5 : 1 CH_2Cl_2/petroleum ether. The extracts were subjected to column chromatography. A brown-red main band was eluted with 5 : 1 CH_2Cl_2/petroleum ether, followed by evaporation of the solvent, to give 0.033 g (23%) of **3a**, as a brown-red viscous oil; anal., calcd. for $C_{15}H_9CoFeMoO_9S$: C, 31.28; H, 1.57%; found: C, 31.26; H, 1.56%; IR (KBr disc): ν_{OH}, 3427(m) cm^{-1}; $\nu_{C\equiv O}$, 2073(s), 2024(vs), 1975(vs), 1885(m) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.53 (d, 3H, J = 5.4 Hz, CH_3), 2.00–2.28 (m, 1H, OH), 4.60–4.92 (m, 1H, CH), 5.20–5.72 (m, 4H, C_5H_4) ppm.

Preparation of 3b

The same procedure as that for **3a** was followed, but 0.162 g (0.25 mmol) of **1b** was used instead of **1a**; 0.033 g (20%) of **3b** was obtained as a brown-red viscous oil, which was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.[2]

Preparation of 4a

To a solution consisting of 6 cm^3 of ethanol and 1 cm^3 of water were added 0.2 g (0.27 mmol) of semicarbazide, 0.034 g (0.41 mmol) of NaOAc and 0.14 g (0.25 mmol) of **1a**. Then, to the reaction mixture was added about 0.1 cm^3 of 37% concentrated HCl to make its pH = 6. After the reaction mixture had been stirred for an additional 30 min at room temperature, solvent was removed at reduced pressure and the residue was extracted with CH_2Cl_2. The extracts were subjected to column chromatography. A yellow-brown main band was eluted with CH_2Cl_2, followed by evaporation of the solvent, to give 0.092 g (60%) of **4a**, as a yellow-brown solid. No m.p. observed; anal., calcd. for $C_{15}H_8CoFeMoN_3O_9S$: C, 29.20; H, 1.31; N, 6.81%; found: C, 28.70; H, 1.25; N, 6.36%; IR (KBr disc): ν_{NH}, 3468(m) cm^{-1}; $\nu_{C\equiv O}$, 2073(s), 2024(vs), 1975(vs), 1885(m) cm^{-1}; $\nu_{C=O}$, 1696(s); $\nu_{C=N}$, 1581(m); ^1H NMR (DMSO-d_6, δ): 4.84–4.98, 5.24–5.40 (m, m, 2H, H^3, H^4), 5.64–5.84 (m, 2H, H^2, H^5), 6.04–6.64 (m, 1H, NH), 7.80 (s, 1H, CH=N), 8.33 (s, 2H, NH_2) ppm.

Preparation of 4b

The same procedure as that for **4a** was followed, but 0.162 g (0.25 mmol) of **1b** was used instead of **1a**; 0.093 g (53%) of **4b** was obtained as a yellow-brown solid. No m.p. observed; anal., calcd. for $C_{15}H_9CoFeN_3O_9SW$: C, 25.56; H, 1.14; N, 5.96%; found: C, 25.36; H, 1.12; N, 5.46%; IR (KBr disc): ν_{NH}, 3476(m) cm^{-1}; $\nu_{C\equiv O}$, 2073(s), 2024(vs), 1983(vs), 1885(m) cm^{-1}; $\nu_{C=O}$, 1696(s) cm^{-1}; $\nu_{C=N}$, 1573(m) cm^{-1}; ^1H NMR (DMSO-d_6, δ): 5.83 (s, 1H, NH), 5.88–5.98, 6.00–6.14 (m, m, 2H, H^3, H^4), 6.44–6.66 (m, 2H, H^2, H^5), 7.80 (s, 1H, CH=N), 8.14, 8.41 (s, s, 2H, NH_2) ppm.

Preparation of 5a

To a solution consisting of 5 cm^3 of ethanol and 0.07 g (0.125 mmol) of **1a** was added 1 cm^3 of 2,4-dinitrophenylhydrazine solution, prepared by dissolving 1.0 g (5 mmol) of 2,4-dinitrophenylhydrazine in 7.5 cm^3 of 98% concentrated H_2SO_4 followed by diluting to 250 cm^3 with 75 cm^3 of 95% ethanol and sufficient water. The reaction mixture was stirred for 30 min at room temperature to give a brown precipitate. The precipitate was filtered off and washed with ethanol until the filtrate was colourless. The washed precipitate was extracted with CH_2Cl_2. The extracts were subjected to column chromatography. A yellow-brown main band was eluted with CH_2Cl_2, followed by evaporation of the solvent to give 0.066 g (71%) of **5a**, as a yellow-brown solid. No m.p. observed; anal., calcd. for $C_{20}H_9CoFeMoN_4O_{12}S$: C, 32.46; H, 1.22; N, 7.57%; found: C, 32.50; H, 1.19; N, 7.37%; IR (KBr disc): ν_{NH}, 3288(m) cm^{-1}; $\nu_{C\equiv O}$, 2073(s), 2032(vs), 1991(vs), 1967(s), 1877(m) cm^{-1}; $\nu_{C=N}$, 1614(s) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 5.40–5.54, 5.56–5.68 (m, m, 2H, H^3, H^4), 5.80–5.96 (m, 2H, H^2, H^5), 7.84 (s, 1H, CH=N), 7.88–8.00 (m, 1H, H^6 of benzene ring), 8.24–8.48 (m, 1H, H^5 of benzene ring), 9.12 (s, 1H, H^3 of benzene ring), 11.30 (s, 1H, NH) ppm.

Preparation of 5b

The same procedure as that for **5a** was followed, but 0.081 g (0.125 mmol) of **1b** was used instead of **1a**; 0.079 g (77%) of **5b** was obtained as a yellow-brown solid. No m.p. observed; anal., calcd. for $C_{20}H_9CoFeN_4O_{12}SW$: C, 29.01; H, 1.09; N, 6.77%; found: C, 28.96; H, 0.80; N, 6.68%; IR (KBr disc): ν_{NH}, 3288 (m) cm^{-1}; $\nu_{C\equiv O}$, 2073(s), 2032(vs), 1991(vs), 1877(s) cm^{-1}; $\nu_{C=N}$, 1614(s) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 5.52–5.66, 5.68–5.80 (m, m, 2H, H^3, H^4), 5.88–6.04 (m, 2H, H^2, H^5), 7.91 (s, 1H, CH=N), 7.93–8.04 (m, 1H, H^6 of benzene ring), 8.30–8.56 (m, 1H, H^5 of benzene ring), 9.20 (s, 1H, H^3 of benzene ring), 11.40 (s, 1H, NH) ppm.

Preparation of 6a and 7a

A solution consisting of 0.333 g (0.59 mmol) of **2a**, 0.337 g (1.77 mmol) of Et_3OBF_4 and 20 cm^3 of CH_2Cl_2 distilled from P_2O_5 was stirred for 10 h at room temperature. Solvents were removed at reduced pressure and the residue was extracted with 2 : 3 CH_2Cl_2/petroleum ether. The extracts were subjected to column chromatography using 2 : 3 CH_2Cl_2/petroleum ether as eluant. Nine brown-red bands were developed. The fourth main band was collected to give 0.044 g (13%) of **6a** as a brown-red viscous oil; anal., calcd. for $C_{16}H_{11}CoFeMoO_9S$: C, 32.57; H, 1.88%; found: C, 32.94; H, 2.05%; IR (KBr disc): $\nu_{C\equiv O}$, 2073(s); 2016(vs), 1975(vs), 1893(s) cm^{-1}; ν_{C-O}, 1122(s) cm^{-1}, ^1H NMR ($CDCl_3$, δ): 1.28 (t, 3H, CH_3), 3.67 (q, 2H, CH_2Me), 4.55 (s, 2H, $CH_2C_5H_4$), 5.31–5.82 (m, 4H, C_5H_4) ppm. The third main band was collected to give 0.242 g (74%) of **7a**, as a brown-red viscous oil; anal., calcd. for $C_{28}H_{12}Co_2Fe_2Mo_2O_{17}S_2$: C, 30.41; H, 1.10%; found: C, 30.80; H, 1.40%; IR (KBr disc): $\nu_{C\equiv O}$, 2073(s), 2016(vs), 1983(vs), 1885(s) cm^{-1}; ν_{C-O}, 1114(m) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 4.44 (s, 4H, $2CH_2$), 5.25–5.57 (m, 8H, $2C_5H_4$) ppm.

Preparation of 6b and 7b

The same procedure as that for **6a** and **7a** was followed, but 1.130 g (1.74 mmol) of **2b**, 1.656 g (8.7 mmol) of Et_3OBF_4 and 40 cm^3 of CH_2Cl_2 were used instead of the corresponding reactants for preparing **6a** and **7a**. The third main band was collected to give 0.433 g (39%) of **6b**, as a brown viscous oil; anal., calcd. for $C_{16}H_{11}CoFeO_9SW$: C, 28.35; H, 1.63%; found: C, 27.99; H, 1.61%; IR (KBr disc): $\nu_{C\equiv O}$, 2073(s), 2024(vs), 1980(vs), 1893(s) cm^{-1}; ν_{C-O}, 1114(s) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.26 (t, 3H, CH_3), 3.66 (q, 2H, CH_2Me), 4.43 (s, 2H, $CH_2C_5H_4$), 5.33–5.83 (m, 4H, C_5H_4) ppm. The fourth main band was collected to give 0.592 g (50%) of **7b**, as a brown-red viscous oil; anal., calcd. for $C_{28}H_{12}Co_2Fe_2O_{17}S_2W_2$: C, 26.24; H, 0.94%; found: C, 26.55; H, 0.96%; IR (KBr disc): $\nu_{C\equiv O}$, 2073(vs), 2024(vs), 1975(vs), 1893(s) cm^{-1}; ν_{C-O}, 1106(s) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 4.57 (s, 4H, $2CH_2$), 5.27–5.87 (m, 8H, $2C_5H_4$) ppm.

Single-crystal Structural Determination of 1b

Single-crystals of **1b** suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2/petroleum ether solution. A single crystal measuring 0.2 × 0.3 × 0.3 mm was mounted on a glass fibre and placed on a Rigaku AFC7R diffractometer with graphite-monochromated Mo*Kα* radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. A total of 4595 independent reflections was collected at 20°C by the ω–θ scan mode, of which 3805 independent reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in subsequent refinement. The data were corrected for Lp factors. Crystal data are listed in Table I.

The structure was solved by direct methods and Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Final refinement by full-matrix least-squares methods converged to give agreement factors of 0.042 (R) and 0.051 (R_w).

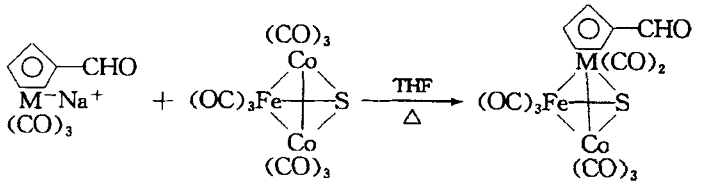
TABLE I Crystal data and details of structure refinement for **1b**

Formula	$C_{28}H_{10}Co_2Fe_2O_{18}S_2W_2$
Formula Weight	1295.76
Crystal Colour, habit	black, prismatic
Crystal System	triclinic
Space Group	$P\bar{1}$(#2)
a (Å)	12.858(4)
b (Å)	15.826(3)
c (Å)	9.097(3)
α (°)	98.95(2)
β (°)	104.09(2)
γ (°)	94.46(2)
Z	2
Dc (g·cm^{-3})	2.444
$F(000)$	1216.00
μ (cm^{-1})	84.34
Data collected	4843
Unique data	4595
Data with $I \geq 3\sigma(I)$	3805
R	0.042
R_w	0.051
(ρ)max (e Å^{-3})	2.36

The highest peak in the final difference Fourier map had a height of 2.36 e Å^{-3}. All calculations were performed on Micro-Vax II computer using the TEXSAN program system.

RESULTS AND DISCUSSION

We have found that sodium salts of formylcyclopentadienyl molybdenum (tungsten) tricarbonyl anions, η^5-$CHOC_5H_4(CO)_3MNa$ (M = Mo, W) generated from $M(CO)_6$ and η^5-$CHOC_5H_4Na$[12] react *in situ* with cluster complex $Co_2Fe(CO)_9(\mu_3\text{-}S)$ in THF at 40–45°C to afford the expected cluster complexes **1a** and **1b**, as shown in (1).



(1)

1a M=Mo 62%
1b M=W 67%

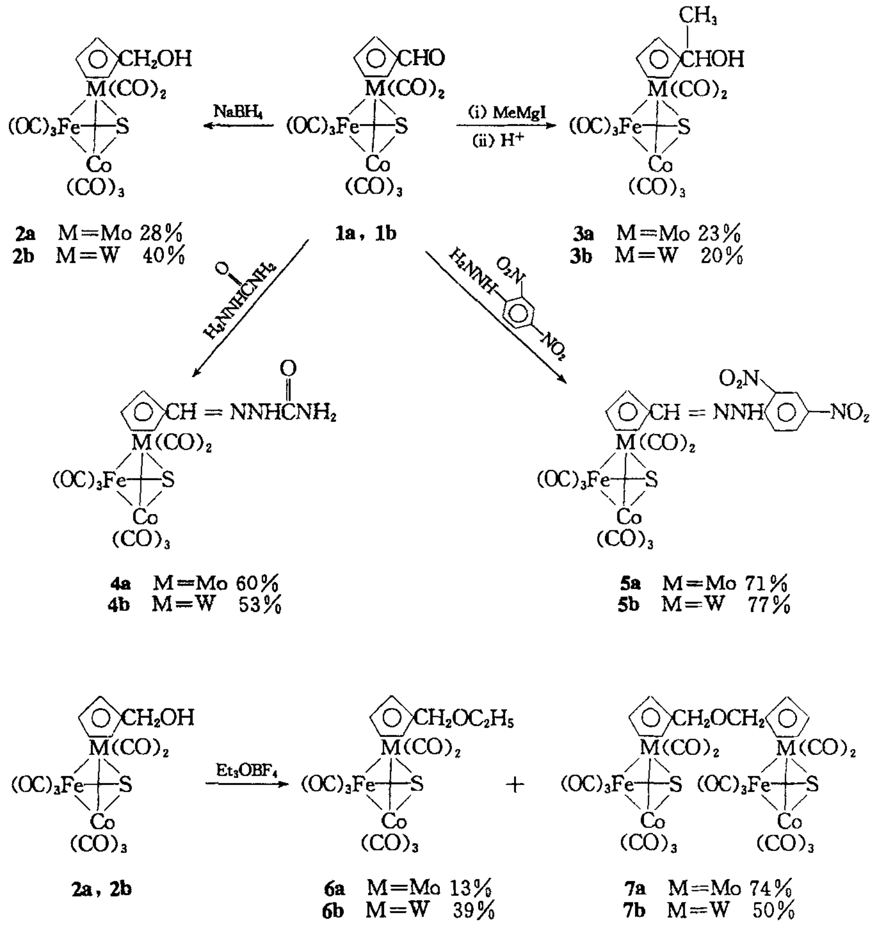
Clusters **1a** and **1b** may be regarded as the products of an isolobal displacement reaction[16–17] of $Co(CO)_3(d^9ML_3)$ in the starting cluster Co_2 $Fe(CO)_9(\mu_3\text{-}S)$ by η^5-$CHOC_5H_4(CO)_2M$ (d^5ML_5) produced *in situ* from the sodium salts η^5-$CHOC_5H_4(CO)_3MNa$. It is worth noting that since **1a** and **1b** contain a sensitive functional group, CHO, the reaction should be carried out at lower temperatures. If the reaction was carried out in refluxing THF for about 0.5 h, most of **1a** and **1b** would be destroyed. Clusters **1a** and **1b** are the first tetrahedral MCoFeS clusters containing the formylcyclopentadienyl ligand, and are somewhat air-sensitive and deep-coloured solids. In their IR spectra there are six absorption bands at about 2082–1877 cm^{-1} and one absorption band at 1688 cm^{-1}, characteristic of CO ligands attached to transition metals and of the aldehyde CO in the formyl substituent, respectively. Their ^{1}H NMR spectra exhibit three multiplets between 5.52–6.12 ppm, of which the upfield two multiplets are assigned to H^3 and H^4 protons and the downfield one to H^2 and H^5 protons of the substituted cyclopentadienyl ring (since the formyl substituent is an electron-withdrawing group). In addition, the ^{1}H NMR spectra of **1a** and **1b** have one singlet at 9.74 ppm attributed to one proton of the CHO group.

The MS spectrum of **1b** shows a molecular ion M^+ at m/z 648, whereas that of **1a** exhibits the largest fragment (M^+-4CO) at m/z 448.

In the course of studying the properties of **1a** and **1b** we found that the tetrahedral cluster core MCoFeS showed a stability difference towards various reagents. For example, treatment of clusters **1a** and **1b** with a 50% aqueous NaOH or with $NH_2OH{\cdot}HCl$ in dilute aqueous NaOH at room temperature failed to produce the products of a Cannizzaro reaction and corresponding oxime derivatives, respectively. Instead, the reactions led to decomposition of the starting clusters, due to the instability of the tetrahedral cluster core MCoFeS towards such strong alkaline conditions. However, treatment of **1a** and **1b** in neutral media with $NaBH_4$ or with MeMgI followed by acidic hydrolysis yielded hydroxyl derivatives **2a**, **2b** and **3a**, **3b**, whereas those with semicarbazide or with 2,4-dinitrophenylhydrazine under weak to strong acidic conditions afforded corresponding semicarbazone derivatives **4a**, **4b** and phenylhydrazone derivatives **5a**, **5b**. In addition, under the action of Et_3OBF_4 the hydroxymethyl derivatives **2a** and **2b** could be converted to both ethylation and dehydration products **6a**, **6b** and **7a**, **7b**, respectively. The reactions mentioned above are summarized in Scheme 1.

It is worth pointing out that although reactions of **1a** and **1b** with semicarbazide occur at about pH = 6 by adding an approximate 0.1 cm^3 of concentrated HCl to give quite high yields of **4a** and **4b**, they do not take place at all without adding 0.1 cm^3 of concentrated HCl. The reactions are actually reversible, since resulting **4a** and **4b** could be completely converted to **1a** and **1b** when the pH was adjusted from 6 to 2–3.

Clusters **2a**–**7a** and **2b**–**7b** are deep-coloured viscous liquids or solids. While clusters **6a**, **7a** and **6b**, **7b** are quite air-stable, clusters **2a**–**5a** and **2b**–**5b** are more air-sensitive than their parent clusters **1a** and **1b**. With the exception of **3b**[2] all the cluster derivatives mentioned above are new and elemental analyses, IR and ^1H NMR data are in good agreement with their respective structures. For example, the IR spectra of **2a**, **2b** and **3a**, **3b** show hydroxyl group absorption bands at 3411–3443 cm^{-1}; those of **4a**, **4b** and **5a**, **5b** exhibit absorption bands characteristic of C=O at 1696 cm^{-1} and C=N at 1573–1614 cm^{-1}, respectively; those of **6a**, **6b** and **7a**, **7b** show C–O–C absorption bands at 1105–1121 cm^{-1}. ^1H NMR spectra of **4a**, **4b** and **5a**, **5b** display three multiplets between 4.84–6.66 ppm, of which the upfield two multiplets are attributed to H^3 and H^4 and the downfield multiplet is attributed to H^2 and H^5 of the substituted cyclopentadienyl ring, since the functional substituents are both electron-withdrawing. For the other derivatives the ^1H NMR spectra exhibit only one multiplet



SCHEME 1

between 5.22–5.87 ppm assigned to all protons on the cyclopentadienyl ring.

The single-crystal molecular structure of **1b** has been studied by X-ray diffraction methods. Atomic coordinates with equivalent isotropic thermal parameters are given in Table II. Figure 1 represents its two crystallographically independent molecules **1b** and **1b′** in the unit cell. Since the bond lengths and angles of **1b** and **1b′** are essentially the same, only those of **1b** are given in Table III and Table IV, respectively.

As seen in Fig. 1, **1b** consists of a distorted tetrahedral core, WCoFeS, which carries a η^5-$CHOC_5H_4$ ligand bound to the W(1) atom and eight

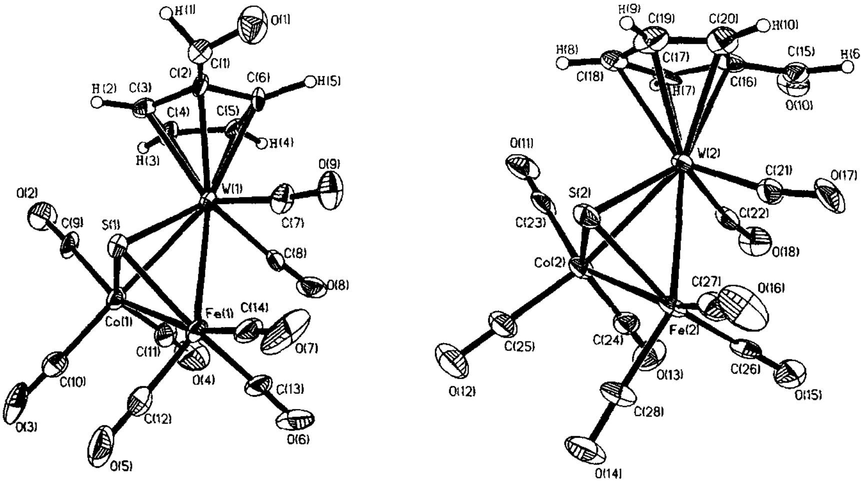
TABLE II Atomic coordinates and equivalent isotropic thermal parameters for **1b**[a]

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
W(1)	0.19832(4)	0.20288(3)	0.01439(5)	2.00(1)
W(2)	0.26782(4)	−0.18396(3)	−0.50466(5)	2.20(1)
Co(1)	0.3231(1)	0.3516(1)	0.0091(2)	2.65(4)
Co(2)	0.2660(1)	−0.2928(1)	−0.7755(2)	2.75(4)
Fe(1)	0.2235(2)	0.2586(1)	−0.2525(2)	2.76(4)
Fe(2)	0.1887(2)	−0.3577(1)	−0.5753(2)	2.73(4)
S(1)	0.1467(3)	0.3254(2)	−0.0862(4)	2.53(7)
S(2)	0.1223(3)	−0.2596(2)	−0.7001(4)	2.72(8)
O(1)	−0.0998(9)	0.1007(7)	0.002(1)	5.3(3)
O(2)	0.3552(10)	0.4308(7)	0.332(1)	5.8(3)
O(3)	0.377(1)	0.5122(8)	−0.095(1)	6.8(4)
O(4)	0.5293(10)	0.2802(9)	0.042(2)	7.1(4)
O(5)	0.234(1)	0.4010(8)	−0.421(1)	6.3(4)
O(6)	0.3995(10)	0.1723(8)	−0.341(1)	5.7(3)
O(7)	0.0550(10)	0.1616(10)	−0.512(1)	7.7(4)
O(8)	0.3854(9)	0.1020(7)	−0.056(1)	4.8(3)
O(9)	0.0503(9)	0.0635(7)	−0.246(1)	4.4(3)
O(10)	0.5409(9)	−0.0426(7)	−0.246(1)	4.8(3)
O(11)	0.3532(9)	−0.1466(7)	−0.890(1)	4.8(3)
O(12)	0.149(1)	−0.4052(8)	−1.067(1)	7.0(4)
O(13)	0.457(1)	−0.3821(8)	−0.711(1)	5.7(3)
O(14)	0.1033(10)	−0.5173(7)	−0.798(1)	5.6(3)
O(15)	0.3733(10)	−0.4245(7)	−0.386(1)	5.2(3)
O(16)	0.024(1)	−0.3870(9)	−0.409(1)	6.8(4)
O(17)	0.2286(9)	−0.2473(7)	−0.214(1)	5.0(3)
O(18)	0.4970(8)	−0.2455(7)	−0.411(1)	4.6(3)
C(1)	−0.043(1)	0.1669(10)	0.061(2)	3.2(4)
C(2)	0.072(1)	0.1749(8)	0.144(1)	2.5(3)
C(3)	0.137(1)	0.2528(9)	0.226(1)	2.9(3)
C(4)	0.241(1)	0.2310(9)	0.286(1)	2.9(3)
C(5)	0.243(1)	0.1418(9)	0.241(1)	2.9(3)
C(6)	0.1352(10)	0.1075(8)	0.150(1)	2.2(3)
C(7)	0.106(1)	0.1182(9)	−0.158(1)	3.0(3)
C(8)	0.319(1)	0.1397(9)	−0.035(1)	3.4(4)
C(9)	0.341(1)	0.4000(9)	0.211(2)	3.5(4)
C(10)	0.355(1)	0.450(1)	−0.061(2)	3.9(4)
C(11)	0.449(1)	0.306(1)	0.028(2)	4.1(4)
C(12)	0.233(1)	0.345(1)	−0.354(1)	3.9(4)
C(13)	0.333(1)	0.2038(10)	−0.303(1)	3.9(4)
C(14)	0.120(1)	0.1995(10)	−0.409(2)	3.7(4)
C(15)	0.451(1)	−0.0523(9)	−0.232(2)	3.6(4)
C(16)	0.354(1)	−0.0539(8)	−0.364(2)	3.0(3)
C(17)	0.359(1)	−0.0565(9)	−0.517(2)	4.0(4)
C(18)	0.250(1)	−0.0570(8)	−0.604(2)	3.8(4)
C(19)	0.180(1)	−0.0587(9)	−0.502(2)	4.2(4)
C(20)	0.243(1)	−0.0557(9)	−0.361(2)	3.9(4)
C(21)	0.242(1)	−0.2327(9)	−0.329(2)	3.7(4)
C(22)	0.411(1)	−0.2285(9)	−0.452(1)	3.0(3)
C(23)	0.316(1)	−0.2025(10)	−0.846(1)	3.5(4)
C(24)	0.383(1)	−0.3479(10)	−0.732(2)	3.7(4)
C(25)	0.196(1)	−0.3619(10)	−0.955(2)	4.0(4)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
C(26)	0.301(1)	−0.3993(9)	−0.459(2)	3.3(4)
C(27)	0.088(1)	−0.3745(10)	−0.471(2)	3.7(4)
C(28)	0.137(1)	−0.4556(10)	−0.715(2)	3.8(4)
H(1)	−0.0772	0.1949	0.1372	3.8159
H(2)	0.1130	0.3090	0.2489	3.6247
H(3)	0.3017	0.2709	0.3530	3.4362
H(4)	0.3061	0.1127	0.2651	3.7273
H(5)	0.1209	0.0391	0.1322	3.7273
H(6)	0.4199	−0.0610	−0.1198	3.7273
H(7)	0.4245	−0.0485	−0.5543	4.6921
H(8)	0.2272	−0.0563	−0.7124	3.7273
H(9)	0.1018	−0.0569	−0.5311	5.0328
H(10)	0.2169	−0.0518	−0.2680	4.8382

[a] $B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.



(a) (b)

FIGURE 1 Molecular structure of **1b**.

carbonyls, two being on the W(1) atom and three on the Fe(1) and Co(1) atoms. So far, few single and double clusters containing a tetrahedral WCoFeS core are reported in the literature. The bond lengths involving the tetrahedral core for the cluster **1b** are comparable with those of $CpWCoFeS(CO)_7L$[18] (L = MePrPhP) and $[WCoFeS(CO)_8]_2(L\text{-}L)[L\text{-}L = \eta^5\text{-}C_5H_4C(O)CH_2CH_2C(O)C_5H_4\text{-}\eta^5]$,[2] as shown in Table V.

TABLE III Selected bondlengths (Å) for **1b**

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
W(1)	Co(1)	2.757(2)	W(1)	Fe(1)	2.789(2)
W(1)	S(1)	2.345(3)	W(1)	C(2)	2.28(1)
W(1)	C(7)	1.97(1)	W(1)	C(8)	2.02(2)
Co(1)	Fe(1)	2.570(2)	Co(1)	S(1)	2.204(4)
Fe(1)	S(1)	2.185(4)	Fe(1)	C(12)	1.78(2)
O(1)	C(1)	1.20(2)	O(8)	C(8)	1.11(2)
O(9)	C(7)	1.14(2)	C(2)	C(3)	1.43(2)
C(1)	C(2)	1.47(2)	Co(1)	C(9)	1.83(1)

TABLE IV Selected bond angles (°) for **1b**

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
Co(1)	W(1)	Fe(1)	55.20(5)	Co(1)	W(1)	S(1)	50.39(9)
Co(1)	W(1)	C(2)	132.8(3)	Fe(1)	W(1)	C(7)	74.2(4)
Fe(1)	W(1)	C(8)	77.0(4)	S(1)	W(1)	C(2)	103.2(3)
W(1)	Co(1)	Fe(1)	63.02(6)	W(1)	Co(1)	S(1)	55.05(10)
W(1)	Co(1)	C(9)	96.4(4)	Fe(1)	Co(1)	S(1)	53.83(10)
Fe(1)	Co(1)	C(9)	155.5(4)	S(1)	Co(1)	C(9)	104.3(5)
W(1)	Fe(1)	Co(1)	61.77(6)	W(1)	Fe(1)	S(1)	54.63(9)
W(1)	Fe(1)	C(12)	148.7(4)	Co(1)	Fe(1)	S(1)	54.5(1)
W(1)	S(1)	Co(1)	74.6(1)	S(1)	Fe(1)	C(12)	96.2(5)
Co(1)	S(1)	Fe(1)	71.7(1)	W(1)	S(1)	Fe(1)	75.9(1)
O(1)	C(1)	C(2)	125(1)	C(1)	C(2)	C(6)	125(1)
W(1)	C(8)	O(8)	176(1)	W(1)	C(7)	O(9)	171(1)

TABLE V Comparison of bondlengths (Å) of the cluster core in **1b** with those of two known clusters

Clusters	*W–Fe*	*W–Co*	*Fe–Co*	*W–S*	*Fe–S*	*Co–S*
1b	2.789(2)	2.757(2)	2.570(2)	2.345(3)	2.185(4)	2.204(4)
CpWCoFeS(CO)$_7$L	2.792(2)	2.730(2)	2.574(2)	2.348(3)	2.187(3)	2.179(4)
[WCoFeS(CO)$_8$]$_2$(L-L)	2.799(2)	2.761(2)	2.558(3)	2.355(4)	2.194(4)	2.187(4)

From Table V it can be seen that all the corresponding bond lengths are almost the same, except that the W–Co and Co–S bonds of **1b** are slightly longer than those of cluster CpWCoFeS(CO)$_7$L.

The dihedral angle between the cyclopentadienyl ring and the triangular plane Fe(1)-Co(1)-S(1) for **1b** (47.56°) is slightly greater than that in the case of [WCoFeS(CO)$_8$]$_2$(L-L) (46.87°), whereas the W atom-Cp ring centroid distance for **1b** (1.989 Å) is virtually the same as that for [WCoFeS(CO)$_8$]$_2$(L-L) (1.998 Å). Since C(1) and O(1) lie in the plane of the cyclopentadienyl ring (the distances C(1) and O(1) to the plane are 0.008 and 0.109 Å, respectively), the formyl group would be quite well conjugated with the Cp ring π-system and thus the bond length C(1)-C(2) (1.47(2) Å) is shorter than a normal C–C single bond.

Supplemental material

Tables of fractional atomic coordinates, thermal parameters, interatomic distances, observed and calculated structure factors are available on request from the authors.

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