Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 78.[1] Reactions of [MoFe(μ-CC₆H₄Me-4)(CO)₆(η-C₅H₅)] with Alkynes; Crystal Structures of [MoFe{μ-C(C₆H₄Me-4)C(O)C(Et)C(Et)}-(μ-CO)(CO)₄(η-C₅H₅)] and [MoFe{μ-C(C₆H₄Me-4)C(Me)C[C(O)Me]}(CO)₅-(η-C₅H₅)] *

M. Esther Garcia, John C. Jeffery, Paul Sherwood, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The dimetal compound [MoFe(μ-CR)(CO)₆(η-C₅H₅)] (R = C₆H₄Me-4) reacts with the alkynes HC≡CH and HC≡CEt at room temperature in light petroleum to afford the complexes [MoFe{μ-C(R)-CHC(R¹)}(CO)₅(η-C₅H₅)] and [MoFe{μ-C(R)CHC(R¹)C(O)}(μ-CO)(CO)₄(η-C₅H₅)](R¹ = H or Et), and with MeC≡CEt to yield a mixture of [MoFe{μ-C(R)C(R¹)C(R²)}(CO)₅(η-C₅H₅)] (two isomers: R¹ = Me, R² = Et; R¹ = Et, R² = Me) and [MoFe{μ-C(R)C(O)C(R¹)C(R²)}(μ-CO)(CO)₄(η-C₅H₅)] (two isomers: R¹ = Me, R² = Et; R¹ = Et, R² = Me). Hex-3-yne and the molybdenum–iron compound react to give a mixture of [MoFe{μ-C(R)C(Et)C(Et)}(CO)₅(η-C₅H₅)] and [MoFe{μ-C(R)C(O)C-(Et)C(Et)}(μ-CO)(CO)₄(η-C₅H₅)]. Treatment of the former species with CO affords the acyl complex [MoFe{μ-C(R)C(Et)C(Et)C(O)}(μ-CO)(CO)₄(η-C₅H₅)], a process which is readily reversed in the presence of a stream of nitrogen. The structure of [MoFe{μ-C(R)C(O)C(Et)C(Et)}(μ-CO)(CO)₄(η-C₅H₅)] has been established by an X-ray diffraction study, which revealed that the asymmetric unit contained two crystallographically independent molecules of similar geometry. The Mo(1)–Fe(1) bond [2.694(1) Å] is spanned by the C(R)C(O)C(Et)C(Et) group in such a manner that the terminal carbon atoms of the chain are each bonded to the molybdenum and the iron atoms but in addition the molybdenum is ligated by the carbon atom of the CEt group adjacent to the ketonic moiety. The iron atom carries three terminal CO ligands, and the molybdenum atom one such group and the C₅H₅ ring. However, another CO group attached to the molybdenum semi-bridges the Mo–Fe bond [Mo(1)–C(9)–O(9) 164.2(8)°]. Reactions between [MoFe(μ-CR)(CO)₆(η-C₅H₅)] and the alkynes MeC≡CEt and EtC≡CEt in large excess (*ca.* 1 : 60) afforded, in addition to the products mentioned above, the species [MoFe{μ-C(R)C(R¹)C(R²)}(CO)₅(η-C₅H₅)] [R¹ = Me, R² = C(O)Me and R¹ = C(O)Me, R² = Me from MeC≡CEt, and R¹ = Et, R² = C(O)Me and R¹ = C(O)Me, R² = Et from EtC≡CEt]. These products arose from the presence of MeC≡CC(O)Me and EtC≡CC(O)Me as impurities in commercial samples of pent-2-yne and hex-3-yne. The structure of [MoFe{μ-C(R)C(Me)C[C(O)Me]}(CO)₅-(η-C₅H₅)] was established by X-ray diffraction. The Mo–Fe bond [2.722(1) Å] is bridged by the C(R)C(Me)C{C(O)Me} fragment. The iron atom is ligated by three terminal CO groups, and the molybdenum atom by two such groups and the η-C₅H₅ ring.

In the preceding paper[1] we described reactions between but-2-yne and the dimetal compounds [MoFe(μ-CC₆H₄Me-4)-(CO)₅L(η-C₅H₅)] [L = CO (**1a**) or PMe₃ (**1b**)] which afforded the complexes [MoFe{μ-C(C₆H₄Me-4)C̅(C̅H̅M̅e̅)̅C̅H̅₂}(CO)₅-(η-C₅H₅)] (**2**) (two isomers) and [MoFe{μ-C(C₆H₄Me-4)C̅(C̅H̅M̅e̅)̅C̅H̅₂C(O)}(μ-CO)(CO)₃(PMe₃)(η-C₅H₅)] (**3**), respectively. These products had unusual structures. Although as expected, coupling occurred between the *p*-tolylmethylidyne groups in (**1**) and the alkyne, there was also the novel feature of hydrogen-atom migration between carbon centres. A similar transformation of a methyl group takes place in the room-temperature reaction between

MeC≡CMe and the dimetal compound [MoW(≡CC₆H₄Me-4)-(CO)₇(η-C₅H₅)], when the complex [MoW{μ-C(C₆H₄-Me-4)C̅(C̅H̅₂)̅C̅H̅(̅M̅e̅)̅C(O)}(CO)₆(η-C₅H₅)] (**4**) is formed.[2] Activation of a methyl substituent of MeC≡CMe in this manner at a dimetal centre is as far as we are aware without precedent. Moreover, the synthesis of (**2**) further illustrates the extraordinary variety of products which may be obtained by treating the heteronuclear compound (**1a**) with various substrate molecules,[3] in accord with the idea that mixed-metal cluster compounds are more reactive than their homonuclear counterparts.

In this paper we describe the results of studies on reactions of compound (**1a**) with the alkynes HC≡CH and RC≡CEt (R = H, Me, or Et), an investigation prompted by the unusual nature of the product (**2**) obtained with MeC≡CMe. In particular, it was thought that RC≡CEt containing alkyl groups might yield complexes related to the products (**2**)—(**4**). In practice, hydrogen-migration processes did not occur. However, new molybdenum–iron compounds were isolated and characterised, some of which have previously received brief mention.[4]

L
(1a) CO
(1b) PMe$_3$

(2a)

(2b)

(3)

(4)

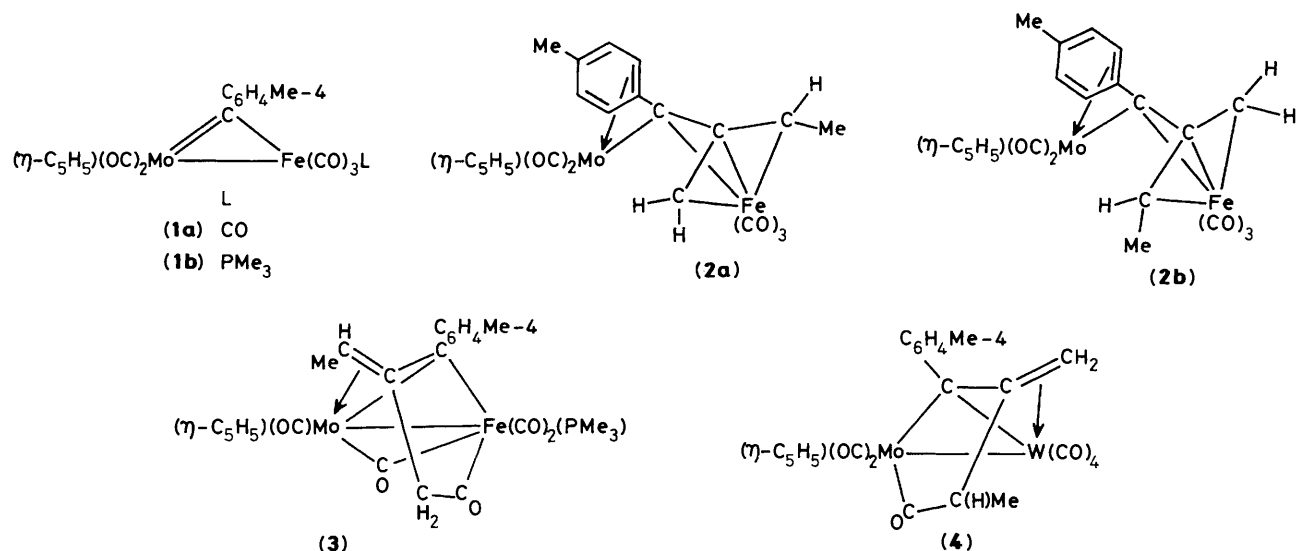**Table 1.** Analytical^a and physical data for the molybdenum–iron complexes

Compound^b	Colour	Yield (%)	$\tilde{v}_{CO}(max.)^c/cm^{-1}$	Analysis (%) C	H
(5a) [MoFe{μ-C(R)CHCH}(CO)$_5$(η-C$_5$H$_5$)]	Red	20	2 052s, 1 991s,br, 1 968w, 1 941w	49.3 (49.4)	3.1 (2.9)
(5b) [MoFe{μ-C(R)CHC(Et)}(CO)$_5$(η-C$_5$H$_5$)]	Red	30	2 049s, 1 987s, 1 963w, 1 939w	50.7 (51.4)	3.8 (3.5)
(5c) [MoFe{μ-C(R)C(Et)C(Me)}(CO)$_5$(η-C$_5$H$_5$)]^d (5d) [MoFe{μ-C(R)C(Me)C(Et)}(CO)$_5$(η-C$_5$H$_5$)]^d	Red	50	2 046s, 1 988s, 1 960w, 1 937w	52.0 (52.3)	3.8 (3.8)
(5e) [MoFe{μ-C(R)C(Et)C(Et)}(CO)$_5$(η-C$_5$H$_5$)]	Red	50	2 048s, 1 998s, 1 958w, 1 937w	53.1 (53.2)	4.3 (4.1)
(5f) [MoFe{μ-C(R)C[C(O)Me]C(Me)}(CO)$_5$(η-C$_5$H$_5$)]	Red	30	^{e}2 049s, 1 991s, 1 986s, 1 938w, 1 697vw(br), 1 669vw(br)	50.8 (51.0)	3.5 (3.4)
(5g) [MoFe{μ-C(R)C(Me)C[C(O)Me]}(CO)$_5$(η-C$_5$H$_5$)]	Red	20	2 054s, 1 996s, 1 970m, 1 942w, 1 644w(br)	51.1 (51.0)	3.7 (3.4)
(5h) [MoFe{μ-C(R)C[C(O)Me]C(Et)}(CO)$_5$(η-C$_5$H$_5$)]	Red	20	^{e}2 048s, 1 992s(br), 1 937w, 1 696vw(br), 1 674vw(br)	51.1 (51.8)	3.9 (3.6)
(5i) [MoFe{μ-C(R)C(Et)C[C(O)Me]}(CO)$_5$(η-C$_5$H$_5$)]	Red	35	2 055s, 1 996s, 1 971w, 1 943w, 1 645vw(br)	51.1 (51.8)	3.7 (3.6)
(6a) [MoFe{μ-C(R)CHCHC(O)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)]	Yellow	75	^{e}2 059s, 2 005s(br), 1 841w(br), 1 610w(br)	48.7 (49.1)	2.8 (2.8)
(6b) [MoFe{μ-C(R)CHC(Et)C(O)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)]	Yellow-orange	60	^{e}2 058s, 1 999s, 1 987m (sh), 1 831w(br), 1 591w(br)	51.0 (51.1)	3.4 (3.4)
(6c) [MoFe{μ-C(R)C(Et)C(Et)C(O)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)]	Yellow	94	^{e}2 055s, 1 999s(br), 1 839w(br), 1 586m(br)	52.6 (52.7)	4.0 (3.9)
(7a) [MoFe{μ-C(R)C(O)C(Me)C(Et)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)]^d (7b) [MoFe{μ-C(R)C(O)C(Et)C(Me)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)]^d	Yellow	40	^{e}2 056vs, 2 002s, 1 994s, 1 895w(br), 1 580w(br)	51.0 (51.8)	3.9 (3.6)
(7c) [MoFe{μ-C(R)C(O)C(Et)C(Et)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)]	Yellow	30	^{e}2 054s, 2 001s(br), 1 886w(br), 1 601w(br)	52.6 (52.7)	3.9 (3.9)

^{a} Calculated values are given in parentheses. ^{b} R = C$_6$H$_4$Me-4. ^{c} Measured in light petroleum, unless otherwise indicated. ^{d} Formed as an inseparable mixture of isomers, see text. ^{e} In CH$_2$Cl$_2$.

Results and Discussion

Complex (1a) and HC≡CH in light petroleum react to give a chromatographically separable mixture of the two compounds [MoFe{μ-C(C$_6$H$_4$Me-4)CHCH}(CO)$_5$(η-C$_5$H$_5$)] (5a) and [MoFe{μ-C(C$_6$H$_4$Me-4)CHCHC(O)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)] (6a), characterised by the data given in Tables 1 and 2. The structure of (5a), in which a three-carbon chain spans the Mo–Fe bond, is similar to that of [MoFe{μ-C(C$_6$H$_4$Me-4)-C(Ph)C(Ph)}(CO)$_5$(η-C$_5$H$_5$)] obtained from (1a) and PhC≡CPh.[1] Moreover, several similar alkyne–alkylidyne

coupling reactions affording μ-C(C$_6$H$_4$Me-4)C(R)C(R) (R = alkyl or aryl) fragments have been observed in reactions between alkynes and dimetal complexes containing W–Fe,[5] W–Co,[6,7] or W–Rh[8] bonds and p-tolylmethylidyne ligands.

In the reaction between (1a) and HC≡CH the acyl complex is the major product. However, (5a) and (6a) are readily interconverted. The former in thf (tetrahydrofuran) at room temperature reacts with CO to afford the latter quantitatively. Moreover, when solutions of (6a) at ca. 40 °C are treated with a stream of nitrogen compound (5a) is formed quantitatively after
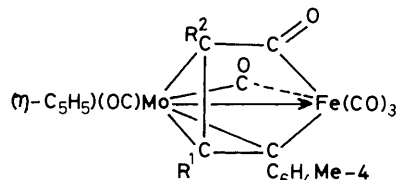
Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

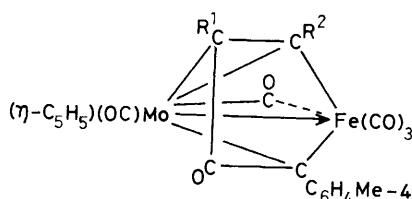| Compound[b]	$^1H(\delta)$[c]	$^{13}C(\delta)$[d]
(5a)	[e] 2.29 (s, 3 H, Me-4), 5.08 (s, 5 H, C_5H_5), 5.74 [d, 1 H, C(R)CHCH, J(HH) 3], 7.00 [d, 1 H, C(R)CHCH, J(HH) 3], 7.04, 7.17 [(AB)$_2$ 4 H, C_6H_4, J(AB) 8]	[f] 233.2, 230.2 (MoCO), 214.0 (FeCO), 145.0 [C^1(C$_6$H$_4$)], 136.2, 129.5, 128.6 (C$_6$H$_4$), 120.8 (CR), 106.1 [C(R)CHCH], 102.8 [C(R)CHCH], 90.6 (C$_5$H$_5$), 21.1 (Me-4)
(5b)	1.09 [d, of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 2.30 (s, 3 H, Me-4), 2.40 [d of q, 1 H, CH$_2$, J(HH), 16, 7], 2.68 [d, of q, 1 H, CH_2Me, J(HH) 16, 7], 5.00 (s, 5 H, C$_5$H$_5$), 7.02 (s, 1 H, CH), 7.04, 7.16 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	233.0, 230.8 (MoCO), 213.7 (FeCO), 144.4 [C^1(C$_6$H$_4$)], 136.0 [C^4(C$_6$H$_4$)], 130.0 (CR), 129.2, 125.7 (C$_6$H$_4$), 115.6 (CEt), 102.4 (CH), 90.0 (C$_5$H$_5$), 35.3 (CH$_2$Et), 21.2 (Me-4), 15.4 (CH$_2$$Me$)
(5c)	[e] 1.15 [d of d, 3 H, CH$_2$$Me$, J(HH) 8, 8], 1.92 (s, 3 H, Me), 2.30 (s, 3 H, Me-4), 2.43 [d of q, 1 H, CH_2Me, J(HH) 15, 8], 2.62 [d of q, 1 H, CH_2Me, J(HH) 15. 8], 5.08 (s, 5 H, C$_5$H$_5$), 7.06, 7.13 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	[g] 233.0, 232.5, 232.4, 232.2 (MoCO), 214.0, 213.0 (FeCO), 144.9 [C^1(C$_6$H$_4$)], 135.5, 129.0, 128.8 (C$_6$H$_4$), 128.5, 126.0, 124.9, 119.0, 116.6, 115.4 [C(R)C(Et)C(Me), C(R)C(Me)C(Et)], 90.7 (C$_5$H$_5$), 90.2 (C$_5$H$_5$), 32.6 (CH$_2$Me), 25.6 (CMe), 24.2 (CH$_2$$Me$), 21.1 (Me-4), 16.9, 16.4, 12.9 (CMe, CH$_2$$Me$)
(5d)	[e] 1.22 [d of d, 3 H, CH$_2$$Me$, J(HH) 8, 8], 2.01 [d of q, 1 H, CH_2Me, J(HH) 15, 8], 2.25 [d of q, 1 H, CH_2Me, J(HH) 15, 8], 2.27 (s, 3 H, Me), 2.30 (s, 3 H, Me-4), 5.03 (s, 5 H, C$_5$H$_5$), 7.04, 7.11 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	
(5e)	1.18 [d of d, 6 H, CH$_2$$Me$, J(HH) 8, 8], 2.08 [d of q, 1 H, CH_2Me, J(HH) 14, 8], 2.30 [d of q, 1 H, CH_2Me, J(HH) 14, 8], 2.33 (2 s, 3 H, Me-4), 2.40 [d of q, 1 H, CH_2Me, J(HH) 16, 8], 2.65 [d of q, 1 H, CH_2Me, J(HH) 16, 8], 5.04 (s, 5 H, C$_5$H$_5$), 7.02, 7.08 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 9]	[h] 232.8, 231.7 (MoCO), 213.3 (FeCO), 144.1 [C^1(C$_6$H$_4$)], 135.0 [C^4(C$_6$H$_4$)], 129.0 [C(R)C(Et)C(Et)], 128.5, 128.4 (C$_6$H$_4$), 125.2 (CR), 115.8 [C(R)C(Et)C(Et)], 89.7 (C$_5$H$_5$), 32.1 [C(R)C(CH$_2$Me)C(Et)], 23.5 [C(R)C(Et)C(CH$_2$Me)], 21.1 (Me-4), 16.4 [C(R)C(CH$_2$$Me$)C(Et)], 12.7 [C(R)-C(Et)C(CH$_2$$Me$)]
(5f)	2.00 (s, 3 H, Me), 2.30 (s, 3 H, Me-4), 2.44 (s, 3 H, Me), 5.04 (s, 5 H, C$_5$H$_5$), 6.98, 7.04 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	229.9, 229.7 (MoCO), 213.0 (FeCO), 197.9 (C=O), 144.2 [C^1(C$_6$H$_4$)], 136.2, 129.1, 128.2 (C$_6$H$_4$), 127.7, 121.2, 120.4 [C(R)C{C(O)Me}C(Me)], 90.7 (C$_5$H$_5$), 29.7, 27.5 [CMe, C(O)Me], 21.1 (Me-4)
(5g)	2.10 (s, 3 H, Me), 2.30, 2.32 (2 × s, 6 H, Me, Me-4), 5.12 (s, 5 H, C$_5$H$_5$), 7.07 (s, 4 H, C$_6$H$_4$)	231.6, 230.6 (MoCO), 213.0 (FeCO), 207.3 (C=O), 143.0 [C^1(C$_6$H$_4$)], 136.4, 129.2, 129.0 (C$_6$H$_4$), 127.9, 120.4, 105.1 [C(R)C(Me)C{C(O)Me}], 90.4 (C$_5$H$_5$), 30.4 [C(O)Me], 21.2 (Me-4), 18.8 (Me)
(5h)	1.13 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 2.02 (s, 3 H, Me), 2.30 (s, 3 H, Me-4), 2.52 [d of q, 1 H, CH_2Me, J(HH) 15, 7], 2.74 [d of q, 1 H, CH_2Me, J(HH) 15, 7], 5.09 (s, 5 H, C$_5$H$_5$), 7.04, 7.97 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	[h] 229.8, 228.8 (MoCO), 212.4 (FeCO), 198.5 (C=O), 143.6 [C^1(C$_6$H$_4$)], 135.9 [C^4(C$_6$H$_4$)], 132.8, 128.9, 127.7, 121.1, 119.9 [C(R)C{C(O)Me}CMe, C$_6$H$_4$], 90.4 (C$_5$H$_5$), 33.4 (CH$_2$Me), 29.5 (Me), 21.1 (Me-4), 16.9 (CH$_2$$Me$)
(5i)	1.14 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 2.25 [d of q, 1 H, CH_2Me, J(HH) 13, 7], 2.31, 2.32 (2 × s, 6 H, Me, Me-4), 2.45 [d of q, 1 H, CH_2Me, J(HH) 13, 7], 5.17 (s, 5 H, C$_5$H$_5$), 6.95, 7.06 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	[h] 231.3, 228.7 (MoCO), 212.0 (FeCO), 207.7 (C=O), 142.4 [C^1(C$_6$H$_4$)], 136.1 [C^4(C$_6$H$_4$)], 132.1, 128.8, 128.7, 121.0, 104.5 [C(R)C(Me)C{C(O)Me}, C$_6$H$_4$], 90.2 (C$_5$H$_5$), 30.4 (Me), 25.0 (CMe), 21.1 (Me-4), 13.3 (CH$_2$Me)
(6a)	[e] 2.33 (s, 3 H, Me), 5.03 [d, 1 H, C(H)C(O), J(HH) 4], 5.18 (s, 5 H, C$_5$H$_5$), 6.18 [d, 1 H, C(R)CH, J(HH) 4], 7.15 (s, 4 H, C$_6$H$_4$)	[f] 239.3 (μ-CO), 226.7, 226.0 (MoCO, C=O), 209.3, 207.3, 206.3 (FeCO), 163.2 (CR), 150.8 [C^1(C$_6$H$_4$)], 136.9, 129.5, 128.7 (C$_6$H$_4$), 103.4 [C(R)CH], 94.3 (C$_5$H$_5$), 80.6 [CHC(O)], 21.1 (Me-4)
(6b)	[i] 1.14 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 2.07 [d of q, 1 H, CH_2Me, J(HH) 15, 7], 2.33 (s, 3 H, Me-4), 2.64 [d of q, 1 H, CH_2Me, J(HH) 15, 7], 5.13 (s, 5 H, C$_5$H$_5$), 6.22 (s, 1 H, CH), 7.11 (s, 4 H, C$_6$H$_4$)	[i] 242.3 (μ-CO), 226.9, 226.5 (MoCO, C=O), 208.2, 205.8, 205.1 (FeCO), 162.0 (CR), 150.0 [C^1(C$_6$H$_4$)], 137.2, 129.2, 128.0 (C$_6$H$_4$), 108.1 (CEt), 104.9 (CH), 93.7 (C$_5$H$_5$), 22.8 (CH$_2$Me), 21.2 (Me-4), 15.6 (CH$_2$$Me$)
(6c)	1.24 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 1.41 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 2.14 (m, 3 H, CH_2Me), 2.33 (s, 3 H, Me-4), 2.53 [d of q, 1 H, CH_2Me, J(HH) 14, 7], 5.24 (s, 5 H, C$_5$H$_5$), 6.57 (br, 1 H, C$_6$H$_4$), 7.10 (m, 3 H, C$_6$H$_4$)	[i,j] 240.0 (μ-CO), 226.3 (MoCO, C=O), 209.2, 206.5, 204.9 (FeCO), 157.9 (CR), 147.9 [C^1(C$_6$H$_4$)], 135.6 [C^4(C$_6$H$_4$)], 130.2 (CEt), 129.4, 128.7, 127.4 (C$_6$H$_4$), 106.8 (CEt), 94.1 (C$_5$H$_5$), 26.3, 23.1 (CH$_2$Me), 21.2 (Me-4), 16.5, 16.2 (CH$_2$$Me$)
(7a)	1.21 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 2.10 (s, 3 H, Me), 2.27 (s, 3 H, Me-4), 2.82 [d of q, 1 H, CH_2Me, J(HH) 13, 7], 3.03 [d of q, 1 H, CH_2Me, J(HH) 13, 7], 5.10 (s, 5 H, C$_5$H$_5$), 7.03 (s, 4 H, C$_6$H$_4$)	237.3 (μ-CO), 225.3 (MoCO), 208.2 (FeCO), 187.4 (C=O), 181.0 (CEt), 148.0 [C^1(C$_6$H$_4$)], 135.0 [C^4(C$_6$H$_4$)], 129.0 (CR), 126.1 (CMe), 128.6 (C$_6$H$_4$), 95.6 (C$_5$H$_5$), 39.8 (CH$_2$Me), 21.1 (Me-4), 16.8 (CMe), 15.8 (CH$_2$$Me$)
(7b)	1.29 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 2.20 [d of q, 1 H, CH_2Me, J(HH) 12, 7], 2.27 (s, 3 H, Me-4), 2.57 [d of q, 1 H, CH_2Me, J(HH) 12, 7], 2.77 (s, 3 H, Me), 5.09 (s, 5 H, C$_5$H$_5$), 7.01 (s, 4 H, C$_6$H$_4$)	234.3 (μ-CO), 226.1 (MoCO), 208.8 (FeCO), 187.7 (C=O), 173.1 (CMe), 148.0 [C^1(C$_6$H$_4$)], 135.0 [C^4(C$_6$H$_4$)], 133.4 (CR), 128.9 (CEt), 128.6 (C$_6$H$_4$), 94.2 (C$_5$H$_5$), 32.4 (CMe), 24.6 (CH$_2$Me), 21.1 (Me-4), 128 (CH$_2$$Me$)
(7c)	[e,g] 1.34 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 1.41 [d of d, 3 H, CH$_2$$Me$, J(HH) 7, 7], 2.22 [d of q, 1 H, CH_2Me, J(HH) 12, 7], 2.31 (s, 3 H, Me-4), 2.53 [d of q, 1 H, CH_2Me, J(HH) 12, 7], 2.80 [d of q, 1 H, CH_2Me, J(HH) 13, 7], 3.14 [d of q, 1 H, CH_2Me, J(HH) 13, 7], 5.20 (s, 5 H, C$_5$H$_5$), 7.00 (br m, 4 H, C$_6$H$_4$)	[h,j] 239.2 (μ-CO), 226.0 (MoCO), 207.1 (FeCO), 186.2 (C=O), 183.4 (CEt), 147.4 [C^1(C$_6$H$_4$)], 134.8 [C^4(C$_6$H$_4$)], 133.6 (CR), 129.2 (CEt), 128.3, 128.1 (C$_6$H$_4$), 95.3 (C$_5$H$_5$), 38.6, 24.6 (CH$_2$Me), 21.1 (Me-4), 19.6, 15.1 (CH$_2$$Me$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature unless otherwise stated. [b] R = C$_6$H$_4$Me-4. [c] Measured in CDCl$_3$ unless otherwise indicated. [d] Hydrogen-1 decoupled with chemical shifts positive to high frequency of SiMe$_4$. Measurements in CD$_2$Cl$_2$–CH$_2$Cl$_2$ unless otherwise indicated. [e] Measured in CD$_2$Cl$_2$. [f] Measured in (CD$_3$)$_2$CO–thf. [g] Data listed are for (5c) and (5d). [h] Measured in CDCl$_3$. [i] Measurements on CO-saturated solutions. [j] Measured at −60 °C.

R^2C—CR^1
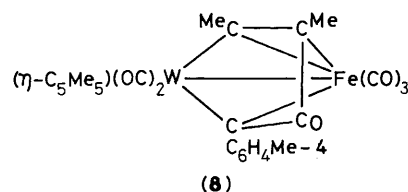
$(\eta\text{-}C_5H_5)(OC)_2Mo$————$Fe(CO)_3$

C

$C_6H_4Me\text{-}4$
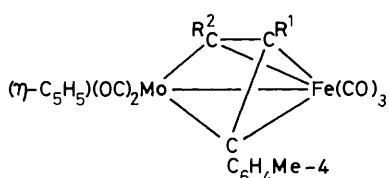
	R^1	R^2
(5a)	H	H
(5b)	H	Et
(5c)	Et	Me
(5d)	Me	Et
(5e)	Et	Et
(5f)	C(O)Me	Me
(5g)	Me	C(O)Me
(5h)	C(O)Me	Et
(5i)	Et	C(O)Me

R^1C—CR^2

O
C

$(\eta\text{-}C_5H_5)(OC)Mo$====$Fe(CO)_3$

O^C—C

$C_6H_4Me\text{-}4$

	R^1	R^2
(7a)	Me	Et
(7b)	Et	Me
(7c)	Et	Et

R^2C—C=O

O
C

$(\eta\text{-}C_5H_5)(OC)Mo$====$Fe(CO)_3$

R^1C—C

$C_6H_4Me\text{-}4$

	R^1	R^2
(6a)	H	H
(6b)	H	Et
(6c)	Et	Et

MeC—CMe

$(\eta\text{-}C_5Me_5)(OC)_2W$————$Fe(CO)_3$

C—CO

$C_6H_4Me\text{-}4$

(8)

ca. 2 h. These results are in principle similar to those recently obtained in a study[7] of the reaction between [WCo(≡CC₆H₄-Me-4)(CO)₈] and MeC≡CSiMe₃. A mixture of [WCo{μ-C(C₆H₄Me-4)C(Me)C(SiMe₃)}(CO)₇] and [WCo{μ-C(C₆H₄Me-4)C(Me)C(SiMe₃)C(O)}(CO)₇] is formed. Exposure of the latter product to vacuum yields the former. This decarbonylation process is readily reversed with CO. However, there is a fundamental difference between the cobalt–tungsten system and those described herein. Carbonylation of the complexes (5) to yield (6) results in the C(C₆H₄Me-4)C(R¹)C(R²) fragment changing from η³ co-ordination to iron to η³ co-ordination to molybdenum. In the formation of [WCo{μ-C(C₆H₄Me-4)C(Me)C(SiMe₃)C(O)}(CO)₇] by carbonylation of [WCo{μ-C(C₆H₄Me-4)C(Me)C(SiMe₃)}(CO)₇] the C(C₆H₄Me-4)C(Me)C(SiMe₃) fragment remains η³ co-ordinated to the W(CO)₄ group.

The reaction between (1a) and HC≡CEt is similar to that with ethyne in affording two products, viz. [MoFe{μ-C(C₆H₄Me-4)-CHC(Et)}(CO)₅(η-C₅H₅)] (5b) and [MoFe{μ-C(C₆H₄-Me-4)CHC(Et)C(O)}(μ-CO)(CO)₄(η-C₅H₅)] (6b), characterised in the usual manner (Tables 1 and 2). If the reaction between (1a) and HC≡CEt is carried out at ca. −40 °C compound (6b) is the sole product, formed in quantitative yield. Solutions of (6b) are, however, readily converted into (5b) when treated with a stream of nitrogen gas, a process that is rapidly reversed with CO.

An interesting feature of the reaction between (1a) and HC≡CEt was the absence of isomers of (5b) and (6b) containing the fragment C(C₆H₄Me-4)C(Et)CH. Reactions of unsymmetrically substituted alkynes R¹C≡CR² with dimetal compounds containing p-tolylmethylidyne ligands generally afford isomeric mixtures of products containing either μ-C(C₆H₄Me-

4)C(R¹)C(R²) or μ-C(C₆H₄Me-4)C(R²)C(R¹) groups.[6,7,9] However, the reaction between HC≡CPh and [WRh(μ-CC₆H₄-Me-4)(CO)₃(η-C₅H₅)(η⁵-C₉H₇)] (C₉H₇ = indenyl) yields a single product [WRh{μ-C(C₆H₄Me-4)CHC(Ph)}(CO)₂(η-C₅H₅)(η⁵-C₉H₇)] having the CH group in the central position in the three-carbon chain,[8] as found with (5b) and (6b). It is possible that formation of a single isomer in reactions with alkynes HC≡CR (R = Et or Ph) is a consequence of a steric effect in one of the several steps in the pathway leading to the products.[1]

In the compounds (6a) and (6b) the presence of a semi-bridging or bridging carbonyl ligand and an acyl group is clearly revealed by the spectroscopic data. In the i.r. spectra bands for the μ-CO ligand are seen at 1 841 (6a) and 1 831 cm⁻¹ (6b), with those for the C=O group at 1 610 (6a) and 1 591 cm⁻¹ (6b). In the ¹³C-{¹H} n.m.r. spectra (Table 2) resonances at δ 239.3 (6a) and 242.3 p.p.m. (6b) are diagnostic for μ-CO ligands. Assignment of the signals for the acyl carbonyl group is more difficult. In the ¹³C-{¹H} n.m.r. spectrum of each compound there are two peaks at ca. δ 226 p.p.m., one of which must be due to the C=O group and the other to the terminal CO ligand co-ordinated to the molybdenum atom. In each spectrum the Fe(CO)₃ groups show three resonances. Evidently in these compounds CO site exchange of the terminal and bridging carbonyl ligands does not occur at room temperature on the n.m.r. time-scale.

The reaction between MeC≡CEt and (1a) was next investigated. When the reactants are taken in approximately equivalent amounts in light petroleum at room temperature a mixture of the compounds [MoFe{μ-C(C₆H₄Me-4)C(R¹)C-(R²)}(CO)₅(η-C₅H₅)] [(5c); R¹ = Et, R² = Me; (5d); R¹ = Me, R² = Et] and [MoFe{μ-C(C₆H₄Me-4)C(O)C(R¹)-

Table 3. Selected internuclear separations (Å) and angles (°) for [MoFe{μ-C(C$_6$H$_4$Me-4)C(O)C(Et)C(Et)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)] (7c) (one of two independent molecules) with estimated standard deviations in parentheses

Mo(1)–Fe(1)	2.694(1)	Mo(1)–C(1)	2.24(1)	Mo(1)···C(2)	2.59	Mo(1)–C(5)	2.44(1)
Mo(1)–C(6)	2.39(1)	Mo(1)–C(9)	2.02(1)	Mo(1)–C(10)	2.02(1)	Mo(1)–X*	1.98
Fe(1)–C(1)	2.01(1)	Fe(1)–C(6)	1.98(1)	Fe(1)···C(9)	2.55	Fe(1)–C(11)	1.80(1)
Fe(1)–C(12)	1.77(1)	Fe(1)–C(13)	1.80(1)	C(1)–C(2)	1.48(1)	C(1)–C(21)	1.51(1)
C(2)–O(2)	1.26(1)	C(2)–C(5)	1.51(1)	C(4)–C(5)	1.50(1)	C(5)–C(6)	1.38(1)
C(6)–C(7)	1.53(1)	C(7)–C(8)	1.51(1)	C(9)–O(9)	1.13(1)	C(10)–O(10)	1.14(1)
C(11)–O(11)	1.14(1)	C(12)–O(12)	1.12(1)	C(13)–O(13)	1.13(1)		
Fe(1)–Mo(1)–C(1)	46.8(2)	Fe(1)–Mo(1)–C(5)	68.0(2)	C(1)–Mo(1)–C(5)	62.5(3)	Fe(1)–Mo(1)–C(6)	45.4(2)
C(1)–Mo(1)–C(6)	68.3(3)	C(5)–Mo(1)–C(6)	33.3(2)	Fe(1)–Mo(1)–C(9)	63.5(3)	Fe(1)–Mo(1)–C(10)	88.1(2)
C(9)–Mo(1)–C(10)	80.0(4)	Fe(1)–Mo(1)–X*	161	C(1)–Mo(1)–X	115	C(5)–Mo(1)–X	112
C(6)–Mo(1)–X	143	C(9)–Mo(1)–X	114	C(10)–Mo(1)–X	110	Mo(1)–Fe(1)–C(1)	54.7(2)
Mo(1)–Fe(1)–C(6)	59.1(2)	C(1)–Fe(1)–C(6)	81.5(3)	Mo(1)–Fe(1)–C(11)	110.1(3)	Mo(1)–Fe(1)–C(12)	134.8(3)
C(11)–Fe(1)–C(12)	100.8(4)	Mo(1)–Fe(1)–C(13)	116.4(3)	C(11)–Fe(1)–C(13)	94.6(4)	C(12)–Fe(1)–C(13)	92.4(4)
Mo(1)–C(1)–Fe(1)	78.5(3)	Mo(1)–C(1)–C(2)	85.7(4)	Fe(1)–C(1)–C(2)	111.7(5)	Mo(1)–C(1)–C(21)	130.6(5)
Fe(1)–C(1)–C(21)	122.8(5)	C(2)–C(1)–C(21)	117.6(6)	C(1)–C(2)–O(2)	127.7(7)	C(1)–C(2)–C(5)	109.6(6)
C(5)–C(2)–O(2)	122.4(7)	C(3)–C(4)–C(5)	113.8(7)	Mo(1)–C(5)–C(4)	124.7(5)	C(2)–C(5)–C(4)	117.7(6)
C(2)–C(5)–C(6)	113.7(6)	C(4)–C(5)–C(6)	128.2(7)	Mo(1)–C(6)–Fe(1)	75.4(2)	Fe(1)–C(6)–C(5)	116.3(6)
Mo(1)–C(6)–C(7)	130.0(5)	Fe(1)–C(6)–C(7)	123.8(6)	C(5)–C(6)–C(7)	118.4(7)	C(6)–C(7)–C(8)	111.9(8)
Mo(1)–C(9)–O(9)	164.2(8)	Mo(1)–C(10)–O(10)	177.1(7)	Fe(1)–C(11)–O(11)	175.5(9)	Fe(1)–C(12)–O(12)	178.9(9)
Fe(1)–C(13)–O(13)	174.8(9)						

* X Is the centroid of the atoms C(31)—C(35).
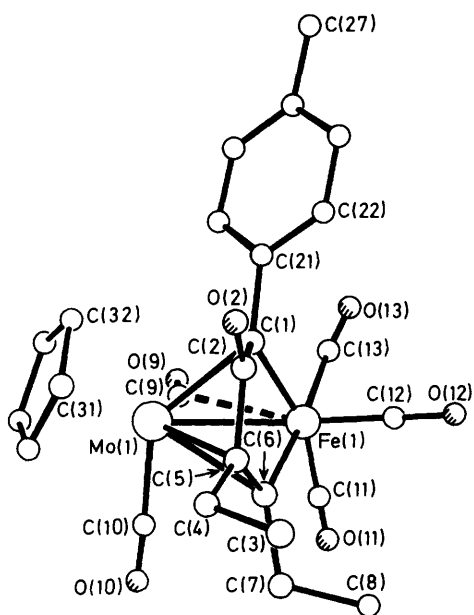
Figure 1. The molecular structure of [MoFe{μ-C(C$_6$H$_4$Me-4)C(O)C-(Et)C(Et)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)] (7c), showing the crystallographic numbering scheme for one of the two independent molecules

C(R^2)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)] [(7a); R^1 = Me, R^2 = Et; (7b); R^1 = Et, R^2 = Me] is produced. The isomers (5c) and (5d) are formed in a ratio of *ca.* 1:1, with (7a) and (7b) produced in a ratio of *ca.* 1:2, based on peak intensities observed in the n.m.r. spectra. It was not possible to separate (5c) from (5d), nor (7a) from (7b). Hence the data for these species given in Tables 1 and 2 relate to the mixtures. The various assignments are in agreement with the structures shown. Moreover, those made for (7a) and (7b) are substantiated by an X-ray crystallographic study on a related complex (7c), described below.

The red isomeric mixture of (5c) and (5d) in CH$_2$Cl$_2$ reacts rapidly with CO to afford a labile yellow product assumed to be

a mixture of the two isomers [MoFe{μ-C(C$_6$H$_4$Me-4)C(R^1)-C(R^2)C(O)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)] (R^1 = Me, R^2 = Et; R^1 = Et, R^2 = Me), acyl species analogous to (6a) or (6b). However, this yellow product [$v_{max.}$(CO) 2 056s, 1 998s(br), 1 830w(br), and 1 589w(br) cm^{-1} (in CH$_2$Cl$_2$)] reverted very readily to the red mixture of (5c) and (5d) in the absence of CO.

Treatment of (1a) with EtC≡CEt in slight excess gave a mixture of [MoFe{μ-C(C$_6$H$_4$Me-4)C(Et)C(Et)}(CO)$_5$(η-C$_5$H$_5$)] (5e) and [MoFe{μ-C(C$_6$H$_4$Me-4)C(O)C(Et)C(Et)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)](7c). Not surprisingly, CH$_2$Cl$_2$ solutions of (5e) react readily with CO gas to afford the acyl complex [MoFe{μ-C(C$_6$H$_4$Me-4)C(Et)C(Et)C(O)}(μ-CO)(CO)$_4$(η-C$_5$-H$_5$)] (6c). The latter in solutions through which nitrogen gas is bubbled reverts to (5e). It may be noted that in the reactions of (5a)—(5e) with CO the product is the one where the acyl group is present between the iron atom and the CR (R = H, Me, or Et) fragment. There was no evidence for the formation of species with a CO group inserted into the Fe–CC$_6$H$_4$Me-4 bond. This is in agreement with results discussed earlier.[7,9]

The structure of the product (7c) was of particular interest since in the bridging organic moiety the C=O group lies between the CEt and CC$_6$H$_4$Me-4 fragments, and is not σ bonded to iron, as in the species (6). This was confirmed by an X-ray diffraction study. The asymmetric unit contains two structurally similar but crystallographically independent molecules, the results for one of which are summarised in Table 3. The structure is shown in Figure 1, from which it is evident that the Mo(1)–Fe(1) bond [2.694(1) Å] is spanned by the C(C$_6$H$_4$Me-4)C(O)C(Et)C(Et) group with C(1) and C(6) bonded to both metal atoms [Mo(1)–C(1) 2.24(1), Mo(1)–C(6) 2.39(1), Fe(1)–C(1) 2.01(1), Fe(1)–C(6) 1.98(1) Å] and C(5) bonded to the molybdenum [Mo(1)–C(5) 2.44(1) Å] but not to the iron. A very similar ligand μ-C(C$_6$H$_4$Me-4)C(O)C(Me)C(Me) has been found previously in the iron–tungsten compound [WFe{μ-C(C$_6$H$_4$Me-4)C(O)C(Me)C(Me)}(CO)$_5$(η-C$_5$Me$_5$)] (8). The latter is a product of the reaction between MeC≡CMe and [WFe(μ-CC$_6$H$_4$Me-4)(CO)$_5$(η-C$_5$Me$_5$)].[5] However, there is a significant difference between the arrangement of the bridging organic fragments in (7c) and (8). In the former the atom C(5) is bonded to the Mo(η-C$_5$H$_5$) fragment, whereas in (8) the comparable carbon atom is attached to the Fe(CO)$_3$ group

Table 4. Selected internuclear separations (Å) and angles (°) for [MoFe{μ-C(C$_6$H$_4$Me-4)C(Me)C[C(O)Me]}(CO)$_5$(η-C$_5$H$_5$)] (5g) with estimated standard deviations in parentheses

Mo–Fe	2.722(1)	Mo–C(1)	2.186(3)	Mo · · · C(3)	2.745	Mo–C(4)	2.183(3)
Mo–C(7)	2.003(4)	Mo–C(8)	2.022(4)	Mo–X*	1.987	Fe–C(1)	2.078(3)
Fe–C(3)	2.127(4)	Fe–C(4)	2.020(4)	Fe–C(9)	1.781(4)	Fe–C(10)	1.777(4)
Fe–C(11)	1.805(4)	C(1)–C(3)	1.427(5)	C(1)–C(21)	1.486(5)	C(3)–C(2)	1.501(5)
C(3)–C(4)	1.427(5)	C(4)–C(5)	1.490(5)	C(5)–O(5)	1.184(5)	C(5)–C(6)	1.496(7)
C(7)–O(7)	1.152(5)	C(8)–O(8)	1.136(5)	C(9)–O(9)	1.141(5)	C(10)–O(10)	1.143(5)
C(11)–O(11)	1.135(5)						
Fe–Mo–C(1)	48.6(1)	Fe–Mo–C(4)	47.1(1)	C(1)–Mo–C(4)	60.8(1)	Fe–Mo–C(7)	80.7(1)
Fe–Mo–C(8)	87.1(1)	C(7)–Mo–C(8)	81.0(2)	Fe–Mo–X*	154.6	C(1)–Mo–X	113.0
C(4)–Mo–X	111.2	C(7)–Mo–X	117.1	C(8)–Mo–X	112.4	Mo–Fe–C(1)	52.1(1)
Mo–Fe–C(3)	67.7(1)	C(1)–Fe–C(3)	39.7(1)	Mo–Fe–C(4)	52.3(1)	C(1)–Fe–C(4)	65.2(1)
C(3)–Fe–C(4)	40.1(1)	Mo–Fe–C(9)	99.5(1)	Mo–Fe–C(10)	154.0(1)	C(9)–Fe–C(10)	95.1(2)
Mo–Fe–C(11)	104.0(1)	C(9)–Fe–C(11)	98.0(2)	C(10)–Fe–C(11)	95.1(2)	Mo–C(1)–Fe	79.3(1)
Mo–C(1)–C(21)	130.5(2)	Fe–C(1)–C(21)	131.8(2)	C(3)–C(1)–C(21)	126.6(3)	Fe–C(3)–C(2)	127.7(3)
C(1)–C(3)–C(2)	129.5(3)	C(1)–C(3)–C(4)	101.5(3)	C(2)–C(3)–C(4)	129.0(3)	Mo–C(4)–Fe	80.6(1)
Mo–C(4)–C(5)	134.2(3)	Fe–C(4)–C(5)	127.1(3)	C(3)–C(4)–C(5)	123.8(3)	C(4)–C(5)–O(5)	121.5(4)
C(4)–C(5)–C(6)	119.8(4)	O(5)–C(5)–C(6)	118.8(4)	Mo–C(7)–O(7)	175.6(3)	Mo–C(8)–O(8)	174.7(3)
Fe–C(9)–O(9)	177.6(4)	Fe–C(10)–O(10)	179.4(4)	Fe–C(11)–O(11)	179.3(4)		

* X Is the centroid of the atoms C(31)–C(35).
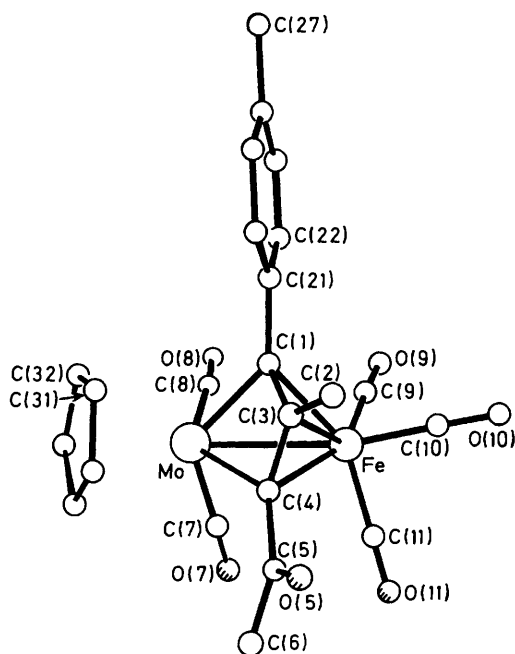
Figure 2. The molecular structure of [MoFe{μ-C(C$_6$H$_4$Me-4)C(Me)-C[C(O)Me]}(CO)$_5$(η-C$_5$H$_5$)] (5g) showing the crystallographic numbering scheme

rather than the W(η-C$_5$Me$_5$) moiety. As a consequence, in (7c) a semi-bridging carbonyl group is present [Mo(1)–C(9)–O(9) 164.2(8)°, Fe(1) · · · C(9) 2.55 Å], and this feature is probably responsible for the band in the i.r. spectrum at 1 886 cm^{-1}, with the band at 1 601 cm^{-1} being attributable to the ketonic group C(2)O(2). In the i.r. spectrum of (8) the absorption for the C=O group occurs at 1 585 cm^{-1}, but in contrast with the spectrum of (7c) there is no CO ligand band at a frequency lower than 1 931 cm^{-1}, in accord with the absence of any carbonyl-bridge bonding.

It seems likely that the complexes (7) are formed via a pathway which involves alkyne attack on a ketenyl ligand

C(C$_6$H$_4$Me-4)C(O) formed by migration of a CO group onto the alkylidyne moiety present in (1a). The overall mechanism would be similar to that discussed earlier to accord for the formation of (8),[5] or products obtained from (1a) and diazomethane.[3a]

In an attempt to obtain the compounds (7) in higher yield, we investigated reactions of (1a) with MeC≡CEt and with EtC≡CEt with the alkyne in very large excess, as described in the Experimental section. Complex mixtures of products were obtained and separated by column chromatography. As in the reactions employing the alkynes in slight excess, the compounds (5c), (5d), (7a), and (7b) were obtained from MeC≡CEt, and (5e) and (7c) from EtC≡CEt. However, in addition unexpected products were isolated. These were characterised as the isomeric pairs of compounds [MoFe{μ-C(C$_6$H$_4$Me-4)C(R^1)C(R^2)}-(CO)$_5$(η-C$_5$H$_5$)] [(5f); R^1 = C(O)Me, R^2 = Me and (5g); R^1 = Me, R^2 = C(O)Me from MeC≡CEt and (5h); R^1 = C(O)Me, R^2 = Et and (5i); R^1 = Et, R^2 = C(O)Me from EtC≡CEt]. Data for (5f)—(5i) are given in Tables 1 and 2. The structures of these species were not, however, recognised until the results of an X-ray diffraction study on (5g) became available. The selected bond distances and angles are given in Table 4, and the structure is shown in Figure 2.

The Mo–Fe bond [2.722(1) Å] is bridged by a C(C$_6$H$_4$-Me-4)C(Me)C{C(O)Me} fragment, with C(1) and C(4) bonded to the molybdenum atom [Mo–C(1) 2.186(3), Mo–C(4) 2.183(3) Å] and all three carbon atoms of the chain attached to the iron atom [Fe–C(1) 2.078(3), Fe–C(3) 2.127(4), Fe–C(4) 2.020(4) Å]. The iron atom carries three terminal CO groups, and the molybdenum two of these ligands and the C$_5$H$_5$ ring. Compound (5g) is thus a member of the growing class of complex in which a three-carbon fragment, formed by the linking of an alkylidyne group with an alkyne, bridges a heteronuclear metal–metal bond. Three other compounds of this type have been the subject of X-ray diffraction studies, viz. [MoFe{μ-C(C$_6$H$_4$Me-4)C(OMe)CH}(CO)$_5$(η-C$_5$H$_5$)],[3a] [WFe{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_5$(η-C$_5$H$_5$)],[6] and [WRh{μ-C(C$_6$H$_4$Me-4)C(Ph)C(Ph)}(CO)$_2$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$)].[8] The core geometries of (5g) and [MoFe{μ-C(C$_6$H$_4$Me-4)C(OMe)CH}(CO)$_5$(η-C$_5$H$_5$)] are very similar as shown by comparing the following molecular parameters for (5g) with those of the latter complex (given in brackets): Mo–Fe 2.722(1) [2.704(1) Å]; C(1)–C(3)–C(4) 101.5(3) [103.4(6)°]. Since the
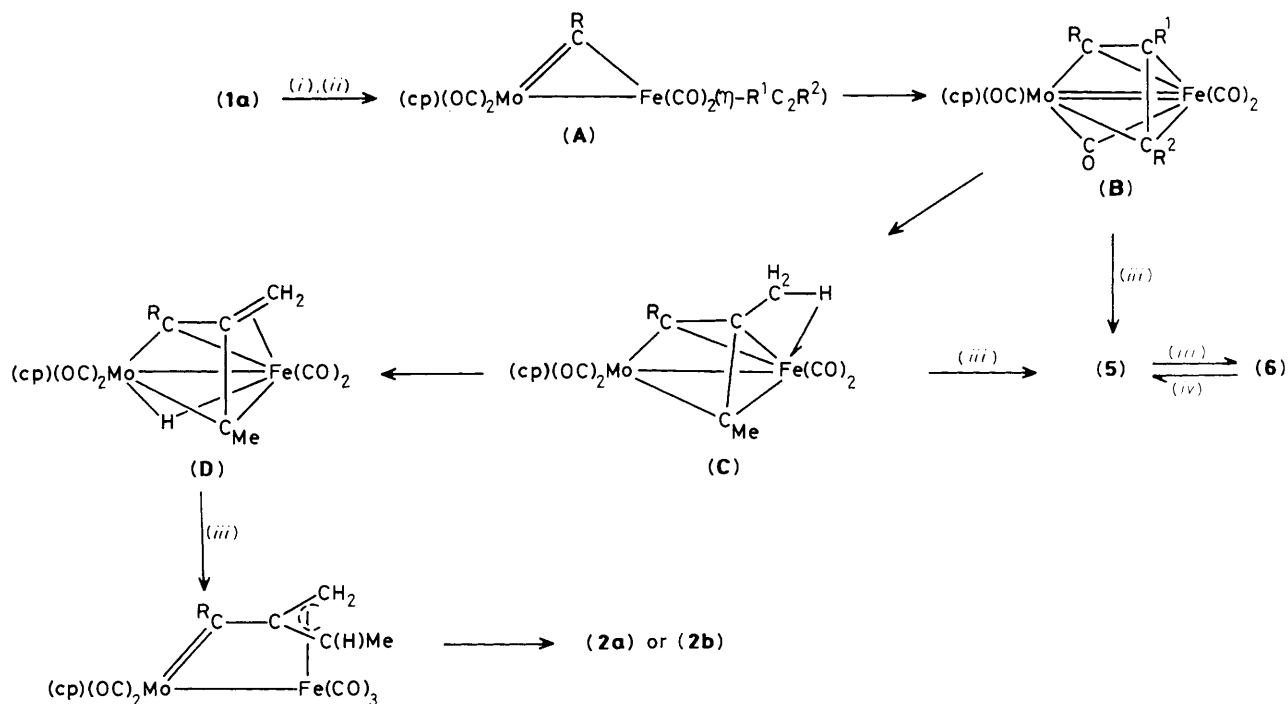
Scheme. cp = η-C_5H_5, R = C_6H_4Me-4, R^1 = R^2 = H, Me, or Et; R^1 = H, R^2 = Et. (i) $-2CO$; (ii) $+R^1C_2R^2$; (iii) $+CO$; (iv) $-CO$

group $Mo(CO)_2(\eta$-$C_5H_5)$ is isolobal with a CR moiety, these two complexes may be regarded as comprising an $Fe(CO)_3$ group co-ordinated by a metallacyclobutadiene fragment.[10,11]

The source of the C(O)Me groups in compounds (5f)—(5i) was of interest, but was eventually traced to small amounts of the alkynes $MeC\equiv CC(O)Me$ and $EtC\equiv CC(O)Me$ present as impurities in commercial samples of $MeC\equiv CEt$ and $EtC\equiv CEt$, respectively. Hence when large ratios of the alkynes $RC\equiv CEt$ (R = Me or Et) are employed in reactions with (1a), a sufficient amount of the impurity $RC\equiv CC(O)Me$ (R = Me or Et) is present to afford the observed species with a C(O)Me substituent in the bridging ligand. Dickson and co-workers[12] have obtained a similar result in studies on the reaction between $[Rh_2(\mu$-$CF_3C_2CF_3)(\mu$-$CO)(\eta$-$C_5H_5)_2]$ and $MeC\equiv CEt$. One product of this reaction is the complex $[Rh_2\{\mu$-$C(CF_3)$-$C(CF_3)C(Me)C[C(O)Me]\}(\eta$-$C_5H_5)_2]$. The impurity $MeC\equiv C$-$C(O)Me$ in pent-2-yne is the source of this product.[13]

The reactions between (1a) and the alkynes $RC\equiv CEt$ (R = H, Me, or Et) differ from those with $MeC\equiv CMe$ in that none of the products described herein involves hydrogen migration from a Me or Et substituent on the alkyne. Evidently $MeC\equiv CMe$ is unique in enabling the reactions to proceed along a different pathway. We have suggested[1] that compound (2) might form from (1a) and but-2-yne via the steps shown in the Scheme. In the unsaturated species (B) (R^1 = R^2 = Me) the methyl group is activated via the intermediate (C) with the agostic C–H$\rightarrow$Fe interaction. In this manner a metal-assisted hydrogen shift between carbon centres becomes possible leading to one or other of the two isomers of (2). Evidently with the other alkynes the preferred pathway leads to the compounds (5), and this could occur via CO addition to either (B) or (C). If these ideas are valid it would suggest that the hydrogen atoms of the methyl group attached to the central carbon of the μ-C_3 group in (C) are more active than those in a similar intermediate involving the alkynes $RC\equiv CEt$ (R = H, Me, or Et). Hence under the condition studied with $MeC\equiv CMe$ the steps (B) $\longrightarrow$ (C) $\longrightarrow$ (D) are faster than CO addition to yield $[MoFe\{\mu C(C_6H_4Me$-

4)$C(Me)C(Me)\}(CO)_5(\eta$-$C_5H_5)]$. As mentioned earlier, formation of the complexes (7) can be rationalised in terms of pathways described previously to account for the synthesis of (8).[5]

Experimental

Details of experimental procedures used, and the instrumentation employed, are given in the preceding paper.[1] The compound $[MoFe(\mu$-CC_6H_4Me-4)$(CO)_6(\eta$-$C_5H_5)]$ was prepared as reported earlier.[3d] Light petroleum refers to that fraction of b.p. 40—60 °C. Analytical and other data for new compounds are given in Table 1.

Reactions of $[MoFe(\mu$-CC_6H_4Me-4)$(CO)_6(\eta$-$C_5H_5)]$ *with Alkynes.*—(i) *Ethyne.* A stream of $HC\equiv CH$ was bubbled through a light petroleum (20 cm³) solution of compound (1a) (0.15 g, 0.30 mmol) at room temperature for 1 h. Solvent was removed *in vacuo,* and the residue was redissolved in thf–light petroleum (10 cm³, 1:4) and chromatographed on a Florisil column (2 × 30 cm) at −30 °C. Elution with the same solvent mixture recovered a red fraction which after removal of solvent *in vacuo* gave red *microcrystals* of $[MoFe\{\mu$-$C(C_6H_4Me$-4)CHCH$\}$-$(CO)_5(\eta$-$C_5H_5)]$ (5a) (0.03 g). Further elution of the column with thf–light petroleum (3:2) gave a yellow eluate, which after removal of solvent *in vacuo* yielded yellow-orange *microcrystals* of $[MoFe\{\mu$-$C(C_6H_4Me$-4)CHCHC(O)\}(\mu$-$CO)(CO)_4(\eta$-$C_5H_5)]$ (6a) (0.12 g).

(ii) *But-1-yne.* A light petroleum (10 cm³) solution of compound (1a) (0.15 g, 0.30 mmol) was treated with a stream of $HC\equiv CEt$ at room temperature for 15 min. Solvent was removed *in vacuo,* and the yellow-orange residue was dissolved in CH_2Cl_2–light petroleum (10 cm³, 2:3) and chromatographed on a Florisil column. Elution with CH_2Cl_2–light petroleum (1:4) gave a red eluate, which after removal of solvent *in vacuo* yielded red *microcrystals* of $[MoFe\{\mu$-$C(C_6H_4Me$-4)CHC(Et)\}$-$(CO)_5(\eta$-$C_5H_5)]$ (5b) (0.05 g). Further elution with thf–light

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for complex (7c) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Mo(1)	1 453(1)	2 878(1)	−9(1)	Mo(2)	5 931(1)	7 062(1)	2 113(1)
Fe(1)	2 902(1)	3 203(1)	−29(1)	Fe(2)	4 497(1)	6 772(1)	2 282(1)
C(1)	2 160(4)	4 458(6)	95(4)	C(51)	5 207(3)	5 479(6)	2 060(3)
C(2)	1 895(4)	4 481(7)	706(3)	C(52)	5 371(4)	5 444(6)	1 439(3)
O(2)	1 604(3)	5 319(5)	973(3)	O(52)	5 626(3)	4 629(4)	1 165(2)
C(3)	1 995(5)	3 270(11)	2 070(5)	C(53)	5 105(7)	6 622(12)	84(6)
C(4)	1 542(4)	3 056(7)	1 529(3)	C(54)	5 619(5)	6 887(8)	591(4)
C(5)	1 940(4)	3 277(7)	965(3)	C(55)	5 306(4)	6 648(7)	1 193(4)
C(6)	2 416(4)	2 545(7)	673(3)	C(56)	4 880(4)	7 409(7)	1 531(4)
C(7)	2 655(5)	1 420(7)	977(4)	C(57)	4 617(5)	8 549(8)	1 250(5)
C(8)	3 359(6)	1 574(11)	1 306(5)	C(58)	3 870(5)	8 382(10)	970(6)
C(9)	1 945(5)	2 735(9)	−798(4)	C(59)	5 590(5)	7 217(9)	2 923(4)
O(9)	2 060(4)	2 623(8)	−1 280(3)	O(59)	5 540(4)	7 414(7)	3 427(3)
C(10)	1 640(4)	1 146(7)	−26(5)	C(60)	5 748(4)	8 803(7)	2 129(4)
O(10)	1 719(4)	166(5)	−48(4)	O(60)	5 655(4)	9 769(5)	2 182(4)
C(11)	3 357(4)	1 852(8)	−195(4)	C(61)	4 092(4)	8 120(7)	2 506(4)
O(11)	3 636(4)	1 011(7)	−338(4)	O(61)	3 806(4)	8 985(6)	2 634(4)
C(12)	3 538(4)	3 854(8)	450(4)	C(62)	3 780(4)	6 101(8)	1 917(4)
O(12)	3 944(3)	4 278(7)	746(4)	O(62)	3 319(3)	5 604(7)	1 668(4)
C(13)	3 260(5)	3 962(8)	−653(4)	C(63)	4 264(4)	6 085(8)	2 975(4)
O(13)	3 519(4)	4 487(7)	−1 018(3)	O(63)	4 092(4)	5 676(6)	3 403(3)
C(22)	2 534(3)	6 540(4)	3(2)	C(72)	4 823(3)	3 425(5)	2 202(2)
C(23)	2 625	7 556	−324	C(73)	4 794	2 397	2 527
C(24)	2 350	7 622	−893	C(74)	5 162	2 316	3 060
C(25)	1 983	6 672	−1 134	C(75)	5 561	3 264	3 268
C(26)	1 893	5 656	−806	C(76)	5 590	4 292	2 943
C(21)	2 168	5 590	−238	C(71)	5 221	4 373	2 410
C(27)	2 456(7)	8 730(10)	−1 252(6)	C(77)	5 099(6)	1 192(10)	3 432(5)
C(31)	406(3)	3 591(6)	433(2)	C(81)	6 911(3)	6 370(6)	1 571(2)
C(32)	507	4 230	−94	C(82)	6 880	5 695	2 092
C(33)	457	3 439	−570	C(83)	6 999	6 452	2 575
C(34)	325	2 311	−339	C(84)	7 104	7 595	2 352
C(35)	293	2 405	281	C(85)	7 050	7 544	1 732

petroleum (3:2) afforded a yellow fraction from which solvent was removed *in vacuo* to give yellow-orange *microcrystals* of [MoFe{μ-C(C₆H₄Me-4)CHC(Et)C(O)}(μ-CO)(CO)₄(η-C₅-H₅)] (6b) (0.10 g).

Treatment of compound (1a) (0.15 g, 0.30 mmol) in light petroleum (10 cm³) at −40 °C with an excess of HC≡CEt, followed by removal of solvent *in vacuo*, gave a yellow-orange residue. The latter was dissolved in CH₂Cl₂–light petroleum (20 cm³, 3:1), and the mixture was filtered through a Celite pad (2 × 3 cm). After removal of solvent *in vacuo*, compound (6b) was obtained (0.15 g) in essentially quantitative yield.

A stream of nitrogen gas was bubbled (1.5 h) through a sample of compound (6b) (0.11 g, 0.20 mmol) in CH₂Cl₂ (10 cm³) affording complex (5b) in quantitative yield. Treatment of CH₂Cl₂ solutions of the latter with CO results in quantitative conversion into (6b).

(*iii*) *Pent-2-yne.* (*a*) A mixture of compound (1a) (0.15 g, 0.30 mmol) and MeC≡CEt (0.40 mmol) in light petroleum (20 cm³) was stirred at room temperature for 2 d. Solvent was removed *in vacuo*, the residue was dissolved in CH₂Cl₂–light petroleum (7 cm³, 3:2), and the mixture was chromatographed on a Florisil column (2 × 40 cm) at 0 °C. Elution of the column with the same solvent mixture gave a red eluate. Removal of solvent *in vacuo* yielded an isomeric mixture (1:1) of red *microcrystals* of [MoFe{μ-C(C₆H₄Me-4)C(R¹)C(R²)}(CO)₅(η-C₅H₅)] [(5c); R¹ = Et, R² = Me; (5d); R¹ = Me, R² = Et] (0.08 g). Further elution of the column with thf–light petroleum (1:4) afforded a yellow eluate. Removal of solvent *in vacuo* gave an isomeric mixture (1:2) of yellow *microcrystals* of [MoFe{μ-C(C₆H₄-Me-4)C(O)C(R¹)C(R²)}(μ-CO)(CO)₄(η-C₅H₅)] [(7a); R¹ = Me, R² = Et; (7b); R¹ = Et, R² = Me].

(*b*) A mixture of compound (1a) (0.15 g, 0.30 mmol) and MeC≡CEt (2.0 cm³, 21 mmol) in light petroleum (20 cm³) was stirred at 10 °C for 20 h. Solvent and excess alkyne were removed *in vacuo*, the residue was dissolved in CH₂Cl₂ (10 cm³), and the solution was adsorbed on Florisil (*ca.* 2 g). This material was transferred to the top of a Florisil chromatography column (2 × 40 cm) maintained at −20 °C. Elution with CH₂Cl₂–light petroleum (1:4) gave in the first eluate traces of the isomers (5c) and (5d), identified by i.r. spectroscopy. Further elution with CH₂Cl₂–light petroleum (3:2) afforded, after removal of solvent *in vacuo*, red *microcrystals* of [MoFe{μ-C(C₆H₄Me-4)C[C(O)-Me]C(Me)}(CO)₅(η-C₅H₅)] (5f) (0.05 g). Elution with CH₂Cl₂–light petroleum (4:1) gave red *microcrystals* of [MoFe{μ-C(C₆H₄Me-4)C(Me)C[C(O)Me]}(CO)₅(η-C₅H₅)] (0.03 g), after removal of solvent. Final elution with thf–light petroleum (1:4) gave an eluate which contained a 1:2 mixture of (7a) and (7b) (0.03 g).

(*iv*) *Hex-3-yne.* (*a*) Compound (1a) (0.15 g, 0.30 mmol) and EtC≡CEt (0.40 mmol) were stirred together in light petroleum (20 cm³) for 2 d. Solvent was removed *in vacuo*, the residue was dissolved in CH₂Cl₂–light petroleum (3:2), and the mixture was chromatographed at 0 °C. Elution with the same mixture of solvents gave a red fraction, which after solvent removal afforded red *microcrystals* of [MoFe{μ-C(C₆H₄Me-4)C(Et)-C(Et)}(CO)₅(η-C₅H₅)] (5e) (0.08 g). Further elution of the column with thf–light petroleum (1:4) afforded, after removal of solvent *in vacuo*, yellow *microcrystals* of [MoFe{μ-C(C₆H₄-Me-4)C(O)C(Et)C(Et)}(μ-CO)(CO)₄(η-C₅H₅)] (7c) (0.05 g).

A CH₂Cl₂ (10 cm³) solution of compound (5e) was treated with a stream of CO gas for 20 min. Solvent was removed *in vacuo*, and the residue was washed with cold (*ca.* −30 °C) light

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for complex (**5g**) with estimated standard deviations in parentheses

Atom	x	y	z
Mo	2 533(1)	8 289(1)	6 000(1)
Fe	868(1)	7 110(1)	6 307(1)
C(1)	3 055(3)	7 196(2)	6 351(1)
C(2)	2 761(4)	6 991(3)	7 328(2)
C(3)	2 488(4)	7 369(2)	6 833(1)
C(4)	1 582(4)	7 998(2)	6 719(1)
C(5)	782(4)	8 438(2)	7 104(1)
O(5)	875(5)	8 290(2)	7 536(1)
C(6)	− 175(7)	9 074(3)	6 946(2)
C(7)	674(4)	8 648(2)	5 728(1)
O(7)	− 349(3)	8 877(2)	5 548(1)
C(8)	2 598(4)	7 772(2)	5 323(1)
O(8)	2 658(4)	7 535(2)	4 928(1)
C(9)	827(4)	6 562(2)	5 745(2)
O(9)	754(4)	6 205(2)	5 389(1)
C(10)	418(4)	6 332(2)	6 706(2)
O(10)	131(3)	5 828(2)	6 958(1)
C(11)	− 902(4)	7 492(2)	6 276(2)
O(11)	− 2 014(3)	7 734(2)	6 261(2)
C(21)	4 199(4)	6 640(2)	6 238(1)
C(22)	4 328(4)	6 268(2)	5 783(1)
C(23)	5 446(4)	5 783(2)	5 684(2)
C(24)	6 501(4)	5 653(2)	6 035(2)
C(25)	6 378(4)	6 018(3)	6 484(2)
C(26)	5 254(4)	6 508(2)	6 589(2)
C(27)	7 725(4)	5 128(3)	5 921(2)
C(31)	4 743(4)	8 643(2)	6 327(2)
C(32)	4 762(4)	8 705(2)	5 802(2)
C(33)	3 804(5)	9 281(2)	5 662(2)
C(34)	3 156(5)	9 554(2)	6 099(2)
C(35)	3 756(4)	9 162(2)	6 511(2)

petroleum (3 × 5 cm³) to afford yellow *crystals* of [MoFe{μ-C(C₆H₄Me-4)C(Et)C(Et)C(O)}(μ-CO)(CO)₄(η-C₅H₅)] (**6c**). Solutions of this product in CH₂Cl₂ under nitrogen rapidly regenerate (**5e**).

(*b*) A mixture of compound (**1a**) (0.15 g, 0.30 mmol) and EtC≡CEt (2.0 cm³, 18 mmol) in light petroleum (20 cm³) at 10 °C was stirred for 24 h. Solvent and excess alkyne were removed *in vacuo*, and the residue in CH₂Cl₂ (10 cm³) was adsorbed on Florisil (*ca.* 2 g). The latter was transferred to the top of a chromatography column (2 × 40 cm) of the same material, maintained at − 20 °C. Elution with CH₂Cl₂–light petroleum (1:4) gave a red fraction from which solvent was removed *in vacuo* to give red *microcrystals* of (**5e**) (0.02 g). Further elution with CH₂Cl₂–light petroleum (3:2), followed by removal of solvent *in vacuo*, gave red *microcrystals* of [MoFe{μ-C(C₆H₄Me-4)C[C(O)Me]C(Et)}(CO)₅(η-C₅H₅)] (**5h**) (0.04 g). Elution with CH₂Cl₂–light petroleum (4:1) gave a fraction which after solvent removal afforded red *microcrystals* of [MoFe{μ-C(C₆H₄Me-4)C(Et)C[C(O)Me]}(CO)₅-(η-C₅H₅)] (**5i**) (0.06 g). A final elution of the column with thf–light petroleum led to the recovery of compound (**7c**) (0.04 g).

Crystal Structure Determinations.—(*a*) [MoFe{μ-C(C₆H₄-Me-4)C(O)C(Et)C(Et)}(μ-CO)(CO)₄(η-C₅H₅)] (**7c**). Crystals of the complex grow on cooling from CH₂Cl₂–light petroleum–Et₂O (1:1:1) as orange plates. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.18 × 0.30 × 0.30 mm on a Nicolet *P*3*m* diffractometer. Of the 5 705 unique data collected (ω—2θ scans, 2θ ≤ 60°, weak data with 40 ≤ 2θ ≤ 60° being skipped on the basis of a preliminary prescan), 4 300 had $I \geqslant 2.0\sigma(I)$ and only these were used in structure solution and refinement. The data were corrected for

X-ray absorption (by an empirical method based on azimuthal scan data[14]), Lorentz and polarisation effects.

Crystal data. C₂₅H₂₂FeMoO₆, $M = 570.21$, orthorhombic, $a = 18.407(3)$, $b = 11.480(2)$, $c = 22.813(4)$ Å, $U = 4\,821(1)$ Å³, $Z = 8$, $D_c = 1.57$ g cm⁻³, $F(000) = 2\,303.4$, space group *Pna*2₁ (no. 33), Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å), $\mu(\text{Mo-}K_\alpha) = 11.45$ cm⁻¹.

The structure was solved by direct methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. There are two chemically identical molecules in the asymmetric unit, being related approximately by a non-crystallographic centre of inversion with fractional co-ordinates *ca.* 0.369, 0.498, and 0.109. All non-hydrogen atoms were refined with anisotropic thermal parameters, all cyclopentadienyl and phenyl rings being constrained to ideal geometries and refined as rigid groups. All hydrogen atoms were included at calculated positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for the methyl hydrogen atoms and fixed isotropic thermal parameters (*ca.* 1.2$U_{\text{equiv.}}$ of the parent carbon atoms) for all other hydrogen atoms. Refinement by blocked-cascade least squares led to $R = 0.045$ ($R' = 0.042$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,6|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.48 or < −0.59 e Å⁻³. As the space group (*Pna*2₁) is chiral an enantiomeric refinement of the type suggested by Rogers[15] was carried out, verifying that the chirality of the initial solution was correct.

(*b*) [MoFe{μ-C(C₆H₄Me-4)C(Me)C[C(O)Me]}(CO)₅(η-C₅H₅)] (**5g**). Crystals were grown as large red blocks from CH₂Cl₂–Et₂O–light petroleum (1:1:2). Diffracted intensities were collected as for (**7c**) from a crystal of dimensions *ca.* 0.50 × 0.45 × 0.35 mm. Of the 3 879 unique data collected (ω–2θ scans, 2θ ≤ 50°), 2 969 had $I \geqslant 2.0\sigma(I)$ and only these were used in structure solution and refinement, after corrections as for (**7c**).

Crystal data. C₂₃H₁₆FeMoO₆, $M = 542.2$, orthorhombic, $a = 9.461(2), b = 17.483(4), c = 26.710(6)$ Å, $U = 4\,418(2)$ Å³, $Z = 8$, $D_c = 1.63$ g cm⁻³, $F(000) = 2\,175.4$, space group *Pbca* (no. 61), $\mu(\text{Mo-}K_\alpha) = 12.5$ cm⁻¹.

The structure was solved and all non-hydrogen atoms located by conventional heavy-atom and difference Fourier methods. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included at calculated positions as for (**7c**). Refinement by blocked-cascade least squares led to $R = 0.035$ ($R' = 0.032$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,1|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.38 or < −0.39 e Å⁻³. All calculations were performed on a Data General Eclipse computer with the SHELXTL system of programs.[14] Scattering factors with corrections for anomalous dispersion were taken from ref. 16. The atom co-ordinates for (**7c**) and (**5g**) are given in Tables 5 and 6 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

References

1 Part 77, M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, preceding paper.
2 E. Delgado, M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 207.

3 (a) M. E. Garcia, N. H. Tran-Huy, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.,* 1987, 2201; (b) P. G. Byrne, M. E. Garcia, N. H. Tran-Huy, J. C. Jeffery, and F. G. A. Stone, *ibid.,* p. 1243; (c) P. G. Byrne, M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *ibid.,* p. 1215; (d) M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *ibid.,* p. 1209.

4 P. G. Byrne, M. E. Garcia, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.,* 1987, 53.

5 J. Hein, J. C. Jeffery, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.,* 1987, 2211.

6 J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.,* 1984, 1383.

7 I. J. Hart and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.,* 1988, 1899.

8 M. Green, J. A. K. Howard, S. J. Porter, F. G. A. Stone, and D. C. Tyler, *J. Chem. Soc., Dalton Trans.,* 1984, 2553.

9 I. J. Hart, J. C. Jeffery, M. J. Grosse-Ophoff, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.,* 1988, 1867.

10 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.,* 1982, **94**, 725.

11 F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.,* 1984, **23**, 89.

12 C. W. Baimbridge, R. S. Dickson, G. D. Fallon, I. Grayson, R. J. Nesbit, and J. Weigold, *Aust. J. Chem.,* 1986, **39**, 1187.

13 R. S. Dickson, personal communication.

14 G. M. Sheldrick, SHELXTL programs for use with the Nicolet X-ray system, Revision 5.1, 1986.

15 D. Rogers, *Acta Crystallogr., Sect. A,* 1981, **37**, 734.

16 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.