Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 56.[1] Synthesis of Iron–Molybdenum Compounds; Crystal Structures of $[FeMo(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ and $[FeMo_2(\mu_3\text{-}RC_2R)(CO)_6\text{-}(\eta\text{-}C_5H_5)_2](R = C_6H_4Me\text{-}4)$ *

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Equivalent amounts of $[Fe_2(CO)_9]$ and $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) react in Et_2O at room temperature to give the dimetal complex $[FeMo(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$, the structure of which has been established by *X*-ray diffraction. Four CO groups are terminally bound to the iron atom and two to the molybdenum, with the latter also carrying the $\eta\text{-}C_5H_5$ ligand. The dimensions of the dimetallacyclopropene ring are Fe–Mo 2.823(1), μ-C–Fe 2.008(5), and μ-C–Mo 1.921(5) Å. Excess of $[Fe_2(CO)_9]$ and $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ react at room temperature in Et_2O to give the trimetal compound $[Fe_2Mo(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$. In contrast, reaction between one equivalent of nonacarbonyldi-iron and two equivalents of the tolylmethylidynemolybdenum compound affords the 46-valence-electron irondimolybdenum cluster $[FeMo_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$, the structure of which was confirmed by an *X*-ray diffraction study. The alkyne ligand adopts a $\mu_3\text{-}(\eta^2\text{-}\perp)$ bonding mode towards the metal triangle [Mo–Mo 2.764(1), Fe–Mo 2.732(1) and 2.761(1) Å], and one carbonyl ligand semi-bridges the molybdenum–molybdenum bond [Mo–C–O 162.5(3)°]. Reaction between one equivalent of the bis(cyclo-octene)iron complex $[Fe(CO)_3(\eta\text{-}C_8H_{14})_2]$ and two equivalents of $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$, in light petroleum at -40 °C, affords the thermally labile heptacarbonylirondimolybdenum compound $[FeMo_2(\mu_3\text{-}RC_2R)(CO)_7(\eta\text{-}C_5H_5)_2]$. The latter readily releases a molecule of CO to give $[FeMo_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$, but this process is reversed at -20 °C. The spectroscopic properties of the new compounds are reported and discussed.

In a previous paper[2] we reported that treatment of the alkylidynetungsten complex $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (**1a**) ($R = C_6H_4Me\text{-}4$) with iron carbonyls affords the dimetal compound (**2a**) and the trimetal complexes (**3a**) and (**4a**), the relative yields of these compounds depending on the reaction conditions. In this paper we describe reactions of the related molybdenum compound (**1b**) with $[Fe_2(CO)_9]$ and $[Fe(CO)_3\text{-}(\eta\text{-}C_8H_{14})_2]$ (C_8H_{14} = cyclo-octene). The products are the iron–molybdenum compounds, $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6\text{-}(\eta\text{-}C_5H_5)]$ (**2b**), $[Fe_2Mo(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**3b**), and $[FeMo_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_n(\eta\text{-}C_5H_5)_2]$ (**4b**, $n = 6$; **5b**, $n = 7$). Moreover, it was found that the saturated 48-valence-electron species (**5b**) readily releases CO to give the unsaturated 46-valence-electron complex (**4b**), while the latter combines with CO at low temperatures to yield (**5b**). These observations reflect interesting differences between the molybdenum and tungsten systems. Thus in the previous work[2] we obtained no evidence for the saturated complex (**5a**), although in related studies we isolated and fully characterised the tungsten–ruthenium and –osmium compounds (**5c**) and (**5d**), and showed that they exist as isomeric mixtures of (**I**) and (**II**).[3] Another interesting feature of the present work is that compound (**2b**) is relatively stable, in contrast with (**2a**), which is a thermally very labile species. The relative stability of (**2b**) makes it a useful reagent for further syntheses.[4]

Results and Discussion

At room temperature in diethyl ether the compounds (**1b**) and $[Fe_2(CO)_9]$ react in 1:1 ratio to afford the dimetal complex (**2b**) in *ca.* 80% yield. The microanalytical and spectroscopic data for (**2b**) (Experimental section) are in accord with the formulation shown. In particular, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum shows a characteristic resonance at δ 362.3 p.p.m. for the μ-C nucleus. The corresponding signal in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**2a**) is at 331.3 p.p.m.[2]

As mentioned above, compound (**2a**) has poor stability, and thus a single-crystal *X*-ray diffraction study was not carried out on this species. There was no such difficulty with (**2b**), and the results of the *X*-ray diffraction work are summarised in Table 1; the structure is shown in Figure 1. This investigation was carried out in order to extend the scope of the structural data available for heteronuclear dimetal compounds in which the metal–metal bonds are spanned by tolylmethylidyne groups.[5]

In (**2b**) the dimensions of the dimetallacyclopropene ring are: Fe–Mo 2.823(1), C(1)–Fe 2.008(5), and C(1)–Mo 1.921(5) Å. Since the radii of molybdenum and tungsten are esssentially the same, it is interesting to compare the metal–metal bond distance in (**2b**) with the significantly shorter Fe–W separation [2.612(2) Å] found in the unsaturated 32-valence-electron complex $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ [$HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate].[5d] The Fe–Mo bond in (**2b**) is also somewhat longer than the similar bonds in $[FeMo\{\mu\text{-}\sigma{:}\eta\text{-}C(R){=}CH_2\}(\mu\text{-}CH_2)(CO)_5(\eta\text{-}C_5H_5)]$ [2.717(1) Å], $[FeMo\{\mu\text{-}\eta^3\text{-}C(R)C(OMe)C(H)\}(CO)_5(\eta\text{-}C_5H_5)]$ [2.704(1)Å], and $[FeMo\{\mu\text{-}\eta^2\text{-}SCR\}(CO)_5(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) [2.765(1) Å].[4] The C(1)–Fe linkage in (**2b**) is significantly longer than the corresponding distance [1.826(6) Å] in $[FeW(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_5\{HB(pz)_3\}]$,[5d] a result also in accord with the electronic unsaturation in the latter complex. The C(1)–Mo distance in (**2b**) [1.921(5) Å] is as expected for a C=Mo bond, based on comparable μ-C=W separations (1.91—2.02 Å) found

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* 1,1,1,2,2-Hexacarbonyl-2-η-cyclopentadienyl-μ-*p*-tolylmethylidyne-ironmolybdenum(*Fe–Mo*) and 2,3-μ-carbonyl-1,1,1,2,3-pentacarbonyl-2,3-bis(η-cyclopentadienyl)-μ_3-[di-*p*-tolylacetylene-C^1(Fe,$Mo^{2,3}$)C^2(Fe,Mo^2)]-irondimolybdenum(2*Fe–Mo*)(*Mo=Mo*) respectively.

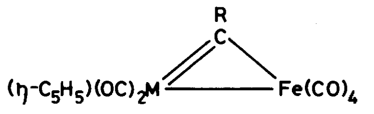
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Selected internuclear distances (Å) and angles (°) for [FeMo(μ-CC$_6$H$_4$Me-4)(CO)$_6$(η-C$_5$H$_5$)] (**2b**) with estimated standard deviations in parentheses

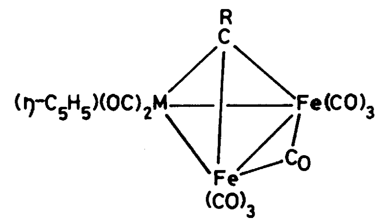
Fe–Mo	2.823(1)	Mo–C(1)	1.921(5)	Mo–C(2)	1.973(7)	Mo–C(3)	1.952(7)
Fe–C(1)	2.008(5)	Fe–C(4)	1.797(7)	Fe–C(5)	1.824(6)	Fe–C(6)	1.804(7)
Fe–C(7)	1.777(6)	C(1)–C(11)	1.450(7)	C(2)–O(2)	1.148(8)	C(3)–O(3)	1.137(9)
C(4)–O(4)	1.137(9)	C(5)–O(5)	1.116(8)	C(6)–O(6)	1.134(8)	C(7)–O(7)	1.137(8)
Mo–C (C_5H_5) mean	2.313	C–C (C_5H_5)	1.38				
Fe–Mo–C(1)	45.3(2)	Fe–Mo–C(2)	71.7(2)	C(1)–Mo–C(2)	115.2(2)	Fe–Mo–C(3)	99.0(2)
C(1)–Mo–C(3)	85.8(2)	C(2)–Mo–C(3)	91.3(3)	Mo–Fe–C(1)	42.8(1)	Mo–Fe–C(4)	81.8(3)
C(1)–Fe–C(4)	84.6(3)	Mo–Fe–C(5)	115.8(2)	C(1)–Fe–C(5)	158.6(3)	C(4)–Fe–C(5)	92.7(3)
Mo–Fe–C(6)	85.3(2)	C(1)–Fe–C(6)	86.3(3)	C(4)–Fe–C(6)	167.0(3)	C(5)–Fe–C(6)	92.4(3)
Mo–Fe–C(7)	142.3(2)	C(1)–Fe–C(7)	99.4(2)	C(4)–Fe–C(7)	97.3(3)	C(5)–Fe–C(7)	102.0(3)
C(6)–Fe–C(7)	93.3(3)	Mo–C(1)–Fe	91.9(2)	Mo–C(1)–C(11)	139.1(4)	Fe–C(1)–C(11)	128.7(4)
Mo–C(2)–O(2)	171.9(5)	Mo–C(3)–O(3)	176.4(6)	Fe–C(4)–O(4)	178.0(6)	Fe–C(5)–O(5)	178.2(6)
Fe–C(6)–O(6)	178.3(5)	Fe–C(7)–O(7)	178.4(7)				

$(\eta\text{-}C_5H_5)(OC)_2M{\equiv}CR$

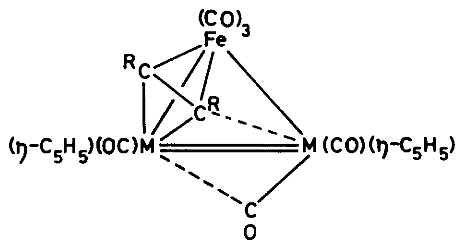
	M
(**1a**)	W
(**1b**)	Mo



	M
(**2a**)	W
(**2b**)	Mo

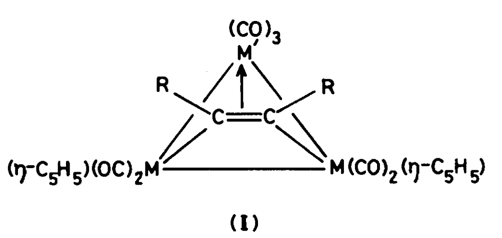


	M
(**3a**)	W
(**3b**)	Mo

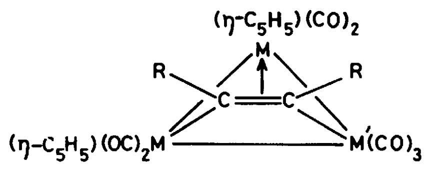


	M
(**4a**)	W
(**4b**)	Mo

R = C$_6$H$_4$Me-4



(**I**)



(**II**)

	M	M′	R
(**5a**)	W	Fe	C$_6$H$_4$Me-4
(**5b**)	Mo	Fe	C$_6$H$_4$Me-4
(**5c**)	W	Ru	C$_6$H$_4$Me-4
(**5d**)	W	Os	C$_6$H$_4$Me-4
(**5e**)	W	Ru	Me

Table 2. Selected internuclear distances (Å) and angles (°) for the complex $[FeMo_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (**4b**)

Mo(1)–Mo(2)	2.764(1)	Mo(1)–Fe	2.732(1)	Mo(1)–C(1)	2.070(3)	Mo(1)–C(2)	2.299(3)
Mo(1)–C(6)	1.949(3)	Mo(1)–C(7)	2.531(4)	Mo(2)–Fe	2.761(1)	Mo(2)–C(2)	2.297(3)
Mo(2)–C(7)	1.971(3)	Mo(2)–C(8)	1.979(3)	Fe–C(1)	2.049(3)	Fe–C(2)	2.016(2)
Fe–C(3)	1.801(3)	Fe–C(4)	1.794(3)	Fe–C(5)	1.783(3)	C(1)–C(2)	1.399(4)
C(1)–C(11)	1.471(4)	C(2)–C(21)	1.504(3)	C(3)–O(3)	1.132(4)	C(4)–O(4)	1.147(4)
C(5)–O(5)	1.143(3)	C(6)–O(6)	1.162(4)	C(7)–O(7)	1.160(4)	C(8)–O(8)	1.145(4)
Mo(1)–C (C_5H_5) mean	2.329	Mo(2)–C (C_5H_5) mean	2.330				

Mo(2)–Mo(1)–Fe	60.3(1)	Mo(2)–Mo(1)–C(1)	87.6(1)	Fe–Mo(1)–C(1)	48.1(1)	Mo(2)–Mo(1)–C(2)	53.0(1)
Fe–Mo(1)–C(2)	46.3(1)	C(1)–Mo(1)–C(2)	36.9(1)	Mo(2)–Mo(1)–C(6)	104.0(1)	Fe–Mo(1)–C(6)	68.9(1)
C(1)–Mo(1)–C(6)	97.5(1)	C(2)–Mo(1)–C(6)	114.9(1)	Mo(2)–Mo(1)–C(7)	43.4(1)	Fe–Mo(1)–C(7)	81.9(1)
C(1)–Mo(1)–C(7)	125.7(1)	C(2)–Mo(1)–C(7)	95.6(1)	C(6)–Mo(1)–C(7)	78.7(1)	Mo(1)–Mo(2)–Fe	59.3(1)
Mo(1)–Mo(2)–C(2)	53.1(1)	Fe–Mo(2)–C(2)	45.9(1)	Mo(1)–Mo(2)–C(7)	62.0(1)	Fe–Mo(2)–C(7)	92.2(1)
C(2)–Mo(2)–C(7)	113.9(1)	Mo(1)–Mo(2)–C(8)	76.8(1)	Fe–Mo(2)–C(8)	131.1(1)	C(2)–Mo(2)–C(8)	91.5(1)
C(7)–Mo(2)–C(8)	84.6(1)	Mo(1)–Fe–Mo(2)	60.4(1)	Mo(1)–Fe–C(1)	48.8(1)	Mo(2)–Fe–C(1)	88.1(1)
Mo(1)–Fe–C(2)	55.5(1)	Mo(2)–Fe–C(2)	54.8(1)	C(1)–Fe–C(2)	40.2(1)	Mo(1)–Fe–C(3)	106.6(1)
Mo(2)–Fe–C(3)	162.9(1)	C(1)–Fe–C(3)	90.5(1)	C(2)–Fe–C(3)	129.2(1)	Mo(1)–Fe–C(4)	99.9(1)
Mo(2)–Fe–C(4)	77.1(1)	C(1)–Fe–C(4)	148.3(1)	C(2)–Fe–C(4)	131.8(1)	C(3)–Fe–C(4)	95.5(1)
Mo(1)–Fe–C(5)	152.5(1)	Mo(2)–Fe–C(5)	102.4(1)	C(1)–Fe–C(5)	114.3(1)	C(2)–Fe–C(5)	97.3(1)
C(3)–Fe–C(5)	93.7(1)	C(4)–Fe–C(5)	96.4(1)	Mo(1)–C(1)–Fe	83.1(1)	Mo(1)–C(1)–C(2)	80.5(2)
Fe–C(1)–C(2)	68.6(1)	Mo(1)–C(1)–C(11)	136.4(2)	Fe–C(1)–C(11)	129.3(2)	C(2)–C(1)–C(11)	133.9(2)
Mo(1)–C(2)–Mo(2)	73.9(1)	Mo(1)–C(2)–Fe	78.2(1)	Mo(2)–C(2)–Fe	79.3(1)	Mo(1)–C(2)–C(1)	62.6(1)
Mo(2)–C(2)–C(1)	131.1(2)	Fe–C(2)–C(1)	71.1(1)	Mo(1)–C(2)–C(21)	142.0(2)	Mo(2)–C(2)–C(21)	104.9(2)
Fe–C(2)–C(21)	139.6(2)	C(1)–C(2)–C(21)	123.0(2)	Fe–C(3)–O(3)	178.2(2)	Fe–C(4)–O(4)	171.9(3)
Fe–C(5)–O(5)	177.5(3)	Mo(1)–C(6)–O(6)	170.4(2)	Mo(1)–C(7)–Mo(2)	74.6(1)	Mo(1)–C(7)–O(7)	122.6(2)
Mo(2)–C(7)–O(7)	162.5(3)	Mo(2)–C(8)–O(8)	172.6(3)				

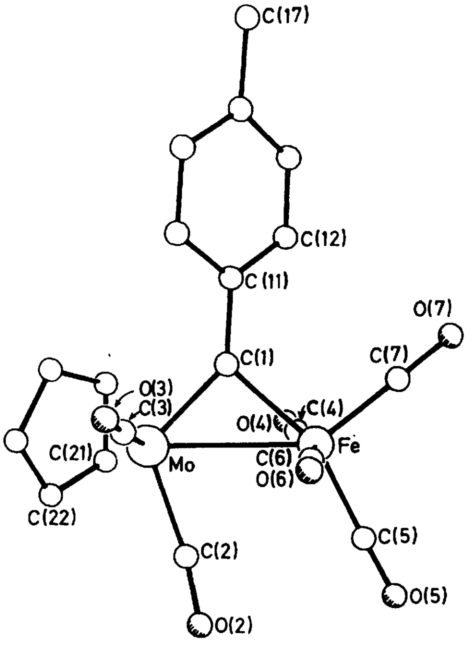


Figure 1. The molecular structure of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ (**2b**) showing the atom-labelling scheme

in several dimetallacyclopropene complexes containing tungsten.[5c]

In (**2b**) the iron atom carries four terminal CO groups and the molybdenum two such ligands, albeit with one group showing a small deviation from linearity [Mo–C(2)–O(2) 171.9(5)°]. As expected, the molybdenum atom is ligated by the $\eta\text{-}C_5H_5$ group. The plane defined by C(1)FeMo is inclined at 40.8° to that of the plane containing the atoms C(1) and C(11)—C(16).

If (**1b**) is treated with a three-fold excess of $[Fe_2(CO)_9]$ in diethyl ether at room temperature the black crystalline trimetal complex $[Fe_2Mo(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**3b**) is formed in high yield. The tungsten analogue (**3a**) has been reported previously.[2] Compound (**3b**) was fully characterised by the analytical and spectroscopic data given in the Experimental section. Examination of the n.m.r. spectra revealed the existence of dynamic behaviour in solution, corresponding to the presence of two isomers (*ca.* 3:1) interconverting on the n.m.r. time-scale. Thus when the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum is measured at ambient temperatures there is a single resonance at δ 295.5 p.p.m. for the μ_3-C nucleus and only one broad signal (217.7 p.p.m.) for the carbonyl ligands. However, in the spectrum measured at −90 °C (400 MHz), there are two alkylidyne resonances (δ 296.0 and 291.2 p.p.m.), two peaks in the bridging CO region (256.4 and 245.9 p.p.m.), and three signals in the terminal CO region [225.5 (MoCO), 212.7 and 210.5 p.p.m. (FeCO)]. Evidently even at −90 °C site exchange of carbonyl ligands at the molybdenum and iron centres persists in each isomer. Probably the isomerism is rotational in nature, resulting from different orientations of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ group with respect to an axis through the molybdenum and the mid-point of the $\mu_3\text{-}CFe_2$ triangle. This property has been observed previously with the related compounds (**3a**)[2] and $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)]$.[6]

The existence of rotational isomers of (**3b**) in solution is also revealed by the appearance of 13 absorptions in the carbonyl region of the i.r. spectrum (see Experimental section). As discussed previously,[2] the i.r. spectrum of (**3a**) also shows 13 carbonyl bands, a number exceeding that expected for the presence of a single species in solution.

By treating an excess of (**1b**) with $[Fe_2(CO)_9]$ in diethyl ether it was possible to prepare the dark red irondimolybdenum complex $[FeMo_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (**4b**) in good yield. The tungsten analogue (**4a**) has been obtained previously, and its structure confirmed by *X*-ray diffraction.[2] However, because the i.r. spectrum of (**4b**) in the carbonyl region displayed a somewhat different pattern to that observed for (**4a**) we were initially unsure of the formulation of this complex. Consequently an *X*-ray diffraction study was carried out on (**4b**). The results are summarised in Table 2 and the structure is shown in Figure 2. The data confirmed that (**4b**) is isostructural and isomorphous with (**4a**).

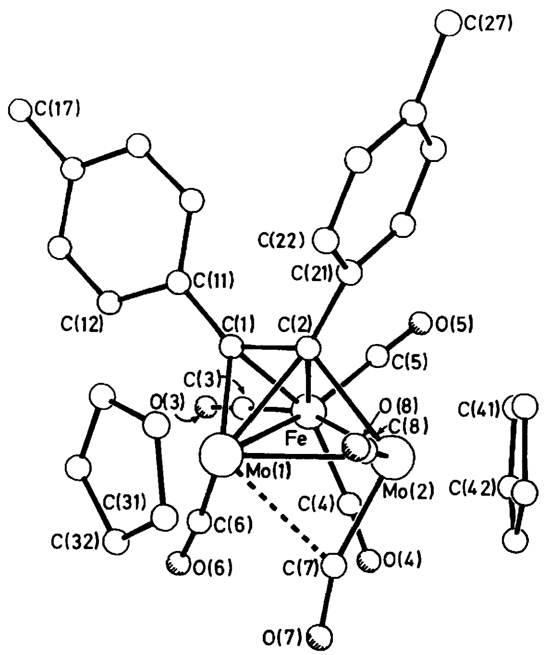


Figure 2. The molecular structure of the electronically unsaturated complex $[FeMo_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ **(4b)** showing the atom-labelling scheme.

The alkyne groups in the complexes **(4)** are formed by coupling of two tolylmethylidyne fragments. The $C_2(C_6H_4Me\text{-}4)_2$ ligand adopts the μ_3-(η^2-$\perp$) bonding mode with the metal triangle,[7] first observed with $[Fe_3(\mu_3\text{-}C_2Ph_2)(CO)_9]$.[8] The bond parameters for **(4a)** and **(4b)** as expected are very similar, as seen by comparison of the data for the metal triangle [**(4a)**, Fe–W 2.731(1) and 2.745(1), W–W 2.747(1) Å;[2] **(4b)**, Fe–Mo 2.732(1) and 2.761(1), Mo–Mo 2.764(1) Å], and the ligated alkyne [**(4a)**, C–C 1.399(9) Å;[2] **(4b)**, 1.399(4) Å]. A carbonyl group in **(4b)** semi-bridges the Mo–Mo vector [Mo(2)–C(7)–O(7) 162.5(3)°], and a similar situation occurs with the W–W bond in **(4a)**.

In **(4b)** the semi-bridging CO ligand reveals itself in the i.r. with a band at 1 792 cm^{-1} and in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (measured at -70 °C) with a resonance at δ 249.9 p.p.m. Variable-temperature n.m.r. studies reveal that both compounds **(4)** undergo dynamic behaviour in solution, probably by a mechanism involving pivoting of the alkyne ligand about the μ_3-C atom [C(2) of Figure 2] from one Fe–M edge to the other, as discussed elsewhere.[2] With **(4b)** this process slows down at -70 °C, as shown by the data given in the Experimental section. For example, resonances for the two non-equivalent C_5H_5 and C_6H_4Me-4 groups are observed in the spectra at -70 °C in accord with the *X*-ray diffraction results, whereas in room-temperature spectra these groups appear to be equivalent.

In the compounds **(4)** the W–W and Mo–Mo separations are short, corresponding to metal–metal double bonds, and in agreement with the electronic unsaturation of these clusters (46-valence-electron species).

Treatment of two equivalents of **(1b)** with one equivalent of $[Fe(CO)_3(\eta\text{-}C_8H_{14})_2]$[9] in light petroleum at -40 °C, followed by low-temperature chromatography, affords a dark green complex $[FeMo_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ **(5b)**. The latter releases CO at room temperature yielding **(4b)**. Interestingly, this process may be reversed. Solutions of red **(4b)** in CH_2Cl_2 at -20 °C react in a stream of CO to give green **(5b)**.

In the saturated 48-valence-electron complex **(5b)** the alkyne would adopt the μ_3-(η^2-$\parallel$) bonding mode, as previously found by *X*-ray diffraction in the ditungsten–osmium[3] and –ruthenium[10] compounds, **(5d)** and **(5e)**, with these species existing as mixtures of isomers [**(I)** and **(II)**]. As mentioned earlier, the ironditungsten compound **(5a)** has not been isolated, perhaps because it is even more labile than its molybdenum analogue **(5b)**. Evidently there is a delicate balance between structures of types **(4)** and **(5)**. Thus although **(5a)** has not as yet been observed in the various reactions, a related complex $[FeW_2(\mu_3\text{-}MeC_2C_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$, containing the unsymmetrically substituted alkyne $MeC{\equiv}CC_6H_4Me$-4, has been prepared, and its structure shown[11] by *X*-ray crystallography to be similar to those of the species **(5d)** and **(5e)** with the alkyne adopting the μ_3-(η^2-$\parallel$) bonding mode.

The formulation for **(5b)** is based on the spectroscopic data. The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (measured at -30 °C) were not limiting, the dynamic processes involving interconversion between two isomers, discussed in detail earlier,[3] presumably occurring. Nevertheless, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum showed resonances at δ 184.8 and 170.4 p.p.m., assigned to the ligated carbon atoms of the alkyne. The quality of the spectrum of **(5c)**, and that of the osmium analogue **(5d)**, was insufficient to reveal signals for the ligated carbon nuclei in these complexes.[3] However, in the related compound **(5e)**, peaks for the alkyne-carbon nuclei in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum are at 154.0 and 141.4 p.p.m.[10]

Experimental

The experimental techniques used, and the instrumentation employed, have been described in previous parts of this series. Light petroleum refers to that fraction of b.p. 40—60 °C. The compound $[Fe(CO)_3(\eta\text{-}C_8H_{14})_2]$ was prepared as described elsewhere.[9] The molybdenum complex $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ **(1b)**[12] was synthesised by the method used to obtain its tungsten analogue **(1a)**.[13]

Synthesis of the Dimetal Complex $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$.—A mixture of $[Fe_2(CO)_9]$ (0.36 g, 1.0 mmol) and **(1b)** (0.32 g, 1.0 mmol) in Et_2O (20 cm^3) was stirred at room temperature for *ca.* 1 h. Solvent was removed *in vacuo* leaving a red-brown residue. The latter was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:2), and chromatographed on a Kieselgel column (*ca.* 2 × 40 cm). Elution with the same solvent mixture recovered a red-brown fraction, from which solvent was removed *in vacuo* affording red-brown *microcrystals* of $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ **(2b)** (0.39 g, 80%). Further elution of the column with neat CH_2Cl_2 gave a dark red solution which after removal of solvent afforded dark red *microcrystals* of $[FeMo_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ **(4b)** (0.038 g, 5%). For complex **(2b)** (Found: C, 47.2; H, 2.5. $C_{19}H_{12}FeMoO_6$ requires C, 46.8; H, 2.5%); $\nu_{max.}$(CO) at 2 074s, 2 020s, 1 995vs, 1 954s, and 1 902m cm^{-1} (in light petroleum). N.m.r.: ^1H ($CDCl_3$), δ 2.36 (s, 3 H, Me-4), 5.33 (s, 5 H, C_5H_5), and 7.23 (br, 4 H, C_6H_4); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 362.3 (μ-C), 231.1 (MoCO), 211.2 (FeCO), 157.0 [C^1 (C_6H_4)], 140.0, 129.1, 128.2 (C_6H_4), 94.9 (C_5H_5), and 21.6 p.p.m. (Me-4).

Synthesis of the Trimetal Complex $[Fe_2Mo(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$.—A mixture of $[Fe_2(CO)_9]$ (0.55 g, 1.5 mmol) and **(1b)** (0.16 g, 0.50 mmol) in Et_2O (30 cm^3) was stirred for *ca.* 12 h. Solvent was removed *in vacuo*, and the black residue dissolved in CH_2Cl_2–light petroleum (10 cm^3, 2:3) and chromatographed on a Florisil column (*ca.* 2 × 30 cm). Elution with the same solvent mixture removed initially a trace of green $[Fe_3(CO)_{12}]$, followed by a greenish-brown solution. Solvent was removed *in vacuo* from the latter, giving black *microcrystals*

Table 3. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**2b**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	2 256(1)	2 119(1)	685(1)	O(7)	6 321(3)	894(5)	1 911(4)
Fe	4 066(1)	575(1)	1 023(1)	C(11)	4 400(4)	3 821(5)	1 717(4)
C(1)	3 716(4)	2 575(5)	1 298(4)	C(12)	5 221(4)	4 161(6)	1 543(4)
C(2)	1 917(5)	17(7)	502(4)	C(13)	5 856(5)	5 332(6)	1 971(4)
O(2)	1 600(4)	−1 154(5)	334(4)	C(14)	5 748(4)	6 205(6)	2 613(4)
C(3)	2 435(4)	2 059(7)	1 973(4)	C(15)	4 932(4)	5 898(6)	2 785(4)
O(3)	2 546(4)	2 101(6)	2 726(3)	C(16)	4 254(4)	4 729(6)	2 334(4)
C(4)	3 740(5)	1 331(7)	−124(4)	C(17)	6 472(5)	7 450(7)	3 112(5)
O(4)	3 554(5)	1 842(6)	−836(3)	C(21)	1 291(5)	2 824(8)	−902(4)
C(5)	3 860(5)	−1 294(7)	573(4)	C(22)	589(5)	2 599(8)	−588(4)
O(5)	3 759(4)	−2 446(5)	314(4)	C(23)	778(6)	3 564(9)	121(5)
C(6)	4 125(4)	20(6)	2 127(4)	C(24)	1 608(6)	4 437(7)	269(5)
O(6)	4 188(4)	−321(5)	2 834(3)	C(25)	1 935(5)	3 995(8)	−379(5)
C(7)	5 441(5)	756(6)	1 555(4)				

Table 4. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**4b**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	535(1)	1 858(1)	3 221(1)	C(15)	−3 305(4)	3 944(3)	5 169(2)
Mo(2)	−524(1)	2 390(1)	1 155(1)	C(16)	−2 785(3)	3 714(2)	4 319(2)
Fe	−2 677(1)	1 499(1)	2 080(1)	C(17)	−3 848(5)	3 506(4)	6 831(3)
C(1)	−1 562(3)	2 450(2)	3 363(2)	C(21)	−1 848(3)	4 054(2)	2 245(2)
C(2)	−1 521(3)	2 927(2)	2 448(2)	C(22)	−641(3)	4 820(2)	2 731(2)
C(3)	−3 585(3)	673(2)	2 838(2)	C(23)	−947(4)	5 874(2)	2 646(3)
O(3)	−4 182(3)	141(2)	3 291(2)	C(24)	−2 435(4)	6 203(2)	2 081(2)
C(4)	−2 516(4)	476(2)	1 210(2)	C(25)	−3 634(4)	5 447(2)	1 599(2)
O(4)	−2 503(4)	−255(2)	717(2)	C(26)	−3 360(4)	4 386(2)	1 666(2)
C(5)	−4 587(3)	1 913(2)	1 279(2)	C(27)	−2 742(4)	7 358(2)	2 016(3)
O(5)	−5 819(3)	2 146(2)	746(2)	C(31)	3 394(4)	2 128(3)	3 827(3)
C(6)	−150(4)	383(2)	3 186(2)	C(32)	2 940(4)	1 231(3)	4 269(3)
O(6)	−340(3)	−512(2)	3 259(2)	C(33)	2 008(4)	1 528(3)	4 914(3)
C(7)	926(4)	1 230(2)	1 541(2)	C(34)	1 904(4)	2 621(3)	4 846(3)
O(7)	1 787(3)	579(2)	1 511(2)	C(35)	2 758(4)	2 986(3)	4 177(3)
C(8)	1 503(4)	3 289(2)	1 744(3)	C(41)	−2 588(5)	2 898(4)	−293(3)
O(8)	2 668(3)	3 829(2)	1 977(3)	C(42)	−2 248(6)	1 906(3)	−541(3)
C(11)	−2 162(3)	2 749(2)	4 222(2)	C(43)	−679(7)	1 937(4)	−561(3)
C(12)	−2 088(4)	2 047(2)	5 011(2)	C(44)	−36(6)	2 946(4)	−338(3)
C(13)	−2 631(4)	2 290(3)	5 840(2)	C(45)	−1 241(6)	3 551(3)	−172(3)
C(14)	−3 255(4)	3 241(3)	5 930(2)				

of [$Fe_2Mo(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_8(\eta-C_5H_5)$] (**3b**) (0.27 g, 80%) (Found: C, 42.7; H, 1.9. $C_{22}H_{12}Fe_2MoO_9$ requires C, 42.1; H, 1.9%); $\nu_{max.}$(CO) at 2 074m, 2 066w, 2 031vs, 2 020m, 2 012s, 2 000m, 1 995m, 1 981m, 1 973m (sh), 1 958w, 1 927w, 1 848w br, and 1 798w br cm^{-1} (in light petroleum). N.m.r.: ^{1}H ($CDCl_3$), δ 2.39 (s, 3 H, Me-4), 5.26 (s, 5 H, C_5H_5), and 7.16, 7.42 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8 Hz]; ^{13}C-{^{1}H} (CD_2Cl_2–CH_2Cl_2), δ 295.5 (μ_3-C), 217.7 (br, CO), 158.3 [C^1 (C_6H_4)], 138.1, 131.4, 128.8 (C_6H_4), 91.7 (C_5H_5), and 21.3 p.p.m. (Me-4); ^{13}C-{^{1}H} (at −90 °C, with peaks of minor isomer labelled *), δ 296.0, 291.2* (μ_3-C), 256.4, 245.9* (μ-CO), 225.5 (MoCO), 212.7, 210.5* (FeCO), 158.5*, 157.1 [C^1 (C_6H_4)], 138.4, 137.8*, 131.8, 130.9*, 129.1, 128.6* (C_6H_4), 91.6 (C_5H_5), and 21.6 p.p.m. (Me-4).

Preparation of the Trimetal Complexes [$FeMo_2\{\mu_3-C_2(C_6H_4Me-4)_2\}(CO)_6(\eta-C_5H_5)_2$] *and* [$FeMo_2\{\mu_3-C_2(C_6H_4Me-4)_2\}(CO)_7(\eta-C_5H_5)_2$].—(*i*) A mixture of [$Fe_2(CO)_9$] (0.11 g, 0.30 mmol) and (**1b**) (0.19 g, 0.60 mmol) in Et_2O (20 cm^3) was stirred at room temperature for 6 h. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 cm^3) and chromatographed on a Kieselgel column (*ca.* 2 × 30 cm). Elution with CH_2Cl_2 gave a dark red solution. Removal of solvent *in vacuo* afforded dark red *microcrystals* of [$FeMo_2\{\mu_3-C_2(C_6H_4Me-4)_2\}(CO)_6(\eta-C_5H_5)_2$] (**4b**) (0.17 g, 75%) (Found: C, 50.9; H, 3.1. $C_{32}H_{24}FeMo_2O_6$ requires C, 51.1; H, 3.2%); $\nu_{max.}$(CO) at 2 016vs, 1 958s (sh), 1 941vs, 1 865w br, and 1 792w br cm^{-1} (in CH_2Cl_2). N.m.r.: ^{1}H (CD_2Cl_2, at −70 °C), δ 2.24 (s, 3 H, Me-4), 2.32 (s, 3 H, Me-4), 5.38 (s, 5 H, C_5H_5), 5.46 (s, 5 H, C_5H_5), 6.16 [d, 1 H, C_6H_4, *J*(HH) 7 Hz], 6.66, 6.95 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7 Hz], 7.03 (br, 2 H, C_6H_4), and 7.21 p.p.m. [d, 1 H, C_6H_4, *J*(HH) 7 Hz]; ^{13}C-{^{1}H} (CD_2Cl_2–CH_2Cl_2, at −70 °C), δ 249.9 (μ-CO), 231.7, 231.4 (MoCO), 217.7, 214.3, 214.0 (FeCO), 155.7—128.8 (CC_6H_4), 96.8, 95.0 (C_5H_5), 21.5 and 21.1 p.p.m. (Me-4).

(*ii*) A mixture of (**1b**) (0.16 g, 0.50 mmol) and [$Fe(CO)_3(\eta-C_8H_{14})_2$] (0.92 g, 0.26 mmol) in light petroleum (50 cm^3) was stirred at −40 °C for 4 h. Solvent was removed at −20 °C. The residue was dissolved in cold (*ca.* −20 °C) CH_2Cl_2–light petroleum (10 cm^3, 2:3) and chromatographed on a Florisil column (*ca.* 2 × 30 cm) at −20 °C. Elution with the same solvent mixture gave a green eluate, which was concentrated *in vacuo* giving dark green *microcrystals* of [$FeMo_2\{\mu_3-C_2(C_6H_4Me-4)_2\}(CO)_7(\eta-C_5H_5)_2$] (**5b**) (0.14 g, 70%), $\nu_{max.}$(CO) at 2 041vw, 2 026vs, 1 989s, 1 967vs, 1 924s, and 1 830vw br cm^{-1} (in light petroleum). N.m.r.: ^{1}H ($CDCl_3$, at −30 °C), δ 2.23 (s, 6 H, Me-4), 4.83 (s, 5 H, C_5H_5), 5.28 (s, 5 H, C_5H_5), and 6.94—7.29 (m br, 8 H, C_6H_4); ^{13}C-{^{1}H} ($C_6D_5CD_3$, at −30 °C), 236.6, 236.3, 231.8, 231.3 (MoCO), 212.0 (br, FeCO), 184.8, 170.4 (μ_3-C_2), 152.6, 152.0 [C^1 (C_6H_4)], 134.9, 133.8 (C_6H_4), 93.7 and 93.6 p.p.m. (C_5H_5); other signals were obscured by solvent peaks.

(*iii*) A red solution of (**4b**) (0.17 g, 0.25 mmol) in CH_2Cl_2 (20 cm^3) at −20 °C was treated with a stream of CO for 1 h; the mixture turned green. Removal of solvent gave a green residue which was extracted (5 × 20 cm^3) with light petroleum at −20 °C. The extracts were filtered through a Celite pad (*ca.* 2 cm). The filtrate was concentrated *in vacuo* affording dark green *microcrystals* of (**5b**) (0.20 g, 100%).

Solutions of (**5b**) under nitrogen revert quantitatively after a few minutes to (**4b**).

Crystal Structure Determinations.—(*a*) $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ (**2b**). Crystals of (**2b**) were grown as black plates from a mixture of CH_2Cl_2, Et_2O, and light petroleum. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.50 × 0.45 × 0.15 mm on a Nicolet *P*3*m* diffractometer. Of the 3 315 unique data collected (Wyckoff ω scans $2\theta \leqslant 50°$), 2 469 had $I \geqslant 2.0\sigma(I)$ and only these were used in structure solution and refinement after the data had been corrected for *X*-ray absorption (by an empirical method based on azimuthal scan data[14]), Lorentz, and polarisation effects.

Crystal data. $C_{19}H_{12}FeMoO_6$, $M = 488.1$, monoclinic, $a = 14.710(2)$, $b = 9.154(1)$, $c = 16.040(3)$ Å, $\beta = 119.29(1)°$, $U = 1\,883.8(5)$ Å^3, $Z = 4$, $D_c = 1.72$ g cm^{-3}, $F(000) = 968$, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 14.5 cm^{-1}.

The structure was solved and all non-hydrogen atoms located by conventional heavy-atom and difference-Fourier methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included at calculated positions (C–H 0.96 Å), with fixed isotropic thermal parameters (1.2 × $U_{\text{equiv.}}$ of the parent carbon atom) for those attached to aromatic carbon atoms, and a common refined isotropic thermal parameter for the methyl hydrogen atoms. Refinement by blocked-cascade least-squares methods led to $R = 0.044$ ($R' = 0.043$) and a weighting scheme of the form $w = [\sigma^2(F) + 0.000\,6|F|^2]^{-1}$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks $\geqslant 0.65$ or $\leqslant -0.37$ e Å^{-3}. The atomic co-ordinates are given in Table 3.

(*b*) $[FeMo_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$ (**4b**). Crystals of (**4b**) grow as black needles from CH_2Cl_2, Et_2O, and light petroleum mixtures. Data collection, and structure solution and refinement were as for (**2b**) except for the following details. Crystal dimensions *ca.* 0.50 × 0.40 × 0.20 mm, with 5 489 unique data collected ($2\theta \leqslant 53°$), of which 4 757 had $I \geqslant 2.5\sigma(I)$.

Crystal data. $C_{32}H_{24}FeMo_2O_6$, $M = 752.2$, triclinic, $a = 8.658(4)$, $b = 12.844(6)$, $c = 13.544(10)$ Å, $\alpha = 90.76(5)$, $\beta = 108.36(4)$, $\gamma = 93.21(3)°$, $U = 1\,426(1)$ Å^3, $Z = 2$, $D_c = 1.75$ g cm^{-3}, $F(000) = 748$, space group $P\bar{1}$ (no. 2), μ(Mo-K_α) = 13.9 cm^{-1}.

Refinement as for (**2b**) led to $R = 0.026$ ($R' = 0.029$) and a weighting scheme of the form $w = [\sigma^2(F) + 0.000\,42|F|^2]^{-1}$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks $\geqslant 0.41$ or $\leqslant -0.45$ e Å^{-3}. Atomic co-ordinates are given in Table 4. Scattering factors and corrections for anomalous dispersion were taken from ref. 15. All calculations were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[14]

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