Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 64.[1] Addition of Methylene Groups to Iron–Molybdenum Complexes; Crystal Structures of $[FeMo(\mu-CH_2)\{\mu-\sigma:\eta-C(C_6H_4Me-4)=CH_2\}(CO)_5(\eta-C_5H_5)]$ and $[FeMo\{\mu-C(C_6H_4Me-4)C(OMe)C(H)\}(CO)_5(\eta-C_5H_5)]$ *

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The reaction between $[FeMo(\mu-CC_6H_4Me-4)(CO)_6(\eta-C_5H_5)]$ and CH_2N_2 in diethyl ether at ambient temperatures affords the complex $[FeMo(\mu-CH_2)\{\mu-\sigma:\eta-C(C_6H_4Me-4)=CH_2\}(CO)_5(\eta-C_5H_5)]$, whereas if the reaction is carried out at *ca.* −40 °C the product is $[FeMo\{\mu-C(C_6H_4Me-4)-C(OMe)C(H)\}(CO)_5(\eta-C_5H_5)]$. Both species correspond to the addition of two CH_2 fragments to the precursor, and their molecular structures have been established by single-crystal *X*-ray diffraction studies. In $[FeMo(\mu-CH_2)\{\mu-\sigma:\eta-C(C_6H_4Me-4)=CH_2\}(CO)_5(\eta-C_5H_5)]$ the Fe–Mo bond [2.717(1) Å] is asymmetrically bridged by the CH_2 group [μ-C–Fe 2.016(3), μ-C–Mo 2.239(3) Å], and the $C(C_6H_4Me-4)=CH_2$ fragment is σ-bonded to molybdenum [C–Mo 2.209(2) Å] and η-co-ordinated to iron [C–Fe 2.055(2) and 2.127(3) Å]. The molecule of $[FeMo\{\mu-C(C_6H_4Me-4)-C(OMe)C(H)\}(CO)_5(\eta-C_5H_5)]$ has an Fe–Mo bond [2.704(1) Å] transversely bridged by a $C(C_6H_4Me-4)C(OMe)C(H)$ fragment, with the latter η^3-co-ordinated to the iron and with the two end carbons of the C_3 chain σ-bonded to the molybdenum. Reactions between the complexes $[FeMo(\mu-CC_6H_4Me-4)(CO)_n(PMe_3)(\eta-C_5H_5)]$ (*n* = 4 and 5) and CH_2N_2 have also been investigated, and the compounds $[FeMo(\mu-CH_2)\{\mu-\sigma:\eta-C(C_6H_4Me-4)=CH_2\}(CO)_4(PMe_3)(\eta-C_5H_5)]$ and $[FeMo\{\mu-C(C_6H_4Me-4)C(OH)C(H)\}(CO)_4(PMe_3)(\eta-C_5H_5)]$ thereby obtained. The ^1H and $^{13}C-\{^1H\}$ n.m.r. spectra of the new compounds are reported and discussed, and pathways proposed for their formation.

Currently there is considerable interest in the synthesis and reactivity of di- and poly-nuclear metal complexes in which the metal–metal bonds are bridged by CH_2 groups.[1–5] Reactions of these species which result in the formation of C–H or C–C bonds are receiving particular attention.[6–8] These studies have in part been prompted by the probable involvement of methylene groups in carbon monoxide reduction on metal surfaces,[9–12] and in the likely participation of metal-bound alkylidene groups in olefin metathesis[13] and other catalytic reactions.

As a consequence of the interest in this area, many compounds have been characterised having one or more CH_2 groups bridging homonuclear bonds of the type Mn–Mn,[14] Fe–Fe,[6,15–17] Ru–Ru,[8,18,19] Os–Os,[20–23] Co–Co,[24–27] Rh–Rh,[28–31] or Ir–Ir.[32] Species in which this ligand bridges a heteronuclear metal–metal bond are fewer in number, but already include Co–Rh,[26–33] Co–Ir,[34] Rh–Ir,[35] Fe–Ir,[36] Fe–Ru,[37] and Fe–W[38] compounds.

We have recently prepared the dimetal complex $[FeMo(\mu-CC_6H_4Me-4)(CO)_6(\eta-C_5H_5)]$ (**1a**),[39] and have shown that it is very reactive towards a variety of nucleophilic compounds. The reactivity of (**1a**) may well be associated with a ready loss of CO to give the unsaturated 32-valence-electron species $[FeMo(\mu-CC_6H_4Me-4)(CO)_5(\eta-C_5H_5)]$ (**2a**) as an intermediate. Although the latter complex has not as yet been isolated, treatment of (**1a**) with PMe_3 affords $[FeMo(\mu-CC_6H_4Me-4)(CO)_5(PMe_3)(\eta-C_5H_5)]$ (**1b**) which readily releases CO to give $[FeMo(\mu-CC_6H_4Me-4)(CO)_4(PMe_3)(\eta-C_5H_5)]$ (**2b**), a stable derivative of (**2a**). Herein we describe reactions of compounds (**1a**), (**1b**), and (**2b**) with diazomethane. This reagent was employed in the expectation of obtaining products in which either transfer of a methylene group to the tolylmethylidyne ligand would occur,[40] or μ-CH_2 complexes would be formed. A preliminary account of the results has been given.[41]

Results and Discussion

In the studies reported herein it became apparent that the reaction between (**1a**) and CH_2N_2 afforded one or other of two products, depending critically on the temperature at which the reactants were mixed. Moreover, these two compounds were produced in very high yield, indeed, essentially quantitatively if due allowance is made for loss during the experimental work-up procedures.

Treatment of compound (**1a**) in diethyl ether at room temperature with an excess of CH_2N_2 afforded the orange-red crystalline compound $[FeMo(\mu-CH_2)\{\mu-\sigma:\eta-C(C_6H_4Me-4)=CH_2\}(CO)_5(\eta-C_5H_5)]$ (**3a**), data for which are given in Tables 1 and 2. The structure of the complex was unambiguously established by an *X*-ray diffraction study, the results of which are summarised in Table 3 with the molecule shown in Figure 1.

The Fe–Mo bond [2.717(1) Å] is shorter than that in (**1a**) [2.823(1) Å][39] and is bridged both by CH_2 and $C(C_6H_4Me-4)=CH_2$ groups. The latter is σ-bonded to the molybdenum [C(1)–Mo 2.209(2) Å] and η-bonded to the iron atom [C(1)–Fe 2.055(2), C(2)–Fe 2.127(3) Å]. This bridging ligand has been identified previously by *X*-ray diffraction in the compounds $[TiW\{\mu-C(C_6H_4Me-4)=CH_2\}(\mu-CO)(CO)(\eta-C_5H_5)_3]$ and $[PtW\{\mu-C(C_6H_4Me-4)=CH_2\}(CO)_2(PMe_3)_2(\eta-C_5H_5)]$.[40] The CH_2 group in (**3a**) asymmetrically bridges the metal–metal bond [Fe–C(3) 2.016(3), Mo–C(3) 2.239(3) Å]. The iron atom is

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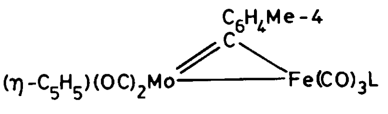
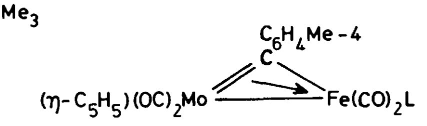
* 1,1,1,2,2-Pentacarbonyl-2-(η-cyclopentadienyl)-μ-methylene-μ-[1-(*p*-tolyl)ethynyl-$C^1(Fe^1,Mo^2),C^2(Fe^1)$]ironmolybdenum(*Fe–Mo*) and 1,1,1,2,2-pentacarbonyl-2-(η-cyclopentadienyl)-μ-[2-methoxy-1-(*p*-tolyl)propan-2-yl-1,3-diylidene-$C^1(Fe^1,Mo^2),C^2(Fe^1),C^3(Fe^1,Mo^2)$]-ironmolybdenum(*Fe–Mo*) respectively.

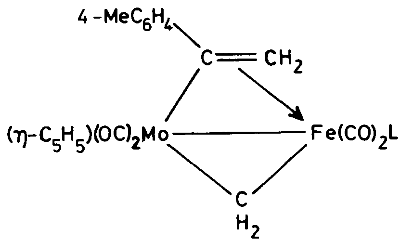
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.



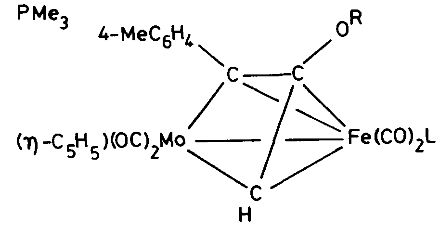
	L
(1a)	CO
(1b)	PMe_3



	L
(2a)	CO
(2b)	PMe_3



	L
(3a)	CO
(3b)	PMe_3



	R	L
(4a)	Me	CO
(4b)	H	PMe_3

ligated by three terminally bound carbonyl groups, and the molybdenum by two such groups and the cyclopentadienyl moiety. The dihedral angle between the planes defined by the atoms C(1)C(2)Fe and C(1)MoFe is 126°, whilst the related angle between the planes MoC(1)Fe and MoC(3)Fe is 123°.

Having established the molecular structure of (**3a**), the ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra (Table 2) may be readily interpreted. In the ^1H n.m.r. spectrum resonances for the μ-CH_2 group occur as doublets [J(HH) 6 Hz] at δ 3.44 and 4.78. The geminal CH_2 group gives singlet signals at δ 1.44 and 3.20, the absence of ^1H–^1H coupling being characteristic for such a group.[42] Compound (**3a**) was also prepared using CD_2N_2 thereby affording [$FeMo(\mu$-$CD_2)\{\mu$-σ:η-$C(C_6H_4Me$-$4)$=$CD_2\}(CO)_5(\eta$-$C_5H_5)$]. Examination of the ^2H n.m.r. spectrum revealed singlet signals at δ 1.42 and 3.20 (=CD_2), and at 3.44 and 4.81 (μ-CD_2). In the ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**3a**) the resonance for the μ-CH_2 ligand occurs at δ 107.4 p.p.m., with signals for the two metal-ligating carbon nuclei of the vinyl group seen at δ 209.2 (μ-CC_6H_4Me-4) and 64.5 p.p.m. [μ-$C(C_6H_4Me$-$4)$=CH_2]. The CO ligands attached to the molybdenum give rise to the expected two resonances (δ 229.4 and 227.7 p.p.m.) but the $Fe(CO)_3$ group shows only one peak

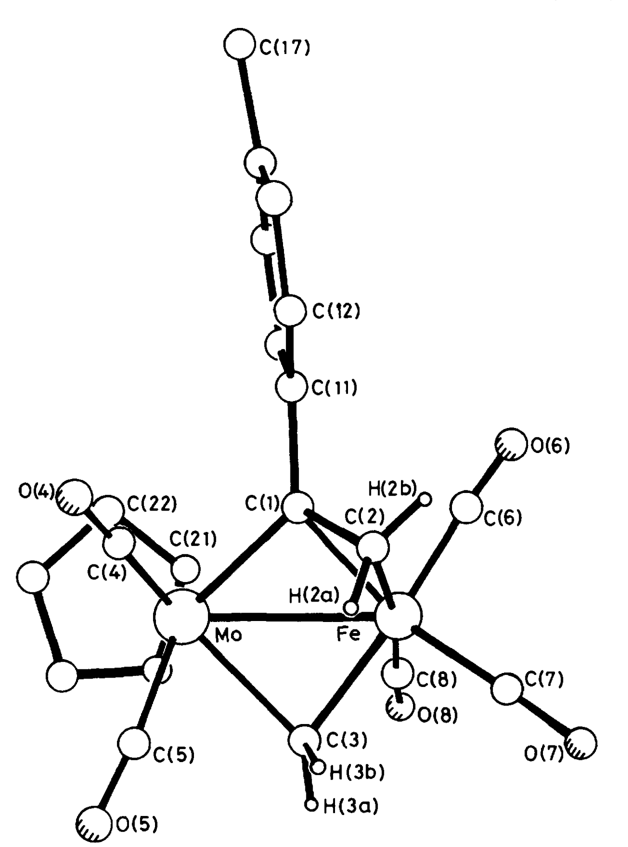


Figure 1. The molecular structure of [$FeMo(\mu$-$CH_2)\{\mu$-σ:η-$C(C_6H_4$-Me-$4)$=$CH_2\}(CO)_5(\eta$-$C_5H_5)$] (**3a**), showing the crystallographic numbering

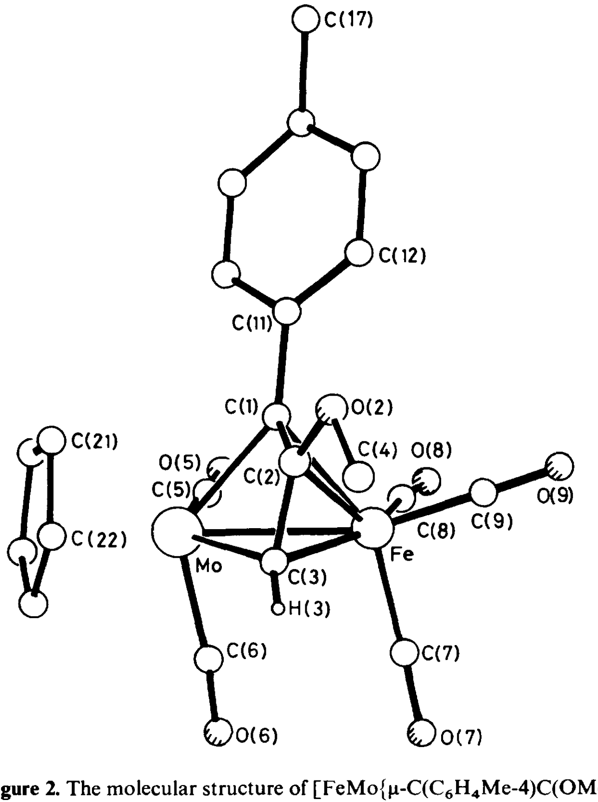


Figure 2. The molecular structure of [$FeMo\{\mu$-$C(C_6H_4Me$-$4)C(OMe)$-$C(H)\}(CO)_5(\eta$-$C_5H_5)$] (**4a**), showing the crystallographic numbering

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

Compound[b,c]	Yield (%)	$\nu_{max.}$(CO)/cm^{-1}	Analysis (%) C	Analysis (%) H
(**3a**) $[FeMo(\mu\text{-}CH_2)\{\mu\text{-}\sigma{:}\eta\text{-}C(R)=CH_2\}(CO)_5(\eta\text{-}C_5H_5)]$	87	[d] 2 049vs, 1 997s, 1 971m, 1 956vs, 1 890m br	49.0 (49.2)	3.3 (3.3)
(**3b**) $[FeMo(\mu\text{-}CH_2)\{\mu\text{-}\sigma{:}\eta\text{-}C(R)=CH_2\}(CO)_4(PMe_3)(\eta\text{-}C_5H_5)]$	79	[e] 1 981m, 1 935vs, 1 921s, 1 863m	48.8 (49.3)	4.7 (4.9)
(**4a**) $[FeMo\{\mu\text{-}C(R)C(OMe)C(H)\}(CO)_5(\eta\text{-}C_5H_5)]$	90	[f] 2 047s, 1 987s br, 1 958vw, 1 931vw	48.1 (48.9)	3.1 (3.1)
(**4b**) $[FeMo\{\mu\text{-}C(R)C(OH)C(H)\}(CO)_4(PMe_3)(\eta\text{-}C_5H_5)]$	73	[f,g] 1 993vs, 1 939m, 1 925s	47.2 (48.0)	4.2 (4.2)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] Complexes are orange or orange-red in colour. [d] In light petroleum. [e] In CH_2Cl_2. [f] In Et_2O. [g] Band at 3 522 cm^{-1} assigned to OH group.

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

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(**3a**)	1.44 (s, 1 H, $C=CH_2$), 2.35 (s, 3 H, Me-4), 3.20 (s, 1 H, $C=CH_2$), 3.44 [d, 1 H, μ-CH_2, J(HH) 6], 4.78 [d, 1 H, μ-CH_2, J(HH) 6], 5.63 (s, 5 H, η-C_5H_5), 7.10 (m br, 4 H, C_6H_4)	229.4, 227.7 (MoCO), 211.6 (FeCO), 209.2 (μ-CC_6H_4Me-4), 150.5 [$C^1(C_6H_4)$], 138.4, 129.9, 128.5 (C_6H_4), 107.4 (μ-CH_2), 98.2 (C_5H_5), 64.5 [μ-$C(C_6H_4Me\text{-}4)=CH_2$], 21.2 (Me-4)
(**3b**)	0.87 [d, 1 H, $C=CH_2$, J(PH) 5], 1.66 [d, 9 H, MeP, J(PH) 9], 2.34 (s, 3 H, Me-4), 2.63 [d of d, 1 H, μ-CH_2, J(PH) 9, J(HH) 5], 2.78 [d, 1 H, $C=CH_2$, J(PH) 7], 4.38 [d of d, 1 H, μ-CH_2, J(HH) 5, J(PH) 3], 5.54 (s, 5 H, C_5H_5), 7.08, 7.18 [$(AB)_2$, 4 H, C_6H_4, J(AB) 7]	232.5 (MoCO), 232.0 [d, MoCO, J(PC) 5], 215.3 [d, FeCO, J(PC) 13], 213.0 [d, FeCO, J(PC) 13], 209.6 [d, μ-CC_6H_4-Me-4, J(PC) 4], 151.6 [$C^1(C_6H_4)$], 137.3, 130.2, 128.2 (C_6H_4), 107.5 [d, μ-CH_2, J(PC) 10], 64.7 [d, μ-$C(C_6H_4Me\text{-}4)=CH_2$, J(PC) 8], 21.2 (Me-4), 21.0 [d, MeP, J(PC) 31]
(**4a**)	[d] 2.28 (s, 3 H, Me-4), 3.57 (s, 3 H, OMe), 4.56 (s, 1 H, μ-CH), 5.09 (s, 5 H, C_5H_5), 7.03, 7.39 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	[e] 233.4, 230.5 (MoCO), 212.4 (FeCO), 148.1 (μ-COMe), 142.8 [$C^1(C_6H_4)$], 135.0, 128.6, 128.5 (C_6H_4), 94.2 (μ-CC_6H_4Me-4), 89.7 (C_5H_5), 65.2 (μ-CH), 53.3 (COMe), 21.1 (Me-4)
(**4b**)	1.23 [d, 9 H, MeP, J(PH) 10], 2.30 (s, 3 H, Me-4), 3.83 (s br, 1 H, OH), 5.30 (s, 1 H, μ-CH), 4.95 (s, 5 H, C_5H_5), 7.00, 7.51 [$(AB)_2$, 4 H, J(AB) 8]	239.9, 238.0 (MoCO), 218.5 [d, FeCO, J(PC) 22], 218.3 [d, FeCO, J(PC) 22], 145.7 [$C^1(C_6H_4)$], 139.5 [d, μ-COH, J(PC) 44], 133.9, 129.1, 128.8 (C_6H_4), 90.6 (C_5H_5), 87.7 (μ-CC_6H_4-Me-4), 65.0 (μ-CH), 21.2 (Me-4), 19.0 [d, MeP, J(PC) 30]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperature. [b] Measured in $CDCl_3$ unless otherwise stated. [c] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2 unless otherwise stated. [d] Measured in CD_2Cl_2. [e] Measured in $CDCl_3$.

(δ 211.6 p.p.m.). This is a common property of the latter fragment, reflecting a low-energy site exchange of the carbonyl ligands.

If compound (**1a**) is treated with CH_2N_2 in diethyl ether with the reactants maintained at a temperature of *ca.* −40 °C, an orange-red product (**4a**) is obtained of different formulation to that of (**3a**). This was immediately apparent from the spectroscopic (i.r. and n.m.r.) properties (Tables 1 and 2), but the latter did not identify the compound. An *X*-ray diffraction study, the results of which are summarised in Table 4, characterised (**4a**) as the complex $[FeMo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(OMe)C(H)\}(CO)_5(\eta\text{-}C_5H_5)]$, the structure of which is shown in Figure 2.

The molecule contains an Fe–Mo bond [2.704(1) Å] transversely bridged by a C_3 fragment $C(C_6H_4Me\text{-}4)C(OMe)C(H)$ such that C(1) and C(3) are each bonded to both metal centres [Fe–C(1) 2.061(6), Mo–C(1) 2.205(6), Fe–C(3) 2.006(8), Mo–C(3) 2.148(7) Å], but C(2) is bonded only to iron [Fe–C(2) 2.167(7), Mo••• C(2) 2.68 Å]. The normal to the plane defined by C(1)C(2)C(3) is inclined at 23° to the Mo–Fe vector. Atom C(2) carries an OMe group, and C(3) a hydrogen atom which was located in the electron-density difference map. The hydrogen atom [H(3)] was also clearly revealed in the n.m.r. studies, discussed below. Three carbonyl ligands are terminally bound to the iron atom and two to the molybdenum, and the latter carries the C_5H_5 group, as expected.

It is interesting to relate the structure of (**4a**) to the isolobal fragment model.[43] Since an $Mo(CO)_2(\eta\text{-}C_5H_5)$ group is isolobal with CH, compound (**4a**) may be regarded as a complex in which a tricarbonyliron moiety is ligated by a substituted cyclobutadiene molecule having one of its ring carbon atoms replaced by molybdenum.

The ^{1}H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**4a**) (Table 2) are in agreement with the structure established by *X*-ray crystallography. The ^{1}H n.m.r. spectrum shows singlet resonances for the OMe and μ-CH groups (relative intensity 3:1) at δ 3.57 and 4.56, respectively, as well as the expected signals for the C_6H_4Me-4 and C_5H_5 fragments. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum, resonances for the μ-C_3 bridge system appear at δ 148.1 (μ-*C*OMe), 94.2 (μ-CC_6H_4Me-4), and 65.2 p.p.m. (μ-CH).

In order to confirm the ^{1}H n.m.r. assignments, and to establish unambiguously the origin of the μ-CH and OMe groups in (**4a**), the complex was prepared from (**1a**) and CD_2N_2 at −40 °C. Measurement of the ^{2}H n.m.r. spectrum revealed signals at δ 3.56 (s, 3 D, OCD_3) and 4.57 (s, 1 D, μ-CD), while in the ^{1}H n.m.r. spectrum the resonances at δ 3.57 and 4.56 were no longer observed. These results established that the μ-CH and OMe groups present in (**4a**) originate from two CH_2 groups derived from CH_2N_2.

To establish the source of the COMe fragment in (**4a**), the complex was prepared from CH_2N_2 and a sample of (**1a**) which had been partially enriched with ^{13}CO. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum was measured. As expected, the resonances due to the ligated CO groups were increased in intensity, compared with the corresponding peaks in the spectrum of the non-^{13}CO enriched complex. More significantly, the peak at δ 148.1 p.p.m., assigned to the *C*OMe group, increased in intensity relative to that at δ 53.3 p.p.m. (CO*Me*). Moreover, the resonance due to the μ-CH group (at 65.2 p.p.m.) appeared as a doublet [*J*(CC)

Table 3. Selected internuclear distances (Å) and angles (°) for [FeMo(μ-CH_2){μ-σ:η-C(C_6H_4Me-4)=CH_2}$(CO)_5$(η-C_5H_5)] (**3a**) with estimated standard deviations in parentheses

Mo–Fe	2.717(1)	Mo–C(1)	2.209(2)	Mo–C(3)	2.239(3)	Mo–C(4)	1.940(2)
Mo–C(5)	1.936(3)	Fe–C(1)	2.055(2)	Fe–C(2)	2.127(3)	Fe–C(3)	2.016(3)
Fe–C(6)	1.806(3)	Fe–C(7)	1.774(3)	Fe–C(8)	1.795(3)	C(1)–C(2)	1.408(4)
C(1)–C(11)	1.495(4)	C(4)–O(4)	1.157(3)	C(5)–O(5)	1.161(4)	C(6)–O(6)	1.141(4)
C(7)–O(7)	1.144(4)	C(8)–O(8)	1.136(3)	Mo–C(cp) (mean)	2.374	C–C(cp) (mean)	1.405
Fe–Mo–C(1)	48.0(1)	Fe–Mo–C(3)	46.8(1)	C(1)–Mo–C(3)	80.6(1)	Fe–Mo–C(4)	110.8(1)
C(1)–Mo–C(4)	67.0(1)	C(3)–Mo–C(4)	109.6(1)	Fe–Mo–C(5)	106.4(1)	C(1)–Mo–C(5)	115.2(1)
C(3)–Mo–C(5)	60.9(1)	C(4)–Mo–C(5)	79.1(1)	Mo–Fe–C(1)	53.0(1)	Mo–Fe–C(2)	80.1(1)
C(1)–Fe–C(2)	39.3(1)	Mo–Fe–C(3)	54.0(1)	C(1)–Fe–C(3)	89.9(1)	C(2)–Fe–C(3)	85.3(1)
Mo–Fe–C(6)	121.7(1)	C(1)–Fe–C(6)	88.8(1)	C(2)–Fe–C(6)	96.8(1)	C(3)–Fe–C(6)	174.9(1)
Mo–Fe–C(7)	137.7(1)	C(1)–Fe–C(7)	124.9(1)	C(2)–Fe–C(7)	85.6(1)	C(3)–Fe–C(7)	85.4(1)
C(6)–Fe–C(7)	99.4(1)	Mo–Fe–C(8)	91.5(1)	C(1)–Fe–C(8)	135.2(1)	C(2)–Fe–C(8)	171.4(1)
C(3)–Fe–C(8)	88.1(1)	C(6)–Fe–C(8)	89.2(1)	C(7)–Fe–C(8)	99.5(1)	Mo–C(1)–Fe	79.1(1)
Mo–C(1)–C(2)	119.4(2)	Fe–C(1)–C(2)	73.1(1)	Mo–C(1)–C(11)	121.5(2)	Fe–C(1)–C(11)	127.7(2)
C(2)–C(1)–C(11)	118.2(2)	Fe–C(2)–C(1)	67.6(1)	Mo–C(3)–Fe	79.2(1)	Mo–C(4)–O(4)	178.7(3)
Mo–C(5)–O(5)	174.3(2)	Fe–C(6)–O(6)	176.1(2)	Fe–C(7)–O(7)	177.3(3)	Fe–C(8)–O(8)	176.9(2)

Table 4. Selected internuclear distances (Å) and angles (°) for [FeMo{μ-C(C_6H_4Me-4)C(OMe)C(H)}$(CO)_5$(η-C_5H_5)] (**4a**) with estimated standard deviations in parentheses

Mo–Fe	2.704(1)	Mo–C(1)	2.205(6)	Mo–C(3)	2.148(7)	Mo–C(5)	1.991(9)
Mo–C(6)	2.004(8)	Fe–C(1)	2.061(6)	Fe–C(2)	2.167(7)	Fe–C(3)	2.006(8)
Fe–C(7)	1.777(7)	Fe–C(8)	1.760(9)	Fe–C(9)	1.765(8)	C(1)–C(2)	1.417(10)
C(1)–C(11)	1.501(8)	C(2)–C(3)	1.400(10)	C(2)–O(2)	1.359(8)	O(2)–C(4)	1.438(12)
C(5)–O(5)	1.151(12)	C(6)–O(6)	1.149(10)	C(7)–O(7)	1.133(9)	C(8)–O(8)	1.156(11)
C(9)–O(9)	1.151(10)	Mo–C(cp) (mean)	2.314				
Fe–Mo–C(1)	48.3(2)	Fe–Mo–C(3)	47.1(2)	C(1)–Mo–C(3)	61.0(3)	Fe–Mo–C(5)	83.8(2)
C(1)–Mo–C(5)	86.4(3)	C(3)–Mo–C(5)	130.9(3)	Fe–Mo–C(6)	81.7(2)	C(1)–Mo–C(6)	129.8(3)
C(3)–Mo–C(6)	90.6(3)	C(5)–Mo–C(6)	83.2(4)	Mo–Fe–C(1)	53.1(2)	Mo–Fe–C(2)	65.6(2)
C(1)–Fe–C(2)	39.1(3)	Mo–Fe–C(3)	51.7(2)	C(1)–Fe–C(3)	65.8(3)	C(2)–Fe–C(3)	39.0(3)
Mo–Fe–C(7)	102.4(2)	C(1)–Fe–C(7)	152.8(3)	C(2)–Fe–C(7)	125.4(3)	C(3)–Fe–C(7)	90.2(3)
Mo–Fe–C(8)	102.2(2)	C(1)–Fe–C(8)	99.6(3)	C(2)–Fe–C(8)	137.1(3)	C(3)–Fe–C(8)	153.9(3)
C(7)–Fe–C(8)	97.0(4)	Mo–Fe–C(9)	151.8(3)	C(1)–Fe–C(9)	103.0(3)	C(2)–Fe–C(9)	86.5(3)
C(3)–Fe–C(9)	108.1(4)	C(7)–Fe–C(9)	96.4(4)	C(8)–Fe–C(9)	96.0(4)	Mo–C(1)–Fe	78.6(2)
Mo–C(1)–C(2)	92.7(4)	Fe–C(1)–C(2)	74.5(4)	Mo–C(1)–C(11)	134.9(4)	Fe–C(1)–C(11)	128.5(4)
C(2)–C(1)–C(11)	126.4(5)	Fe–C(2)–C(1)	66.4(4)	Fe–C(2)–C(3)	64.3(4)	C(1)–C(2)–C(3)	103.4(6)
Fe–C(2)–O(2)	131.0(5)	C(1)–C(2)–O(2)	125.6(6)	C(3)–C(2)–O(2)	131.0(7)	Mo–C(3)–Fe	81.2(3)
Mo–C(3)–C(2)	95.6(5)	Fe–C(3)–C(2)	76.7(5)	C(2)–O(2)–C(4)	115.0(6)	Mo–C(5)–O(5)	177.7(7)
Mo–C(6)–O(6)	174.9(7)	Fe–C(7)–O(7)	177.6(8)	Fe–C(8)–O(8)	175.8(7)	Fe–C(9)–O(9)	179.6(9)

32 Hz] superimposed on a singlet; this pattern resulting from the presence in solution of both ^{13}C-enriched and non-enriched molecules of (**4a**). It is thus evident that the COMe fragment in (**4a**) has formed *via* a process which involves incorporation of a carbonyl group, as discussed further below.

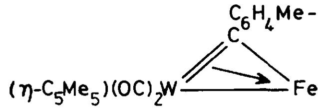
There are several aspects of the syntheses of (**3a**) and (**4a**) which are of interest. Thus the formation of both complexes corresponds to the addition of two CH_2 fragments to the dimetal compound (**1a**). Double addition of methylene groups to di- or tri-nuclear metal complexes using the reagent CH_2N_2 is rare, and we are only aware of two other examples.[8,27] Moreover, the pathways to these products are intriguing, especially that leading to (**4a**). In order to investigate these matters further, the reactions between CH_2N_2 and (**1b**), and between CH_2N_2 and (**2b**) were studied. It was thought that the presence of the PMe_3 ligand on the iron centres in (**1b**) and (**2b**) might introduce new electronic and steric factors which would affect the nature of the products obtained with CH_2N_2, and thereby increase our understanding of methylene-addition reactions at dimetal centres.

In contrast with the results presented above, the nature of the products obtained from the reactions between CH_2N_2 and either (**1b**) or (**2b**) were the same, whether or not the reactants were brought together at or below room temperature. Treatment of (**2b**) with an excess of CH_2N_2 in diethyl ether afforded the compound [FeMo(μ-CH_2){μ-σ:η-C(C_6H_4Me-4)=CH_2}$(CO)_4$(PMe_3)(η-C_5H_5)] (**3b**), in high yield. The complex was characterised by the data given in Tables 1 and 2. The n.m.r. spectra (Table 2) establish that (**3b**) is structurally similar to (**3a**).

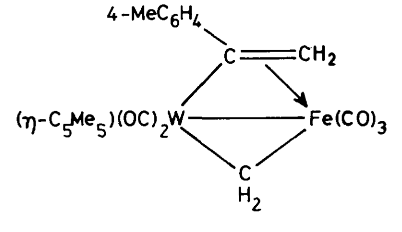
The reaction between the electronically saturated complex (**1b**) and CH_2N_2 gave in good yield a compound (**4b**) formulated as [FeMo{μ-C(C_6H_4Me-4)C(OH)C(H)}$(CO)_4$(PMe_3)(η-C_5H_5)]. The i.r. spectrum of the latter showed a broad band at 3 522 cm^{-1} attributable to the OH group, which revealed itself in the ^1H n.m.r. spectrum (Table 2) as a broad signal at δ 3.83. The ^1H spectrum also showed a resonance at δ 5.30 for the μ-CH group, as well as the expected peaks for the MeP, C_6H_4Me-4, and C_5H_5 fragments. In the ^{13}C-{^1H} n.m.r. spectrum of (**4b**) resonances for the μ-C_3 fragment occur at 139.5 [d, μ-COH, *J*(PC) 44 Hz], 87.7 (μ-CC_6H_4Me-4), and 65.0 p.p.m. (μ-CH). The complex does not undergo site-exchange of CO groups at room temperature on the n.m.r. time-scale since four carbonyl resonances are observed (Table 2). The two peaks appearing as singlets may be ascribed to the Mo$(CO)_2$ fragment, and the two seen as doublets [*J*(PC) 22 Hz] to the Fe$(CO)_2$ group. The absence of any resonance in the ^1H or ^{13}C-{^1H} n.m.r. spectra of (**4b**) due to an OMe group means that

Table 5. Fractional atomic co-ordinates (× 10^4), with estimated deviations in parentheses, for complex (**3a**)

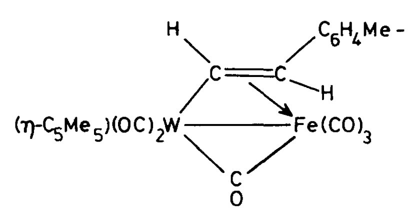
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	3 424(1)	2 195(1)	971(1)	O(8)	6 043(3)	−1 687(2)	3 391(2)
Fe	6 348(1)	1 334(1)	3 018(1)	C(11)	3 667(3)	4 044(2)	2 793(2)
C(1)	4 666(3)	3 314(2)	2 287(2)	C(12)	3 697(4)	5 485(3)	2 761(2)
C(2)	6 336(3)	3 566(3)	2 510(2)	C(13)	2 671(4)	6 263(3)	3 117(2)
C(3)	6 217(3)	1 332(3)	1 456(2)	C(14)	1 590(4)	5 648(3)	3 520(2)
C(4)	2 871(3)	4 275(3)	336(2)	C(15)	1 592(4)	4 203(3)	3 593(2)
O(4)	2 534(3)	5 513(2)	−62(2)	C(16)	2 613(3)	3 414(3)	3 240(2)
C(5)	4 190(4)	2 388(3)	−234(2)	C(17)	411(5)	6 521(4)	3 865(4)
O(5)	4 507(3)	2 513(2)	−1 021(2)	C(21)	1 967(3)	610(3)	1 742(2)
C(6)	6 275(3)	1 297(3)	4 374(2)	C(22)	789(3)	1 937(3)	1 095(2)
O(6)	6 275(3)	1 195(2)	5 253(2)	C(23)	487(3)	2 165(3)	−66(2)
C(7)	8 629(3)	1 055(3)	3 496(2)	C(24)	1 451(4)	966(3)	−137(3)
O(7)	10 089(3)	900(3)	3 761(2)	C(25)	2 387(4)	15(3)	973(3)
C(8)	6 113(3)	−505(3)	3 228(2)				



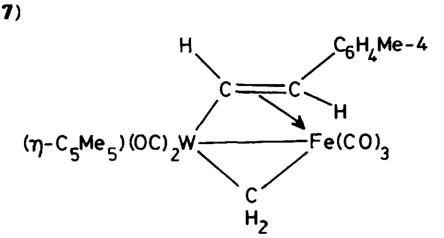
(**5**)



(**6**)



(**7**)



(**8**)

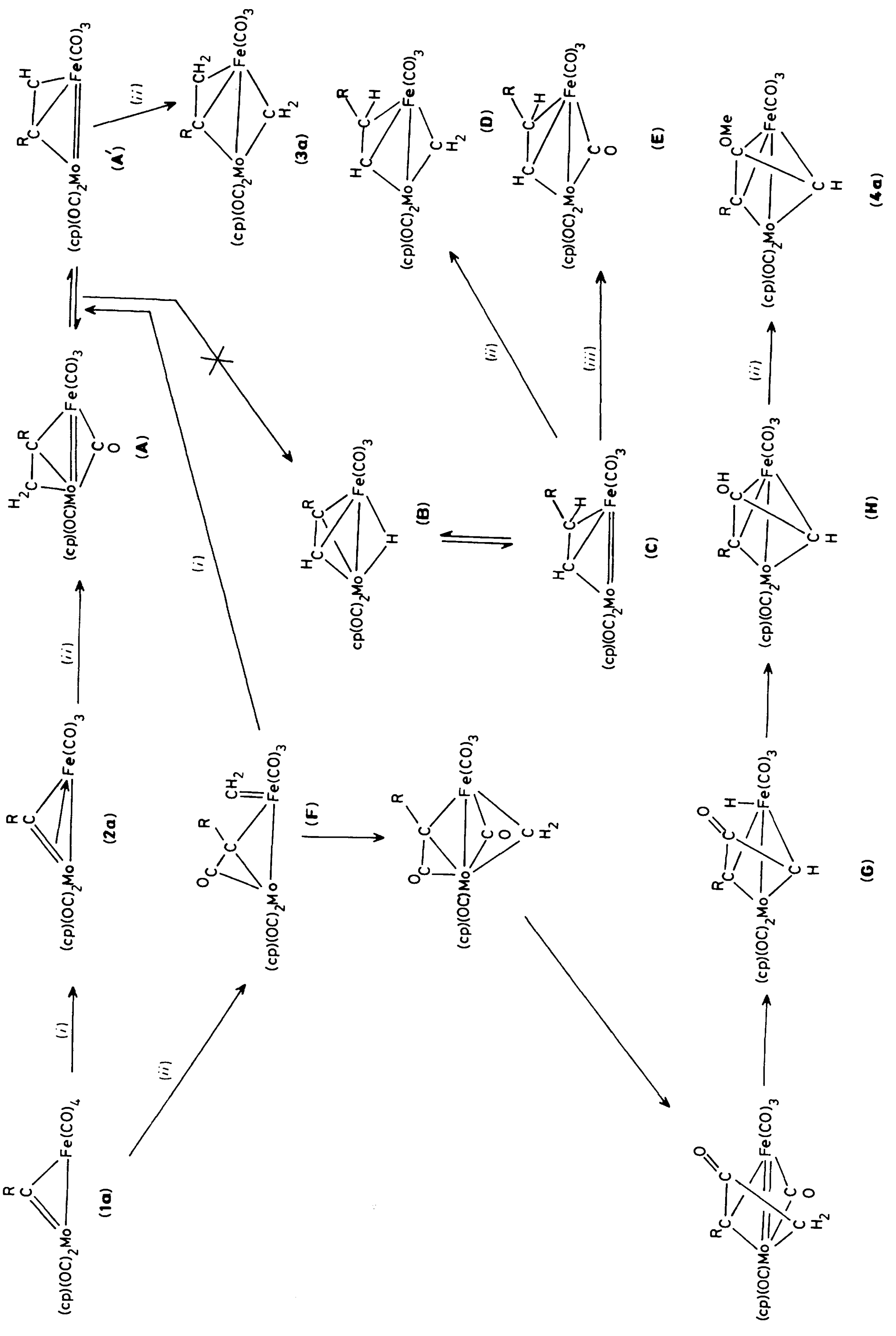
it is formed by addition of a single CH_2 fragment to (**1b**). The ^{31}P-{^1H} n.m.r. spectrum of (**4b**) shows a singlet resonance at δ 42.9 p.p.m.

The pathways by which compounds (**3**) and (**4**) are formed, in the reactions described above, are of considerable interest. Earlier we reported[38] a study of reactions between the unsaturated complex [FeW(μ-CC_6H_4Me-4)$(CO)_5$(η-C_5Me_5)] (**5**) and CH_2N_2 which resulted in characterisation of the products [FeW(μ-CH_2){μ-σ:η-C(C_6H_4Me-4)=CH_2}$(CO)_5$(η-C_5Me_5)] (**6**), [FeW{μ-σ:η-C(H)=C(C_6H_4Me-4)H}(μ-CO)-$(CO)_5$(η-C_5Me_5)] (**7**), and [FeW(μ-CH_2){μ-σ:η-C(H)=C-(C_6H_4Me-4)H}$(CO)_5$(η-C_5Me_5)] (**8**). The structure of (**6**) is similar to that of (**3a**) and (**3b**) and it is likely that similar steps are involved in the formation of these species.

Possible routes to compounds (**3a**) and (**4**) are shown in the accompanying Scheme. It is suggested that the room-temperature reaction, affording (**3a**) as the product, proceeds *via* (**2a**), which is electronically unsaturated like the recently characterised complex (**5**).[38] Transfer of a methylene fragment to (**2a**) from CH_2N_2 might involve more than one step but the bridged-vinyl species (**A**) and (**A′**) are likely to form, and to equilibrate *via* a pivoting mechanism.[42] Addition of a methylene group to (**A′**) would afford the observed product (**3a**); the tungsten analogue of which, (**6**), has been prepared, as mentioned above. It is interesting to note in passing that the intermediates (**A**) and (**A′**) might have rearranged *via* (**B**) to the *trans*-vinyl unsaturated species (**C**). Reaction of the latter with CH_2 or CO might then have produced compounds (**D**) and (**E**), the molybdenum-containing analogues of the previously characterised iron–tungsten complexes (**7**) and (**8**). That this does not occur in the molybdenum system would be due to the process (**A′**) ⟶ (**3a**) being very fast so that there is insufficient time for the rearrangement (**A**) or (**A′**) ⟶ (**B**) ⟶ (**C**) to occur.

A key step in the formation of (**3a**), according to the Scheme, is release of a CO molecule from (**1a**). In the low-temperature reaction, however, there was no evidence for the formation of (**3a**); instead, complex (**4a**) is produced. As shown by the studies employing ^{13}CO-enriched (**1a**), the COMe group in (**4a**) is derived from a carbonyl ligand in the former compound. Hence (**4a**) incorporates all six carbonyl groups of its precursor, and thus the pathway to its synthesis must depend on retention of these ligands about the dimetal centre. It is possible that under the reaction conditions of *ca.* −40 °C, (**F**) is an intermediate. The μ-C(C_6H_4Me-4)C(O) group present in (**F**) would form *via* CO transfer to the tolylmethylidyne ligand present in the precursor (**1a**), a process firmly established previously.[44] A coupling of μ-C(C_6H_4Me-4)C(O) and μ-CH_2 ligands at the dimetal centre, accompanied by hydride migration to iron could yield intermediate (**G**). The μ-C(C_6H_4Me-4)C(O)C(H) bridge system present in the latter has a structural precedent in the compound [W_2{μ-C(C_6H_4Me-4)C(O)C(C_6H_4Me-4)}$(CO)_4$(η-$C_5H_5)_2$].[45] Transfer of hydride from iron to the 'organic' carbonyl group would afford intermediate (**H**), which in the presence of an excess of CH_2N_2 would yield the product (**4a**).

The formation of (**3b**) from the 32-valence-electron dimetal compound (**2b**) is readily explained in terms of the pathway proposed for the synthesis of (**3a**). The initial dissociation of a CO molecule would be unnecessary since the precursor is



Scheme. cp = η-C_5H_5, R = C_6H_4Me-4; (*i*) −CO, (*ii*) +CH_2, (*iii*) +CO

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

Atom	x	y	z	Atom	x	y	z
Mo	1 715(1)	2 094(1)	1 522(1)	C(9)	3 596(7)	−188(10)	3 518(5)
Fe	2 580(1)	320(1)	2 750(1)	O(9)	4 263(5)	−512(9)	4 017(4)
C(1)	2 750(5)	2 577(7)	2 667(4)	C(12)*	3 599(3)	3 764(5)	3 968(3)
C(2)	3 580(5)	1 951(8)	2 388(4)	C(13)	3 641	4 852	4 561
C(3)	3 134(6)	972(8)	1 782(4)	C(14)	2 875	5 899	4 505
O(2)	4 561(4)	2 256(6)	2 684(4)	C(15)	2 068	5 858	3 856
C(4)	5 266(6)	1 357(11)	2 360(7)	C(16)	2 027	4 770	3 262
C(5)	617(6)	2 240(9)	2 155(5)	C(11)	2 793	3 723	3 318
O(5)	−35(5)	2 357(8)	2 502(4)	C(17)	2 914(10)	7 114(10)	5 138(6)
C(6)	1 022(6)	202(9)	1 128(5)	C(21)*	2 279(4)	4 362(5)	1 086(3)
O(6)	606(5)	−834(6)	846(4)	C(22)	2 496	3 241	552
C(7)	2 350(5)	−1 474(8)	2 324(5)	C(23)	1 573	2 602	168
O(7)	2 214(5)	−2 600(5)	2 028(4)	C(24)	786	3 327	465
C(8)	1 662(6)	266(8)	3 363(5)	C(25)	1 223	4 415	1 032
O(8)	1 082(5)	146(8)	3 782(4)				

* Pivot atom of a rigid group; remaining atoms in the group have identical standard deviations.

unsaturated. Reaction between CH$_2$N$_2$ and the 34-valence-electron compound (**1b**) gives (**4b**), a complex structurally akin to intermediate (**H**) (Scheme) but containing an Fe(CO)$_2$(PMe$_3$) group. Surprisingly, compound (**4b**) does not react further with diazomethane to afford a product containing a COMe group. This may be due to a steric effect arising from substitution of CO by PMe$_3$, or perhaps more likely to reduction in acidity of the C–OH function upon introduction of a strongly electron-releasing ligand (PMe$_3$) into the structure.

The results described herein further illustrate the reactivity of the dimetal species (**1**).[39] Moreover, formation of the compounds (**3**) and (**4**) provides new examples of C–C bond-forming reactions involving coupling of alkylidyne, methylene, and CO fragments.

Experimental

The experimental techniques used, and the instrumentation employed, have been described in previous parts of this series.[39] Light petroleum refers to that fraction of b.p. 40—60 °C. The compounds [FeMo(μ-CC$_6$H$_4$Me-4)(CO)$_6$(η-C$_5$H$_5$)] and [FeMo(μ-CC$_6$H$_4$Me-4)(CO)$_4$(PMe$_3$)(η-C$_5$H$_5$)] were prepared as described earlier.[39] Diazomethane and CD$_2$N$_2$ were prepared using Aldrich Chemical Co. Diazald kits. Analytical data for the iron–molybdenum compounds are given in Table 1. Phosphorus-31 n.m.r. chemical shifts (hydrogen-1 decoupled) given in p.p.m., positive values being to high frequency of 85% H$_3$PO$_4$ (external).

Reactions between [FeMo(μ-CC$_6$H$_4$Me-4)(CO)$_6$(η-C$_5$H$_5$)] *and Diazomethane.*—(*i*) An Et$_2$O (10 cm^3) solution of (**1a**) (0.15 g, 0.30 mmol) was treated dropwise at room temperature with an excess of CH$_2$N$_2$ (*ca.* 8 mmol) in the same solvent (*ca.* 15 cm^3). The red solution was purged with a stream of nitrogen, and then the solvent was removed *in vacuo*. The residue was extracted with light petroleum (2 × 10 cm^3), and the extracts filtered through a Celite pad (*ca.* 2 × 2 cm). Removal of solvent *in vacuo* afforded orange-red *microcrystals* of [FeMo(μ-CH$_2$){μ-σ:η-C(C$_6$H$_4$Me-4)=CH$_2$}(CO)$_5$(η-C$_5$H$_5$)] (**3a**) (0.13 g).

The reaction was also carried out using CD$_2$N$_2$ (*ca.* 0.50 mmol) and (**1a**) (0.05 g, 0.10 mmol) thereby affording [FeMo(μ-CD$_2$){μ-σ:η-C(C$_6$H$_4$Me-4)=CD$_2$}(CO)$_5$(η-C$_5$H$_5$)] (0.04 g, *ca.* 90%). Hydrogen-1 n.m.r. (CDCl$_3$): δ 2.35 (s, 3 H, Me-4), 5.63 (s, 5 H, η-C$_5$H$_5$), and 7.10 (br, 4 H, C$_6$H$_4$); ^{2}H-{^{1}H} n.m.r. (CH$_2$Cl$_2$), δ 1.42 (s, 1 D, C=CD$_2$), 3.20 (s, 1 D, C=CD$_2$), 3.44 (s, 1 D, μ-CD$_2$), and 4.81 (s, 1 D, μ-CD$_2$).

(*ii*) An Et$_2$O (20 cm^3) solution of (**1a**) (0.15 g, 0.30 mmol) at −40 °C was treated with an excess of CH$_2$N$_2$ (*ca.* 8 mmol) in Et$_2$O (10 cm^3) for 10 min. The red solution obtained was warmed to room temperature and was purged with a stream of nitrogen, and then solvent was removed *in vacuo*. The residue was extracted with light petroleum (4 × 10 cm^3), and filtered through a Celite pad (*ca.* 2 × 2 cm). Removal of solvent *in vacuo* afforded orange *microcrystals* of [FeMo{μ-C(C$_6$H$_4$Me-4)C(OMe)C(H)}(CO)$_5$(η-C$_5$H$_5$)] (**4a**) (0.14 g).

A similar synthesis, also at −40 °C, using (**1a**) (0.05 g, 0.10 mmol) and CD$_2$N$_2$ (*ca.* 0.50 mmol) in Et$_2$O (15 cm^3) gave [FeMo{μ-C(C$_6$H$_4$Me-4)C(OCD$_3$)C(D)}(CO)$_5$(η-C$_5$H$_5$)] (0.05 g, *ca.* 90%). Hydrogen-1 n.m.r. (CD$_2$Cl$_2$), δ 2.28 (s, 3 H, Me-4), 5.09 (s, 5 H, C$_5$H$_5$), and 7.04, 7.39 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8 Hz]; ^{2}H-{^{1}H} n.m.r. (CH$_2$Cl$_2$), δ 3.56 (s, 3 D, OCD$_3$) and 4.57 (s, 1 D, CD).

Reaction between the Compounds [FeMo(μ-CC$_6$H$_4$Me-4)(CO)$_n$(PMe$_3$)(η-C$_5$H$_5$)] (*n* = 4 *or* 5) *and Diazomethane.*—(*i*) An Et$_2$O (20 cm^3) solution of (**2b**) (0.18 g, 0.35 mmol) at 0 °C was treated with excess of CH$_2$N$_2$, as in the preparation of (**3a**). The mixture changes from purple to red in colour during addition of diazomethane. Solvent was removed *in vacuo*, and the residue was extracted with Et$_2$O–light petroleum (5 × 10 cm^3, 2:1) and the extracts passed through a Celite pad (*ca.* 2 × 2 cm). Removal of solvent *in vacuo* gave orange-red *microcrystals* of [FeMo(μ-CH$_2$){μ-σ:η-C(C$_6$H$_4$Me-4)=CH$_2$}(CO)$_4$(PMe$_3$)(η-C$_5$H$_5$)] (**3b**) (0.15 g). The complex may be obtained crystalline from Et$_2$O–light petroleum (1:1). Phosphorus-31 n.m.r. (CDCl$_3$), δ 25.0 (s) p.p.m.

(*ii*) An Et$_2$O (30 cm^3) solution of (**1b**) (0.20 g, 0.37 mmol) at 0 °C was treated with an excess of CH$_2$N$_2$. Solvent was removed *in vacuo*, and the residue extracted with Et$_2$O–light petroleum (2 × 25 cm^3, 2:1) and the extracts passed through a Celite pad (2 × 2 cm). Removal of solvent *in vacuo*, followed by crystallisation of the residue from Et$_2$O–light petroleum (2:1), afforded orange-red *crystals* of [FeMo{μ-C(C$_6$H$_4$Me-4)C(OH)C(H)}(CO)$_4$(PMe$_3$)(η-C$_5$H$_5$)] (**4b**) (0.15 g). Phosphorus-31 n.m.r. (CDCl$_3$, δ 42.9 (s) p.p.m.

Crystal Structure Determinations.—(*a*) [FeMo(μ-CH$_2$){μ-σ:η-C(C$_6$H$_4$Me-4)=CH$_2$}(CO)$_5$(η-C$_5$H$_5$)] (**3a**). Crystals grow on cooling from a mixture of CH$_2$Cl$_2$, light petroleum, and Et$_2$O as orange-red parallelepipeds. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.50 × 0.25 × 0.15 mm on a Nicolet *P*3*m* diffractometer. Of the 4 439 unique data collected (ω—2θ scans, $2\theta \leqslant 55°$), 3 710 had $I \geqslant 2.5\sigma(I)$, 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[46]), Lorentz, and polarisation effects.

Crystal data. $C_{20}H_{16}FeMoO_5$, $M = 488.1$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.624(1)$, $b = 9.725(1)$, $c = 13.178(2)$ Å, $\alpha = 77.53(1)$, $\beta = 114.04(1)$, $\gamma = 84.04(1)°$, $U = 962.4(2)$ Å^3, $Z = 2$, $D_c = 1.68$ g cm^{-3}, $F(000) = 488$, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 14.2 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and successive difference Fourier syntheses were used to locate all non-hydrogen atoms and H(2a), H(2b), H(3a), and H(3b). All non-hydrogen atoms were refined with anisotropic thermal parameters. Atoms H(2a), H(2b), H(3a), and H(3b) were refined with fixed isotropic thermal parameters (*ca.* 1.2 × $U_{\text{equiv.}}$ of the parent carbon atom). All other hydrogen atoms were included at calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (*ca.* 1.2 × $U_{\text{equiv.}}$ of the parent carbon atom) for the aromatic hydrogen atoms, and a common isotropic thermal parameter for the methyl hydrogen atoms H(17a), H(17b), and H(17c). Refinement by blocked-cascade least squares converged at R 0.026 (R' 0.025), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,09|F|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $\geqslant 0.36$ or $\leqslant -0.25$ e Å^{-3}.

(*b*) $[FeMo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(OMe)C(H)\}(CO)_5(\eta\text{-}C_5H_5)]$ (**4a**). Crystals grow on cooling from a mixture of CH_2Cl_2, light petroleum, and Et_2O as orange plates. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.07 × 0.30 × 0.22 mm with principal faces (1 0 0), (−1 0 0), (0 1 0), (0 −1 0), (0 0 1), and (0 0 −1). Of the 2 864 unique data collected [ω—2θ scans, $2\theta \leqslant 55°$; weak data with $40 \leqslant 2\theta \leqslant 55°$ were not collected if a prescan showed that $I \lesssim 2\sigma(I)$], 2 336 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 analytical method), Lorentz, and polarisation effects.

Crystal data. $C_{21}H_{16}FeMoO_6$, $M = 516.1$, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.566(5)$, $b = 9.038(3)$, $c = 16.825(4)$ Å, $\beta = 100.78(3)°$, $U = 2\,026(1)$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 1\,032$, μ(Mo-K_α) = 13.5 cm^{-1}.

The structure was solved as for (**3a**) and thereby all non-hydrogen atoms and H(3) were located. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom H(3) was refined with an isotropic thermal parameter and all other hydrogen atoms were included at calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (*ca.* 1.2 × $U_{\text{equiv.}}$ of the parent carbon atoms) for all aromatic hydrogen atoms and a common refined thermal parameter for all methyl hydrogen atoms. Cyclopentadienyl and phenyl rings were constrained to ideal geometries and refined as rigid groups. Refinement by blocked-cascade least squares led to R 0.049 (R' 0.049), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,86|F|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $\geqslant 0.94$ or $\leqslant -0.69$ e Å^{-3}. All calculations were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[46] Scattering factors and corrections for anomalous dispersion were taken from ref. 47. The atom co-ordinates for (**3a**) and (**4a**) are given in Tables 5 and 6, respectively.

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