Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 61.[1] Reactions of Iron–Molybdenum Compounds with Tertiary Phosphines

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Treatment of [FeMo(μ-CR)(CO)$_6$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4) with PMe$_3$ affords the compound [FeMo(μ-CR)(CO)$_5$(PMe$_3$)(η-C$_5$H$_5$)], which readily releases a molecule of CO to give the unsaturated species [FeMo(μ-CR)(CO)$_4$(PMe$_3$)(η-C$_5$H$_5$)]; a process which can be readily reversed. The compound [Mo(≡CR)(CO)$_2$(η-C$_5$H$_5$)] reacts with PMe$_3$ to give [Mo(≡CR)(CO)(PMe$_3$)(η-C$_5$H$_5$)]. The latter on treatment with one equivalent of [Fe$_2$(CO)$_9$] yields a mixture of the complexes [FeMo(μ-CR)(CO)$_n$(PMe$_3$)(η-C$_5$H$_5$)] (n = 4 or 5), and with excess of [Fe$_2$(CO)$_9$] affords [Fe$_2$Mo(μ$_3$-CR)(μ-CO)(CO)$_7$(PMe$_3$)(η-C$_5$H$_5$)]. This di-ironmolybdenum compound may also be obtained from the reaction of PMe$_3$ with [Fe$_2$Mo(μ$_3$-CR)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)], while the latter with dppm (Ph$_2$PCH$_2$PPh$_2$) affords [Fe$_2$Mo(μ-CR)(μ-CO)(μ-dppm)(CO)$_6$(η-C$_5$H$_5$)]. The reaction between PMe$_3$ and [FeMo$_2$(μ$_3$-RC$_2$R)(CO)$_6$(η-C$_5$H$_5$)$_2$] gives [FeMo$_2$(μ$_3$-RC$_2$R)(CO)$_5$(PMe$_3$)(η-C$_5$H$_5$)$_2$]. Spectroscopic data for the new compounds are reported and discussed in the context of the structures proposed.

We have shown previously that treatment of the complex [Mo(≡CR)(CO)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4) with [Fe$_2$(CO)$_9$] in a 1:1 ratio affords in high yield the dimetal compound [FeMo(μ-CR)(CO)$_6$(η-C$_5$H$_5$)] (**1a**).[2] In contrast, if the reaction is carried out using an excess of [Fe$_2$(CO)$_9$], the trimetal compound [Fe$_2$Mo(μ$_3$-CR)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] (**2a**) is formed. Moreover, by employing [Fe$_2$(CO)$_9$] and [Mo(≡CR)(CO)$_2$(η-C$_5$H$_5$)] in a 1:2 ratio, the reaction product is the irondimolybdenum complex [FeMo$_2$(μ$_3$-RC$_2$R)(CO)$_6$(η-C$_5$H$_5$)$_2$] (**3a**). The analogous iron–tungsten species (**1b**)—(**3b**) were prepared earlier, and some reactions with PMe$_3$ and Ph$_2$PCH$_2$PPh$_2$ (dppm) have been investigated.[3,4] In this paper we report reactions of the iron–molybdenum compounds with these tertiary phosphines. The results obtained establish both similarities and differences between the behaviour of the iron–molybdenum species and iron–tungsten compounds.

Results and Discussion

Addition of one equivalent of PMe$_3$ to a light petroleum solution of (**1a**) affords the brown crystalline complex [FeMo(μ-CR)(CO)$_5$(PMe$_3$)(η-C$_5$H$_5$)] (**4a**). If diethyl ether solutions of the latter are treated with a stream of nitrogen gas the purple compound [FeMo(μ-CR)(CO)$_4$(PMe$_3$)(η-C$_5$H$_5$)] (**5a**) is formed, but the latter readily reverts to (**4a**) in the presence of CO. An alternative synthesis of (**4a**) and (**5a**) involves treatment of the compound [Mo(≡CR)(CO)(PMe$_3$)(η-C$_5$H$_5$)] (**6**), described below, with [Fe$_2$(CO)$_9$] in diethyl ether; a reaction which results in transfer of a PMe$_3$ group from molybdenum to iron.

Compounds (**4a**) and (**5a**) are characterised by the data given in Tables 1 and 2. Complex (**5a**) is a formally unsaturated 32 valence electron species. The iron–tungsten analogues (**4b**) and (**5b**) were prepared earlier by treating (**1b**) with PMe$_3$, and they also may be readily interconverted.[4]

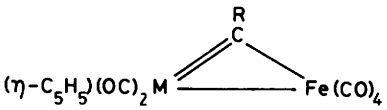
In the ^{13}C-{^{1}H} n.m.r. spectrum of (**4a**) the resonance for the alkylidyne carbon nucleus is at δ 385.5 p.p.m., whereas in the spectrum of (**5a**) the corresponding signal is at 407.1 p.p.m. This difference in chemical shifts is in the direction expected. In the spectra of 32 valence electron dimetal species with bridging carbyne groups the resonances for the μ-C fragments are more deshielded than those of their 34 valence electron counterparts.[4,5] Thus for (**4b**) and (**5b**) the signals for the μ-C groups occur at δ 354.4 and 388.1 p.p.m., respectively.

During the course of our studies it was found that the molybdenum complex [Mo(≡CR)(CO)$_2$(η-C$_5$H$_5$)] reacts with PMe$_3$ to afford the compound [Mo(≡CR)(CO)(PMe$_3$)(η-C$_5$H$_5$)] (**6**), data for which are given in Tables 1 and 2. Although satisfactory microanalytical data could not be obtained, because crystals could not be freed from oily impurities, the nature of compound (**6**) is well established by its spectroscopic properties. The i.r. spectrum in the carbonyl region shows a single band at 1 900 cm^{-1}, and the ^{13}C-{^{1}H} n.m.r. spectrum has a resonance for the alkylidyne carbon atom at δ 294.0 p.p.m., appearing as a doublet due to ^{31}P–^{13}C coupling (22 Hz). In the ^{13}C-{^{1}H} n.m.r. spectrum of the precursor [Mo(≡CR)(CO)$_2$(η-C$_5$H$_5$)] the resonance for the ligated *C*R group is at δ 311.2 p.p.m. The signal for the ligated carbonyl group in (**6**) is a doublet at 248.1 p.p.m. [*J*(PC) 22 Hz].

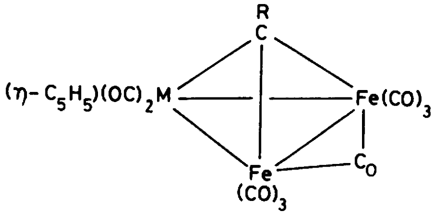
Formation of (**6**) is of some interest, since the corresponding reaction between [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] and one equivalent of PMe$_3$ affords the 'ketenyl' complex [W{η^2-C(R)C(O)}(CO)(PMe$_3$)(η-C$_5$H$_5$)] (**7**).[6,7] The tungsten analogue of (**6**) has not been reported, although a related species [W(≡CR)(CO)(PMe$_3$){HB(pz)$_3$}] [HB(pz)$_3$ = hydrotris(pyrazol-1-yl)borate] has been isolated from the reaction between PMe$_3$ and [FeW(μ-CR)(CO)$_4$(PMe$_3$){HB(pz)$_3$}].[4]

Treatment of compound (**1a**) with excess of PMe$_3$ in CH$_2$Cl$_2$ affords the bis(trimethylphosphine) complex [FeMo(μ-CR)(CO)$_4$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (**8a**). The tungsten analogue (**8b**) has been prepared from (**5b**) and PMe$_3$,[4] and the spectroscopic data for the two species are very similar. In their i.r. spectra, both compounds show four bands in the CO stretching region, with one peak at relatively low frequency [1 788 (**8a**), 1 780 cm^{-1} (**8b**)] indicative of the presence of a semi-bridging CO ligand. In the ^{13}C-{^{1}H} n.m.r. spectra of compounds (**8a**) and (**8b**) resonances for the μ-C nuclei occur as triplets at δ 397.0 and 365.7 p.p.m., respectively, with ^{31}P–^{13}C couplings of *ca.* 18 Hz.

Both molecules (**8a**) and (**8b**) undergo dynamic behaviour in solution. Thus the ^{31}P-{^{1}H} n.m.r. spectrum of each species shows a single resonance [δ 17.3 (**8a**), 18.7 p.p.m. (**8b**)], implying that the PMe$_3$ ligands on iron occupy equivalent sites at

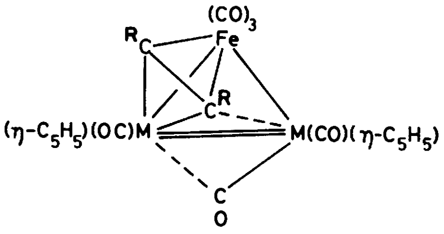


	M
(1a)	Mo
(1b)	W

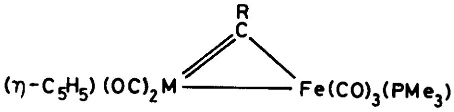


	M
(2a)	Mo
(2b)	W

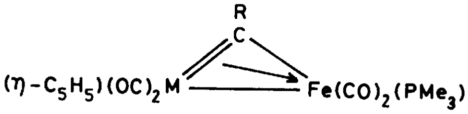
R = C_6H_4Me-4



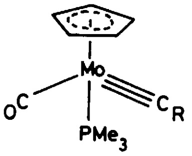
	M
(3a)	Mo
(3b)	W



	M
(4a)	Mo
(4b)	W



	M
(5a)	Mo
(5b)	W



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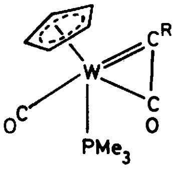

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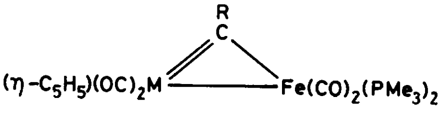

	M
(8a)	Mo
(8b)	W

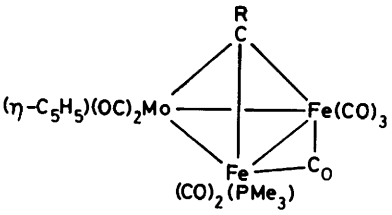

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Table 1. Analytical[a] and physical data for the complexes

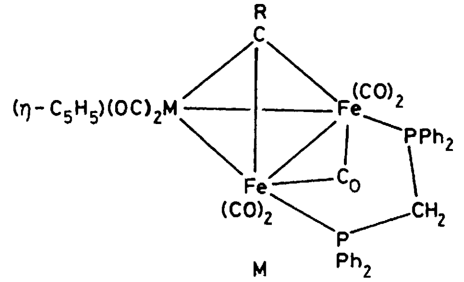
	Compound[b]	Colour	Yield (%)	$\nu_{max.}$(CO)/cm^{-1}	Analysis (%)	
					C	H
(**4a**)	$[FeMo(\mu\text{-}CR)(CO)_5(PMe_3)(\eta\text{-}C_5H_5)]$	Brown	62	[c] 2 020s, 1 962s, 1 943s, 1 908s, 1 850m	46.2 (47.0)	4.2 (3.9)
(**5a**)	$[FeMo(\mu\text{-}CR)(CO)_4(PMe_3)(\eta\text{-}C_5H_5)]$	Purple	23	[c] 1 993vs, 1 962w, 1 923s, 1 854m	46.8 (47.3)	4.2 (4.1)
(**6**)	$[Mo(\equiv CR)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$[d]	Dark red	95	[e] 1 900vs		
(**8a**)	$[FeMo(\mu\text{-}CR)(CO)_4(PMe_3)_2(\eta\text{-}C_5H_5)]$	Green	70	[f] 1 958s, 1 894vs, 1 869s, 1 788w	46.4 (47.3)	5.2 (5.1)
(**9**)	$[Fe_2Mo(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta\text{-}C_5H_5)]$	Brown	70	[e] 2 051w, 2 038w, 2 013m, 1 997vs, 1 978vs, 1 970s, 1 949m, 1 942m, 1 912vw, 1 863vw, 1 793vw, 1 767vw	42.6 (42.6)	3.1 (3.1)
(**10a**)	$[Fe_2Mo(\mu_3\text{-}CR)(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6(\eta\text{-}C_5H_5)]$[g]	Brown	55	[f] 2 011s, 1 961vs, 1 941 (sh), 1 880w br, 1 798w br, 1 783w br, 1 752w br	54.7 (54.7)	3.5 (3.5)
(**11**)	$[FeMo_2(\mu_3\text{-}RC_2R)(CO)_5(PMe_3)(\eta\text{-}C_5H_5)_2]$	Black	88	[e] 1 952m, 1 929s, 1 900vs, 1 840w br, 1 800vw	51.6 (51.0)	4.5 (4.2)

[a] Calculated values are given in parentheses. [b] $R = C_6H_4Me\text{-}4$. [c] In Et_2O. [d] Compound failed to crystallise, see text. [e] In light petroleum. [f] In CH_2Cl_2. [g] Crystallises with 0.5 of a molecule of CH_2Cl_2.

Table 2. Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. data[a] for the complexes

Compound	$^1H(\delta)$[b]	$^{13}C\text{-}\{H\}(\delta)$[c]	$^{31}P\text{-}\{^1H\}$ (δ)[b,d]
(**4a**)	1.23 [d, 9 H, MeP, *J*(PH) 9], 2.33 (s, 3 H, Me-4), 5.18 (s, 5 H, C_5H_5), 7.11, 7.26 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[e] 385.5 [d, μ-C, *J*(PC) 22], 241.7, 236.9 (MoCO), 219.5 [d, FeCO, *J*(PC) 33], 215.2 [d, FeCO, *J*(PC) 27], 208.8 [d, FeCO, *J*(PC) 56], 158.6 [C^1 (C_6H_4)], 137.9, 128.7, 126.0 (C_6H_4), 94.6 (C_5H_5), 21.6 (Me-4), 17.1 [d, MeP, *J*(PC) 27]	15.0
(**5a**)	[f] 1.12 [d, 9 H, MeP, *J*(PH) 11], 2.43 (s, 3 H, Me-4), 5.62 (s, 5 H, C_5H_5), 7.20, 7.26 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[e] 407.1 (br, μ-C), 234.6 (MoCO), 221.3 [d, FeCO, *J*(PC) 21], 162.8 [C^1 (C_6H_4)], 135.9, 128.5, 120.7 (C_6H_4), 95.1 (C_5H_5), 21.5 (Me-4), 19.7 [d, MeP, *J*(PC) 30]	40.6
(**6**)	1.49 [d, 9 H, MeP, *J*(PH) 9], 2.24 (s, 3 H, Me-4), 5.41 [d, 5 H, C_5H_5, *J*(PH) 1], 6.94, 7.20 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[g] 294.0 [d, C≡Mo, *J*(PC) 22], 248.1 [d, CO, *J*(PC) 22], 145.1 [C^1 (C_6H_4)], 136.4, 128.3, 127.8 (C_6H_4), 91.1 (C_5H_5), 24.0 [d, MeP, *J*(PC) 28], 21.6 (Me-4)	20.8
(**8a**)	1.19 (m, 18 H, MeP), 2.31 (s, 3 H, Me-4), 5.16 (s, 5 H, C_5H_5), 7.11, 7.30 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[h] 397.0 [t, μ-C, *J*(PC) 18], 247.3, 246.6 (MoCO), 222.6 [t, FeCO, *J*(PC) 30], 220.2 [t, FeCO, *J*(PC) 28], 157.4 [C^1 (C_6H_4)], 136.9, 128.4, 128.0 (C_6H_4), 93.9 (C_5H_5), 21.6 (Me-4), 19.8 [d, MeP, *J*(PC) 21], 17.6 [d, MeP, *J*(PC) 21]	17.3
(**9**)	1.60 [d, 9 H, MeP, *J*(PH) 10], 2.38 (s, 3 H, Me-4), 5.19 (s, 5 H, C_5H_5), 7.12, 7.45 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[i] 281.9 (μ_3-C), 231.1 (MoCO), 214.0 (br, FeCO), 159.6 [C^1 (C_6H_4)], 136.3, 130.1, 128.0 (C_6H_4), 94.1 (C_5H_5), 21.3 (Me-4), 18.0 [d, MeP, *J*(PC) 34]	23.9
(**10a**)	2.37 (s, 3 H, Me-4), 3.14 [apparent t, 2 H, CH_2, *J*(PH) 10], 5.02 (s, 5 H, C_5H_5), 6.83—7.89 (m, 24 H, C_6H_4 and Ph)	[i] 283.4 (μ_3-C), 230.9 (MoCO), 220.6 (FeCO), 160.1 [C^1 (C_6H_4)], 137.1—127.6 (C_6H_4 and Ph), 92.8 (C_5H_5), 35.4 [t, CH_2, *J*(PC) 21], 21.1 (Me-4)	52.5
(**11**)	[h] 1.12 [d, 9 H, MeP, *J*(PH) 8], 2.17 (s, 3 H, Me-4), 2.27 (s, 3 H, Me-4), 5.35, 5.43 (s × 2, 10 H, C_5H_5), 5.99 [d, 1 H, C_6H_4, *J*(HH) 6], 6.66, 6.86 [$(AB)_2$, 4 H C_6H_4, *J*(AB) 6], 6.99 (br, 2 H, C_6H_4), 7.32 [d, 1 H, C_6H_4, *J*(HH) 6]	[h] 253.0 (μ-CO), 237.3, 232.2 (MoCO), 221.9 [d, FeCO, *J*(PC) 16], 218.0 [d, FeCO, *J*(PC) 10], 159.1 [d, μ-C, *J*(PC) 7], 146.4—128.2 (C_6H_4), 101.6 [d, μ-C, *J*(PC) 7], 96.2, 94.8 (C_5H_5), 21.4, 21.0 (Me-4), 16.4 [d, MeP, *J*(PC) 28]	15.9

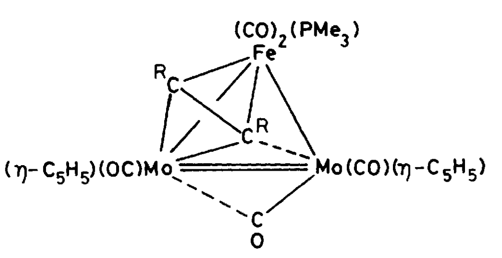
[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature unless otherwise stated. [b] Measured in $CDCl_3$. [c] Hydrogen-1 decoupled, to high frequency of $SiMe_4$; measured in CD_2Cl_2–CH_2Cl_2. [d] Hydrogen-1 decoupled, chemical shifts to high frequency of 85% H_3PO_4 (external) taken as positive. [e] Measured at −50 °C. [f] Measured in $(CD_3)_2CO$. [g] Measured at −20 °C. [h] Measured at −70 °C. [i] Measured at −40 °C.



M

(10a) Mo

(10b) W



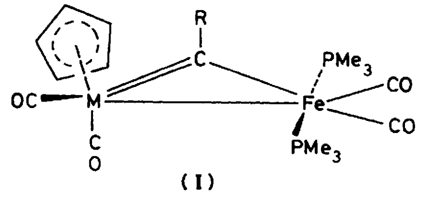
(11)

R = C_6H_4Me-4

ambient temperatures. In contrast, the ^{13}C-$\{^1H\}$ n.m.r. spectra at −70 °C reveal the presence of inequivalent PMe_3 groups, and the low symmetry of the complexes at this temperature is further emphasised by the observation of four resonances for the inequivalent carbonyl ligands at iron and molybdenum or tungsten. These data suggest a low-temperature limiting structure of the type (**I**) shown below. Moreover, the proposed stereochemistry at the two metal centres closely resembles that established[2] by *X*-ray diffraction for the related $Fe(CO)_4$ derivative (**1a**). The presence of equivalent PMe_3 ligands at ambient temperature may be readily understood if rotation of the $M(CO)_2(\eta-C_5H_5)$ fragments about the Fe–M axis is rapid on the n.m.r. time-scale under these conditions of measurement.

Compound (**2a**) reacts with one equivalent of PMe_3 to give $[Fe_2Mo(\mu_3-CR)(\mu-CO)(CO)_7(PMe_3)(\eta-C_5H_5)]$ (**9**), characterised by the data given in Tables 1 and 2. A related compound $[Fe_2W(\mu_3-CR)(\mu-CO)(CO)_6(PMe_2Ph)_2(\eta-C_5H_5)]$ has been obtained by treating (**2b**) with an excess of PMe_2Ph.[3] The observation of 12 bands in the i.r. spectrum of (**9**) indicates the presence of rotational isomers in solution, a property in complexes of this type discussed previously.[3,8] However, the isomers of (**9**) interconvert rapidly on the n.m.r. time-scale since in the ^{13}C-$\{^1H\}$ n.m.r. spectrum only two CO resonances are observed (Table 2). The resonance for the μ_3-C nucleus is seen at δ 281.9 p.p.m., in the range expected for a triply bridging alkylidyne ligand. In the spectrum of the precursor (**2a**) the μ_3-C signal is at 295.5 p.p.m.[2]

Interestingly, compound (**9**) may also be prepared by treating (**6**) with an excess of $[Fe_2(CO)_9]$, a process involving transfer of the PMe_3 ligand from molybdenum to iron. It is likely this reaction proceeds *via* (**5a**) as an intermediate, which then adds an $Fe(CO)_4$ fragment derived from $[Fe_2(CO)_9]$. It was mentioned above that treatment of (**6**) with one equivalent of $[Fe_2(CO)_9]$ gives a mixture of (**4a**) and (**5a**); transfer of the PMe_3 ligand between metal centres in reactions of this kind has precedent. Thus compound (**7**) reacts with $[Co_2(CO)_8]$ to give a complex $[Co_2W(\mu_3-CR)(CO)_7(PMe_3)(\eta-C_5H_5)]$ in which the PMe_3 group ligates the tungsten atom. However, in solution this species isomerises, the phosphine group migrating to a cobalt centre.[7] Similarly, (**7**) reacts with $[Rh(C_2H_4)_2(\eta^5-C_9H_7)]$ to give $[RhW(\mu-CR)(CO)_2(PMe_3)(\eta-C_5H_5)(\eta^5-C_9H_7)]$, but an *X*-ray diffraction study showed that the PMe_3 group was bonded to the rhodium atom.[7]



(**I**)

Reaction between (**2a**) and dppm ($Ph_2PCH_2PPh_2$) affords $[Fe_2Mo(\mu_3-CR)(\mu-CO)(\mu-dppm)(CO)_6(\eta-C_5H_5)]$ (**10a**). The tungsten analogue (**10b**) has been similarly prepared from dppm and (**2b**).[3] The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**10a**) (Table 2), like that of (**10b**), showed only one resonance, indicating that the dppm ligand is bridging the Fe–Fe bond and not an Fe–Mo vector. In the ^{13}C-$\{^1H\}$ n.m.r. spectrum, the resonance for the μ_3-C nucleus is at δ 283.4 p.p.m., compared with the corresponding signal in the spectrum of (**10b**) at 272.1 p.p.m. The carbonyl ligands in the species (**10**) undergo site exchange. Thus when the ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**10a**) was measured at −40 °C, the lower limit based on the solubility of the compound, only two peaks were observed in the carbonyl region (Table 2). The complexity of the i.r. spectrum in the carbonyl stretching region indicates that isomers are present in solution.

Finally, the reaction between PMe_3 and the unsaturated compound (**3a**) was investigated. Since (**3a**) is a 46 valence electron cluster it seemed possible that it would add a molecule of PMe_3 to afford a 48 valence electron species. In practice, however, CO is displaced and the compound $[FeMo_2(\mu_3-RC_2R)(CO)_5(PMe_3)(\eta-C_5H_5)_2]$ (**11**) is formed. Like the complexes (**3**), compound (**11**) in solution undergoes dynamic behaviour, as evidenced by the temperature dependence of the ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra. At −70 °C, however, limiting spectra for (**11**) are observed (Table 2). The ^{13}C-$\{^1H\}$ data are especially informative. In the carbonyl region a peak at δ 253.0 p.p.m. may be assigned to the semi-bridging carbonyl group, further support for the presence of which is given by the appearance of a band at 1 800 cm^{-1} in the i.r. spectrum. An *X*-ray diffraction study has revealed that this structural feature is present in the precursors (**3**).[2,3] Signals at δ 237.3 and 232.2 p.p.m. in the ^{13}C-$\{^1H\}$ n.m.r. spectrum may be assigned to the two non-equivalent MoCO groups. The presence of the $Fe(CO)_2(PMe_3)$ fragment is confirmed by the appearance of two CO resonances at 221.9 and 218.0 p.p.m. which appear as doublets due to ^{31}P–^{13}C coupling. In accord with the proposed structure, there are two signals for the pairs of non-equivalent C_5H_5 and Me-4 groups. Resonances for the ligated carbon atoms of the alkyne occur as doublets at δ 159.1 and 101.6 p.p.m., with ^{31}P–^{13}C couplings of 7 Hz.

The ^1H spectrum also reveals the presence of two Me-4 and two C_5H_5 groups in different environments. Moreover, whereas one C_6H_4 group of complex (**11**) gives rise to the customary $(AB)_2$ pattern of peaks, the other displays three signals. These are a doublet, a broad resonance, and a doublet, with relative intensities 1:2:1. The limiting low-temperature ^1H n.m.r. spectrum of (**3a**) showed an identical pattern for the two C_6H_4 groups. In compounds (**3**) and (**11**) the dynamic behaviour probably takes the form of pivoting of the alkyne about the

μ_3 carbon atom from one Fe–M (M = Mo or W) edge to the other, with a concomitant transfer of the semi-bridging carbonyl between the two molybdenum or two tungsten centres, a process discussed previously.[3]

Experimental

The experimental techniques used and the instrumentation employed have been described in previous parts of this series.[4,5,8] Light petroleum refers to that fraction of b.p. 40—60 °C. Compounds (**1a**)—(**3a**) and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ were prepared as previously described.[2] Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Complexes $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_n(PMe_3)(\eta\text{-}C_5H_5)]$ (*n* = 4 *or* 5).—(*i*) A light petroleum (15 cm^3) solution of (**1a**) (0.15 g, 0.30 mmol) at −20 °C was treated with PMe_3 (0.30 mmol). After stirring for 15 min, solvent was removed *in vacuo*, and the brown residue extracted with light petroleum (3 × 20 cm^3) and the extracts filtered through a Celite pad (*ca.* 2 × 2 cm). Removal of solvent *in vacuo* afforded brown *microcrystals* of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMe_3)(\eta\text{-}C_5H_5)]$ (**4a**) (0.15 g).

Diethyl ether solutions of (**4a**) treated with a stream of nitrogen gas give mixtures containing (**4a**) and purple $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)(\eta\text{-}C_5H_5)]$ (**5a**).

(*ii*) A mixture of the compounds $[Fe_2(CO)_9]$ (1.1 g, 3.0 mmol) and (**6**) (1.1 g, 3.0 mmol) in Et_2O (150 cm^3) was stirred at room temperature for 40 min. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (5 cm^3) and chromatographed at *ca.* −20 °C on Florisil. Elution with light petroleum–CH_2Cl_2 mixtures, initially 4:1 changing to 1:1, afforded first a black-brown eluate, and secondly a purple eluate. Removal of solvent *in vacuo* from the former afforded brown *microcrystals* of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMe_3)(\eta\text{-}C_5H_5)]$ (**4a**) (1.0 g). Removal of solvent *in vacuo* from the latter gave purple *microcrystals* of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)(\eta\text{-}C_5H_5)]$ (**5a**) (0.35 g).

Reaction of $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ *with* PMe_3.—A tetrahydrofuran (20 cm^3) solution of $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.32 g, 1.0 mmol) was treated with PMe_3 (1.0 mmol) at room temperature. Evolution of CO was observed, and after 5 min the reaction was complete, as revealed by i.r. Solvent was removed *in vacuo*, and the residue dissolved in light petroleum (50 cm^3) and filtered through a Celite pad (*ca.* 2 × 2 cm). Solvent was removed *in vacuo* giving $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**6**) (0.35 g) as a dark red oil which did not crystallise in spite of repeated attempts.

Synthesis of the Complex $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)_2(\eta\text{-}C_5H_5)]$.—Compound (**1a**) (0.15 g, 0.30 mmol) in CH_2Cl_2 (10 cm^3) was treated with PMe_3 (0.60 mmol) at room temperature. After 5 min solvent was removed *in vacuo* and the residue washed with light petroleum (2 × 10 cm^3) at 0 °C and dried *in vacuo* affording green *microcrystals* of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**8a**) (0.12 g).

Synthesis of the Complex $[Fe_2Mo(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta\text{-}C_5H_5)]$.—(*i*) A mixture of (**2a**) (0.11 g, 0.17 mmol) and PMe_3 (0.17 mmol) in $CHCl_2$–light petroleum (10 cm^3, 1:1) at 0 °C was stirred for 1 h. Solvent was removed *in vacuo*, and the brown residue washed with light petroleum (3 × 10 cm^3) at −20 °C and then redissolved in CH_2Cl_2–light petroleum (20 cm^3, 1 : 1), and filtered through a Celite pad (2 × 2 cm) affording a red-brown solution. Removal of solvent *in vacuo* gave red-brown *microcrystals* of $[Fe_2Mo(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta\text{-}C_5H_5)]$ (**9**) (0.08 g).

(*ii*) An Et_2O (25 cm^3) solution of (**6**) (0.11 g, 0.30 mmol) was treated with $[Fe_2(CO)_9]$ (0.36 g, 1.0 mmol), and the mixture stirred for 8 h at room temperature. Volatile material was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed on Florisil. Elution with the same solvent mixture removed first a trace of green $[Fe_3(CO)_{12}]$ (identified by i.r.) and then a brown band. Removal of solvent *in vacuo* from the latter afforded brown *microcrystals* of $[Fe_2Mo(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta\text{-}C_5H_5)]$ (**9**) (0.18 g).

Reaction of $[Fe_2Mo(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ *with* $Ph_2PCH_2PPh_2$.—A solution of (**2a**) (0.084 g, 0.13 mmol) in Et_2O (30 cm^3) was treated with dppm (0.052 g, 0.13 mmol), and the mixture stirred at room temperature for 1 d. Solvent was removed *in vacuo*, and the brown residue dissolved in light petroleum (10 cm^3) and chromatographed on alumina. Elution with Et_2O–light petroleum (1:1) gave a green eluate. Solvent was removed *in vacuo* and the residue was crystallised from CH_2Cl_2–light petroleum (10 cm^3, 1:4) at *ca.* −20 °C to yield brown *crystals* of $[Fe_2Mo(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6(\eta\text{-}C_5H_5)]$ (**10a**) (0.07 g).

Reaction of $[FeMo_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ *with* PMe_3.—A CH_2Cl_2 (15 cm^3) solution of (**3a**) (0.15 g, 0.20 mmol) was treated with PMe_3 (0.20 mmol). After 15 min the reaction was complete, as shown by i.r. Solvent was removed *in vacuo*, and the residue dissolved in light petroleum (60 cm^3), filtered through a Celite pad (*ca.* 3 × 2 cm), and the solution concentrated to *ca.* 10 cm^3 and cooled to *ca.* −70 °C. Black *microcrystals* of $[FeMo_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_5(PMe_3)(\eta\text{-}C_5H_5)_2]$ (**11**) (0.14 g) were thereby obtained.

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