Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 79.[1] Synthesis and Reactions of the Alkylidynemetal Complexes $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = $C_6H_3Me_2$-2,6, M = Cr, Mo, or W; R = C_6H_4Me-2, C_6H_4OMe-2, or $C_6H_4NMe_2$-4, M = Mo); Crystal Structure of the Compound $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ *

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The alkylidynemetal complexes $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Cr, Mo, or W, R = $C_6H_3Me_2$-2,6; M = Mo, R = C_6H_4Me-2, C_6H_4OMe-2, or $C_6H_4NMe_2$-4) have been prepared, and several of their reactions have been studied. New compounds characterised include $[M\{C(C_6H_3Me_2\text{-}2,6)C(O)\}(CO)(PR'_3)(\eta\text{-}C_5H_5)]$ (M = Mo, R′ = Ph; M = W, R′ = Me), $[M(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PR'_3)(\eta\text{-}C_5H_5)]$ (M = Mo, R′ = Ph; M = W, R′ = Ph or Me), and $[MCo_2(\mu_3\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_8(\eta\text{-}C_5H_5)]$ (M = Mo or W). However, the main study involved reactions of the alkylidynemetal compounds with $[Fe_2(CO)_9]$. The latter with $[M(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ yields the electronically unsaturated (32 valence electron) dimetal compounds $[MFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$. In CO-saturated solutions, these products afford labile saturated (34 valence electron) complexes $[MFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_6(\eta\text{-}C_5H_5)]$, which readily revert to the unsaturated species in the absence of CO. In contrast, reactions between $[Fe_2(CO)_9]$ and $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-2 or C_6H_4OMe-2) afford the saturated dimetal compounds $[MoFe(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$. However, the species with R = C_6H_4Me-2 in CH_2Cl_2 solution under a stream of nitrogen yields the labile unsaturated compound $[MoFe(\mu\text{-}CC_6H_4Me\text{-}2)(CO)_5(\eta\text{-}C_5H_5)]$. Moreover, an additional feature of the reaction between $[Fe_2(CO)_9]$ and $[Mo(\equiv CC_6H_4Me\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ is the formation of the trimetal compound $[MoFe_2(\mu_3\text{-}CC_6H_4Me\text{-}2)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$, a product produced in high yield if an excess of the iron carbonyl is used. The reaction between $[Mo(\equiv CC_6H_4NMe_2\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Fe_2(CO)_9]$ gives a mixture of $[MoFe(\mu\text{-}CC_6H_4NMe_2\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$, $[MoFe_2(\mu_3\text{-}CC_6H_4NMe_2\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$, and $[Mo_2\{\mu\text{-}C_2(C_6H_4NMe_2\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$. The n.m.r. spectra of the various complexes are discussed. The molecular structure of the unsaturated compound $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ has been established by an *X*-ray diffraction study [Mo–Fe 2.577(1), μ-C–Mo 1.976(2), and μ-C–Fe 1.861(2) Å]. Extended-Hückel molecular-orbital calculations have been carried out on model compounds, in an attempt to understand the nature of the bonding between the core M(μ-C)Fe atoms in the 32- and 34-valence-electron dimetal compounds. The results favour a dimetallacyclopropene description for the saturated complexes, and in affect a four-electron donation from the C≡M unit to the $Fe(CO)_3$ groups in the unsaturated compounds. During the course of the work the complexes $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_4(PMe_3)(\eta\text{-}C_5H_5)]$, $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}CO)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$, and $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-dppm})(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$ (dppm = $Ph_2PCH_2PPh_2$) were also prepared.

We have made extensive use of the compounds $[M(\equiv CR)(CO)_2L]$ {M = Cr, Mo, or W; R = alkyl or aryl; L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]} as reagents for the synthesis of polynuclear metal compounds with bonds between dissimilar transition elements.[2] A major objective of these studies has been to investigate the reactivity of the bridging CR ligands present in the various products.[1] Our work has largely focused on the *p*-tolylmethylidyne species $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2L]$ [L = η-C_5H_5, M = Cr (**1a**), Mo (**1b**), or W (**1c**); L = $HB(pz)_3$ or η-C_5Me_5, M = W (**1d**) or (**1e**)], but the vast majority of the research has been with molybdenum and tungsten compounds. It has become increasingly apparent that the reactivity patterns depend

$[L(OC)_2M\equiv CR]$

	M	R	L
(**1a**)	Cr	C_6H_4Me-4	η-C_5H_5
(**1b**)	Mo	C_6H_4Me-4	η-C_5H_5
(**1c**)	W	C_6H_4Me-4	η-C_5H_5
(**1d**)	W	C_6H_4Me-4	$HB(pz)_3$
(**1e**)	W	C_6H_4Me-4	η-C_5Me_5
(**1f**)	Cr	$C_6H_3Me_2$-2,6	η-C_5H_5
(**1g**)	Mo	$C_6H_3Me_2$-2,6	η-C_5H_5
(**1h**)	W	$C_6H_3Me_2$-2,6	η-C_5H_5
(**1i**)	Mo	C_6H_4Me-2	η-C_5H_5
(**1j**)	Mo	C_6H_4OMe-2	η-C_5H_5
(**1k**)	Mo	$C_6H_4NMe_2$-4	η-C_5H_5

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* 1,1,1,2,2-Pentacarbonyl-2-η-cyclopentadienyl-μ-2′,6′-dimethylphenylmethylidyne-ironmolybdenum (*Fe–Mo*)

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: eV ≈ 1.60 × 10^{-19} J.

critically on the nature of the groups R and the ligands L in [M(≡CR)(CO)$_2$L], and also whether the metal atom is Cr, Mo, or W. In order to define more precisely the effect of the R group, we have prepared several compounds in which the C$_6$H$_4$Me-4 fragment has been replaced by another aryl group, *viz.* [M(≡CR)(CO)$_2$(η-C$_5$H$_5$)] [R = C$_6$H$_3$Me$_2$-2,6, M = Cr (**1f**), Mo (**1g**), or W (**1h**); R = C$_6$H$_4$Me-2, C$_6$H$_4$OMe-2, or C$_6$H$_4$NMe$_2$-4, M = Mo (**1i**)—(**1k**)]. The choice of the R groups was motivated by a desire to distinguish between electronic and steric effects in reactivity patterns. The presence of one or two substituents in the arene ring *ortho* to the ligating alkylidyne-carbon atom introduces a steric constraint. The presence of the NMe$_2$-4 group in (**1k**) should enhance the donor ability of the C≡Mo moiety compared with (**1b**).

Results and Discussion

The alkylidynemetal compounds (**1f**), (**1g**), and (**1i**)—(**1k**) were prepared in yields of 60—80% by an extension of procedures

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

Compound	Colour	Yield (%)	$\nu_{max.}$(CO)[b]/cm^{-1}	Analysis (%)	
				C	H
(**1f**) [Cr(≡CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(η-C$_5$H$_5$)]	Orange	80	1 992s, 1 924s	[c] 67.8 (66.2)	5.5 (4.9)
(**1g**) [Mo(≡CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(η-C$_5$H$_5$)]	Orange	75	1 992s, 1 919s	[c] 56.6 (57.5)	4.3 (4.2)
(**1h**) [W(≡CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(η-C$_5$H$_5$)]	Orange	73	[d] 1 992s, 1 922s	45.7 (45.2)	3.4 (3.4)
(**1i**) [Mo(≡CC$_6$H$_4$Me-2)(CO)$_2$(η-C$_5$H$_5$)]	Orange	75	1 995s, 1 920s	[c] 58.3 (56.3)	4.3 (3.8)
(**1j**) [Mo(≡CC$_6$H$_4$OMe-2)(CO)$_2$(η-C$_5$H$_5$)]	Orange	80	1 995s, 1 919s	[c] 53.3 (53.6)	3.7 (3.6)
(**1k**) [Mo(≡CC$_6$H$_4$NMe$_2$-4)(CO)$_2$(η-C$_5$H$_5$)]	Orange	60	1 991s, 1 924s	[e] 55.3 (55.0)	4.5 (4.3)
(**2c**) [Mo{C(C$_6$H$_3$Me$_2$-2,6)C(O)}(CO)(PPh$_3$)(η-C$_5$H$_5$)]	Violet	20	1 898s, 1 724w	66.2 (68.5)	5.2 (4.9)
(**2d**) [W{C(C$_6$H$_3$Me$_2$-2,6)C(O)}(CO)(PMe$_3$)(η-C$_5$H$_5$)]	Red	35	1 891s, 1 702w	46.0 (45.8)	4.7 (4.7)
(**3d**) [Mo(≡CC$_6$H$_3$Me$_2$-2,6)(CO)(PPh$_3$)(η-C$_5$H$_5$)]	Black	48	1 889s	68.8 (69.7)	5.5 (5.1)
(**3e**) [W(≡CC$_6$H$_3$Me$_2$-2,6)(CO)(PPh$_3$)(η-C$_5$H$_5$)]	Black	28	1 879s	61.1 (61.2)	4.7 (4.7)
(**3f**) [W(≡CC$_6$H$_3$Me$_2$-2,6)(CO)(PMe$_3$)(η-C$_5$H$_5$)]	Orange	30	1 868s	46.3 (46.0)	4.9 (4.9)

[a] Calculated values are given in parentheses. [b] Measured in CH$_2$Cl$_2$ unless otherwise stated. [c] Molecular ion observed in mass spectrum. [d] In light petroleum. [e] N 3.8 (4.0%).

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

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]	^{31}P(δ)[d]
(**1f**)	[e] 2.60 (s, 6 H, Me), 5.05 (s, 5 H, C$_5$H$_5$), 7.02—7.07 (m, 3 H, C$_6$H$_3$)	[e] 329.7 (C≡Cr), 238.8 (CO), 141.2 [C^1(C$_6$H$_3$)], 128.8, 127.3, 126.7 (C$_6$H$_3$), 89.2 (C$_5$H$_5$), 20.8 (Me$_2$-2,6)	
(**1g**)	[e] 2.53 (s, 6 H, Me), 5.61 (s, 5 H, C$_5$H$_5$), 6.90—7.10 (m, 3 H, C$_6$H$_3$)	[e] 310.5 (C≡Mo), 228.7 (CO), 143.6 [C^1(C$_6$H$_3$)], 139.3, 128.1, 126.7 (C$_6$H$_3$), 92.1 (C$_5$H$_5$), 20.9 (Me$_2$-2,6)	
(**1h**)	2.43 (s, 6 H, Me), 5.63 (s, 5 H, C$_5$H$_5$), 6.90 [(AB$_2$), 2 H, C$_6$H$_3$, *J*(AB) 8], 7.13 [(AB$_2$), 1 H, C$_6$H$_3$, *J*(AB) 8]	297.4 [C≡W, *J*(WC) 207], 220.2 [WCO, *J*(WC) 197], 147.1 [C^1(C$_6$H$_3$), *J*(WC) 38], 138.2, 127.4, 126.8 (C$_6$H$_3$), 91.0 (C$_5$H$_5$), 21.1 (Me$_2$-2,6)	
(**1i**)	[e] 2.50 (s, 3 H, Me-2), 5.53 (s, 5 H, C$_5$H$_5$), 6.90—7.20 (m, 4 H, C$_6$H$_4$)	[e] 309.5 (C≡Mo), 227.5 (MoCO), 144.6 [C^1(C$_6$H$_4$)], 138.0, 129.9, 128.9, 128.5, 124.6 (C$_6$H$_4$), 92.1 (C$_5$H$_5$), 20.1 (Me-2)	
(**1j**)	[e] 3.83 (s, 3 H, OMe), 5.60 (s, 5 H, C$_5$H$_5$), 6.71—7.37 (m, 4 H, C$_6$H$_4$)	[e] 305.9 (C≡Mo), 229.2 (MoCO), 160.0 [C^1(C$_6$H$_4$)], 135.9, 131.6, 130.6, 119.8, 110.8 (C$_6$H$_4$), 92.6 (C$_5$H$_5$), 55.5 (OMe)	
(**1k**)	[e] 2.97 (s, 6 H, NMe$_2$), 5.56 (s, 5 H, C$_5$H$_5$), 6.44, 7.38 [(AB)$_2$, 4 H, C$_6$H$_4$, *J*(AB) 9]	[e] 312.7 (C≡Mo), 228.6 (MoCO), 149.8 [C^1(C$_6$H$_4$)], 135.5, 131.3, 109.7 (C$_6$H$_4$), 91.9 (C$_5$H$_5$), 39.8 (NMe$_2$)	
(**2c**)	1.68 (s, 6 H, Me), 5.26 (s, 5 H, C$_5$H$_5$), 7.20—7.50 (m, 18 H, C$_6$H$_3$, Ph)	234.9 (MoCO), 225.3 (*C*C$_6$H$_3$Me$_2$-2,6), 200.2 [*C*(O)CC$_6$H$_3$Me$_2$-2,6], 146.2 [C^1(C$_6$H$_3$)], 133.4—126.8 (C$_6$H$_3$, Ph), 96.3 (C$_5$H$_5$), 21.6 (Me$_2$-2,6)	57.03
(**2d**)	1.58 [d, 9 H, PMe$_3$ *J*(PH) 10], 2.02 (s, 6 H, Me$_2$-2,6), 5.51 (s, 5 H, C$_5$H$_5$), 6.94—7.06 (m, 3 H, C$_6$H$_3$)	228.8 [d, WCO, *J*(PC) 8], 199.2 [d, *C*C$_6$H$_3$Me$_2$-2,6, *J*(PC) 5], 198.8 [*C*(O)CC$_6$H$_3$Me$_2$-2,6], 146.0 [C^1(C$_6$H$_3$)], 129.8, 126.5, 125.0 (C$_6$H$_3$), 93.9 (C$_5$H$_5$), 21.8 (Me$_2$-2,6), 20.9 [d, MeP, *J*(PC) 36]	−16.67 [*J*(WP) 400]
(**3d**)	[e] 2.24 (s, 6 H, Me), 5.27 (s, 5 H, C$_5$H$_5$), 7.20—7.50 (m, 18 H, C$_6$H$_3$, Ph)	[e] 303.7 [d, C≡Mo, *J*(PC) 17], 249.2 [d, MoCO, *J*(PC) 12], 145.5 [C^1(C$_6$H$_3$)], 138.6—127.1 (C$_6$H$_3$, Ph), 92.3 (C$_5$H$_5$), 21.2 (Me$_2$-2,6)	[e] 73.70
(**3e**)	2.15 (s, 6 H, Me), 5.30 (s, 5 H, C$_5$H$_5$), 6.77—7.00 (m, 3 H, C$_6$H$_3$), 7.29—7.48 (m, 15 H, Ph)	289.6 [d, C≡W, *J*(PC) 10], 241.6 [d, WCO, *J*(PC) 5], 149.0 [C^1(C$_6$H$_3$)], 139.3—124.8 (C$_6$H$_3$, Ph), 90.8 (C$_5$H$_5$), 21.2 (Me$_2$-2,6)	49.2 [*J*(WP) 437]
(**3f**)	1.61 [d, 9 H, MeP, *J*(PH) 9], 2.33 (s, 6 H, Me$_2$-2,6), 5.45 [d, 5 H, C$_5$H$_5$, *J*(PH) 1], 6.80—7.10 (m, 3 H, C$_6$H$_3$)	285.2 [d, C≡W, *J*(PC) 10], 243.3 [d, WCO, *J*(PC) 5], 149.0 [C^1(C$_6$H$_3$)], 135.0, 126.8, 123.8 (C$_6$H$_3$), 89.5 (C$_5$H$_5$), 26.0 [d, MeP, *J*(PC) 32], 21.5 (Me$_2$-2,6)	−12.23 [*J*(WP) 439]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures. [b] Measured in CD$_2$Cl$_2$ unless otherwise stated. [c] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of SiMe$_4$. Measurements in CD$_2$Cl$_2$–CH$_2$Cl$_2$ unless otherwise stated. [d] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of 85% H$_3$PO$_4$ (external). [e] Measured in CDCl$_3$.

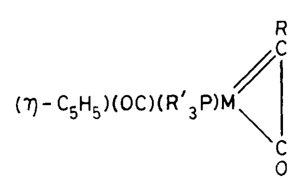
developed by Mayr and co-workers.[3] The metal hexacarbonyls, suspended in diethyl ether, were treated with an equivalent amount of the organolithium reagent LiR (R = $C_6H_3Me_2$-2,6, C_6H_4Me-2, C_6H_4OMe-2, or $C_6H_4NMe_2$-4). Trifluoroacetic anhydride was then added so as to obtain *in situ* the species $[M(\equiv CR)(O_2CCF_3)(CO)_4]$. The latter complexes were treated with the reagent $Na(C_5H_5)\cdot$dme (dme = 1,2-dimethoxyethane)[4] to obtain the desired product, which was purified by column chromatography. Whilst leading to no significant increase in yield, it is sometimes convenient to add tmen (*N,N,N',N'*-tetramethylethylenediamine) following addition of $(CF_3CO)_2O$ and isolate the species $[M(\equiv CR)(O_2CCF_3)(CO)_2(tmen)]$ (M = Cr or Mo) before proceeding to the reaction with $Na(C_5H_5)\cdot$dme. This allows ready removal of unreacted hexacarbonyl, aryl halide, and other species which may impede purification of the desired product. The tungsten compound (**1h**) was also prepared from $[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_4]$ and $NaC_5H_5\cdot$dme by the method of Fischer *et al.*[5]

The compounds (**1f**)—(**1k**) were characterised by the data given in Tables 1 and 2. The ^{13}C-{^1H} n.m.r. spectra show characteristic resonances for the terminally bound alkylidyne-carbon ligands in the range *ca.* 297—330 p.p.m. Reactions of (**1f**) and (**1g**) with tertiary phosphines were investigated, in order to compare the results obtained with those obtained previously. In general, compounds of type (**1**) react with tertiary phosphines to give ketenyl complexes (**2**), or the substitution products (**3**).[6,7] Thus (**1b**) with PMe_3 affords either $[Mo\{C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**2a**) or $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**3a**), depending on the conditions.[6,8] However, whereas (**1c**) with PMe_3 yields the ketenyl complex $[W\{C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**2b**), complex (**3b**), the analogue of (**3a**), is less well defined.[6]

Reactions between (**1g**) and PPh_3 afford either $[Mo\{C(C_6H_3Me_2\text{-}2,6)C(O)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (**2c**) or $[Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (**3d**), depending on the conditions. The former species is produced if light petroleum solutions containing (**1a**) and PPh_3 are exposed to strong light. The latter may be obtained by refluxing thf (tetrahydrofuran) solutions of (**1g**) and PPh_3. Moreover, solutions of (**2c**) in organic solvents slowly (days) decarbonylate to give (**3d**). The complex $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (**3e**) is readily obtained by refluxing in thf a mixture of (**1h**) and PPh_3. Treatment of (**1h**) in light petroleum with PMe_3 at room temperature affords a chromatographically separable mixture of $[W\{C(C_6H_3Me_2\text{-}2,6)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**2d**) and $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**3f**). Data characterising compounds (**2c**), (**2d**), and (**3d**)—(**3f**) are given in Tables 1 and 2. It is evident that reactions of (**1g**) or (**1h**) with tertiary phosphines are similar to those of (**1b**) or (**1c**), and the presence of the more bulky $C_6H_3Me_2$-2,6 group introduces no difference in the nature of products obtained.

A reaction the compounds (**1a**)—(**1e**) have in common is that with $[Co_2(CO)_8]$. The products formed in high yield are the trimetal complexes $[MCo_2(\mu_3\text{-}CR)(CO)_8L]$ (**4a**)—(**4e**).[9] Similarly, treatment of (**1g**) or (**1h**) with $[Co_2(CO)_8]$ in light petroleum at room temperature gives the compounds $[MCo_2(\mu_3\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_8(\eta\text{-}C_5H_5)]$ [M = Mo (**4f**) or W (**4g**)], characterised by the data given in Tables 3 and 4. The ^{13}C-{^1H} n.m.r. spectra show diagnostic signals for the μ_3-C nuclei at δ 274.3 (**4f**) and 270.0 p.p.m. (**4g**). The spectra were measured at low temperatures (Table 4), since at room temperatures the signals are very broad, due to the ^{59}Co quadrupolar effect. The corresponding resonances in the ^{13}C-{^1H} n.m.r. spectra of (**4b**) and (**4c**) occur at δ 270.7 and 257.0 p.p.m., respectively.[9]

Of most interest are results of studies on reactions between compounds (**1f**)—(**1k**) and $[Fe_2(CO)_9]$. Earlier we have shown[10,11] that the compounds (**1b**) and (**1c**) with $[Fe_2(CO)_9]$ give as products the dimetal compounds $[MFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ [M = Mo (**5a**) or W (**5b**)]. However, whereas (**5a**) is a relatively stable species, with an extensive derivative chemistry,[12] compound (**5b**) is unstable. In other work, reactions between (**1d**) or (**1e**) and $[Fe_2(CO)_9]$ gave the electronically unsaturated 32-valence-electron complexes $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5L]$ [L = $HB(pz)_3$ (**6c**)[13] or η-C_5Me_5 (**6d**)[9b]]. In the reaction between (**1e**) and $[Fe_2(CO)_9]$ the saturated 34-valence-electron compound $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5Me_5)]$ (**5d**) is also formed, and in the presence of CO complex (**6d**) exists in equilibrium with (**5d**). In contrast, although there is n.m.r. evidence that (**6c**) in solutions saturated with CO gives (**5c**), the latter cannot be isolated.[13] Moreover during the course of studies on (**5b**), evidence was obtained for the existence of the unsaturated dimetal complex $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)]$ (**6b**), although it proved to have only a fleeting existence. So far no evidence has been obtained for the formation of (**6a**), although many of the varied reactions of (**5a**) may proceed *via* the intermediacy of the former species.[12]



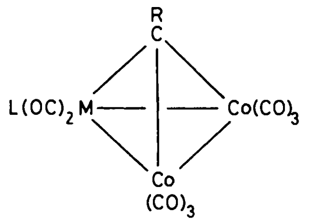
	M	R	R'
(**2a**)	Mo	C_6H_4Me-4	Me
(**2b**)	W	C_6H_4Me-4	Me
(**2c**)	Mo	$C_6H_3Me_2$-2,6	Ph
(**2d**)	W	$C_6H_3Me_2$-2,6	Me

$[(\eta\text{-}C_5H_5)(OC)(R'_3P)M\equiv CR]$

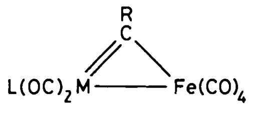
	M	R	R'
(**3a**)	Mo	C_6H_4Me-4	Me
(**3b**)	W	C_6H_4Me-4	Me
(**3d**)	Mo	$C_6H_3Me_2$-2,6	Ph
(**3e**)	W	$C_6H_3Me_2$-2,6	Ph
(**3f**)	W	$C_6H_3Me_2$-2,6	Me

The existence of the pairs of compounds (**5b**) and (**6b**), (**5c**) and (**6c**), and (**5d**) and (**6d**) is of considerable interest, and as discussed previously[13] would appear to indicate that the C≡M groups in (**1c**)—(**1e**) can act formally as four-electron donors to an $Fe(CO)_3$ group in (**6b**)—(**6d**). Because the ability with which the 32-valence-electron compounds add CO to give the saturated 34-valence-electron complexes increases in the order (**6c**) < (**6d**) < (**6b**), it seems likely that steric effects are important. It is well established that the bulkiness of the ligands increases in the order η-C_5H_5 < η-C_5Me_5 < $HB(pz)_3$. With this in mind, studies of reactions between $[Fe_2(CO)_9]$ and (**1f**)—(**1j**) were of considerable interest since, as mentioned earlier, the presence of *ortho*-substituents on the six-membered ring attached to the ligating alkylidyne-carbon atom introduces a steric effect which should favour the formation of the 32-valence-electron dimetal compounds (**6**).

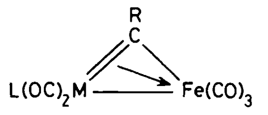
In accord with these ideas, the three mononuclear metal compounds (**1f**)—(**1h**) containing bulky $C_6H_3Me_2$-2,6 groups



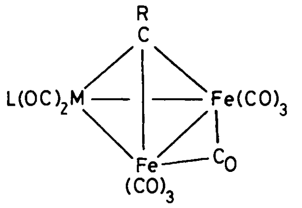
	M	L	R
(4a)	Cr	η-C_5H_5	C_6H_4Me-4
(4b)	Mo	η-C_5H_5	C_6H_4Me-4
(4c)	W	η-C_5H_5	C_6H_4Me-4
(4d)	W	η-C_5Me_5	C_6H_4Me-4
(4e)	W	$HB(pz)_3$	C_6H_4Me-4
(4f)	Mo	η-C_5H_5	$C_6H_3Me_2$-2,6
(4g)	W	η-C_5H_5	$C_6H_3Me_2$-2,6



	M	L	R
(5a)	Mo	η-C_5H_5	C_6H_4Me-4
(5b)	W	η-C_5H_5	C_6H_4Me-4
(5c)	W	$HB(pz)_3$	C_6H_4Me-4
(5d)	W	η-C_5Me_5	C_6H_4Me-4
(5e)	Cr	η-C_5H_5	$C_6H_3Me_2$-2,6
(5f)	Mo	η-C_5H_5	$C_6H_3Me_2$-2,6
(5g)	W	η-C_5H_5	$C_6H_3Me_2$-2,6
(5h)	Mo	η-C_5H_5	C_6H_4Me-2
(5i)	Mo	η-C_5H_5	C_6H_4OMe-2
(5j)	Mo	η-C_5H_5	$C_6H_4NMe_2$-4



	M	L	R
(6a)	Mo	η-C_5H_5	C_6H_4Me-4
(6b)	W	η-C_5H_5	C_6H_4Me-4
(6c)	W	$HB(pz)_3$	C_6H_4Me-4
(6d)	W	η-C_5Me_5	C_6H_4Me-4
(6e)	Cr	η-C_5H_5	$C_6H_3Me_2$-2,6
(6f)	Mo	η-C_5H_5	$C_6H_3Me_2$-2,6
(6g)	W	η-C_5H_5	$C_6H_3Me_2$-2,6
(6h)	Mo	η-C_5H_5	C_6H_4Me-2



	M	L	R
(7a)	Mo	η-C_5H_5	C_6H_4Me-4
(7b)	W	η-C_5H_5	C_6H_4Me-4
(7c)	W	η-C_5Me_5	C_6H_4Me-4
(7d)	Mo	η-C_5H_5	C_6H_4Me-2
(7e)	Mo	η-C_5H_5	$C_6H_4NMe_2$-4

all react with $[Fe_2(CO)_9]$ in Et_2O or thf to give the unsaturated compounds $[MFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ [M = Cr (**6e**), Mo (**6f**), or W (**6g**)], data for which are given in Tables 3 and 4. Spectroscopic evidence was obtained for the existence of the 34-valence-electron complexes $[MFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_6(\eta\text{-}C_5H_5)]$ [M = Cr (**5e**), Mo (**5f**), or W (**5g**)] when solutions of (**6e**), (**6f**), or (**6g**) were treated with CO gas at atmospheric pressure. It was not, however, possible to isolate (**5e**)—(**5g**) as solids from the solutions, because they readily released CO, reverting to (**6e**)—(**6g**), respectively.

Examination of the i.r. and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of CO-saturated solutions of compounds (**6e**)—(**6g**) was informative. Thus a $^{13}C\text{-}\{^1H\}$ spectrum of (**6e**) measured at −90 °C in the presence of CO showed additional signals at δ 367.4 (μ-C), 243.6 (CrCO), 212.0, 209.7 (FeCO), 204.7 (2 FeCO), 160.9 $[C^1(C_6H_3)]$, 91.3 (C_5H_5), and 21.9 p.p.m. (Me_2-2,6) which we attribute to (**5e**). Similar studies on CO-saturated solutions of (**6f**) and (**6g**) revealed new peaks due to μ-C nuclei at δ 345.3 (**5f**) and 311.7 p.p.m. (**5g**), in addition to the signals at δ 407.4 (**6f**) and 391.8 p.p.m. (**6g**). If nitrogen is passed through the CO-saturated solutions the μ-C resonances at δ 367.4, 345.3, and 311.7 p.p.m. disappear. Carbon monoxide-saturated solutions of (**6e**)—(**6g**) also display in their i.r. spectra additional CO stretching bands compared with those of solutions measured (Table 3) under nitrogen in the absence of CO. For compound (**6e**) the new peaks occur at 2 074m, 2 010 (sh), 1 994vs, 1 952m, and 1 866w (br) cm^{-1}, and these are assigned to (**5e**).

Of special interest is the observed difference in $^{13}C\text{-}\{^1H\}$ n.m.r. chemical shift for the μ-C nuclei between the various pairs of saturated and unsaturated dimetal compounds. The resonances in the spectra of the 32-valence-electron compounds are very significantly more deshielded with Δδ (Table 5) ranging from *ca.* 50 to 120 p.p.m. We have commented on this feature previously,[13] and drawn an analogy with alkynemetal complexes. Compounds in which the alkyne formally donates four electrons to a metal centre have ligated-carbon resonances *ca.* 80 p.p.m. more deshielded than those in which the ligand donates two electrons.[14] With the substantial amount of data

Table 3. Analytical[a] and physical data for the mixed-metal compounds

Compound	Colour	Yield (%)	$\tilde{\nu}_{max.}(CO)$[b]/cm^{-1}	Analysis (%) C	H
(**4f**) $[MoCo_2(\mu_3\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_8(\eta\text{-}C_5H_5)]$	Black	82	[c] 2 081s, 2 041s, 2 029s, 2 014m, 2 002m, 1 991w (sh), 1 933m, 1 883w	42.8 (42.6)	2.5 (2.3)
(**4g**) $[WCo_2(\mu_3\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_8(\eta\text{-}C_5H_5)]$	Black	87	2 078s, 2 065w, 2 039s, 2 022s, 2 010s, 2 000m (sh), 1 913w, 1 860w	37.4 (37.3)	2.7 (2.0)
(**5h**) $[MoFe(\mu\text{-}CC_6H_4Me\text{-}2)(CO)_6(\eta\text{-}C_5H_5)]$	Brown	54	[c] 2 074s, 2 018s, 2 000vs, 1 990s, 1 959s, 1 899m	47.7 (46.8)	2.7 (2.5)
(**5i**) $[MoFe(\mu\text{-}CC_6H_4OMe\text{-}2)(CO)_6(\eta\text{-}C_5H_5)]$	Brown	76	2 071m, 1 997s (br), 1 946m, 1 878w	45.0 (45.3)	2.5 (2.4)
(**5j**) $[MoFe(\mu\text{-}CC_6H_4NMe_2\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$	Black	85	2 064m, 2 004m (sh), 1 985s, 1 944m, 1 873w	[d] 46.0 (46.5)	3.1 (2.9)
(**6e**) $[CrFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$	Black	88	2 054s, 1 996vs, 1 979s, 1 933m, 1 883w (br)	54.1 (53.1)	3.6 (3.3)
(**6f**) $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$	Black	95	[c] 2 053s, 1 995s, 1 977s, 1 933w, 1 896w (br)	47.6 (48.1)	3.0 (3.0)
(**6g**) $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$	Purple	75	[c] 2 052s, 1 992s, 1 975s, 1 946w, 1 890w (br)	40.5 (40.6)	2.5 (2.5)
(**7d**) $[MoFe_2(\mu_3\text{-}CC_6H_4Me\text{-}2)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$	Green	80	[c] 2 072m, 2 064m (sh), 2 059s, 2 029s, 2 023m, 2 010s, 2 000s, 1 990m, 1 980s, 1 964s, 1 930w, 1 921m, 1 844w (br), 1 804w (br)	41.5 (42.1)	2.0 (1.9)
(**7e**) $[MoFe_2(\mu_3\text{-}CC_6H_4NMe_2\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$	Brown	63	2 066w, 2 058w, 2 023s, 2 006s, 1 989s, 1 940w (sh), 1 880w (br), 1 780w (br)	[e] 41.3 (42.0)	2.9 (2.3)
(**8c**) $[Mo_2Fe\{\mu\text{-}C_2(C_6H_4NMe_2\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)_2]$	Brown	11	2 041w, 2 012s, 1 948s (sh), 1 935s, 1 858w (br), 1 782w (br)	[f] 43.9 (44.1)	3.8 (3.5)
(**9c**) $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_4(PMe_3)(\eta\text{-}C_5H_5)]$	Brown	40	[g] 2 044w, 1 984vs, 1 916m (br), 1 805w (br)	42.5 (41.3)	4.1 (3.8)
(**11b**) $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}CO)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$	Green	20	1 947vs, 1 888vs, 1 708m (br)	42.3 (42.0)	4.8 (4.9)
(**12b**) $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$	Black	90	1 965vs, 1 910s, 1 770m	57.2 (56.7)	4.1 (4.8)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2 unless otherwise stated. [c] In light petroleum. [d] N 2.6 (2.7%). [e] N 2.1 (2.1%). [f] N 3.0 (2.9%). Crystallises with two molecules of CH_2Cl_2. [g] In thf.

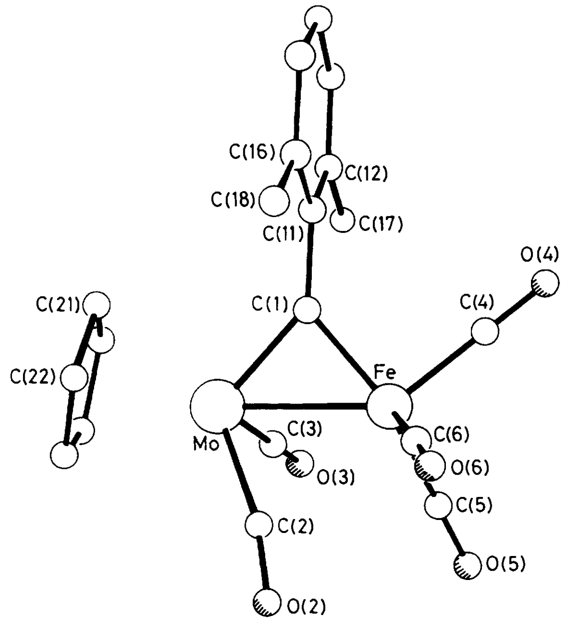


Figure 1. The molecular structure of $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ (**6f**) showing the atom-labelling scheme

now available (Table 5), a similar empirical relationship is seen to exist between pairs of compounds wherein an $RC{\equiv}M(CO)_2L$ fragment isolobal with an alkyne functions as either a two- or a four-electron donor to an $Fe(CO)_3$ group.

The nature of the bonding between the $RC{\equiv}M(CO)_2L$ fragments and the $Fe(CO)_n$ groups in the compounds of types (**5**) and (**6**) is of interest. To allow a comparison structural studies are required. The structure of (**5a**) has been established by *X*-ray diffraction,[11] and serves as a model for species of this class. The structure of (**6c**) has also been determined [13] but is not directly comparable with (**5a**) because the former contains a tungsten atom and the $HB(pz)_3$ ligand. Accordingly we have determined the structure of (**6f**). The results are listed in Table 6, and the structure is shown in Figure 1.

As expected, the molecule of (**6f**) contains an $Fe(CO)_3$ group. A comparison of structural parameters between (**5a**) and (**6f**) is instructive. As expected, in view of its unsaturation, (**6f**) has shorter Mo–Fe [2.557(1) Å] and μ-C(1)–Fe [1.861(2) Å] separations than (**5a**), for which the comparable distances are Mo–Fe [2.823(1)] and μ-C(1)–Fe [2.008(5) Å]. The opposite trend is observed for the μ-C(1)–Mo distances; that for (**5a**) [1.921(5) Å] is slightly shorter than that for (**6f**) [1.976(2) Å]. However, the Mo–C(1)–C(11) angles are the same [(**5a**) 139.1(4), (**6f**) 139.4(2)°].

Table 4. Hydrogen-1 and carbon-13 n.m.r. data[a] for the mixed-metal compounds

Compound	$^1H(\delta)$[b]	$^{13}C(\delta)$[c]
(4f)	[d] 2.32 (s, 6 H, Me), 4.50 (s, 5 H, C_5H_5), 6.70—6.90 (m, 3 H, C_6H_3)	[e] 274.3 (μ_3-C), 235.2 (MoCO), 201.0 (br, CoCO), 160.9 [$C^1(C_6H_3)$], 131.8, 130.1, 126.5 (C_6H_3), 96.2 (C_5H_5), 28.2 (Me_2-2,6)
(4g)	2.46 (s, 6H, Me), 5.37 (s, 5H, C_5H_5), 6.96—7.10 (m, 3H, C_6H_3)	[f] 270.0 (br, μ_3-C), 221.4 (WCO), 200.6 (br, CoCO), 132.1, 129.9, 128.5, 126.2 (C_6H_3), 93.7 (C_5H_5), 29.0 (Me_2-2,6)
(5h)	2.12 (s, 3 H, Me), 5.38 (s, 5 H, C_5H_5), 6.60—7.40 (m, 4 H, C_6H_4)	354.4 (μ-C), 231.4 (MoCO), 210.4 (br, FeCO), 163.5 [$C^1(C_6H_4)$], 130.7, 126.6, 125.9, 125.4, 118.9 (C_6H_4), 95.2 (C_5H_5), 21.1 (Me-2)
(5i)	3.83 (s, 3 H, OMe), 5.33 (s, 5 H, C_5H_5), 6.80—7.20 (m, 4 H, C_6H_4)	354.1 (μ-C), 232.3 (MoCO), 210.5 (FeCO), 151.8 [$C^1(C_6H_4)$], 147.8, 129.0, 123.4, 120.6, 110.7 (C_6H_4), 94.8 (C_5H_5), 54.9 (OMe)
(5j)	[g] 3.12 (s, 6 H, NMe_2), 5.33 (s, 5 H, C_5H_5), 6.67, 7.56 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7]	358.9 (μ-C), 231.6 (MoCO), 212.5 (FeCO), 152.2 [$C^1(C_6H_4)$], 148.0, 137.2, 110.5 (C_6H_4), 94.1 (C_5H_5), 40.4 (NMe_2)
(6e)	1.63 (s, 6 H, Me), 5.16 (s, 5 H, C_5H_5), 7.15—7.22 (m, 3 H, C_6H_3)	438.5 (μ-C), 246.7 (CrCO), 211.7 (FeCO), 165.0 [$C^1(C_6H_3)$], 128.1, 127.4, 124.7 (C_6H_3), 96.6 (C_5H_5), 21.7 (Me_2-2,6)
(6f)	[g] 1.71 (s, 6 H, Me), 5.58 (s, 5 H, C_5H_5), 7.10—7.20 (m, 3 H, C_6H_3)	407.4 (μ-C), 231.7 (MoCO), 213.4 (FeCO), 163.6 [$C^1(C_6H_3)$], 127.5, 126.6, 124.6 (C_6H_3), 94.5 (C_5H_5), 21.9 (Me_2-2,6)
(6g)	1.73 (s, 6 H, Me), 5.70 (s, 5 H, C_5H_5), 7.07—7.18 (m, 3 H, C_6H_3)	391.8 [μ-C, *J*(WC) 149], 221.7 [WCO, *J*(WC) 174], 215.2 (FeCO), 163.9 [$C^1(C_6H_3)$], 127.5, 126.8, 125.3 (C_6H_3), 95.1 (C_5H_5), 22.3 (Me_2-2,6)
(6h)	1.96 (s, 3 H, Me), 5.57 (s, 5 H, C_5H_5), 6.60—7.40 (m, 4 H, C_6H_4)	407.5 (μ-C), 231.4 (MoCO), 213.4 (FeCO), 164.5 [$C^1(C_6H_4)$], 130.1, 127.7, 126.9, 125.3, 119.3 (C_6H_4), 96.4 (C_5H_5), 21.1 (Me-2)
(7d)	2.52 (s, 3 H, Me), 5.27 (s, 5 H, C_5H_5), 7.00—7.20 (m, 4 H, C_6H_4)	[e,h] 289.1 (μ_3-C), 253.5 (μ-CO), 224.2 (MoCO), 215.3, 213.1, 206.6 (FeCO), 155.5 [$C^1(C_6H_4)$], 135.9, 132.5, 132.2, 128.3, 125.0 (C_6H_4), 92.2 (C_5H_5), 23.7 (Me-2)
(7e)	3.06 (s, 6 H, NMe_2), 5.29 (s, 5 H, C_5H_5), 6.66, 7.46 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[e] 297.3 (μ_3-C), 256.9 (μ-CO), 224.7 (MoCO), 214.5 (FeCO), 147.7 [$C^1(C_6H_4)$], 91.1 (C_5H_5), 40.5 (NMe_2)
(8c)	2.88 (s, 6 H, NMe_2), 2.92 (s, 6 H, NMe_2), 5.32 (s, 5 H, C_5H_5), 6.30—6.80 (m, 8 H, C_6H_4)	247.5 (μ-CO), 232.4 (MoCO), 231.1 (MoCO), 213.0 (br, FeCO), 158.4, 155.7 [$C^1(C_6H_4)$], 148.2, 147.7, 130.1, 129.4, 111.9, 110.1 (C_6H_4), 95.8, 93.7 (C_5H_5), 39.5, 39.2 (NMe_2)
(9c)	1.25 [d, 9 H, MeP, *J*(PH) 35], 1.77 (s, 6 H, Me), 5.52 (s, 5 H, C_5H_5), 7.10 (br, 3 H, C_6H_3)	383.6 [μ-C, *J*(WC) 156], 224.2 [WCO, *J*(WC) 177], 220.5 [d, FeCO, *J*(PC) 28], 165.5 [$C^1(C_6H_3)$], 126.7, 124.3, 123.5 (C_6H_3), 93.7 (C_5H_5), 22.3 (Me_2-2,6), 19.9 [d, MeP, *J*(PC) 31]
(11b)	1.24 [d, 9 H, MeP, *J*(PH) 10], 1.25 [d, 9 H, MeP, *J*(PH) 9], 1.48 (s, 3 H, Me), 1.90 (s, 3 H, Me), 5.11 [d, 5 H, C_5H_5, *J*(PH) 2], 6.88—7.15 (m, 3 H, C_6H_3)	347.8 (μ-C), 272.0 [WCO, *J*(WC) 121], 225.9 [d, FeCO, *J*(PC) 15], 222.4 [d, FeCO, *J*(PC) 27], 165.3 [$C^1(C_6H_3)$], 128.6, 127.2, 126.7, 125.7, 123.6 (C_6H_3), 91.3 (C_5H_5), 24.0 [d, MeP, *J*(PC) 37], 21.9 (Me_2-2,6), 20.7 [d, MeP, *J*(PC) 28]
(12b)	1.88 (s, 3 H, Me), 1.95 (s, 3 H, Me), 4.99 [d, 5 H, C_5H_5, *J*(PH) 1], 5.33 (m, 2 H, CH_2), 6.61—7.87 (m, 23 H, Ph, C_6H_3)	372.8 [d, μ-C, *J*(PC) 13], 234.0 [d, WCO, *J*(PC) 13], 223.0 (FeCO), 218.4 [d, FeCO, *J*(PC) 13], 166.9 [$C^1(C_6H_3)$], 142.6—124.2 (C_6H_3, Ph), 93.6 (C_5H_5), 43.9 [d of d, CH_2, *J*(PC) 38, 23], 23.0, 22.7 (Me)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures, unless otherwise stated. [b] Measured in CD_2Cl_2 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. [d] In C_6D_6. [e] Measured at −80 °C. [f] Measured at −40 °C. [g] In $CDCl_3$. [h] Peaks for major isomer are listed (see text).

Table 5. Comparison of carbon-13 chemical shifts, δ (p.p.m.), for μ-alkylidyne-carbon nuclei in electronically saturated and unsaturated dimetal compounds

34-Valence-electron compound	δ	32-Valence-electron compound	δ	δΔ
(5b)[a]	331.3	**(6b)**[a,b]	392.5	61.2
(5c)[a]	290.9	**(6c)**[a]	408.8	117.9
(5d)[c]	341.8	**(6d)**[c]	395.4	53.6
(5e)[d]	367.4	**(6e)**[d]	438.5	71.1
(5f)[d]	345.3	**(6f)**[d]	407.4	62.1
(5g)[d]	311.7	**(6g)**[d]	391.8	80.1
(5h)[d]	354.4	**(6h)**[d]	407.5	53.1

[a] Data from ref. 13. [b] Data from ref. 10. [c] Data from ref. 9*b*. [d] This work.

The xylyl ring in **(6f)** is almost orthogonal to the Mo(μ-C)Fe ring. A similar arrangement occurs[15] in the anion $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]^-$, and is probably imposed by the presence of the *o*-methyl groups. In **(6f)** the torsion angle Mo–C(1)–C(11)–C(12) is 85.1(3)°, to be compared with 103(1)° in $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]^-$, 53° in $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PBu^t{}_2H)(\eta^5\text{-}C_5H_5)]$,[16] and 154(1)° in **(6c)**.

In order to investigate the origin of the structural differences between compounds of class **(5)** and **(6)**, a series of extended-

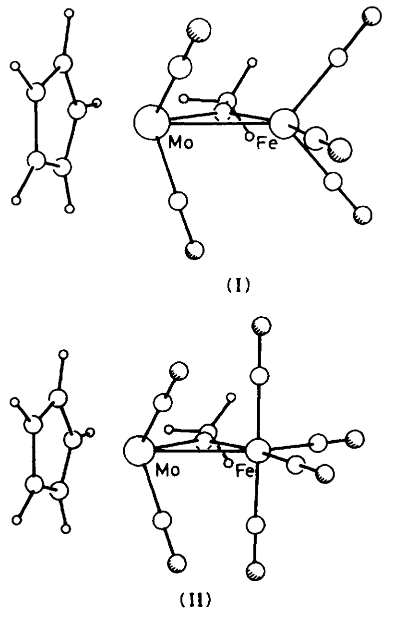


Figure 2. Model geometries for **(I)** and **(II)** as used in the extended Hückel calculations

Table 6. Selected internuclear distances (Å) and angles (°) for [MoFe(μ-CC$_6$H$_3$Me$_2$-2,6)(CO)$_5$(η-C$_5$H$_5$)] (**6f**) with estimated standard deviations in parentheses

Mo–Fe	2.577(1)	Mo–C(1)	1.976(2)	Mo–C(2)	1.964(2)	Mo–C(3)	1.997(3)
Mo–X*	2.021	Fe–C(1)	1.861(2)	Fe···C(2)	2.534	Fe–C(4)	1.782(3)
Fe–C(5)	1.799(3)	Fe–C(6)	1.757(4)	C(1)–C(11)	1.461(3)	C(2)–O(2)	1.157(3)
C(3)–O(3)	1.133(4)	C(4)–O(4)	1.135(4)	C(5)–O(5)	1.140(4)	C(6)–O(6)	1.134(5)
Fe–Mo–C(1)	46.0(1)	Fe–Mo–C(2)	66.3(1)	C(1)–Mo–C(2)	109.6(1)	Fe–Mo–C(3)	80.9(1)
C(1)–Mo–C(3)	97.8(1)	C(2)–Mo–C(3)	86.7(1)	Fe–Mo–X*	163	C(1)–Mo–X	122
C(2)–Mo–X	118	C(3)–Mo–X	115	Mo–Fe–C(1)	49.7(1)	Mo–Fe–C(4)	137.5(1)
C(1)–Fe–C(4)	91.1(1)	Mo–Fe–C(5)	107.8(1)	C(1)–Fe–C(5)	147.4(1)	C(4)–Fe–C(5)	98.3(1)
Mo–Fe–C(6)	114.0(1)	C(1)–Fe–C(6)	115.8(1)	C(4)–Fe–C(6)	96.3(2)	C(5)–Fe–C(6)	94.2(2)
Mo–C(1)–Fe	84.3(1)	Mo–C(1)–C(11)	139.4(2)	Fe–C(1)–C(11)	136.3(2)	Mo–C(2)–O(2)	167.8(2)
Mo–C(3)–O(3)	178.0(3)	Fe–C(4)–O(4)	178.9(3)	Fe–C(5)–O(5)	177.1(3)	Fe–C(6)–O(6)	176.7(3)
C(1)–C(11)–C(12)	119.9(2)	C(1)–C(11)–C(16)	119.9(2)				

* X is the centroid of the η-C$_5$H$_5$ ligand.

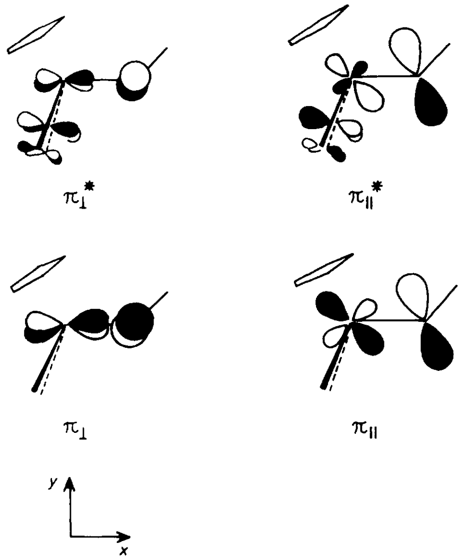


Figure 3. The frontier orbitals of the distorted MeC≡Mo(CO)$_2$(η-C$_5$H$_5$) fragment

Table 7. Mulliken fragment orbital populations for the molybdenum carbon π orbitals in models (**I**) and (**II**)

	Isolated fragment	Model (**I**)	Model (**II**)
$\pi_{\perp}$*	0.00	0.07	0.08
$\pi_{\parallel}$*	0.00	0.87	0.78
$\pi_{\perp}$	2.00	1.23	1.95
$\pi_{\parallel}$	2.00	1.81	1.69

Hückel molecular-orbital calculations have been carried out. The compounds (**6**) were modelled by [MoFe(μ-CMe)(CO)$_5$(η-C$_5$H$_5$)] (**I**) in an idealised mirror-symmetric geometry, based on that observed for [FeW(μ-CC$_6$H$_4$Me-4)(CO)$_4$(PBu$^t{}_2$H)(η-C$_5$H$_5$)][16] since the data for (**6f**) were not available at the time the calculations were performed. This, however, is not expected to affect the conclusions. The model class (**5**) complex was [MoFe(μ-CMe)(CO)$_6$(η-C$_5$H$_5$)] (**II**) with exactly the same geometry as (**I**), but with replacement of the Fe(CO)$_3$ group by Fe(CO)$_4$. This model differs from the lower-symmetry structure observed crystallographically for (**5a**) in the relative orientation of the Mo(CO)$_2$(η-C$_5$H$_5$) group and the Fe-μ-(C) bond, but equivalence of the two molybdenum carbonyls from n.m.r. data, even at low temperature, suggests that the two conformations are of similar energy. We have used a mirror-symmetric model geometry to simplify the analysis of the calculations and facilitate direct comparison with the model structure (**I**). The geometries of (**I**) and (**II**) are depicted in Figure 2. Geometrical data are given in the Appendix, together with the extended-Hückel parameters used in the calculations.

The results will be discussed in terms of the interactions between the frontier orbitals of a distorted MeC≡Mo(CO)$_2$(η-C$_5$H$_5$) fragment, and the Fe(CO)$_n$ (n = 3 or 4) fragments. The important frontier orbitals for the molybdenum–carbyne moiety are, as expected from the isolobal analogy,[17] similar in form to those for an alkyne (Figure 3). They comprise two C–Mo π-bonding orbitals and two π* orbitals. One component of each pair lies in the symmetry plane of the 'ligand' ($\pi_{\parallel}$ and $\pi_{\parallel}$*), and the other components are perpendicular to and antisymmetric with respect to this plane ($\pi_{\perp}$ and $\pi_{\perp}$*).[18] The frontier orbitals of the iron carbonyl fragments have been previously discussed,[19] and are shown on either side of the simplifed interaction diagram (Figure 4).

We have chosen to consider the inter-fragment bonding in two stages. (*i*) Interaction between those orbitals which are symmetric with respect to the molecular symmetry plane gives rise to the metallacycle Mo(μ-C)Fe σ-bonded framework. The interaction of the C≡Mo $\pi_{\parallel}$ and $\pi_{\parallel}$* orbitals with the Fe(CO)$_n$ groups is qualitatively similar in (**I**) and (**II**). Both Fe(CO)$_3$ and Fe(CO)$_4$ have σ-symmetry acceptor orbitals (2a_1 in Figure 4), and in-plane π-donor orbitals [1b_2 in Fe(CO)$_4$, and the symmetric component of 2e in Fe(CO)$_3$]. The result is a reduction in the strength of the C–Mo $\pi_{\parallel}$ bonding, and the formation of Mo–Fe and C–Fe σ bonds. This process is analogous to the Dewar–Chatt–Duncanson[20] model for alkene–metal bonding since it involves synergic $\pi_{\parallel}$→Fe dative and Fe→$\pi_{\parallel}$* retrodative components. The fragment orbital populations (Table 7) from a Mulliken[21] analysis provide an estimate of the relative magnitudes of these effects.

(*ii*) Those orbitals which are antisymmetric with respect to the molecular plane interact to afford the π bonding in the unsaturated ring system Mo(μ-C)Fe. The most important orbital of this type of the C≡Mo fragment is the out-of-plane π-bonding orbital $\pi_{\perp}$. In the model complex (**II**) the only iron frontier orbital of the required symmetry is 1b_1, and as this orbital is occupied a destabilising four-electron interaction results. The highest occupied molecular orbital (h.o.m.o.) of (**II**) is thus both Mo–Fe and C–Fe antibonding, and as expected from electron-counting considerations the π bonding remains

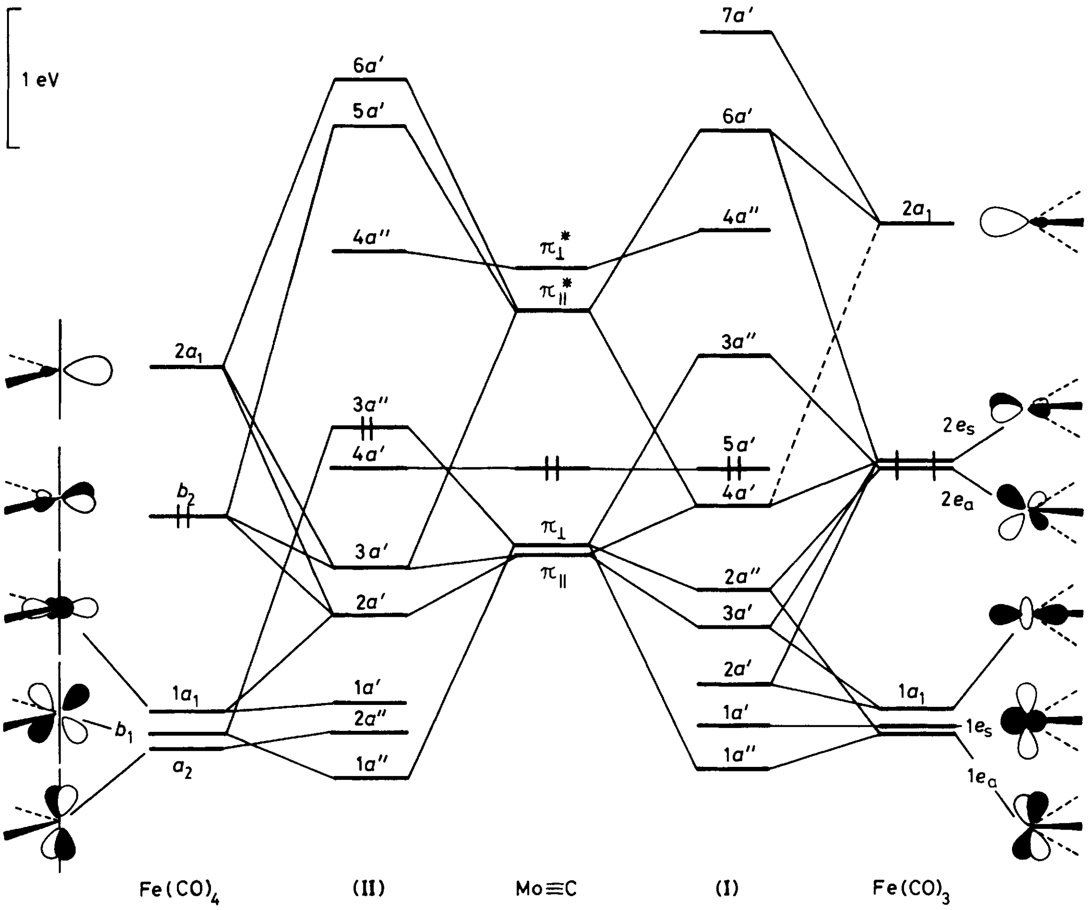
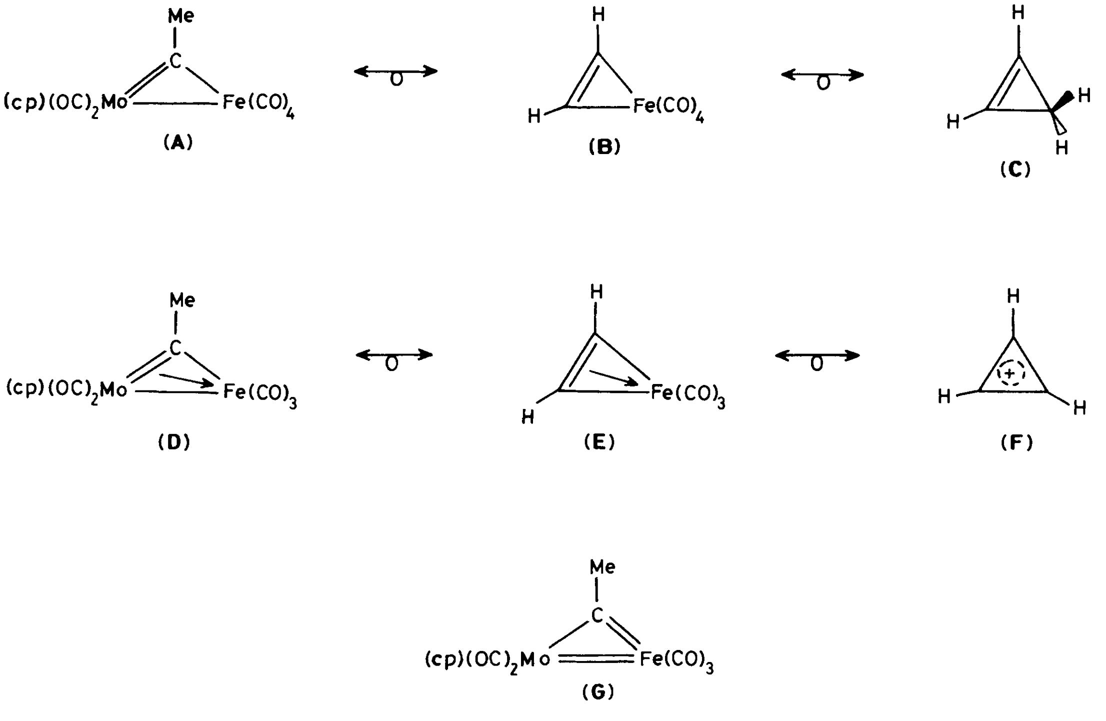


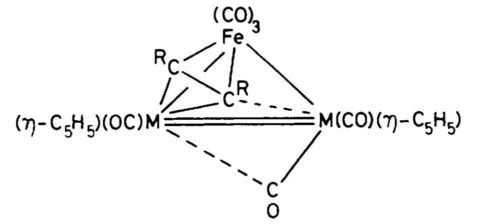
Figure 4. Simplifed interaction diagram for (I) and (II)



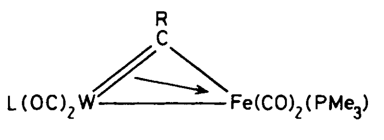
Scheme. cp = η-C_5H_5

Table 8. Mulliken interatomic overlap populations for the model complexes (**I**) and (**II**); *a′* and *a″* denote summations over those molecular orbitals which are symmetric and antisymmetric respectively, with respect to the molecular symmetry plane

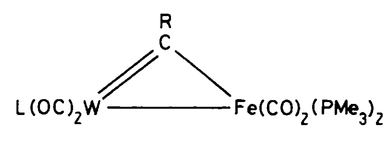
		(I)	(II)
Mo–Fe	*a′*	0.109	0.087
	a″	0.055	−0.070
	Total	0.164	0.017
Mo–μ-C	*a′*	0.598	0.593
	a″	0.123	0.266
	Total	0.721	0.859
Fe–μ-C	*a′*	0.532	0.472
	a″	0.155	−0.030
	Total	0.687	0.442



	M	R
(**8a**)	Mo	C_6H_4Me-4
(**8b**)	W	C_6H_4Me-4
(**8c**)	Mo	$C_6H_4NMe_2$-4



	L	R
(**9a**)	η-C_5H_5	C_6H_4Me-4
(**9b**)	HB(pz)$_3$	C_6H_4Me-4
(**9c**)	η-C_5H_5	$C_6H_3Me_2$-2,6



	L	R
(**10a**)	η-C_5H_5	C_6H_4Me-4
(**10b**)	HB(pz)$_3$	C_6H_4Me-4

localised between Mo and the μ-C atom. In contrast, the $Fe(CO)_3$ fragment has an acceptor orbital of suitable symmetry ($2e_a$), and hence a stabilising $\pi_\perp \rightarrow$Fe dative interaction results. The C≡Mo $\pi_\perp{}^*$ orbital is a potential acceptor of approximately δ symmetry towards iron. However, it is evident from the fragment orbital populations (Table 7) that in both (**I**) and (**II**) this orbital makes only a small contribution to the bonding. Similar conclusions have been reached in studies on some alkynemolybdenum complexes.[22,23]

The calculations support the dimetallacyclopropene formulation (**A**) (Scheme) for the bonding in (**II**) and the isolobal mapping with (**B**) or (**C**). For (**I**), representation (**D**) seems particularly appropriate, involving a two-electron π system, as in the isolobal species (**E**) and (**F**). The formulation (**G**) implies the contribution of a second pair of π electrons from iron and occupation of the Mo–Fe $\pi_\perp{}^*$ orbital. In view of the fragment orbital population given in Table 7, it seems likely that (**G**) may considerably underestimate the extent of the residual C–Mo multiple bonding. In support of this the Mo–C bond length in (**6f**) [1.976(2) Å] is similar to that observed in the terminal-carbene complex [$Mo_2(=CR_2)(N_2CR_2)(CO)_3$(η-$C_5H_5)_2$] (R = C_6H_4Me-4).[24]

The Mulliken interatomic overlap populations for the Mo-(μ-C)Fe cores of (**I**) and (**II**) are given in Table 8. The relative magnitudes of the Mo–Fe, μ-C–Mo, and μ-C–Fe overlap populations will be rather sensitive to the basis set parametrisation, and the interatomic separations used. However, since (**I**) and (**II**) have the same core geometries, differences between corresponding values should be due mainly to the different bonding requirements of the $Fe(CO)_3$ and $Fe(CO)_4$ fragments. The breaking into *a′* and *a″* components provides more evidence for the suggestion that the differences in core bonding between (**I**) and (**II**), and hence the molecular dimensions for (**5a**) and (**6f**), stem largely from the different out-of-plane π-bonding requirements of the two iron carbonyl fragments.

An interesting feature of the reactions between [$Fe_2(CO)_9$] and compounds (**1f**)—(**1h**) was the absence of products containing three metal atoms. This is also true of the reaction between (**1d**) and [$Fe_2(CO)_9$].[13] In contrast, in the presence of an excess of the iron carbonyl, the compounds (**1b**), (**1c**), and (**1e**) readily afford the trimetal complexes [$MFe_2(\mu_3$-CC_6H_4-Me-4)(μ-CO)$(CO)_8$L] [L = η-C_5H_5, M = Mo (**7a**) or W (**7b**); L = η-C_5Me_5, M = W (**7c**)].[9–11] Moreover, the latter may also be obtained by treating the dimetal species (**5a**), (**5b**), and (**5d**) with [$Fe_2(CO)_9$]. If an excess of the monoalkylidyne compounds (**1b**) or (**1c**) is used in reactions with [$Fe_2(CO)_9$] the trimetal compounds [M_2Fe{μ-$C_2(C_6H_4Me$-$4)_2$}$(CO)_6$(η-$C_5H_5)_2$] [M = Mo (**8a**) or W (**8b**)] are obtained. The absence of trimetal compounds analogous to (**7a**)—(**7c**) and (**8a**) and (**8b**) when the reagents (**1d**) and (**1f**)—(**1g**) are used in reactions with iron carbonyls may be attributed to the steric effect of the HB(pz)$_3$ or $C_6H_3Me_2$-2,6 groups inhibiting attack of an iron carbonyl fragment on a species of type (**5**) or (**6**).

In view of these results, reactions between (**1i**) and (**1j**) and [$Fe_2(CO)_9$] were next investigated, since the presence in these mononuclear metal alkylidyne compounds of one substituent in the *ortho* position in the arene ring, rather than two as in (**1f**)—(**1h**), was expected to favour formation of complexes of type (**5**) and also the trimetal compounds, if steric factors are important. In Et_2O at room temperature the compounds (**1i**) and [$Fe_2(CO)_9$] afford a mixture of the three complexes [MoFe(μ-CC_6H_4Me-2)$(CO)_n$(η-C_5H_5)] (**5h**, *n* = 6; **6h**, *n* = 5) and [$MoFe_2(\mu_3$-CC_6H_4Me-2)(μ-CO)$(CO)_8$(η-C_5H_5)] (**7d**). The latter species can be obtained in *ca.* 80% yield by treating (**1i**) with 2 equivalents of [$Fe_2(CO)_9$]. Although (**5h**) and (**6h**) cannot be separated by column chromatography, crystals of (**5h**) can be obtained from CO-saturated solutions of mixtures of the two dimetal compounds in CH_2Cl_2–light petroleum at −78 °C. Complex (**6h**) can be recovered from mixtures of the two dimetal compounds by bubbling nitrogen through solutions. Data for (**5h**), (**6h**), and (**7d**) are given in Tables 3 and 4. However, for (**6h**), microanalyses were not obtained because of its ready conversion into (**5h**), and so its formulation rests on n.m.r. data and the i.r. spectrum [$\nu_{max.}$(CO) at 2 054s, 1 990s, 1 978m, 1 934s, and 1 899w cm^{-1} (in light petroleum)], which is very similar to that of (**6f**).

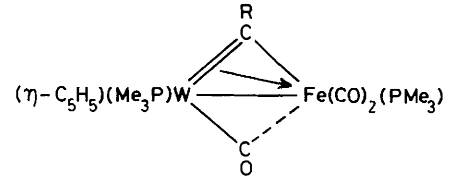
The $^{13}C-\{^1H\}$ n.m.r. spectrum of (**7d**), measured at -80 °C, showed the presence of two isomers. Peaks for the major isomer (*ca.* 75%) are listed in Table 4, with the diagnostic peak for the μ_3-C nucleus at δ 289.1 p.p.m. Resonances for the minor isomer occur at δ 286.0 (μ_3-C), 243.3 (μ-CO), 228.6 (MoCO), 221.2, 210.1, 204.3 (FeCO), 158 [$C^1(C_6H_4)$], 134.3, 132.7, 131.2, 127.5, 124.7 (C_6H_4), 92.2 (C_5H_5), and 24.1 (Me-2). The existence of isomers of (**7d**) arises as a consequence of the $Mo(CO)_2(\eta-C_5H_5)$ fragment occupying different configurations with respect to the μ_3-CFe_2 framework, as discussed previously,[9b,10,11] The existence of rotational isomers in complexes of this structural type is also revealed by the appearance of additional CO stretching bands in the i.r. spectra. For (**7d**) (Table 3) there are fourteen such bands, with two in the bridging or semi-bridging region of the spectrum.

The reaction between (**1j**) and $[Fe_2(CO)_9]$ afforded the electronically saturated compound $[MoFe(\mu-CC_6H_4OMe-2)-(CO)_6(\eta-C_5H_5)]$ (**5i**), and no trimetal species was identified. Moreover, we obtained no evidence of a compound of type (**6**), although in work-up procedures some decomposition was observed and it may be that other products are formed. The results with (**1i**) and (**1j**) seem to support the idea that steric effects are important, since these reagents favour formation of species of type (**5**) rather than those of type (**6**).

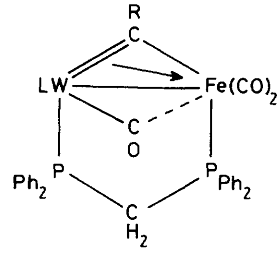
As mentioned earlier, it was hoped that the presence of the NMe_2 group in the *para* position of the C_6H_4 fragment in compound (**1k**) would enhance the donor ability of the $RC{\equiv}Mo(CO)_2(\eta-C_5H_5)$ group and thereby favour formation with $[Fe_2(CO)_9]$ of a product of type (**6**) in which the C≡Mo formally contributes four electrons to the iron centre. In practice reactions between (**1k**) and $[Fe_2(CO)_9]$ afforded the three products $[MoFe(\mu-CC_6H_4NMe_2-4)(CO)_6(\eta-C_5H_5)]$ (**5j**), $[MoFe_2(\mu_3-CC_6H_4NMe_2-4)(\mu-CO)(CO)_8(\eta-C_5H_5)]$ (**7e**), and $[Mo_2Fe\{\mu-C_2(C_6H_4NMe_2-4)_2\}(CO)_6(\eta-C_5H_5)_2]$ (**8c**). Data characterising these complexes are given in Tables 3 and 4. There was no evidence for the existence of an unsaturated dimetal compound of type (**6**). Moreover, formation of the trimetal compounds confirms that such products are obtained if in the precursors (**1**) the arene ring does not have substituents *ortho* to the ligating alkylidyne-carbon atom. It should be noted that (**1j**), however, with only one substituent in the ring *ortho* to the alkylidyne carbon, affords a trimetal product (**7d**).

During the course of our work we have also studied reactions of compound (**6g**) with PMe_3 and with dppm ($Ph_2PCH_2PPh_2$). We have earlier observed[13] that treatment of (**6b**) with 1 equivalent of PMe_3 yields $[WFe(\mu-CC_6H_4Me-4)(CO)_4(PMe_3)-(\eta-C_5H_5)]$ (**9a**), which with a further equivalent of PMe_3 affords $[WFe(\mu-CC_6H_4Me-4)(CO)_4(PMe_3)_2(\eta-C_5H_5)]$ (**10a**) and $[WFe(\mu-CC_6H_4Me-4)(CO)_3(PMe_3)_2(\eta-C_5H_5)]$ (**11a**) in a stepwise process. Compound (**9b**) was also prepared by treating (**6c**) with 1 equivalent of PMe_3, but an excess of the phosphine led to fragmentation of the dimetal species and formation of $[W(\equiv CC_6H_4Me-4)(CO)(PMe_3)\{HB(pz)_3\}]$.

Compound (**6g**) reacts with 2 equivalents of PMe_3 in CH_2Cl_2 to give a chromatographically separable mixture of the complexes $[WFe(\mu-CC_6H_3Me_2-2,6)(CO)_4(PMe_3)(\eta-C_5H_5)]$ (**9c**) and $[WFe(\mu-CC_6H_3Me_2-2,6)(CO)_3(PMe_3)_2(\eta-C_5H_5)]$ (**11b**), which were characterised by microanalysis and spectroscopic data (Tables 2 and 3). We have previously prepared the compound $[WFe(\mu-CC_6H_4Me-4)(\mu-dppm)-(\mu-CO)(CO)_2\{HB(pz)_3\}]$ (**12a**) by treating (**6c**) with dppm. Similarly, (**6g**) with dppm affords $[WFe(\mu-CC_6H_3Me_2-2,6)(\mu-dppm)(\mu-CO)(CO)_2(\eta-C_5H_5)]$ (**12b**). The i.r. spectra of (**11b**) and (**12b**) show three CO stretching bands, one of which [1 708 (**11b**) and 1 770 cm^{-1} (**12b**)] is in the bridging region. The $^{13}C-\{^1H\}$ n.m.r. spectra also show resonances for three CO ligands at δ 272.0, 225.9, and 222.4 p.p.m. for (**11b**), and at δ 234.0, 223.0, and 218.4 p.p.m. for (**12b**). The resonances for the FeCO groups (see Table 4) occur as doublets due to $^{31}P-^{13}C$ coupling, and confirm that the phosphine ligates the iron atoms. Moreover, as expected, in the spectrum of (**12b**) the resonance for the WCO group is also a doublet. Signals for the μ-C nuclei occur at δ 347.8 (**11b**) and 372.8 p.p.m. (**12b**). These chemical shifts may be compared with those at δ 354.7 p.p.m. in the spectrum of (**11a**), and 377.2 p.p.m. in the spectrum of (**12a**).[13] The $^{31}P-\{^1H\}$ n.m.r. spectra of compounds (**9c**) and (**11b**) are also in accord with the formulations shown, with signals at δ 43.4 (**9c**), and δ 35.5 (FeP) and -17.9 p.p.m. [WP, J(WP) 400 Hz] (**11b**). The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**12b**) has resonances at δ 40.4 [d, FeP, J(PP) 83] and 25.7 p.p.m. [d, WP, J(PP) 85, J(WP) 327 Hz]. These data are very similar to those reported for compounds (**9a**), (**11a**), and (**12a**).



	R
(**11a**)	C_6H_4Me-4
(**11b**)	$C_6H_3Me_2-2,6$



	L	R
(**12a**)	$HB(pz)_3$	C_6H_4Me-4
(**12b**)	$\eta-C_5H_5$	$C_6H_3Me_2-2,6$

Experimental

All reactions were carried out under oxygen-free nitrogen. Light petroleum refers to that fraction of b.p. 40—60 °C. The complex $[W(\equiv CC_6H_3Me_2-2,6)Br(CO)_4]$ was prepared as described previously.[5,15] The new alkylidynemolybdenum compounds were prepared, as described below, by a modification of procedures described by Mayr and co-workers.[3] The reagent $Na(C_5H_5)\cdot dme$ was obtained as described elsewhere.[4] Analytical and other data for new compounds are given in Tables 1 and 2. The instrumentation used to record spectroscopic data has been listed in previous parts of this series.

Synthesis of the Molybdenum and Tungsten Alkylidyne Compounds.—(*i*) The compound $[W(\equiv CC_6H_3Me_2-2,6)-Br(CO)_4]$ (2.0 g, 4.0 mmol) in thf (20 cm^3) was treated with $Na(C_5H_5)\cdot dme$ (0.36 g, 4.0 mmol). After 0.5 h, solvent was removed *in vacuo* and the residue was suspended in light petroleum (6 cm^3). The solution was chromatographed on an alumina column (3 × 15 cm) eluting with light petroleum. The orange fraction was collected and the volume of solvent reduced *in vacuo* to *ca.* 20 cm^3. Cooling to −78 °C afforded bright orange crystals of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ (**1h**) (1.23 g).

(*ii*) The compounds (**1f**), (**1g**), and (**1i**)—(**1k**) were all prepared *via* the species $[M(\equiv CR)(O_2CCF_3)(CO)_4]$ (M = Cr or Mo) which were not isolated but used *in situ*. The general procedure is described. A 1-l three-necked round-bottom flask, the contents of which could be magnetically stirred, was fitted with a dropping funnel, a nitrogen inlet, and an exit *via* a bubbler. Diethyl ether (400 cm^3) and $[Mo(CO)_6]$ (7.9 g, 30 mmol) were added to the flask. The suspension was then treated, *via* the dropping funnel, with an equimolar amount of a *ca.* 1 mol dm^{-3} Et_2O solution of the appropriate LiR reagent. Completion of the reaction may be monitored by observing the disappearance of i.r. bands due to $[Mo(CO)_6]$. The yellow mixture was cooled to *ca.* −78 °C, and an Et_2O (20 cm^3) solution of trifluoroacetic anhydride (4.5 cm^3, 32 mmol) was added dropwise *via* the funnel. Carbon monoxide is evolved, and the colour changes through red to yellow. In the synthesis of compound (**1k**) the temperature must be raised to *ca.* −20 °C.

When CO evolution had ceased, solid $Na(C_5H_5)\cdot$dme (5.7 g, 32 mmol) was added, and the mixture was allowed to warm to ambient temperatures during which time further CO evolution occurred, and the contents of the flask turned red. After the reaction had ceased (monitored by i.r. spectroscopy), the volume of solvent was reduced *in vacuo* to *ca.* 20 cm^3, and the residue was extracted with CH_2Cl_2–light petroleum (5 × 50 cm^3, 1:4). The extracts were chromatographed on an alumina column (8 × 10 cm), eluting with the same solvent mixture. Removal of solvent *in vacuo* afforded the desired alkylidynemolybdenum complex in yields of 60—80%.

Reactions of the Complexes $[M(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ *with Tertiary Phosphines.*—(*i*) A light petroleum (20 cm^3) solution of compound (**1g**) (0.32 g, 0.95 mmol) was treated with PPh_3 (0.25 g, 0.95 mmol), and the mixture was stirred for 3 d while exposed to light from a 100-W electric light bulb. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (10 cm^3) and chromatographed on an alumina column (3 × 15 cm). Elution with CH_2Cl_2 afforded a violet eluate. Removal of solvent *in vacuo* gave violet *microcrystals* of $[Mo\{C(C_6H_3Me_2\text{-}2,6)C(O)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (**2c**) (0.13 g). This compound slowly decomposes in CH_2Cl_2 to give (**3d**).

(*ii*) Compound (**1g**) (0.50 g, 1.5 mmol) and PPh_3 (0.25 g, 0.95 mmol) were refluxed in thf (10 cm^3) for several days in the dark. Solvent was removed *in vacuo* and the oily red residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:3) and chromatographed on an alumina column (3 × 15 cm). Elution with the same solvent mixture removed initially some unreacted (**1g**). The second eluate afforded a red solution. Removal of solvent *in vacuo* gave dark red or black *microcrystals* of $[Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (**3d**) (0.26 g).

(*iii*) A thf (50 cm^3) solution of PPh_3 (0.50 g, 1.9 mmol) and compound (**1h**) (0.40 g, 0.95 mmol) was refluxed for 6 d. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (2 cm^3, 1:1) and chromatographed on an alumina column (2 × 15 cm). Elution with CH_2Cl_2–light petroleum (1:10) developed two fast-moving bands. The first contained unreacted (**1h**). The second contained the product, which was recovered by removing the solvent *in vacuo*, dissolving the residue in CH_2Cl_2 (2 cm^3), adding light petroleum (20 cm^3), and cooling to −20 °C to give black *crystals* of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (**3e**) (0.17 g).

(*iv*) A light petroleum (10 cm^3) solution of compound (**1h**) (0.40 g, 0.95 mmol) and PMe_3 (2 mmol) was stirred for 3 h giving a red precipitate. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2–light petroleum (2 cm^3, 1:1) and chromatographed on alumina. Elution with the same solvent removed initially an orange band and this was followed by a slowly moving red fraction. The former, after removing solvent *in vacuo*, yielded orange *microcrystals* of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**3f**) (0.13 g). The red fraction was removed from the column with CH_2Cl_2–thf (1:5), and after removal of solvent *in vacuo* gave red *microcrystals* of $[W\{C(C_6H_3Me_2\text{-}2,6)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**2d**) (0.19 g).

Reaction with $[Co_2(CO)_8]$.—(*i*) Compound (**1g**) (0.20 g, 0.60 mmol) and $[Co_2(CO)_8]$ (0.20 g, 0.58 mmol) were dissolved in light petroleum, and the mixture was stirred for 2 h. Solvent was removed *in vacuo* and the black residue was dissolved in CH_2Cl_2 (2 cm^3). Light petroleum (4 cm^3) was added, and the solution was chromatographed at −60 °C on a Kieselgel column (2 × 10 cm). Elution with CH_2Cl_2–light petroleum (1:2) afforded a dark green eluate. Removal of solvent *in vacuo* gave black *microcrystals* of $[MoCo_2(\mu_3\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_8(\eta\text{-}C_5H_5)]$ (**4f**) (0.30 g).

(*ii*) The compounds (**1h**) (0.30 g, 0.71 mmol) and $[Co_2(CO)_8]$ (0.24 g, 0.71 mmol) were dissolved in light petroleum (20 cm^3). After 0.5 h, the volume was reduced *in vacuo* to *ca.* 15 cm^3, and the mixture was cooled to −78 °C. The supernatant was then removed to give black *microcrystals* of $[WCo_2(\mu_3\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_8(\eta\text{-}C_5H_5)]$ (**4g**) (0.36 g).

Reactions of the Alkylidyne Chromium, Molybdenum, and Tungsten Compounds with $[Fe_2(CO)_9]$.—(*i*) A mixture of compound (**1f**) (0.15 g, 0.42 mmol) and $[Fe_2(CO)_9]$ (0.30 g, 0.84 mmol) in thf (50 cm^3) was stirred for 6 h at room temperature. Volatiles were removed *in vacuo* {**CAUTION**: $[Fe(CO)_5]$}. The black residue was dissolved in CH_2Cl_2 (5 cm^3), light petroleum (5 cm^3) was added, and the solution was chromatographed on an alumina column (3 × 10 cm). Elution with the same solvent mixture removed initially a yellow solution containing $[Fe(CO)_5]$ and a green eluate containing $[Fe_3(CO)_{12}]$ (i.r.). Further elution recovered a violet fraction from which solvent was removed *in vacuo* to give black *microcrystals* of $[CrFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ (**6e**) (0.16 g).

(*ii*) Similarly compound (**1g**) (0.20 g, 0.60 mmol) and $[Fe_2(CO)_9]$ (0.28 g, 0.77 mmol) in thf (30 cm^3) afforded after stirring for 5 h a dark violet solution. Volatile material was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (3 cm^3) and light petroleum (15 cm^3) and chromatographed on alumina (3 × 15 cm column). Elution with CH_2Cl_2–light petroleum (1:5) followed by removal of solvent *in vacuo* afforded black *microcrystals* of $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ (**6f**) (0.27 g).

(*iii*) An Et_2O (25 cm^3) solution containing compound (**1h**) (2.00 g, 4.74 mmol) and $[Fe_2(CO)_9]$ (1.72 g, 9.48 mmol) was stirred for 3 h. Solvent was removed *in vacuo* from the deep purple solution. The residue was dissolved in CH_2Cl_2–light petroleum (2 cm^3, 1:1) and chromatographed on an alumina column (3 × 15 cm). Elution with the same solvent mixture removed a deep purple fraction from which solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (2 cm^3) to which light petroleum (10 cm^3) was added, and the mixture was cooled to −78 °C. This treatment gave purple *microcrystals* of $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ (**6g**) (1.98 g).

(*iv*) A mixture of compound (**1i**) (0.85 g, 2.66 mmol) and $[Fe_2(CO)_9]$ (1.0 g, 2.75 mmol) in Et_2O (50 cm^3) was stirred for 4 h at ambient temperature. Volatile material was removed *in vacuo*. The black residue was dissolved in CH_2Cl_2 (4 cm^3) and light petroleum (20 cm^3), and chromatographed on a water-cooled Kieselgel column (2 × 20 cm). Elution with CH_2Cl_2–light petroleum (1:5) gave initially a green fraction containing $[Fe_3(CO)_{12}]$. This was followed by a broad red-brown to violet band which did not separate on the column. This fraction was collected and solvent was removed *in vacuo* giving (0.70 g) of a mixture of $[MoFe(\mu-CC_6H_4Me-2)(CO)_n(\eta-C_5H_5)]$ [(**5h**), $n = 6$; (**6h**), $n = 5$]. Crystals of $[MoFe(\mu-CC_6H_4Me-2)(CO)_6(\eta-C_5H_5)]$ (**5h**) can be obtained from the mixture by recrystallisation from a solution of CH_2Cl_2–light petroleum (1:5) saturated with CO at −78 °C.

Further elution of the column with the same solvent removed a green-brown eluate from which solvent was removed *in vacuo* to yield dark green *microcrystals* of $[MoFe_2(\mu_3-CC_6H_4Me-2)(\mu-CO)(CO)_8(\eta-C_5H_5)]$ (**7d**) (0.27 g). This product can be obtained in *ca.* 80% yield by treating (**1i**) with 2 equivalents of $[Fe_2(CO)_9]$.

The complex (**6h**) can be recovered in *ca.* 30% yield by bubbling nitrogen through CH_2Cl_2 solutions of (**5h**) at room temperature. The reaction is readily reversed by addition of CO.

(*v*) A mixture of $[Fe_2(CO)_9]$ (0.58 g, 1.5 mmol) and compound (**1j**) (0.50 g, 1.5 mmol) in Et_2O (50 cm^3) was stirred at room temperature for 4 h. Volatile material was removed *in vacuo*, and the dark brown residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:5) and chromatographed on a water-cooled Kieselgel column (3 × 40 cm). Elution with the same solvent mixture removed fractions containing traces of yellow $[Fe(CO)_5]$ and green $[Fe_3(CO)_{12}]$. A third dark brown eluate was removed with CH_2Cl_2–light petroleum (1:1). Evaporation of solvent *in vacuo* afforded an oily product which was recrystallised from light petroleum at −78 °C to give brown *microcrystals* of $[MoFe(\mu-CC_6H_4OMe-2)(CO)_6(\eta-C_5H_5)]$ (**5i**) (0.58 g). No other product was identified but some decomposition on the chromatography column was observed.

(*vi*) Similarly, compound (**1k**) (0.50 g, 1.43 mmol) and $[Fe_2(CO)_9]$ (0.55 g, 1.51 mmol) were stirred in Et_2O (50 cm^3) for 5 h. Solvent was removed *in vacuo*, and the black residue was dissolved in CH_2Cl_2 (10 cm^3). Light petroleum (20 cm^3) was added and the mixture was chromatographed on a water-cooled Kieselgel column (3 × 20 cm). Elution with the same solvent mixture removed initially a yellow fraction containing traces of $[Fe(CO)_5]$, identified by i.r. spectroscopy. A second eluate was dark violet which, after solvent was removed *in vacuo*, afforded black *microcrystals* of $[MoFe(\mu-CC_6H_4NMe_2-4)(CO)_6(\eta-C_5H_5)]$ (**5j**) (0.63 g). Further elution of the column with CH_2Cl_2–thf (1:1) gave a dark brown fraction which after removal of solvent *in vacuo* gave brown *microcrystals* of $[Mo_2Fe\{\mu-C_2(C_6H_4NMe_2-4)_2\}(CO)_6(\eta-C_5H_5)_2]$ (**8c**) (0.01 g).

Treatment of compound (**5j**) (0.15 g, 0.43 mmol) with $[Fe_2(CO)_9]$ (0.08 g, 0.22 mmol) in Et_2O (20 cm^3) for 5 h gave after chromatography, as described above, $[MoFe_2(\mu_3-CC_6H_4NMe_2-4)(\mu-CO)(CO)_8(\eta-C_5H_5)]$ (**7e**) (0.08 g) and unreacted (**5j**) (0.02 g). The compound (**7e**) may be obtained in *ca.* 65% yield from (**1k**) and two equivalents of $[Fe_2(CO)_9]$.

Compound (**8c**) can also be obtained (*ca.* 10% yield) by treating (**5j**) with an equivalent amount of (**1k**) in Et_2O. The desired product was isolated by chromatography on Kieselgel, as described above.

Reactions of $[WFe(\mu-CC_6H_3Me_2-2,6)(CO)_5(\eta-C_5H_5)]$ *with Tertiary Phosphines.*—(*i*) A CH_2Cl_2 (15 cm^3) solution of compound (**6g**) (0.50 g, 0.89 mmol) and PMe_3 (1.78 mmol) was stirred for 0.5 h. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2–light petroleum (2 cm^3, 1:1) and chromatographed on an alumina column (2 × 15 cm). Elution with the same solvent mixture gave a red-brown fraction followed by a green eluate. Solvent was removed from the former *in vacuo* and the residue was dissolved in CH_2Cl_2 (*ca.* 2 cm^3). Addition of light petroleum (*ca.* 5 cm^3) and cooling to −78 °C afforded brown-black *microcrystals* of $[WFe(\mu-CC_6H_3Me_2-2,6)(CO)_4(PMe_3)(\eta-C_5H_5)]$ (**9c**) (0.22 g).

Table 9. Atomic fractional co-ordinates (× 10^4) for compound (**6f**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo	2 140(1)	2 195(1)	4 278(1)
Fe	−42(1)	3 332(1)	3 525(1)
C(1)	2 124(3)	3 174(2)	3 398(1)
C(2)	−76(3)	1 756(2)	4 361(2)
O(2)	−1 246(2)	1 354(2)	4 483(1)
C(3)	1 868(4)	3 162(2)	5 154(2)
O(3)	1 760(4)	3 707(2)	5 660(2)
C(4)	−129(3)	4 494(2)	3 002(2)
O(4)	−188(3)	5 227(2)	2 657(2)
C(5)	−1 500(3)	3 605(2)	4 192(2)
O(5)	−2 374(3)	3 800(2)	4 636(2)
C(6)	−1 429(4)	2 696(3)	2 829(2)
O(6)	−2 280(4)	2 245(3)	2 387(2)
C(11)	3 233(3)	3 604(2)	2 887(1)
C(12)	4 195(3)	4 434(2)	3 156(2)
C(13)	5 258(3)	4 825(2)	2 673(2)
C(14)	5 386(4)	4 417(3)	1 933(2)
C(15)	4 459(4)	3 607(3)	1 666(2)
C(16)	3 355(3)	3 177(2)	2 133(2)
C(17)	4 072(4)	4 895(2)	3 955(2)
C(18)	2 356(5)	2 297(3)	1 832(2)
C(21)	4 557(3)	1 510(2)	3 981(2)
C(22)	3 438(3)	725(2)	3 951(2)
C(23)	3 053(4)	591(2)	4 728(2)
C(24)	3 872(4)	1 279(3)	5 232(2)
C(25)	4 830(3)	1 867(3)	4 765(2)

Solvent was removed *in vacuo* from the green eluate. The residue was crystallised from CH_2Cl_2–light petroleum (1:3) at −78 °C to give dark green *crystals* of $[WFe(\mu-CC_6H_3Me_2-2,6)(CO)_3(PMe_3)_2(\eta-C_5H_5)]$ (**11b**) (0.11 g).

(*ii*) The compounds (**6g**) (0.20 g, 0.36 mmol) and dppm (0.13 g, 0.36 mmol) were stirred together in Et_2O (10 cm^3) for 10 min. Solvent was removed *in vacuo* and the residue was dissolved Et_2O–thf (10 cm^3, 10:1) and cooled to −78 °C. This treatment afforded black *microcrystals* of $[WFe(\mu-CC_6H_3Me_2-2,6)(\mu-dppm)(\mu-CO)(CO)_2(\eta-C_5H_5)]$ (**12b**) (0.29 g).

Crystal Structure Determination.—Black prisms of compound (**6f**) were grown from CH_2Cl_2–light petroleum (1:5) at −10 °C. Diffracted intensities were collected at 293 K on a Nicolet $R3m/\mu$ diffractometer from a crystal of dimensions *ca.* 0.25 × 0.45 × 0.50 mm. Of the 5 463 unique data collected (ω—2θ scans, $2\theta \leqslant 60°$), 4 198 had $I \geqslant 2.0\sigma(I)$, and only these were used for structure solution and refinement. The data were corrected empirically for *X*-ray absorption (using azimuthal scan data)[25] and extinction, and for Lorentz and polarisation effects. Preliminary structure solution and refinement were performed on a Digital μ-Vax computer using the SHELXPLUS package.[25]

Crystal data. $C_{19}H_{14}FeMoO_5$, $M = 474.1$, monoclinic, $a = 8.354(2)$, $b = 13.352(3)$, $c = 16.845(3)$ Å, $\beta = 97.44(2)°$, $U = 1\,863(1)$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 944$, 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) = 14.6 cm^{-1}.

The structure was solved, and all non-hydrogen atoms located, by conventional heavy-atom and difference Fourier methods. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included at calculated positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for those belonging to methyl groups, and fixed isotropic thermal parameters (*ca.* $1.2U_{equiv.}$ of the parent carbon atom) for the remainder. The reflections (−5,3,10) and (−6,6,1) were not included in the final stages of refinement, since they showed large values of $(F_c - F_o)/\sigma(F)$

(27.2 and 14.5, respectively) which could not be explained. Refinement by blocked-cascade least squares led to $R = 0.029$ ($R' = 0.027$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,1|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.30 or < -0.47 e Å^{-3}. Scattering factors with corrections for anomalous dispersion were taken from ref. 26. The later stages of refinements were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs. Atomic co-ordinates are given in Table 9.

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

Appendix

All molecular orbital calculations were of the extended-Hückel type,[27] with the weighted H_{ij} formalism.[28] They were performed on the I.C.L. 2980 and Series 39 Level 80 machines of the South Western Universities Regional Computer Centre, using the programs ICON8 and FMO.[29] The basis-set parameters given below were taken from ref. 30.

	Orbital	H_{ii}/eV	ζ_1	ζ_2	c_1*	c_2
H	1*s*	−13.60	1.300			
C	2*s*	−21.40	1.625			
	2*p*	−11.40	1.625			
O	2*s*	−32.30	2.275			
	2*p*	−14.80	2.275			
Fe	3*d*	−12.60	5.350	2.00	0.5505	0.6260
	4*s*	−9.10	1.900			
	4*p*	−5.32	1.900			
Mo	4*d*	−10.50	4.54	1.90	0.6097	0.6097
	5*s*	−8.34	1.960			
	5*p*	−5.24	1.900			

* Coefficients in the double-ζ expansion.

The model geometries (**I**) and (**II**) had dimensions Mo–Fe 2.61, Mo–μ-C 2.02, Fe–μ-C 1.85, Mo–C_{co} 1.98, Fe–C_{co} 1.78, C–O 1.15, C–C_{cp} 1.41, Mo–C_{cp} 2.35, μ-C–C_{Me} 1.46, and C–H 1.09 Å; Mo–μ-C–C_{Me} 139.4, C_{co}–Mo–C_{co} 83.7, C_{co}–Mo–μ-C 106.4, and cp(centroid)–Mo–μ-C 120.0°. The $Fe(CO)_3$ fragment, in (**I**), had C_{3v} symmetry with C–Fe–C 96.2°. The $Fe(CO)_4$ group in (**II**) had C_{2v} symmetry with C_{ax}–Fe–C_{ax} 180.0° and C_{eq}–Fe–C_{eq} 102.°. The iron carbonyl and C≡Mo fragments were oriented such that the principal rotation axis of the $Fe(CO)_{3,4}$ fragment intersected the Mo–μ-C vector at a distance of 0.813 Å from Mo.

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