Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 57.[1] Reactions of Iron–Molybdenum Complexes with Oxygen and Sulphur; Crystal Structure of $[FeMo(\mu\text{-}\eta^2\text{-}SCC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)]$ *

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The compound $[FeMo(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4), in diethyl ether at room temperature, reacts with molecular oxygen to give the complex $[FeMo\{\mu\text{-}C(R)C(O)O\}(CO)_5(\eta\text{-}C_5H_5)]$ in which the bridging ligand has formed by coupling of an oxygen atom with CO and CR groups. Treatment of tetrahydrofuran (thf) solutions of $[FeMo(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ with elemental sulphur at room temperature affords a mixture of the complexes $[FeMo\{\mu\text{-}C(R)C(O)S\}(CO)_5(\eta\text{-}C_5H_5)]$ and $[FeMo(\mu\text{-}\eta^2\text{-}SCR)(CO)_5(\eta\text{-}C_5H_5)]$. The structure of the latter has been established by an *X*-ray diffraction study. The Fe–Mo bond [2.765(1) Å] is transversely bridged by the SCR group [μ-C–S 1.735(2), Fe–S 2.248(1), Mo–S 2.441(1), μ-C–Fe 1.942(2), and μ-C–Mo 2.153(2) Å]. The iron atom carries three terminally bonded CO groups, and the molybdenum atom is ligated by the $\eta\text{-}C_5H_5$ ring and two CO groups, one Mo–C–O bond being slightly bent [170.4(2)°]. The reaction between sulphur and the trimetal complex $[Fe_2Mo(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ in thf at room temperature gives a mixture of the two trimetal complexes $[Fe_2Mo(\mu_3\text{-}\eta^2\text{-}SCR)(CO)_8(\eta\text{-}C_5H_5)]$ and $[Fe_2Mo(\mu\text{-}CR)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$. The former is quantitatively converted into the latter with loss of CO on heating in toluene. Spectroscopic data for the new compounds are reported and discussed.

In the preceding paper[1] we described the synthesis of the iron–molybdenum complexes $[FeMo(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ (**1a**) and $[Fe_2Mo(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**2a**) (R = C_6H_4-Me-4), having earlier reported[2] the preparation of their tungsten analogues. In this paper we describe the reaction between (**1a**) and oxygen, and also reactions between (**1a**) and (**2a**) and elemental sulphur. It was anticipated that the reactivity of (**1a**) and (**2a**) would differ from that of the analogous iron–tungsten compounds (**1b**) and (**2b**). Indeed, studies on the iron–tungsten dimetal complex (**1b**) are limited by its instability. In contrast, (**1a**) is stable, can be prepared in good yield, and can apparently serve as a useful precursor to other compounds.[3]

Results and Discussion

Treatment of a diethyl ether solution of (**1a**) at room temperature with a stream of oxygen affords the yellow-orange complex $[FeMo\{\mu\text{-}C(C_6H_4Me\text{-}4)\ C(O)O\}(CO)_5(\eta\text{-}C_5H_5)]$ (**3a**) in high yield. A similar complex (**3b**) has been prepared by treating $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)]$ (**4**) with oxygen, and its structure has been established by an *X*-ray diffraction study.[4] Data for (**3a**) are given in Tables 1 and 2. The i.r. spectrum shows a band for the ketonic carbonyl group at 1 698 cm^{-1}. The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra are in accord with the structure shown. Resonances for the two CO groups bonded to the molybdenum occur at δ 232.0 and 228.2 p.p.m., and the CO groups ligating the iron atom give a signal at 208.9 p.p.m. The appearance of one signal for the $Fe(CO)_3$ fragment indicates rapid site exchange of CO groups attached to the iron on the n.m.r. time-scale, a common property for this group. Peaks in the spectrum at δ 162.4 and 92.6 p.p.m. may be assigned to the C=O and μ-CC_6H_4Me-4 groups in (**3a**), respectively. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of the iron–tungsten compound (**3b**) the corresponding resonances occur at 163.4 and 82.0 p.p.m.[4]

Formation of (**3a**) is of some interest since it involves C–C and C–O bond formation at a dimetal centre between alkylidyne and carbonyl groups and an oxygen atom, a process only observed previously in the synthesis of (**3b**).[4] The preparation of the oxo-bridged species (**3a**) occurs stoicheiometrically and proceeds in high yield. In contrast, formation of (**3b**) from (**4**) and oxygen occurs in *ca.* 20% yield and is non-stoicheiometric. However, since (**4**) readily captures CO to give the saturated dimetal complex $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5Me_5)]$, structurally akin to (**1a**), it is possible that the hexacarbonyl irontungsten compound plays a role in the formation of (**3b**).

Compound (**1a**) reacts with elemental sulphur in tetrahydrofuran (thf) at room temperature to give a mixture of two complexes, $[FeMo\{\mu\text{-}C(R)C(O)S\}(CO)_5(\eta\text{-}C_5H_5)]$ (**3c**) and $[FeMo(\mu\text{-}\eta^2\text{-}SCR)(CO)_5(\eta\text{-}C_5H_5)]$ (**5a**) (R = C_6H_4Me-4), separated by column chromatography. Compound (**3c**) was characterised by the data given in Tables 1 and 2.. The i.r. spectrum showed a characteristic band for the ketonic carbonyl group at 1 665 cm^{-1}, and in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum the resonance for this moiety occurs at δ 175.0 p.p.m. The signal for the bridging μ-CC_6H_4Me-4 nucleus, at 109.7 p.p.m., is in the expected chemical shift range. The similarities between the spectroscopic properties of the complexes (**3**) indicated that they are structurally similar and, as mentioned above, the structure of (**3b**) has been confirmed by an *X*-ray diffraction study.

Compound (**5a**), the other product of the reaction between (**1a**) and sulphur, appeared to be similar in character to (**5b**), obtained from (**4**) and sulphur.[4] Neither (**5a**) nor (**5b**) shows in their i.r. or $^{13}C\text{-}\{^1H\}$ n.m.r. spectra bands or resonances characteristic for a C=O group. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of both complexes, however, there are resonances [(**5a**), δ 111.3; (**5b**), 95.6 p.p.m.] suggesting the possible presence of a thioacyl ligand S*C*R bridging a dimetal centre. In order to resolve the structure of these species an *X*-ray diffraction study was carried out on (**5a**). The results are summarised in Table 3, and the molecule is shown in the Figure.

It is immediately apparent that in the dimetal compound the

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* 1,1,1,2,2-Pentacarbonyl-2-(η-cyclopentadienyl)-μ-[η^2-*p*-thiotoluoyl-*S*(Fe, Mo),*C*(Fe, Mo)]-ironmolybdenum(*Fe–Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

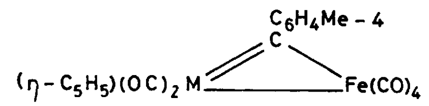
thioacyl ligand [with C(1)–S 1.735(2) Å] transversely bridges the Fe–Mo bond [2.765(1) Å]. The latter separation may be compared with the appreciably longer metal–metal distance [2.823(1) Å] found in (**1a**).[1] We have previously reported[5] an *X*-ray diffraction study on the complex $[Fe_2W(\mu_3\text{-}\eta^2\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)]$ (**6c**) in which a SCMe ligand triply bridges and lies parallel to the face of the metal atom triangle. The C–S distance in this species [1.755(8) Å] is similar to that in (**5a**) [1.735(2) Å]. The Fe–S [2.248(1) Å] and Mo–S [2.441(1) Å] distances in (**5a**) are also very similar to the Fe–S [2.233(2) Å] and W–S [2.439(2) Å] separations in (**6c**). Similar relationships hold for the μ-C–Fe and μ-C–Mo (or W) distances [μ-C–Fe, (**5a**) 1.942(2), (**6c**) 1.951(8); μ-C–Mo (or W), (**5a**) 2.153(2), (**6c**) 2.195(8) Å]. Since molybdenum and tungsten have similar covalent radii, it is evident that the parameters for the thioacyl ligands SCR ($R = C_6H_4Me\text{-}4$ or Me) are essentially the same whether this group is transversely bridging a metal–metal bond, or adopting a $\mu_3\text{-}(\eta^2\text{-}\|)$ bonding mode with a Fe_2W metal triangle as in (**6c**).

The iron atom in (**5a**) is linked to three essentially linear CO groups. The molybdenum atom carries the $\eta\text{-}C_5H_5$ ring and two carbonyl groups. However, whereas Mo–C(3)–O(3) [177.4(2)°] is close to linear, Mo–C(2)–O(2) [170.4(2)°] just perceptibly semi-bridges the Fe–Mo vector.

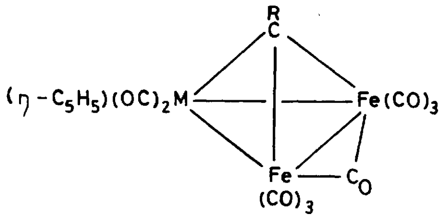
The reaction between (**2a**) and sulphur was also investigated as part of the work described herein. In thf at room temperature, these reagents afforded a chromatographically separable mixture of $[Fe_2Mo(\mu_3\text{-}\eta^2\text{-}SCC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (**6a**) and $[Fe_2Mo(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$ (**7a**), data for which are given in Tables 1 and 2.

Complex (**6a**) is related to the di-irontungsten compound (**6c**), mentioned above. In (**6c**) the two CO groups attached to tungsten semi-bridge the Fe–W bonds. Similar CO semi-bridging of the Fe–Mo linkages probably occurs in (**6a**) also. In the i.r. spectrum of (**6a**) there is a broad band at 1 846 cm^{-1} in the semi-bridging region, and in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum the Mo(CO) resonances are relatively deshielded at δ 243.1 and 235.3 p.p.m. The shifts for terminally bound Mo(CO) groups are less deshielded at *ca.* 228 p.p.m., as observed in the spectrum of (**5a**).

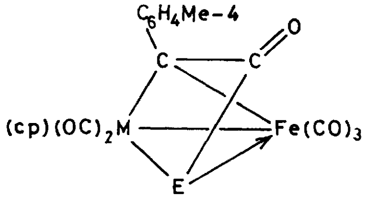
Compound (**7a**) is the molybdenum analogue of the di-irontungsten compound (**7b**) obtained from the reaction between (**2b**) and sulphur.[5] The spectroscopic data for (**7a**) are in accord with the proposed structure, confirmed in the case of (**7b**)



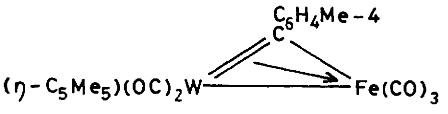
	M
(**1a**)	Mo
(**1b**)	W



	M	R
(**2a**)	Mo	$C_6H_4Me\text{-}4$
(**2b**)	W	$C_6H_4Me\text{-}4$
(**2c**)	W	Me



	M	cp	E
(**3a**)	Mo	$\eta\text{-}C_5H_5$	O
(**3b**)	W	$\eta\text{-}C_5Me_5$	O
(**3c**)	Mo	$\eta\text{-}C_5H_5$	S



(**4**)

Table 1. Analytical[a] and physical data for the iron–molybdenum complexes

	Compound[b]	Colour	Yield (%)	ν(CO)/cm^{-1} [c]	Analysis (%) C	Analysis (%) H
(**3a**)	$[FeMo\{\mu\text{-}C(R)C(O)O\}(CO)_5(\eta\text{-}C_5H_5)]$	Yellow-orange	84	2 070vs, 2 018s, 1 998s, 1 954vw, 1 698w,br	45.0 (45.3)	2.4 (2.4)
(**3c**)	$[FeMo\{\mu\text{-}C(R)C(O)S\}(CO)_5(\eta\text{-}C_5H_5)]$	Yellow-orange	34	2 064vs, 2 010s, 1 995s, 1 950vw, 1 665m,br	43.5 (43.8)	2.3 (2.3)
(**5a**)	$[FeMo(\mu\text{-}\eta^2\text{-}SCR)(CO)_5(\eta\text{-}C_5H_5)]$	Red	60	2 051vs, 1 991vs,br, 1 970s,br	43.9 (43.9)	2.5 (2.5)
(**6a**)	$[Fe_2Mo(\mu_3\text{-}\eta^2\text{-}SCR)(CO)_8(\eta\text{-}C_5H_5)]$	Brown	31	2 059s, 2 015vs, 1 991s, 1 925m,br, 1 846w,br	39.6 (39.9)	2.2 (1.9)
(**7a**)	$[Fe_2Mo(\mu\text{-}CR)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$	Red	47	2 060s, 2 018vs, 1 996m, 1 979m, 1 868w,br	39.5 (39.7)	2.1 (2.0)

[a] Calculated values are given in parentheses. [b] $R = C_6H_4Me\text{-}4$. [c] In CH_2Cl_2.

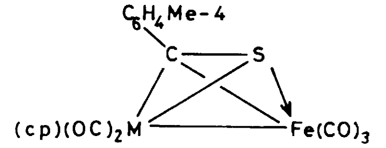
Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the iron–molybdenum complexes

Compound	$^1H(\delta)$[b]	$^{13}C(\delta)$[c]
(3a)	2.31 (s, 3 H, Me-4), 5.51 (s, 5 H, C_5H_5), 7.10, 7.63 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	232.0, 228.2 (MoCO), 208.9 (FeCO), 162.4 (C=O), 142.7 [$C^1(C_6H_4)$], 136.5, 129.7, 128.5 (C_6H_4), 95.6 (C_5H_5), 92.6 (CC_6H_4Me-4), 21.3 (Me-4)
(3c)	2.28 (s, 3 H, Me-4), 5.44 (s, 5 H, C_5H_5), 7.05, 7.33 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	230.8, 227.9 (MoCO), 210.4 (FeCO), 175.0 (C=O), 144.6 [$C^1(C_6H_4)$], 136.2, 129.2, 128.7 (C_6H_4), 109.7 (CC_6H_4Me-4), 93.9 (C_5H_5), 21.2 (Me-4)
(5a)	[d] 2.32 (s, 3 H, Me-4), 5.32 (s, 5 H, C_5H_5), 7.05, 7.24 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	[e] 229.3, 227.3 (MoCO), 211.6 (FeCO), 146.2 [$C^1(C_6H_4)$], 136.5, 129.3, 128.3 (C_6H_4), 111.3 (CC_6H_4Me-4), 92.6 (C_5H_5), 21.4 (Me-4)
(6a)	2.34 (s, 3 H, Me-4), 5.20 (s, 5 H, C_5H_5), 7.12, 7.40 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	243.1, 235.3 (MoCO), 212.4 (br, FeCO), 187.9 (μ-CC_6H_4Me-4), 149.7 [$C^1(C_6H_4)$], 139.7, 129.7, 124.2 (C_6H_4), 96.9 (C_5H_5), 21.2 (Me-4)
(7a)	2.34 (s, 3 H, Me-4), 5.69 (s, 5 H, C_5H_5), 7.20 (br m, 4 H, C_6H_4)	[f] 339.0 (μ-C), 246.9 (MoCO), 214.2 (br, FeCO), 150.3 [$C^1(C_6H_4)$], 141.4, 130.0, 129.7 (C_6H_4), 97.0 (C_5H_5), 21.9 (Me-4)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at ambient temperatures unless otherwise stated. [b] Measured in $CDCl_3$ unless otherwise indicated. [c] Measured in CD_2Cl_2–CH_2Cl_2. [d] Measured in CD_2Cl_2. [e] Measured at −40 °C. [f] Measured at −30 °C.

Table 3. Selected internuclear distances (Å) and angles (°) for [$FeMo(\mu$-η^2-SCC_6H_4Me-4$)(CO)_5(\eta$-$C_5H_5)$] **(5a)** with estimated standard deviations in parentheses

Mo–Fe	2.765(1)	Mo–S	2.441(1)	Mo–C(1)	2.153(2)	Mo–C(2)	1.974(2)
Mo–C(3)	2.017(3)	Fe–S	2.248(1)	Fe–C(1)	1.942(2)	Fe–C(4)	1.830(3)
Fe–C(5)	1.777(3)	Fe–C(6)	1.760(3)	S–C(1)	1.735(2)	C(1)–C(11)	1.465(3)
C(2)–O(2)	1.154(3)	C(3)–O(3)	1.133(4)	C(4)–O(4)	1.132(3)	C(5)–O(5)	1.138(4)
C(6)–O(6)	1.145(3)	Mo–C(cp) mean	2.321	C–C(cp) mean	1.408		
Fe–Mo–S	50.7(1)	Fe–Mo–C(1)	44.4(1)	S–Mo–C(1)	43.8(1)	Fe–Mo–C(2)	69.7(1)
S–Mo–C(2)	120.0(1)	C(1)–Mo–C(2)	98.3(1)	Fe–Mo–C(3)	84.2(1)	S–Mo–C(3)	86.2(1)
C(1)–Mo–C(3)	122.1(1)	C(2)–Mo–C(3)	81.6(1)	Mo–Fe–S	57.2(1)	Mo–Fe–C(1)	50.8(1)
S–Fe–C(1)	48.3(1)	Mo–Fe–C(4)	104.6(1)	S–Fe–C(4)	108.7(1)	C(1)–Fe–C(4)	151.4(1)
Mo–Fe–C(5)	102.5(1)	S–Fe–C(5)	144.1(1)	C(1)–Fe–C(5)	95.9(1)	C(4)–Fe–C(5)	104.9(1)
Mo–Fe–C(6)	148.9(1)	S–Fe–C(6)	95.5(1)	C(1)–Fe–C(6)	100.9(1)	C(4)–Fe–C(6)	97.9(1)
C(5)–Fe–C(6)	91.9(1)	Mo–S–Fe	72.1(1)	Mo–S–C(1)	59.2(1)	Fe–S–C(1)	56.6(1)
Mo–C(1)–Fe	84.8(1)	Mo–C(1)–S	76.9(1)	Fe–C(1)–S	75.1(1)	Mo–C(1)–C(11)	139.6(2)
Fe–C(1)–C(11)	129.0(2)	S–C(1)–C(11)	127.6(1)	Mo–C(2)–O(2)	170.4(2)	Mo–C(3)–O(3)	177.4(2)
Fe–C(4)–O(4)	178.6(2)	Fe–C(5)–O(5)	175.6(3)	Fe–C(6)–O(6)	178.3(3)		



	M	cp
(5a)	Mo	η-C_5H_5
(5b)	W	η-C_5Me_5

by an X-ray diffraction study. The ^{13}C-{^1H} n.m.r. spectrum of **(7a)** has a resonance for a μ-C nucleus at δ 339.0 p.p.m. The corresponding signal in the spectrum of **(7b)** is at 313.7 p.p.m. The Mo(CO) resonance for **(7a)**, at 246.9 p.p.m., is relatively deshielded, approaching the chemical shift range for a bridging carbonyl group. In compound **(7b)**, the X-ray study revealed that the CO ligand bonded to tungsten strongly semi-bridges the W–Fe vector, and in agreement the resonance for the W(CO) group in the ^{13}C-{^1H} n.m.r. spectrum is deshielded at 241.8 p.p.m.

Formation of **(7a)** from **(2a)** results in migration of the alkylidyne group from a triply bridging to an edge-bridging site. A similar transformation occurs in the synthesis of **(7b)**. The

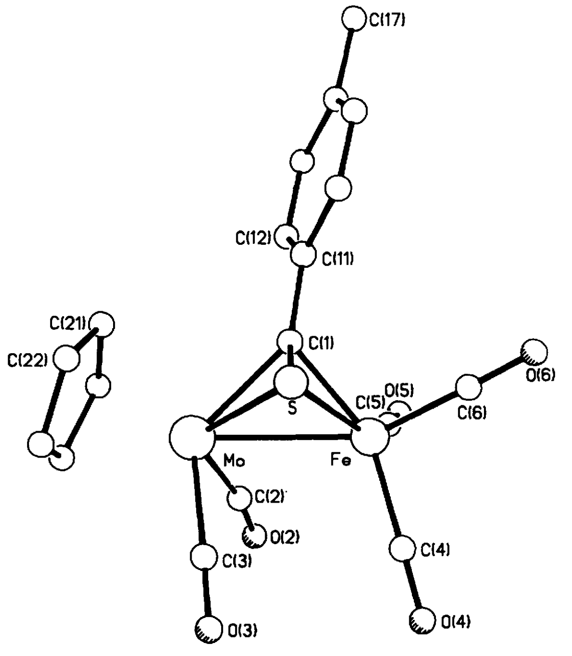
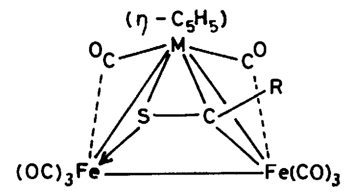
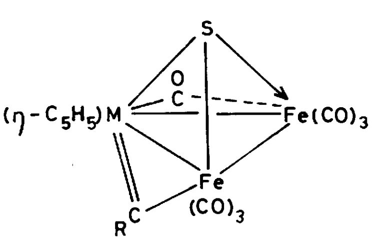


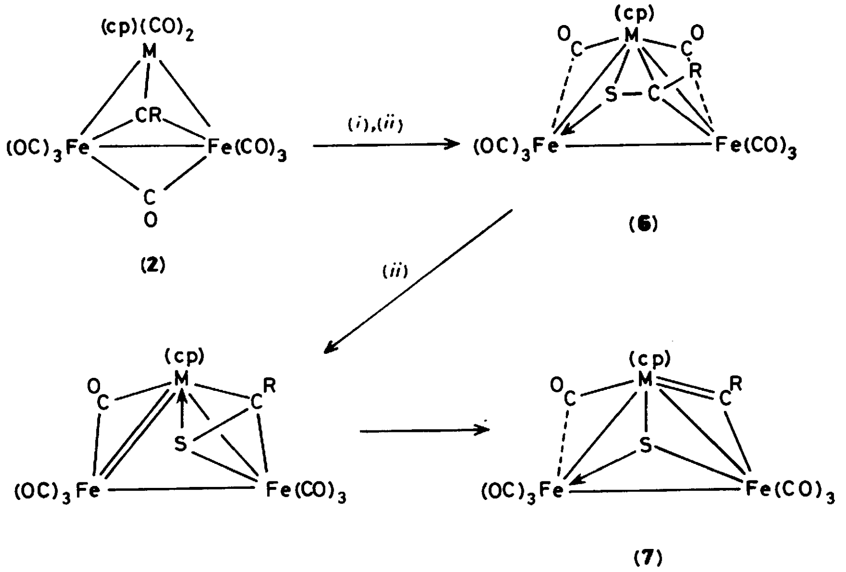
Figure. The molecular structure of [$FeMo(\mu$-η^2-SCC_6H_4Me-4$)(CO)_5(\eta$-$C_5H_5)$] **(5a)** showing the atom-labelling scheme



	M	R
(6a)	Mo	C_6H_4Me-4
(6b)	W	C_6H_4Me-4
(6c)	W	Me



	M	R
(7a)	Mo	C_6H_4Me-4
(7b)	W	C_6H_4Me-4
(7c)	W	Me



Scheme. cp = η-C_5H_5, M = Mo or W; (*i*) +S_8, (*ii*) −CO

pathway for these μ_3-CR to μ-CR migrations, however, involves the intermediacy of triply-bridging thioacyl complexes. Thus it was shown that if (**6a**) were heated in toluene at *ca.* 60 °C for 2 h it was quantitatively converted into (**7a**), with release of carbon monoxide. Indeed, if the reaction between (**2a**) and sulphur is carried out in refluxing thf, compound (**7a**) is the only product. Interestingly, in the reaction of (**2b**) with sulphur, compound (**7b**) was the sole product, and the thioacyl complex (**6b**) was not observed. In contrast, however, the reaction between (**2c**) and sulphur afforded a mixture of (**6c**) and (**7c**).[5] Moreover, it was shown that on heating complex (**6c**) was converted into (**7c**).

The work described herein, and that reported earlier,[5] thus establishes a novel reaction sequence between sulphur and a triply bridging alkylidyne group. Initially C–S bond formation occurs with generation of a thioacyl ligand, but this is followed by cleavage of the C–S linkage leading to a triply bridging sulphur atom and an edge-bridging alkylidyne ligand. A possible pathway is shown in the Scheme in which the intermediate is a 46-valence-electron trimetal cluster in which the thioacyl group adopts an edge-bridging bonding mode with the metal triangle. The overall transformation bears a striking resemblance to the mechanism proposed[6] for the formation of bis(alkylidyne)trimetal compounds *via* cleavage of the C–C bonds of ligated alkyne groups when the latter are co-ordinated in the μ_3-(η^2-‖) bonding mode to a metal triangle.

Experimental

The experimental techniques used and the instrumentation employed have been described in previous parts of this series.[5] Light petroleum refers to that fraction of b.p. 40—60 °C. The compounds [FeMo(μ-CC_6H_4Me-4)$(CO)_6$(η-C_5H_5)] and [Fe_2Mo(μ_3-CC_6H_4Me-4)(μ-CO)$(CO)_8$(η-C_5H_5)] were prepared as previously described.[1] Analytical data for the new compounds are given in Table 1.

Synthesis of Complex [FeMo{μ-C(C_6H_4Me-4)C(O)O}$(CO)_5$(η-C_5H_5)] (**3a**).—A stream of oxygen was passed for 15 min through an Et_2O (10 cm^3) solution of (**1a**) (0.15 g, 0.30 mmol). Solvent was removed *in vacuo*, and the yellow-brown residue was dissolved in CH_2Cl_2–light petroleum (20 cm^3, 2:1), and filtered through a Celite pad (2 × 4 cm). The resulting solution was reduced in volume *in vacuo* to *ca.* 10 cm^3, and cooled to *ca.* −20 °C. Yellow-orange *microcrystals* of [FeMo{μ-C(C_6H_4Me-4)C(O)O}$(CO)_5$(η-C_5H_5)] (**3a**) (0.13 g) were thereby obtained.

Reaction of [FeMo(μ-CC_6H_4Me-4)$(CO)_6$(η-C_5H_5)] *with Sulphur.*—A mixture of (**1a**) (0.15 g, 0.30 mmol) and sulphur (0.015 g, 0.50 mmol) was stirred in thf (15 cm^3) at room temperature for 5 min, affording a dark red solution. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–

Table 4. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$), with estimated standard deviations in parentheses, for **(5a)**

Atom	x	y	z
Mo	147(1)	2 639(1)	2 269(1)
Fe	−2 441(1)	3 137(1)	812(1)
S	−1 877(1)	4 235(1)	3 058(1)
C(1)	−2 136(3)	2 901(2)	3 134(3)
C(2)	174(3)	1 573(2)	168(3)
O(2)	398(2)	919(2)	−1 057(2)
C(3)	898(3)	3 503(2)	570(3)
O(3)	1 360(2)	3 953(2)	−411(3)
C(4)	−1 938(3)	3 647(2)	−1 145(3)
O(4)	−1 620(2)	3 981(2)	−2 335(2)
C(5)	−2 791(3)	1 803(2)	104(3)
O(5)	−3 056(3)	952(2)	−248(3)
C(6)	−4 313(3)	3 750(2)	1 054(3)
O(6)	−5 536(2)	4 130(2)	1 236(3)
C(11)	−3 094(2)	2 546(2)	4 379(3)
C(12)	−2 991(3)	1 420(2)	4 437(3)
C(13)	−3 945(3)	1 075(2)	5 546(3)
C(14)	−5 027(3)	1 823(2)	6 623(3)
C(15)	−5 118(3)	2 943(2)	6 572(3)
C(16)	−4 172(3)	3 296(2)	5 477(3)
C(17)	−6 083(3)	1 439(3)	7 802(4)
C(21)	512(3)	1 955(2)	4 833(3)
C(22)	1 135(3)	2 898(3)	4 910(3)
C(23)	2 275(3)	2 672(3)	3 578(4)
C(24)	2 350(3)	1 598(3)	2 680(4)
C(25)	1 250(3)	1 156(2)	3 459(4)

light petroleum (2:1, 10 cm^3) and chromatographed on a Florisil column (2 × 40 cm) at −20 °C. Elution with the same solvent mixture eluted a deep red band. Solvent was removed *in vacuo* affording red *microcrystals* of [$FeMo(\mu$-η^2-SCC_6H_4Me-4)$(CO)_5(\eta$-$C_5H_5)$] **(5a)** (0.09 g). Elution of the column with neat CH_2Cl_2 gave a yellow-orange solution. Removal of solvent *in vacuo* from this eluate gave yellow-orange *microcrystals* of [$FeMo\{\mu$-$C(C_6H_4Me$-4)$C(O)S\}(CO)_5(\eta$-$C_5H_5)$] **(3c)** (0.052 g).

Reaction between [$Fe_2Mo(\mu_3$-CC_6H_4Me-4)$(\mu$-$CO)(CO)_8(\eta$-$C_5H_5)$] *and Sulphur*.—A mixture of **(2a)** (0.145 g, 0.23 mmol) and elemental sulphur (0.027 g, 0.85 mmol) in thf (20 cm^3) was stirred at room temperature under a slow purge of nitrogen for 24 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (1:1, 10 cm^3) and chromatographed on an alumina column (2 × 40 cm). Elution with Et_2O–light petroleum (2:1) gave a red solution from which solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (1:1, 5 cm^3), and the solution cooled to *ca.* −20 °C yielding red *crystals* of [$Fe_2Mo(\mu$-CC_6H_4Me-4)$(\mu_3$-$S)(CO)_7(\eta$-$C_5H_5)$] **(7a)** (0.062 g). Elution of the chromatography column with Et_2O gave a brown eluate. Removal of solvent *in vacuo*, and crystallisation from CH_2Cl_2–light petroleum (1:1, *ca.* 5 cm^3) afforded brown *crystals* of [$Fe_2Mo(\mu_3$-η^2-SCC_6H_4Me-4)$(CO)_8(\eta$-$C_5H_5)$] **(6a)** (0.040 g).

Crystal Structure Determination of [$FeMo(\mu$-η^2-SCC_6H_4Me-4)$(CO)_5(\eta$-$C_5H_5)$] **(5a)**.—Crystals of **(5a)** grow on cooling from a mixture of CH_2Cl_2, light petroleum, and Et_2O as orange-red parallelepipeds. Diffracted intensities were collected at 293 K on a Nicolet *P*3*m* diffractometer from a crystal of dimensions *ca.* 0.45 × 0.15 × 0.13 mm. Of the 3 186 unique data collected (ω–2θ scans, $2\theta \leqslant 50°$) 2 793 had $I \geqslant 2.5\sigma(I)$, and only these were used in the structure solution and refinement. The data were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[7]

Crystal data. $C_{18}H_{12}FeMoO_5S$, $M = 492.1$, triclinic, $a = 9.397(1)$, $b = 12.461(1)$, $c = 7.948(1)$ Å, $\alpha = 98.29(1)$, $\beta = 86.02(1)$, $\gamma = 78.67(1)°$, $U = 898.4(2)$ Å^3, $Z = 2$, $D_c = 1.82$ g cm^{-3}, $F(000) = 488$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 16.3 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and successive difference-Fourier syntheses were used to locate all non-hydrogen atoms. These were refined with anisotropic thermal parameters. All hydrogen atoms were included at calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (1.2 × $U_{\text{equiv.}}$ of the parent carbon atom) for all aromatic hydrogen atoms and a common refined isotropic thermal parameter for the methyl hydrogen atoms. The reflection (−1, −1, 1) was not included in the last stages of refinement due to a large value of $(F_c - F_o)/\sigma(F)$, attributed to extinction. Refinement by blocked-cascade least squares led to $R = 0.021$ ($R' = 0.022$) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,2|F|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $\geqslant 0.23$ or $\leqslant -0.36$ e Å^{-3}. Scattering factors and corrections for anomalous dispersion were taken from ref. 8. All calculations were carried out with an Eclipse (Data General) computer with the SHELXTL system of programs.[7] Atomic co-ordinates are given in Table 4.

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References

1 Part 56, M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, preceding paper.

2 L. Busetto, J. C. Jeffery, R. M. Mills, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 101.

3 M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1986, 802; P. G. Byrne, M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *ibid.*, 1987, 53.

4 E. Delgado, L. J. Farrugia, J. Hein, J. C. Jeffery, A. L. Ratermann, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 1191.

5 E. Delgado, A. T. Emo, J. C. Jeffery, N. D. Simmons, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 1323.

6 A. D. Clauss, J. R. Shapley, C. N. Wilker, and R. Hoffmann, *Organometallics*, 1984, 3, 619; Y. Chi and J. R. Shapley, *ibid.*, 1985, 4, 1900.

7 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-ray system, Cambridge, 1976; updated, Göttingen, 1981.

8 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

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