Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 77.[1] Reactions of Iron–Molybdenum Compounds with Alkynes; Crystal Structures of $\mathrm{[MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CHMe)CH_2C(Me)C(Me)\}(CO)_4(\eta\text{-}C_5H_5)]}$, $\mathrm{[MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CHMe)CH_2\}(CO)_5(\eta\text{-}C_5H_5)]}$, and $\mathrm{[MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CH_2PMe_3)CHMe\}(CO)_5(\eta\text{-}C_5H_5)]}$ *

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The compounds $\mathrm{[MoFe(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]}$ (**1a**) and $\mathrm{[MoFe_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]}$ (**2a**) ($\mathrm{R = C_6H_4Me\text{-}4}$) react with PhC≡CPh to give the same molybdenum–iron complex $\mathrm{[MoFe\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_5(\eta\text{-}C_5H_5)]}$ (**3a**). In contrast, MeC≡CMe reacts with (**2a**) to yield $\mathrm{[MoFe\{\mu\text{-}C(R)C(CHMe)CH_2C(Me)C(Me)\}(CO)_4(\eta\text{-}C_5H_5)]}$ (**4**), and with (**1a**) to yield $\mathrm{[MoFe\{\mu\text{-}C(R)C(CHMe)CH_2\}(CO)_5(\eta\text{-}C_5H_5)]}$ [two isomers, (**5a**) and (**5b**)]. The molecular structures of (**4**) and (**5a**) have been established by *X*-ray diffraction. In (**4**) the Mo–Fe bond [2.784(1) Å] is bridged by the branched six-carbon atom chain of the *C*(R)*C*(*C*HMe)*C*H$_2$*C*(Me)*C*(Me) ligand, with the *C*(R)*C*(*C*HMe) fragment η^3 co-ordinated to the molybdenum atom. This metal centre is also σ bonded to the terminal CMe group, and co-ordinated by one carbonyl and an $\eta\text{-C}_5\text{H}_5$ ligand. Both CMe groups are bonded to the iron centre, as is also the CR fragment and three terminal carbonyls. In (**5a**) the Mo–Fe separation (4.027 Å) is non-bonding, the two metal atoms being linked *via* a $\mathrm{C(R)C(CHMe)CH_2}$ unit. The molybdenum atom is η^3 co-ordinated by the $\mathrm{CC_6H_4Me\text{-}4}$ group, while the $\mathrm{Fe(CO)_3}$ fragment is η^4 co-ordinated by four carbon atoms of the substituted trimethylenemethane moiety $(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{Mo}C(\text{R})C(C\text{HMe})C\text{H}_2$. In (**5a**) the $\mathrm{Mo(CO)_2(\eta\text{-}C_5H_5)}$ and CH$_2$ groups are cisoid, whereas in (**5b**) they are transoid. Treatment of the isomers (**5**) with PMe$_3$ yields two zwitterionic complexes $\mathrm{[MoFe\{\mu\text{-}C(R)C[C(H)Me(PMe_3)]CH_2\}(CO)_5(\eta\text{-}C_5H_5)]}$ (**6a**) and $\mathrm{[MoFe\{\mu\text{-}C(R)C(CH_2PMe_3)CHMe\}(CO)_5(\eta\text{-}C_5H_5)]}$ (**6b**), of which the latter isomer is the more stable, allowing an *X*-ray diffraction study to be made. In (**6b**) a long Mo–Fe [2.831(2) Å] single bond is spanned by the $\mathrm{C(R)C(CH_2PMe_3)CHMe}$ group, with the $\mathrm{Mo(CO)_2(\eta\text{-}C_5H_5)}$ fragment attached to *C*R [2.20(1) Å] and with the Fe(CO)$_3$ moiety η^3 co-ordinated by the three atoms *C*(R)*C*(CH$_2$PMe$_3$)*C*HMe. With CO, compound (**5**) yields $\mathrm{[MoFe\{\mu\text{-}C(O)C(R)C(CHMe)CH_2\}(CO)_6(\eta\text{-}C_5H_5)]}$ formed as a 1 : 1 mixture of two isomers, (**7a**) and (**7b**). In these isomers an Fe(CO)$_3$ group is ligated by a substituted trimethylenemethane, the central carbon of which carries CH$_2$, CHMe, and $\mathrm{C(R)C(O)Mo(CO)_3(\eta\text{-}C_5H_5)}$ groups as substituents; there being no molybdenum–iron bond. Isomers arise according to whether the CH$_2$ and CHMe groups are cisoid or transoid to those of R or $\mathrm{C(O)Mo(CO)_3(\eta\text{-}C_5H_5)}$. Treatment of the dimetal compound $\mathrm{[MoFe(\mu\text{-}CR)(CO)_5(PMe_3)(\eta\text{-}C_5H_5)]}$ with MeC≡CMe affords the complex $\mathrm{[MoFe\{\mu\text{-}C(R)C(CHMe)CH_2C(O)\}(\mu\text{-}CO)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]}$. The n.m.r. (^{1}H and ^{13}C-{^{1}H}) data for the new compounds are reported and discussed in terms of the structures.

We have previously reported the synthesis of the compounds $\mathrm{[MFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]}$ (**1**) and $\mathrm{[MFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]}$ (**2**) (M = Mo or W),[2,3] and have described a number of reactions of these species.[4–6] These studies fall within the ambit of a growing body of work, involving several groups,[7] concerned with the reactivity of C$_1$ fragments when bridging metal–metal bonds. Most of the research in this area, however, has been with homonuclear di- or tri-metal compounds. A distinctive feature of the complexes (**1**) and (**2**) is that the C$_1$ fragment, in this instance a *p*-tolylmethylidyne group, spans heteronuclear metal–metal bonds. This raises the possibility of observing unusual transformations of organic groups. The presence in close proximity of two or more metal centres possessing their own unique bonding properties should result in hitherto unobserved reactivity patterns towards substrate molecules. While our earlier results[4–6] indicated that this expectation was correct, the reactions of (**1a**) and (**2a**) with alkynes, described in this and the following paper,[8] amply confirm the possibility of observing novel reactions when compounds having bonds between different transition elements are employed. A preliminary account of some of the work described herein has been given.[9]

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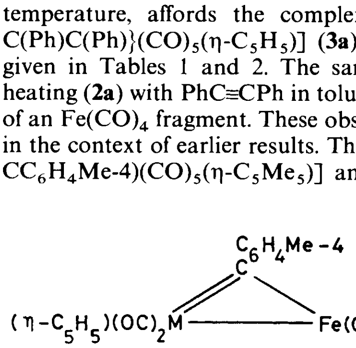
* 1,1,2,2-Tetracarbonyl-2-(η-cyclopentadienyl)-μ-[4-ethylidene-1,2-dimethyl-5-*p*-tolylpentan-2-yl-1,5-diylidene-C^1(Mo,Fe)C^2(Fe)$C^{4,4\alpha}$-(Mo)C^5(Mo,Fe)]-ironmolybdenum(*Fe–Mo*), 1,1,1,2,2-pentacarbonyl-2-(η-cyclopentadienyl)-μ-[2-ethylidene-3-tolylpropan-1-yl-3-ylidene-C^1(Fe)$C^{2,2\alpha}$(Fe)C^3(Mo,Fe)-$C^{1',2'}$(Mo)]-ironmolybdenum(*Fe–Mo*), and 1,1,1,2,2-pentacarbonyl-2-(η-cyclopentadienyl)-μ-[3-methyl-1-*p*-tolyl-2-(trimethylphosphoniomethyl)prop-1-ene-1,3-diyl-C^1(Mo)-C^{1-3}(Fe)]-ironmolybdate(*Fe–Mo*) respectively.

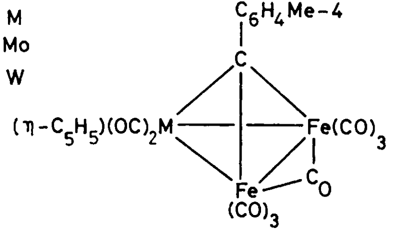
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Results and Discussion

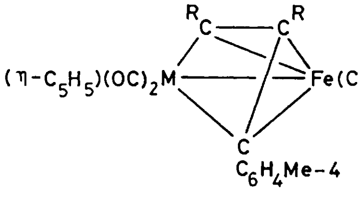
Treatment of (**1a**) with PhC≡CPh, in light petroleum at room temperature, affords the complex [MoFe{μ-C(C_6H_4Me-4)C(Ph)C(Ph)}$(CO)_5$(η-C_5H_5)] (**3a**), characterised by the data given in Tables 1 and 2. The same product is obtained by heating (**2a**) with PhC≡CPh in toluene; a process involving loss of an $Fe(CO)_4$ fragment. These observations are not surprising in the context of earlier results. Thus the compounds [WFe(μ-CC_6H_4Me-4)$(CO)_5$(η-C_5Me_5)] and [WFe_2($μ_3$-CC_6H_4Me-4)(μ-CO)$(CO)_8$(η-C_5Me_5)] react with PhC≡CPh to yield the complex [WFe{μ-C(C_6H_4Me-4)C(Ph)C(Ph)}$(CO)_5$(η-C_5Me_5)], structurally similar to (**3a**).[10] Moreover, (**2b**) and PhC≡CPh afford (**3b**), together with its isomer [WFe{μ-C(Ph)C(C_6H_4Me-4)C(Ph)}$(CO)_5$(η-C_5H_5)]. We obtained no evidence for formation of a similar isomer of (**3a**) in reactions of (**1a**) or (**2a**) with PhC≡CPh. Moreover, compound (**3a**) does not react with CO (3×10^5 Pa) to give an acyl complex [MoFe{μ-C(C_6H_4Me-4)C(Ph)C(Ph)C(O)}$(CO)_5$(η-C_5H_5)], a not unexpected result in the light of previous work.[1] It should be noted that because (**1b**) readily disproportionates into the trimetal compounds (**2b**) and [W_2Fe{$μ_3$-C_2(C_6H_4Me-4$)_2$}-$(CO)_6$(η-$C_5H_5$$)_2$],[3] reactions of (**1b**) with alkynes cannot be studied. For this reason the existence of the much more stable molybdenum analogue (**1a**) is fortunate.



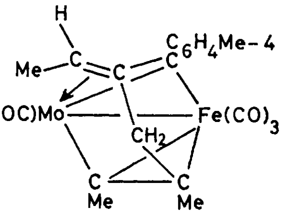
M
(**1a**) Mo
(**1b**) W



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



M R
(**3a**) Mo Ph
(**3b**) W Ph
(**3c**) W Me



(**4**)

Reactions of the alkyne MeC≡CMe with (**1a**) or (**2a**) proved to be much more interesting. Previously we had observed[4] that (**2b**) with MeC≡CMe gives the dimetal compound [WFe{μ-C(C_6H_4Me-4)C(Me)C(Me)}$(CO)_5$(η-C_5H_5)] (**3c**). In contrast, the reaction between (**2a**) and MeC≡CMe in light petroleum at room temperature affords the novel dimetal complex [MoFe{μ-C(C_6H_4Me-4)C(CHMe)-CH_2C(Me)C(Me)}$(CO)_4$(η-C_5H_5)] (**4**).

Analytical and spectroscopic data for (**4**) are listed in Tables 1 and 2. The peaks observed in the ^1H and ^{13}C-{^1H} n.m.r. spectra are in agreement with the structure established by an *X*-ray diffraction study. Results for the latter are listed in Table 3, and the structure is shown in Figure 1.

The Mo–Fe bond [2.784(1) Å] is bridged by a branched six-carbon chain [C(1), C(4), C(3), C(5), C(7), and C(8)] of a ligand *C*(C_6H_4Me-4)*C*(*C*HMe)*C*H_2*C*(Me)*C*(Me). The latter is attached to the iron at C(1), C(7), and C(8), and to the molybdenum at C(1), C(3), C(4), and C(8). This unusual organic moiety has evidently formed *via* a coupling of the *p*-tolylmethylidyne group in (**2a**) with two molecules of MeC≡CMe, in an overall process which also results in migration of a hydrogen atom between the carbon centres. The bonding of the organic ligand to the dimetal fragment may be viewed in the following way. The C(1)C(4)C(3) atoms η^3 ligate the molybdenum as part of a *trans*-type σ,η^3-allylidene group, since the substituents C_6H_4Me-4 on C(1) and CH_2 on C(4) are transoid to one another. However, this ligand arrangement may also be considered as a vinylcarbene. This formulation is supported by a considerable twist about the C(1)–C(4) bond as reflected by a

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

	Compound[b]	Colour	Yield (%)	$\nu_{max.}$(CO)[c]/cm^{-1}	Analysis (%) C	H
(**3a**)	[MoFe{μ-C(R)C(Ph)C(Ph)}$(CO)_5$(η-C_5H_5)]	Red	95	2 051vs, 1 992s, 1 966w, 1 940w	60.4 (60.0)	3.6 (3.8)
(**4**)	[MoFe{μ-C(R)C(CHMe)CH_2C(Me)C(Me)}$(CO)_4$-(η-C_5H_5)]	Green	20	2 031vs, 1 979s, 1 955m, 1 924s	55.1 (55.6)	4.6 (4.5)
(**5a**), (**5b**)[d]	[MoFe{μ-C(R)C(CHMe)CH_2}$(CO)_5$(η-C_5H_5)]	Red	95	2 041s, 1 979s, 1 968s, 1 958vs, 1 892s	51.3 (51.4)	3.7 (3.5)
(**6a**)[d] (**6b**)	[MoFe{μ-C(R)C[C(H)Me(PMe_3)]CH_2}$(CO)_5$(η-C_5H_5)] [MoFe{μ-C(R)C(CH_2PMe_3)CHMe}$(CO)_5$(η-C_5H_5)]	Orange-red	96	[e]1 977s, 1 900vs, 1 863s, 1 772m	50.1 (50.9)	4.8 (4.6)
(**7a**), (**7b**)[d]	[MoFe{μ-C(O)C(R)C(CHMe)CH_2}$(CO)_6$(η-C_5H_5)]	Yellow	72	2 058vs, 2 022s, 2 000s, 1 987vs, 1 953s, 1 936vs, 1 643w	49.2 (50.6)	3.4 (3.2)
(**8**)	[MoFe{μ-C(R)C(CHMe)CH_2C(O)}(μ-CO)$(CO)_3$-(PMe_3)(η-C_5H_5)]	Orange	40	[e]2 000s, 1 933s, 1 783w br, 1 606w br	50.9 (50.9)	4.6 (4.6)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] Measured in light petroleum, unless otherwise stated. [d] Mixture of isomers, see text. [e] In CH_2Cl_2.

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

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]
(3a)	2.26 (s, 3 H, Me-4), 5.08 (s, 5 H, C_5H_5), 6.88—7.25 (br, 14 H, C_6H_4 and 2Ph)	231.6, 231.5 (MoCO), 212.7 (FeCO), 146.5—125.4 [C_6H_4, Ph, and C(R)*C*(Ph)C(Ph)], 115.7, 115.1 [*C*(R)C(Ph)*C*(Ph)], 91.0 (C_5H_5), 21.0 (Me-4)
(4)	1.57 [d, 3 H, CH*Me*, *J*(HH) 6], 1.74 (s, 3 H, CMe), 2.29 (s, 3 H, Me-4), 2.40 [q, 1 H, C*H*Me, *J*(HH) 6], 2.47 [d, 1 H, CH_2, *J*(HH) 15], 2.95 [d, 1 H, CH_2, *J*(HH) 15], 3.00 (s, 3 H, CMe), 5.45 (s, 5 H, C_5H_5), 6.99, 7.13 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	234.4 (MoCO), 213.5 (FeCO), 212.0 (μ-*C*Me), 185.7 (*C*C_6H_4-Me-4), 149.5 [C^{1}(C_6H_4)], 136.3, 130.8, 128.3 (C_6H_4), 102.8 (C), 98.1 (*C*Me), 95.5 (C_5H_5), 48.9 (*C*HMe), 45.8 (CH_2), 33.8 (C*Me*), 23.5 (C*Me*), 21.1 (Me-4), 18.5 (CH*Me*)
(5a)[d]	1.57 [d, 3 H, CH*Me*, *J*(H^{a}H) 7], 2.29 (s, 3 H, Me-4), 2.73 [d, 1 H^{b}, CH_2, *J*(H^{a}H^{b}) 1], 2.82 (s, 1 H^{c}, CH_2), 3.90 [d of q, 1 H^{a}, C*H*Me, *J*(HH^{a}) 7, *J*(H^{b}H^{a}) 1], 5.48 (s, 5 H, C_5H_5), 5.70 (m, 1 H, C_6H_4), 6.98 (m, 3 H, C_6H_4)	[e] 245.1, 243.4 (MoCO), 213.0 (FeCO), 139.4, 137.8 (C_6H_4), 131.2 (2 C, C_6H_4), 116.3 [C^{1}(C_6H_4)], 99.8 (*C*C_6H_4Me-4), 95.4 (C_5H_5), 93.5 (C), 89.3 [C^{2}(C_6H_4)], 77.8 (*C*HMe), 55.1 (CH_2), 21.6 (Me-4), 15.7 (CH*Me*)
(5b)[d]	1.44 [d, 3 H, CH*Me*, *J*(H^{a}H) 7], 2.29 (s, 3 H, Me-4), 2.88 [d, 1 H^{b}, CH_2, *J*(H^{a}H^{b}) 1], 2.96 (s, 1 H^{c}, CH_2), 3.61 [d of q, 1 H^{a}, C*H*Me, *J*(HH^{a}) 7, *J*(H^{b}H^{a}) 1], 5.48 (s, 5 H, C_5H_5), 5.70 (m, 1 H, C_6H_4), 6.98 (m, 3 H, C_6H_4)	[e] 245.1, 243.4 (MoCO), 213.0 (FeCO), 139.4, 137.8 (C_6H_4), 131.8 (2 C, C_6H_4), 115.0 [C^{1}(C_6H_4)], 100.3 (*C*C_6H_4Me-4), 95.4 (C_5H_5), 93.2 (C), 89.9 [C^{2}(C_6H_4)], 75.9 (*C*HMe), 55.6 (CH_2), 21.6 (Me-4), 16.1 (CH*Me*)
(6a)[f,g]	1.56 [d, 9 H, PMe_3, *J*(PH) 14], 2.37 (s, 3 H, Me-4), 4.88 (s, 5 H, C_5H_5)	250.4, 249.8 (MoCO), 225.6 (FeCO), 185.9 (*C*C_6H_4Me-4), 152.5 [C^{1}(C_6H_4)], 134.8 [C^{4}(C_6H_4)], 133.6, 128.5 (C_6H_4), 104.9 [d, C, *J*(PC) 4], 95.3 (C_5H_5), 37.8 (CH_2), 32.4 [d, *C*HMePMe_3, *J*(PC) 46], 21.0 (Me-4), 15.3 (CH*Me*), 7.9 [d, PMe_3, *J*(PC) 53]
(6b)[f,g]	0.95 [d of q, 1 H, C*H*Me, *J*(PH) 3, *J*(HH) 7], 1.44 [d, 3 H, CH*Me*, *J*(HH) 7], 1.76 [d, 9 H, PMe_3, *J*(PH) 14], 2.36 (s, 3 H, Me-4), 2.86 [d of d, 1 H, C$H_2$$PMe_3$, *J*(HH) 15, *J*(PH) 15], 3.68 [d of d, 1 H, C$H_2$$PMe_3$, *J*(HH) 15, *J*(PH) 13], 4.80 (s, 5 H, C_5H_5), 7.12 [d, 1 H, C_6H_4, *J*(HH) 8], 7.25 [d, 1 H, C_6H_4, *J*(HH) 8], 7.39 [d of d, 1 H, C_6H_4, *J*(HH) 8, *J*(HH) 2], 7.86 [d of d, 1 H, C_6H_4, *J*(HH) 8, *J*(HH) 2]	252.0, 250.0 (MoCO), 221.4 (FeCO), 182.6 (*C*C_6H_4Me-4), 152.9 [C^{1}(C_6H_4)], 134.8 [C^{4}(C_6H_4)], 134.1, 128.9, 128.4, 128.3 (C_6H_4), 96.6 (C), 94.8 (C_5H_5), 57.6 (*C*HMe), 27.1 [*C*H_2P-Me_3, *J*(PC) 45], 21.0 (Me-4), 19.3 (CH*Me*), 9.8 [PMe_3, *J*(PC) 53]
(7a),[h] **(7b)**	1.42 [d, 3 H, CH*Me*, *J*(H^{a}H) 7], 1.43 [d, 3 H, CH*Me*, *J*(H^{a}H) 7], 2.30 (s, 6 H, Me-4), 2.33 [d of d, 1 H^{b}, CH_2, *J*(H^{a}H^{b}) 3, *J*(H^{c}H^{b}) 2], 2.46 [d of d, 1 H^{b}, CH_2, *J*(H^{a}H^{b}) 3, *J*(H^{c}H^{b}) 1], 2.56 [d, 1 H^{c}, CH_2, *J*(H^{b}H^{c}) 2], 3.26 [d of q, 1 H^{a}, C*H*Me, *J*(HH^{a}) 7, *J*(H^{b}H^{a}) 3], 3.42 [d of q, 1 H^{a}, C*H*Me, *J*(HH^{a}) 7, *J*(H^{b}H^{a}) 3], 5.12 (s, 5 H, C_5H_5), 5.13 (s, 5 H, C_5H_5), 7.05, 7.19 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 8]	[i] 248.8, 248.1 (C=O), 238.6, 229.8, 229.3, 229.2, 229.1 (MoCO), 213.2, 212.7, 211.5, 210.9 (FeCO), 137.7 [C^{1}(C_6H_4)], 134.3, 131.0, 130.9, 130.8, 130.5, 129.5, 129.4, 128.4, 128.3 (C_6H_4), 117.5, 117.3 (*C*C_6H_4Me-4), 98.2, 97.8 (C), 94.1 (C_5H_5), 67.3, 66.0 (*C*HMe), 47.9, 46.3 (CH_2), 21.3 (Me-4), 15.1, 14.3 (CH*Me*)
(8)	[j] 1.21 [d, 9 H, PMe_3, *J*(PH) 10], 1.93 [d, 3 H, CH*Me*, *J*(HH) 6], 2.27 [d, 1 H, CH_2, *J*(HH) 19], 2.32 (s, 3 H, Me-4), 3.14 [d, 1 H, CH_2, *J*(HH) 19], 3.86 [q, 1 H, C*H*Me, *J*(HH) 6], 5.24 (s, 5 H, C_5H_5), 6.98, 7.03 [AB, 2 H, C_6H_4, *J*(AB) 8], 7.19 [d, 1 H, C_6H_4, *J*(HH) 8], 7.69 [d, 1 H, C_6H_4, *J*(HH) 8]	[j] 279.1 [d, C=O, *J*(PC) 29], 254.2 [d, μ-CO, *J*(PC) 6], 234.2 (MoCO), 214.6 [d, FeCO, *J*(PC) 15], 208.1 [d, FeCO, *J*(PC) 13], 177.2 [d, *C*C_6H_4Me-4, *J*(PC) 20], 152.6 [C^{1}(C_6H_4)], 135.8, 133.1, 129.7, 128.5, 126.2 (C_6H_4), 110.0 (C), 97.8 (C_5H_5), 66.3 (*C*HMe), 57.3 (CH_2), 21.3 (Me-4), 17.6 [d, MeP, *J*(PC) 32], 17.2 (CH*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 $SiMe_4$. Measured in CD_2Cl_2–CH_2Cl_2 unless otherwise stated. [d] Data obtained from measurements on the isomeric mixture. [e] In $(CD_3)_2CO$–Me_2CO. [f] Data for (**6b**) obtained from a pure sample, that for (**6a**) from a mixture. Some resonances for (**6a**) were obscured by those of (**6b**). [g] Measured in $(CD_3)_2CO$. [h] Data taken from spectra of isomeric mixture (see text). Many signals overlap. [i] Measured at −40 °C. [j] Measured at −60 °C.

Table 3. Selected internuclear distances (Å) and angles (°) for [MoFe{μ-C(C_6H_4Me-4)C(CHMe)CH_2C(Me)C(Me)}$(CO)_4$(η-C_5H_5)] (**4**) with estimated standard deviations in parentheses

Mo–Fe	2.784(1)	Mo–C(1)	2.172(3)	Mo–C(3)	2.337(4)	Mo–C(4)	2.204(3)
Mo–C(8)	2.176(3)	Mo–C(10)	1.961(3)	Fe–C(1)	1.999(3)	Fe–C(7)	2.172(3)
Fe–C(8)	2.056(3)	Fe–C(11)	1.774(3)	Fe–C(12)	1.778(3)	Fe–C(13)	1.791(4)
C(1)–C(4)	1.435(4)	C(1)–C(21)	1.490(4)	C(2)–C(3)	1.511(5)	C(3)–C(4)	1.429(4)
C(4)–C(5)	1.497(4)	C(5)–C(7)	1.524(5)	C(6)–C(7)	1.523(4)	C(7)–C(8)	1.415(4)
C(8)–C(9)	1.525(6)	C(10)–O(10)	1.149(4)	C(11)–O(11)	1.152(4)	C(12)–O(12)	1.144(4)
C(13)–O(13)	1.144(6)						
Fe–Mo–C(1)	45.5(1)	C(1)–Mo–C(3)	63.4(1)	C(1)–Mo–C(4)	38.3(1)	C(3)–Mo–C(4)	36.5(1)
Fe–Mo–C(8)	47.0(1)	C(1)–Mo–C(8)	82.5(1)	C(3)–Mo–C(8)	109.1(1)	C(4)–Mo–C(8)	78.2(1)
Fe–Mo–C(10)	109.1(1)	Mo–Fe–C(1)	50.8(1)	Mo–Fe–C(7)	74.3(1)	C(1)–Fe–C(7)	84.7(1)
Mo–Fe–C(8)	50.7(1)	C(1)–Fe–C(8)	90.0(1)	C(7)–Fe–C(8)	39.0(1)	Mo–Fe–C(11)	96.8(1)
Mo–Fe–C(12)	130.0(1)	C(11)–Fe–C(12)	103.7(2)	Mo–Fe–C(13)	128.7(1)	C(1)–Fe–C(13)	179.0(1)
C(11)–Fe–C(13)	85.4(2)	C(12)–Fe–C(13)	98.3(2)	Mo–C(1)–Fe	83.7(1)	Mo–C(1)–C(21)	127.6(2)
Fe–C(1)–C(21)	125.3(2)	C(4)–C(1)–C(21)	121.0(3)	Mo–C(3)–H(3)	105(2)	C(2)–C(3)–H(3)	111(2)
C(2)–C(3)–C(4)	124.3(3)	C(4)–C(3)–H(3)	118(2)	Mo–C(4)–C(1)	69.6(2)	Mo–C(4)–C(3)	76.8(2)
C(1)–C(4)–C(3)	111.8(2)	Mo–C(4)–C(5)	111.7(2)	C(1)–C(4)–C(5)	117.2(3)	C(3)–C(4)–C(5)	130.1(3)
C(4)–C(5)–C(7)	108.2(2)	H(5a)–C(5)–H(5b)	101(2)	Fe–C(7)–C(5)	105.8(2)	Fe–C(7)–C(6)	119.7(2)
C(5)–C(7)–C(6)	114.1(3)	Fe–C(7)–C(8)	66.1(2)	C(5)–C(7)–C(8)	116.3(3)	C(6)–C(7)–C(8)	124.3(3)
Mo–C(8)–Fe	82.2(1)	Mo–C(8)–C(9)	124.0(2)	Fe–C(8)–C(9)	121.8(2)	C(7)–C(8)–C(9)	121.2(3)
Mo–C(10)–O(10)	174.2(3)	Fe–C(11)–O(11)	175.3(4)	Fe–C(12)–O(12)	176.1(3)	Fe–C(13)–O(13)	175.9(4)

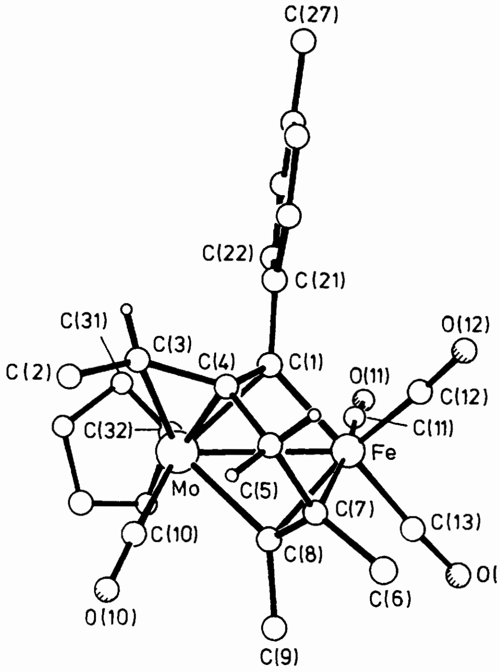
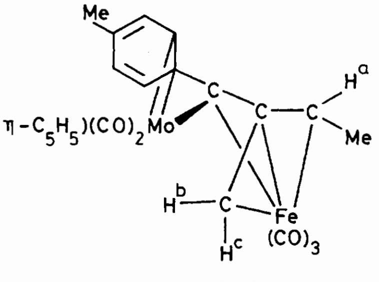
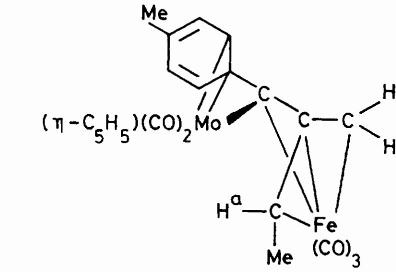


Figure 1. The molecular structure of [$MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CHMe)CH_2C(Me)C(Me)\}(CO)_4(\eta\text{-}C_5H_5)$] (**4**)



(5a)



(5b)

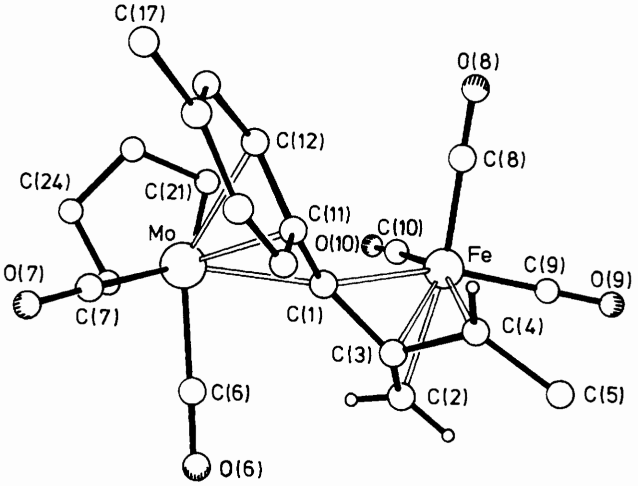


Figure 2. The molecular structure of [$MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CHMe)CH_2\}(CO)_5(\eta\text{-}C_5H_5)$] (**5a**)

C(21)–C(1)–C(4)–C(3) torsion angle of 58°. The C(7) and C(8) atoms may be regarded as being part of a vinyl group σ bonded to the molybdenum at C(8) and η^2 co-ordinated to the iron at C(7)C(8), with C(5), C(6), and C(9) as substituents.

The Mo–Fe separation in (**4**) lies between those found in the complexes (**1a**) [2.823(1) Å][2] and [$MoFe(\mu\text{-}\eta^2\text{-}SCC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)$] [2.765(1) Å].[6] These distances may be assumed to correspond to single bonds since each metal centre has a closed 18 electron shell, based on the electron contributions from the ligating groups.

In contrast with the reaction of (**2a**) with MeC≡CMe, compound (**1a**) affords the complex [$MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CHMe)CH_2\}(CO)_5(\eta\text{-}C_5H_5)$] (**5**) in essentially quantitative yield. In solution (**5**) exists as a *ca.* 3:2 mixture of two isomers (**5a**) and (**5b**), a property revealed by the relative intensities of peaks in the n.m.r. spectra. Fortunately it was possible to obtain suitable crystals for an *X*-ray diffraction study. The results (Table 4) established that isomer (**5a**) is present in the crystal studied, and the structure is shown in Figure 2.

The Mo–Fe separation (4.027 Å) is non-bonding, and the $Mo(CO)_2(\eta\text{-}C_5H_5)$ and $Fe(CO)_3$ fragments are linked by a $C(C_6H_4Me\text{-}4)C(CHMe)CH_2$ group. The latter has arisen from a coupling of the $\mu\text{-}C(C_6H_4Me\text{-}4)$ ligand in (**1a**) with one molecule of but-2-yne, but the alkyne has rearranged to produce the $C(CHMe)CH_2$ moiety.[11] The structure is best discussed in terms of bonding of the bridging organic group to each metal centre in turn.

The molybdenum atom is η^3 ligated by C(1), C(11), and C(12), but the bonding becomes progressively weaker, *viz.* Mo–C(1) 2.188(4), Mo–C(11) 2.393(4), and Mo–C(12) 2.520(5) Å. There are several new complexes now known in which an arene ring forms part of an 'allylic' group attached to a Mo or W atom. These include the mononuclear metal compounds [$Mo(CO)_2(\eta^3\text{-}CH_2C_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)$][12] and [$W(CO)_2\{\eta^3\text{-}CH(C_6H_4Me\text{-}4)Ph\}(\eta\text{-}C_5H_5)$],[13] and the binuclear complexes [$PtW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)$][$BF_4$],[14] [$Mo_2\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2$],[15] [$RhW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$][$BF_4$] ($\eta^5\text{-}C_9H_7$ = indenyl),[16] and [$Ru_2(\mu\text{-}CPh_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2$].[17]

The $Fe(CO)_3$ group is co-ordinated by the atoms C(1), C(2), C(3), and C(4) which form the core of a trimethylenemethane ligand[18] with a Me substituent at C(4), and C_6H_4Me-4 and $Mo(CO)_2(\eta\text{-}C_5H_5)$ substituents at C(1). The bonding at the iron centre [Fe–C(3) 1.945(5), mean Fe–C(1,2,4) 2.15 Å; mean Fe–C(3)–C(1,2,4) 77.7°, mean OC–Fe–CO 98.8°] is very similar to that found in the trimethylenemethane–iron complex [$Fe\{\eta^4\text{-}C(CH_2)_2CHPh\}(CO)_3$].[19] For the latter the comparable parameters are 1.93(1) and 2.13 Å, and 77.1 and 99.1°. The iron–carbonyl groups in (**5a**) are staggered with respect to the C–C bonds of the trimethylenemethane moiety, as expected from theory.[20]

The existence of two isomers of (**5**) is a consequence of the fact that the $C(2)H_2$ group can be either cisoid (**5a**) or transoid (**5b**) to the molybdenum atom. It is possible that (**5**) exists exclusively as isomer (**5a**) in the solid state, subsequently equilibrating in solution to give some (**5b**). Alternatively it may be purely

Table 4. Selected internuclear distances (Å) and angles (°) for $[MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CHMe)CH_2\}(CO)_5(\eta\text{-}C_5H_5)]$ (**5a**) with estimated standard deviations in parentheses

Mo···Fe	4.027	Mo–C(1)	2.188(4)	Mo–C(6)	1.943(5)	Mo–C(7)	1.949(5)
Mo–C(11)	2.393(4)	Mo–C(12)	2.520(5)	Fe–C(1)	2.188(4)	Fe–C(2)	2.122(5)
Fe–C(3)	1.945(5)	Fe–C(4)	2.142(5)	Fe–C(8)	1.790(5)	Fe–C(9)	1.799(5)
Fe–C(10)	1.791(5)	C(1)–C(3)	1.441(6)	C(1)–C(11)	1.449(5)	C(2)–C(3)	1.407(6)
C(3)–C(4)	1.418(7)	C(4)–C(5)	1.518(8)	C(6)–O(6)	1.152(6)	C(7)–O(7)	1.151(6)
C(8)–O(8)	1.132(6)	C(9)–O(9)	1.136(6)	C(10)–O(10)	1.139(6)		
C(6)–Mo–C(7)	75.8(2)	C(1)–Mo–C(11)	36.5(1)	C(11)–Mo–C(12)	33.2(2)	C(1)–Fe–C(3)	40.3(2)
C(2)–Fe–C(3)	40.2(2)	C(3)–Fe–C(4)	40.2(2)	C(3)–Fe–C(8)	118.6(2)	C(3)–Fe–C(9)	117.7(2)
C(8)–Fe–C(9)	98.8(2)	C(3)–Fe–C(10)	119.9(2)	C(8)–Fe–C(10)	102.0(2)	C(9)–Fe–C(10)	95.5(2)
Mo–C(1)–Fe	133.9(2)	Mo–C(1)–C(3)	140.8(3)	Fe–C(1)–C(3)	60.8(2)	Mo–C(1)–C(11)	79.5(3)
Fe–C(1)–C(11)	126.6(3)	C(3)–C(1)–C(11)	124.1(4)	Fe–C(2)–C(3)	63.1(3)	Fe–C(3)–C(1)	78.9(3)
Fe–C(3)–C(2)	76.7(3)	C(1)–C(3)–C(2)	115.3(4)	Fe–C(3)–C(4)	77.4(3)	C(1)–C(3)–C(4)	114.9(4)
C(2)–C(3)–C(4)	116.5(4)	Fe–C(4)–C(3)	62.4(3)	Fe–C(4)–C(5)	120.1(4)	C(3)–C(4)–C(5)	124.6(4)
Mo–C(6)–O(6)	177.8(4)	Mo–C(7)–O(7)	176.1(4)	Fe–C(8)–O(8)	179.1(4)	Fe–C(9)–O(9)	179.6(5)
Fe–C(10)–O(10)	174.9(4)	Mo–C(11)–C(1)	64.0(2)	Mo–C(11)–C(12)	78.3(3)	C(1)–C(11)–C(12)	118.2(4)
Mo–C(11)–C(16)	119.9(3)	C(1)–C(11)–C(16)	124.7(4)	C(12)–C(11)–C(16)	116.1(4)	Mo–C(12)–C(11)	68.5(2)

fortuitous that the crystal of (**5a**) chosen for the *X*-ray study came from a mixture of crystalline (**5a**) and (**5b**). The available data do not allow a clear distinction to be made between these possibilities. The various n.m.r. resonances and their assignments (Table 2) are in accord with the structures. Moreover, the assignments for the peaks due to the CH_2 and *C*HMe groups in the $^{13}C\text{-}\{^1H\}$ spectra were confirmed by measurement of proton-coupled ^{13}C spectra. Thus the signals for the CH_2 [(**5a**), 55.1; (**5b**), 55.6 p.p.m.] and *C*HMe [(**5a**), 77.8; (**5b**), 75.9 p.p.m.] groups became triplets [(**5a**), *J*(HC) 158; (**5b**), *J*(HC) 158 Hz] and doublets [(**5a**), *J*(HC) 166; (**5b**), *J*(HC) 164 Hz], respectively, in the fully coupled spectra.

A possible pathway by which the compounds (**5**) may be formed is shown in the Scheme. Loss of two molecules of carbon monoxide from (**1a**) and co-ordination of one molecule of but-2-yne could give rise to intermediate (**A**), in which the $Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$ and alkyne groups together formally donate six electrons to the $Fe(CO)_2$ fragment. Addition of CO to (**B**) would provide a route to compounds of type (**3**), several other examples of which are reported in the following paper.[8] However, with the molybdenum–but-2-yne system, the intermediate (**B**) may undergo a metal-assisted hydrogen shift reaction leading *via* (**C**) to (**D**), similar in some respects to that invoked[11] earlier to account for the synthesis of $[MoW\{\mu\text{-}C\text{-}(C_6H_4Me\text{-}4)C(CH_2)CH(Me)C(O)\}(CO)_6(\eta\text{-}C_5H_5)]$ from $[MoW(\equiv CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)]$ and but-2-yne. The allylcarbene fragment in (**D**) is very similar to that found and structurally characterised in $[W_2\{\mu\text{-}C(SiMe_3)C(CH_2)CHMe\}\text{-}(\mu\text{-}CSiMe_3)(CH_2SiMe_3)_4]$.[21] Collapse of (**D**) *via* the two intermediates shown, with cleavage of the metal–metal bond, could lead to the isomeric mixture of products (**5a**) and (**5b**).

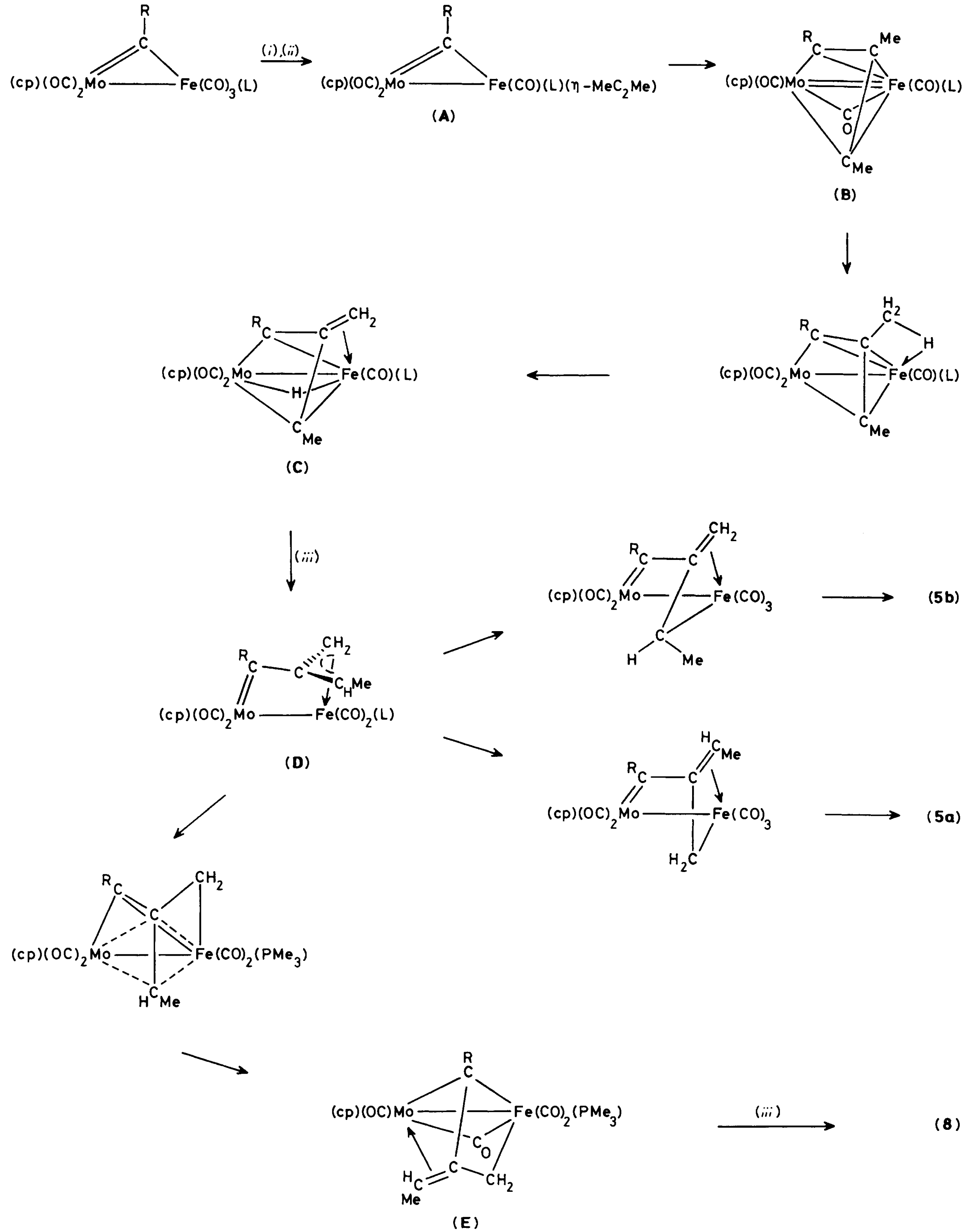
The presence of a $C_6H_4Me\text{-}4$ group η^2 co-ordinated to the molybdenum atom in (**5**) prompted us to study reactions with PMe_3 and with CO to see whether the attachment of the arene ring to the molybdenum would be displaced. We have previously shown that the similar interaction between the $C_6H_4Me\text{-}4$ group and the tungsten atom in $[PtW\{\mu\text{-}\sigma:\eta^3\text{-}CH\text{-}(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ is displaced in reactions of the latter with CO or tertiary phosphines.[22] In practice, compound (**5**) reacted with PMe_3 and with CO with displacement of the $\sigma:\eta^3$ bonding mode at the molybdenum centre, but the structures of the products obtained were unexpected.

Treatment of the isomeric mixture (**5**) in light petroleum with PMe_3 at room temperature afforded a *ca.* 1:1 mixture of two isomeric compounds $[MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C[C(H)Me\text{-}(PMe_3)]CH_2\}(CO)_5(\eta\text{-}C_5H_5)]$ (**6a**) and $[MoFe\{\mu\text{-}C(C_6H_4\text{-}Me\text{-}4)C(CH_2PMe_3)CHMe\}(CO)_5(\eta\text{-}C_5H_5)]$ (**6b**). Identification of these products as zwitterionic complexes was made possible by an *X*-ray diffraction study on (**6b**), and consideration of the n.m.r. data (Table 2) for both species. In practice, (**6a**) was unstable in acetone solution, thus allowing (**6b**) to be isolated, and crystals obtained. The results of the *X*-ray diffraction study are summarised in Table 5, and the structure is shown in Figure 3.

The Mo–Fe separation [2.831(2) Å] is appreciably longer than that found in (**4**) [2.784(1) Å], and in other molybdenum–iron complexes discussed earlier. Moreover, the Mo–C(1) distance [2.20(1) Å] is intermediate between that of the formal Mo=C double bond [1.921(5) Å] in (**1a**)[2] and that expected (2.29—2.40 Å) for a Mo–C single bond.[23] The data for (**6b**) are consistent with the negative charge in this zwitterionic compound residing largely on the molybdenum centre, with C(1), C(3), and C(4) adopting an η^3-bonding mode to the iron atom. The σ,η^3-linkage of the C(1)C(3)C(4) group to the Mo–Fe fragment is of the *cis* type. This conformation for an allylidene ligand bridging two metal centres is more commonly observed[24] than the *trans*, although examples of the latter configuration for a μ-allylidene ligand include $[W_2\{\mu\text{-}C(H)\text{-}C(H)CMe_2\}(CO)_9]$[25] and $[Re_2\{\mu\text{-}C(H)C(H)CMe_2\}(CO)_8]$.[26] Moreover, as mentioned earlier, the C(1), C(4), C(3) group in (**4**) while σ bonded to the iron at C(1), has a transoid η^3 attachment to the molybdenum.

Since a $[Mo(CO)_2(\eta\text{-}C_5H_5)]^-$ group is isolobal with CH_2, the structure of (**6b**) is analogous to that of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ in which the butadiene ligand has a *cis* configuration. For the latter the orientation of the three carbonyl groups with respect to the butadiene ligand is determined by electronic factors.[20] Interestingly, in (**6b**) the $Fe(CO)_3$ group adopts a similar configuration with respect to the MoC(1)C(3)C(4) fragment.

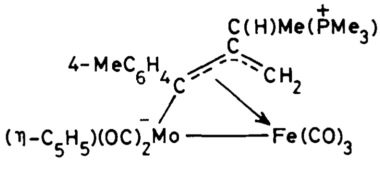
The n.m.r. data for (**6b**) (Table 2) were obtained from a pure sample, that for (**6a**) was taken from a mixture of the two isomers. The peaks observed are in accord with the structures depicted. It may be noted that for the unstable species (**6a**) two diastereoisomers are possible because of the asymmetry at the central carbon of the *C*(H)Me(PMe_3) group. However, only one diastereoisomer is formed. Examination of the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**6b**) reveals four and six signals, respectively, for the C_6H_4 group. This implies that there is restricted rotation at the C(1)–C(11) bond, a feature found in some other species containing a $CC_6H_4Me\text{-}4$ fragment. The origins of this property may be steric or electronic in nature.[24,27]



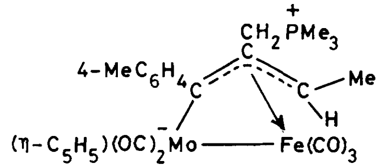
Scheme. R = C_6H_4Me-4, cp = η-C_5H_5, L = CO or PMe_3 (see text). (*i*) −2CO; (*ii*) +MeC≡CMe; (*iii*) +CO

Table 5. Selected internuclear distances (Å) and angles (°) for $[MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CH_2PMe_3)CHMe\}(CO)_5(\eta\text{-}C_5H_5)]$ (**6b**) with estimated standard deviations in parentheses

Mo–Fe	2.831(2)	Mo–C(1)	2.20(1)	Mo–C(6)	1.89(2)	Mo–C(7)	1.88(2)
Fe–C(1)	2.07(1)	Fe–C(3)	2.05(1)	Fe–C(4)	2.09(2)	Fe–C(8)	1.73(2)
Fe–C(9)	1.74(2)	Fe–C(10)	1.67(2)	P–C(2)	1.83(1)	P–C(31)	1.76(2)
P–C(32)	1.78(2)	P–C(33)	1.77(2)	C(1)–C(3)	1.43(2)	C(1)–C(11)	1.52(2)
C(2)–C(3)	1.51(2)	C(3)–C(4)	1.43(2)	C(4)–C(5)	1.54(2)	C(6)–O(6)	1.20(2)
C(7)–O(7)	1.20(2)	C(8)–O(8)	1.16(2)	C(9)–O(9)	1.17(2)	C(10)–O(10)	1.22(2)
Fe–Mo–C(1)	46.5(3)	Fe–Mo–C(6)	108.9(5)	Fe–Mo–C(7)	91.3(4)	C(6)–Mo–C(7)	74.4(7)
Mo–Fe–C(1)	50.4(4)	Mo–Fe–C(3)	81.8(4)	C(1)–Fe–C(3)	40.6(5)	Mo–Fe–C(4)	85.7(4)
C(1)–Fe–C(4)	71.1(5)	C(3)–Fe–C(4)	40.3(6)	Mo–Fe–C(8)	92.1(5)	Mo–Fe–C(9)	75.4(5)
C(8)–Fe–C(9)	100.1(8)	Mo–Fe–C(10)	175.2(6)	C(8)–Fe–C(10)	90.8(8)	C(9)–Fe–C(10)	100.3(8)
C(2)–P–C(31)	108.3(8)	C(2)–P–C(32)	110.6(7)	C(2)–P–C(33)	111.4(7)	C(31)–P–C(32)	109.4(8)
C(31)–P–C(33)	108.0(8)	C(32)–P–C(33)	108.9(8)	Mo–C(1)–Fe	83.2(5)	Mo–C(1)–C(3)	126(1)
Fe–C(1)–C(3)	69.0(7)	Mo–C(1)–C(11)	115.7(8)	Fe–C(1)–C(11)	131.7(8)	C(3)–C(1)–C(11)	117(1)
P–C(2)–C(3)	114.1(9)	Fe–C(3)–C(2)	124.1(9)	C(1)–C(3)–C(2)	122(1)	C(1)–C(3)–C(4)	116(1)
C(2)–C(3)–C(4)	122(1)	Fe–C(4)–C(5)	125(1)	C(3)–C(4)–C(5)	123(1)	Mo–C(6)–O(6)	179.3(8)
Mo–C(7)–O(7)	176(1)	Fe–C(8)–O(8)	180(2)	Fe–C(9)–O(9)	171(1)	Fe–C(10)–O(10)	178(2)



(**6a**)



(**6b**)

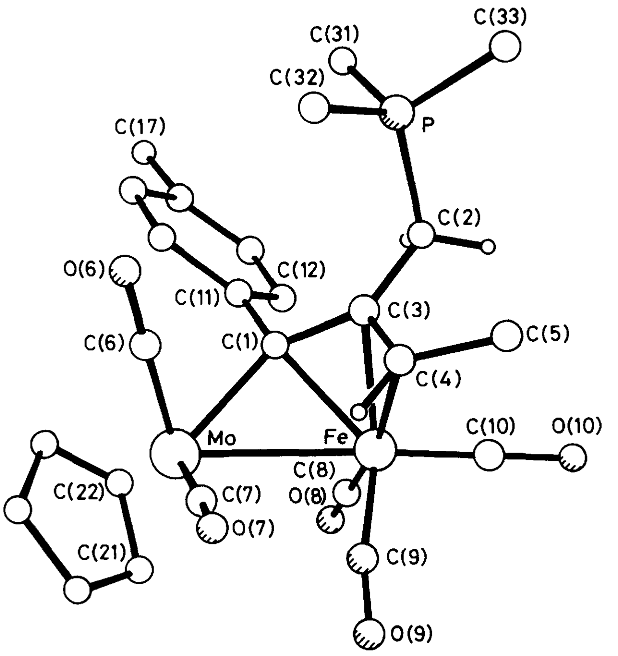


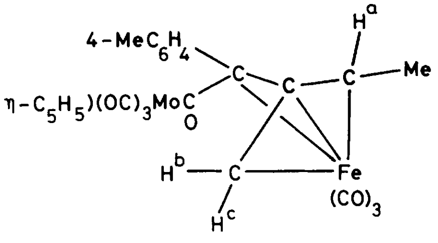
Figure 3. The molecular structure of $[MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CH_2PMe_3)CHMe\}(CO)_5(\eta\text{-}C_5H_5)]$ (**6b**). Hydrogen atoms attached to C(2) and C(4) are shown at calculated positions

Some of the $^{13}C\text{-}\{^1H\}$ resonance assignments for the isomers (**6**) were confirmed by recording proton-coupled ^{13}C spectra. For (**6b**) the following data establish the assignments for the *C*HMe, *C*H$_2$PMe$_3$, and PMe$_3$ groups: δ 57.6 [d, *C*HMe, *J*(HC) 165], 27.1 [d of t, *C*H$_2$PMe$_3$, *J*(PC) 45, *J*(HC) 132 Hz]. Similarly, for (**6a**): δ 37.8 [d of d, CH$_2$, *J*(HC) 167 and 163] and 7.9 p.p.m. [d of q, PMe$_3$, *J*(PC) 53, *J*(HC) 132 Hz]. In the ^{13}C spectrum of (**6a**), the signal for the *C*(H)Me nucleus is obscured by the $(CD_3)_2CO$ peaks. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the isomeric mixture shows one resonance at δ 30.4 p.p.m.

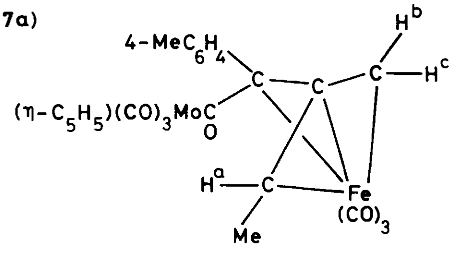
Compound (**5**) reacts with CO in light petroleum at room temperature to form the complex $[MoFe\{\mu\text{-}C(O)C(C_6H_4\text{-}Me\text{-}4)C(CHMe)CH_2\}(CO)_6(\eta\text{-}C_5H_5)]$ (**7**). The latter exists in solution as a 1 : 1 mixture of the two isomers (**7a**) and (**7b**), as inferred from the relative intensity of peaks in the n.m.r. spectra (Table 2). The isomerism, as with (**5a**) and (**5b**), arises because the CH$_2$ and CHMe groups can adopt transoid or cisoid orientations with respect to the C_6H_4Me-4 group.

The structures of (**7a**) and (**7b**) are assigned on the basis of the spectroscopic properties. The i.r. spectrum shows six bands in the terminal CO stretching region (Table 1), and a band at 1 643 cm^{-1} attributable to the acyl carbonyl group bonded to the molybdenum. The presence of the latter in the two isomers is further revealed by the observation of two resonances in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table 2) at δ 248.8 and 248.1 p.p.m. The terminal CO ligands give rise to nine peaks. Those at δ 238.6 and 211.5 p.p.m., however, correspond to two and three groups, respectively, based on their relative intensities. Thus the overall pattern of bands is indicative of the presence of twelve CO ligands, as expected, since there are six in each isomer. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum is also informative in showing (Table 2) two signals for each of the groups C=O, *C*(C_6H_4Me-4), C, *C*HMe, CH$_2$, and CH*Me*. In the ^1H n.m.r. spectrum the observed couplings between H^a, H^b, and H^c are as expected for the presence of the CH$_2$CC(H)Me moiety with a 'W' relationship between H^a and H^b. As with (**5**), the species (**7**) can be regarded as a novel substituted trimethylenemethane complex of iron.[18]

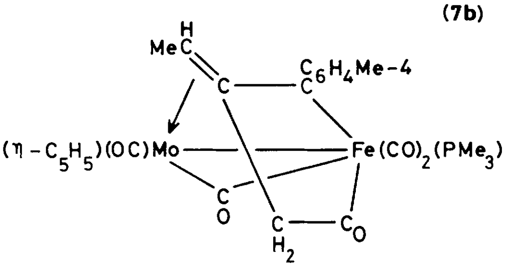
The final reaction studied in this series was that between MeC≡CMe and $[MoFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMe_3)(\eta\text{-}C_5H_5)]$. The latter is a derivative of (**1a**) with the PMe$_3$ group ligating the iron atom.[6] The reaction with but-2-yne occurred readily in light petroleum at room temperature to yield the complex $[MoFe\{\mu\text{-}C(C_6H_4Me\text{-}4)C(CHMe)CH_2C(O)\}(\mu\text{-}CO)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]$ (**8**), data for which are given in Tables 1 and 2. An *X*-ray diffraction study was carried out on (**8**)



(7a)



(7b)



(8)

in order to confirm the molecular structure. There are two crystallographically independent molecules, one of which is shown in Figure 4. Unfortunately, there were unresolved peculiarities in the refinement of the structure (see Experimental section), and it is imprudent to discuss structural parameters. Nevertheless, the overall molecular structure is apparent, and is in agreement with the spectroscopic data. Thus the i.r. spectrum indicates the presence of the bridging CO ligand with a band at 1 783 cm^{-1}, and the presence of the acyl carbonyl group with a band at 1 606 cm^{-1}. The ^{31}P-{^{1}H} n.m.r. spectrum shows a singlet resonance at δ 23.0 p.p.m.

The ^{1}H and ^{13}C-{^{1}H} specta (Table 2) show the expected signals. Moreover, the CO resonances for the $Fe(CO)_2(PMe_3)$ group appear as doublets as a result of ^{31}P–^{13}C coupling, thereby confirming that the PMe_3 ligand is attached to the iron atom. A proton-coupled ^{13}C spectrum (measured in $CDCl_3$) confirmed the assignments for the *C*HMe (δ 64.7 p.p.m.) and CH_2 (δ 57.6 p.p.m.) groups. These resonances appeared as a doublet [*J*(HC) 157 Hz] and a triplet [*J*(HC) 128 Hz], respectively.

The structure of compound (**8**) has features similar to those of (**4**). The bridge system in (**8**) is produced by a combination of processes involving coupling of one molecule of but-2-yne with a μ-CC_6H_4Me-4 group, hydrogen atom migration between carbon centres, and CO insertion between the CH_2 group and the iron atom. It is possible that the early stages of the formation of (**8**) are similar to those suggested in the Scheme for (**5**), but with L = PMe_3.

From intermediate (**D**), a 'windscreen-wiper' motion of the 'C_4' organic fragment C(R)C(CH_2)CHMe would lead to (**E**), with subsequent insertion of CO into the Fe–CH_2 bond giving (**8**). Alternatively, (**E**) could arise directly by the uptake of CO by (**C**) if the transfer of the hydride ligand to the CMe carbon atom is accompanied by C–Fe rather than C–Mo bond cleavage. The CO insertion step is very probably the last in the overall reaction sequence.[28] It is interesting to contrast the reaction which affords (**8**) with the synthesis of the isomeric compounds (**6**). Treatment of (**5**) with PMe_3 might have involved attack of the phosphine at the iron atom, with rearrangement of the bridging organic moiety to yield (**8**).

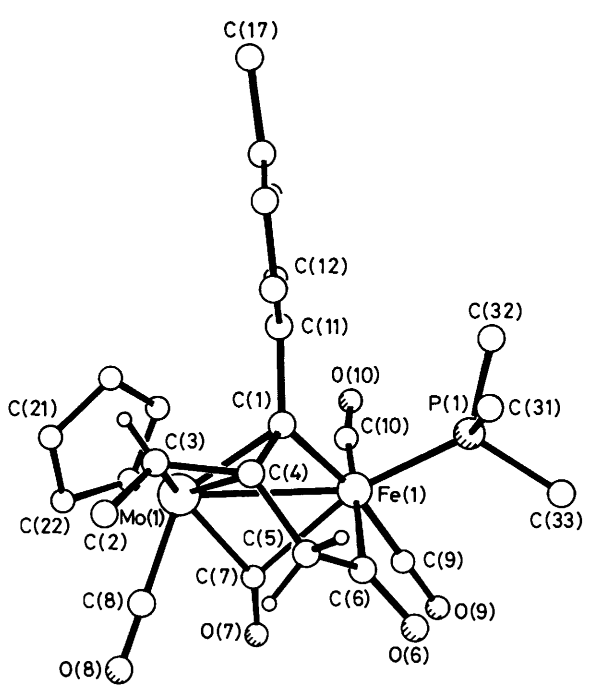


Figure 4. The molecular structure of [MoFe{μ-C(C_6H_4Me-4)-C(CHMe)CH_2C(O)}(μ-CO)$(CO)_3(PMe_3)$(η-C_5H_5)] (**8**). Hydrogen atoms attached to C(3) and C(5) are shown at calculated positions

The reactions described herein demonstrate an unusual variety of facile chemical processes associated with the molybdenum–iron compounds (**1a**) or (**2a**) and the alkynes MeC≡CMe and PhC≡CPh. As mentioned earlier, the tungsten–iron compound (**1b**) is too labile for its reactions with alkynes to be studied and (**2b**) with MeC≡CMe affords the structurally simple product (**3c**) rather than a tungsten–iron analogue of (**4**). In the succeeding paper[8] we show how reactions between (**1a**) and MeC≡CEt or EtC≡CEt give dimetal complexes very different in nature from those obtained with MeC≡CMe.

Experimental

All reactions were carried out under oxygen-free nitrogen, using Schlenk-tube techniques. Solvents were dried before use, and light petroleum refers to that fraction of b.p. 40—60 °C. The i.r. spectra were measured with Nicolet 10-MX and 5Z-DX spectrophotometers, and n.m.r. spectra with JNM JEOL FX90Q, FX200, GX270, and GX400 instruments. The ^{31}P-{^{1}H} n.m.r. chemical shifts are relative to 85% H_3PO_4 (external); positive values representing shifts to high frequency of the reference. Florisil used for chromatography columns was Fluka 100—200 mesh. The compounds (**1a**), (**2a**), and [MoFe(μ-CC_6H_4Me-4)$(CO)_5(PMe_3)$(η-C_5H_5)] were prepared as previously described.[2,6]

Synthesis of the Complex [MoFe{μ-C(C_6H_4Me-4)C(Ph)-C(Ph)}$(CO)_5$(η-C_5H_5)].—(*i*) A mixture of (**1a**) (0.15 g, 0.30

mmol) and PhC≡CPh (0.09 g, 0.50 mmol) was stirred in light petroleum (20 cm^3) for 48 h. Solvent was removed *in vacuo*; the red residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 2:3) and chromatographed (2 × 10 cm column). Elution with the same solvent mixture afforded a red eluate. Removal of solvent *in vacuo* gave red *microcrystals* of [$MoFe\{\mu$-$C(C_6H_4$-Me-4)C(Ph)C(Ph)$\}(CO)_5(\eta$-$C_5H_5)$] (**3a**) (0.18 g).

(*ii*) A mixture of (**2a**) (0.16 g, 0.25 mmol) and PhC≡CPh (0.10 g, 0.53 mmol) in toluene (60 cm^3) was heated at 70 °C for 24 h. Forcing conditions were required, since no reaction occurred in Et_2O or light petroleum at room temperature. Solvent was removed *in vacuo* from the dark brown toluene solution, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed (3 × 20 cm column). Elution with the same solvent mixture afforded a red eluate. Solvent was removed *in vacuo* to obtain *microcrystals* of (**3a**) (0.02 g).

Reactions with But-2-yne.—(*i*) A light petroleum (50 cm^3) solution of (**2a**) (0.29 g, 0.46 mmol) and a large excess of MeC≡CMe (3 cm^3, 38 mmol) were stirred for 24 h at room temperature. Solvent was removed *in vacuo*, and the brown residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed using the same solvent mixture as eluant. A green band and traces of a brown band were observed on the column. The latter was eluted and identified as unreacted (**2a**). The green band was removed with Et_2O–light petroleum (4:1). Solvent was removed *in vacuo* affording a green powder. The latter was dissolved in toluene–light petroleum (3 cm^3, 2:1) and cooled to *ca.* −20 °C thereby yielding green *crystals* of [$MoFe\{\mu$-$C(C_6H_4Me$-4)C(CHMe)CH_2C(Me)C(Me)$\}(CO)_4$-(η-C_5H_5)] (**4**) (0.05 g).

(*ii*) A light petroleum (10 cm^3) solution of (**1a**) (0.15 g, 0.30 mmol) was stirred (5 min) with an excess of MeC≡CMe (0.25 cm^3, 3.0 mmol). Solvent was removed *in vacuo*, and the red residue was extracted with light petroleum (25 cm^3). The extracts were filtered through a Celite pad (2 × 2 cm). Solvent was removed *in vacuo*, the residue dissolved in Et_2O (2 cm^3) and cooled to *ca.* −10 °C, affording red *microcrystals* of [$MoFe\{\mu$-$C(C_6H_4Me$-4)C(CHMe)$CH_2\}(CO)_5(\eta$-$C_5H_5)$] (**5**) (0.15 g).

(*iii*) A light petroleum (20 cm^3) solution of [MoFe(μ-CC_6H_4Me-4)$(CO)_5(PMe_3)(\eta$-$C_5H_5)$] (0.16 g, 0.30 mmol) at room temperature was treated with an excess of MeC≡CMe (0.50 cm^3, 6.0 mmol). After 1 h, solvent was removed *in vacuo*, and the brown residue in CH_2Cl_2–light petroleum (10 cm^3, 2:3) was chromatographed. Elution with the same solvent mixture removed traces of three unidentified compounds. Further elution with tetrahydrofuran–light petroleum (2:3) afforded an orange eluate. Removal of solvent *in vacuo* gave orange *microcrystals* of [$MoFe\{\mu$-$C(C_6H_4Me$-4)C(CHMe)CH_2C(O)$\}$-(μ-CO)$(CO)_3(PMe_3)(\eta$-$C_5H_5)$] (**8**) (0.07 g).

Reactions of [$MoFe\{\mu$-$C(C_6H_4Me$-4)C(CHMe)$CH_2\}(CO)_5$-(η-C_5H_5)].—(*i*) An isomeric mixture of (**5**) (0.10 g, 0.20 mmol) in light petroleum (15 cm^3) was treated with PMe_3 (0.02 cm^3, 0.20 mmol), and the reactants were stirred for 15 min at room temperature. Solvent was decanted from an orange precipitate which formed. The latter was washed with Et_2O (3 × 5 cm^3), and dried *in vacuo*. The precipitate was dissolved in acetone (20 cm^3). After filtration through a Celite pad (2 × 2 cm), solvent was removed *in vacuo* to give orange *microcrystals* of [MoFe(μ-$C(C_6H_4Me$-4)C[C(H)Me$(PMe_3)]CH_2\}(CO)_5(\eta$-$C_5H_5)$] (**6a**) and [$MoFe\{\mu$-$C(C_6H_4Me$-4)$C(CH_2PMe_3)CHMe\}(CO)_5(\eta$-$C_5H_5)$] (**6b**) (0.11 g), as a 1:1 mixture (see Discussion). If the mixture of isomers is stirred in acetone (25 cm^3) for 48 h pure (**6b**) may be recovered.

(*ii*) A light petroleum (20 cm^3) solution of (**5**) (0.16 g, 0.30 mmol) was stirred at room temperature for 3 d under CO (3×10^5 Pa), affording an orange solution and a yellow precipitate. After removal of solvent *in vacuo*, the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed at 10 °C. Elution with the same solvent mixture removed traces of an unidentified red compound. Further elution with CH_2Cl_2–light petroleum (4:1) gave a yellow eluate. Removal of solvent *in vacuo* afforded yellow *microcrystals* of the isomeric mixture of [$MoFe\{\mu$-$C(O)C(C_6H_4Me$-4)C(CHMe)$CH_2\}(CO)_6(\eta$-$C_5H_5)$] (**7**) (0.12 g).

Crystal Structure Determinations.—(*a*) [$MoFe\{\mu$-$C(C_6H_4$-Me-4)C(CHMe)CH_2C(Me)C(Me)$\}(CO)_4(\eta$-$C_5H_5)$] (**4**). Crystals grow on cooling from a mixture of CH_2Cl_2, light petroleum, and Et_2O (1:2:1) as black prisms. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.40 × 0.28 × 0.25 mm on a Nicolet *P*3*m* diffractometer. Of the 5 222 unique data collected (ω–2θ scans, $2\theta \leqslant 55°$), 3 866 had $I \geqslant 2.5\sigma(I)$ and only these were used in structure solution and refinement. The data were corrected for *X*-ray absorption (by an empirical method based on azimuthal scan data[29]), Lorentz and polarisation effects.

Crystal data. $C_{25}H_{24}FeMoO_4$, $M = 540.23$, monoclinic, $a = 14.166(3)$, $b = 8.714(1)$, $c = 18.645(3)$ Å, $\beta = 100.95(1)°$, $U = 2\,259.8(6)$ Å^3, $Z = 4$, $D_c = 1.59$ g cm^{-3}, $F(000) = 1\,096$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 12.11 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and successive difference-Fourier syntheses were used to locate all non-hydrogen atoms, and the atoms H(3), H(5a), and H(5b). All non-hydrogen atoms were refined with anisotropic thermal parameters. Atoms H(3), H(5a), and H(5b) were refined with isotropic thermal parameters. All remaining hydrogen atoms were included at calculated positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for the methyl hydrogen atoms [attached to C(2), C(6), C(9), and C(27)], and fixed isotropic thermal parameters (*ca.* 1.2 × $U_{equiv.}$ of the parent carbon atoms) for all other hydrogen atoms. Refinement by blocked-cascade least squares led to $R = 0.032$ ($R' = 0.032$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,36|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks > 0.45 or < -0.28 e Å^{-3}.

(*b*) [$MoFe\{\mu$-$C(C_6H_4Me$-4)C(CHMe)$CH_2\}(CO)_5(\eta$-$C_5H_5)$] (**5a**). Crystals grow as red needles by solvent diffusion from Et_2O–light petroleum at room temperature. Diffracted intensities were collected from a crystal of dimensions *ca.* 0.60 × 0.20 × 0.15 mm as for (**4**). Of the 3 277 unique data collected (ω–2θ scans, $2\theta \leqslant 50°$, weak data with $40 \leqslant 2\theta \leqslant 50°$ being skipped on the basis of a preliminary prescan), 2 575 had $I \geqslant 2.0\sigma(I)$ and only these were used for structure solution and refinement, after corrections as for (**4**).[29]

Crystal data. $C_{22}H_{18}FeMoO_5$, $M = 514.2$, monoclinic, $a = 7.950(1)$, $b = 26.558(7)$, $c = 9.889(4)$ Å, $\beta = 99.67(3)°$, $U = 2\,058(1)$ Å^3, $Z = 4$, $D_c = 1.66$ g cm^{-3}, $F(000) = 1\,032$, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), μ(Mo-K_α) = 13.28 cm^{-1}.

The structure was solved as for (**4**), and thereby all non-hydrogen atoms and H(2a), H(2b), H(4), and H(12) were located. All non-hydrogen atoms were refined with anisotropic thermal parameters. Atoms H(2a), H(2b), H(4), and H(12) were refined with fixed isotropic thermal parameters (*ca.* 1.2 × $U_{equiv.}$ of the parent carbon atoms), the parent carbon–hydrogen distances being constrained to 0.96 Å. All other hydrogen atoms were included at calculated positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for the methyl hydrogen atoms [attached to C(5) and C(17)] and fixed isotropic thermal parameters (*ca.* 1.2 × $U_{equiv.}$ of the parent carbon atoms) for all remaining hydrogen atoms. Refinement by blocked-cascade least squares led to $R = 0.038$ ($R' = 0.032$) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,15|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks > 0.49 or < -0.35 e Å^{-3}.

(*c*) [MoFe{μ-C(C_6H_4Me-4)C(CH_2PMe_3)CHMe}$(CO)_5$(η-C_5H_5)] (**6b**). Crystals were grown, with some difficulty, from a mixture of acetone, CH_2Cl_2, and light petroleum (3:1:1), as small orange parallelepipeds. Diffracted intensities were collected from a crystal of dimensions *ca.* 0.1 × 0.1 × 0.2 mm on a Nicolet *R*3*m*/μ diffractometer. Of the 3 342 unique data collected (ω–2θ scans, $2\theta \leqslant 45°$), 1 747 had $I \geqslant 2.0\sigma(I)$ and only these were used for structure solution and refinement. The data were corrected for Lorentz and polarisation effects,[29] but an absorption correction was not applied.

Crystal data. $C_{25}H_{27}FeMoO_5P$, $M = 590.3$, monoclinic, $a = 25.121(8)$, $b = 10.796(3)$, $c = 19.411(6)$ Å, $\beta = 101.26(2)°$, $U = 5\,163(3)$ Å^3, $Z = 8$, $D_c = 1.52$ g cm^{-3}, $F(000) = 2\,400$, space group *I*2/*a* (non-standard setting of *C*2/*c*, no. 15), $\mu(\text{Mo-}K_\alpha) = 11.3$ cm^{-1}.

The structure was solved and non-hydrogen atoms located as for (**4**). The number of observed data was small (as a result of the small crystal size), and anisotropic thermal parameters were refined for the molybdenum, iron, and phosphorus atoms only. The remaining non-hydrogen atoms were refined with isotropic thermal parameters, the C_5H_5 and C_6H_4 groups being constrained to rigid, idealised geometries. Hydrogen atoms were included at calculated positions, with a common refined isotropic thermal parameter for the methyl hydrogen atoms and fixed isotropic thermal parameters (0.08 Å^2) for the remainder. Refinement by blocked-cascade least squares led to $R = 0.076$ ($R' = 0.065$) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,4|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks > 1.02 or < -0.74 e Å^{-3}.

(*d*) [MoFe{μ-C(C_6H_4Me-4)C(CHMe)CH_2C(O)}(μ-CO)$(CO)_3(PMe_3)$(η-C_5H_5)] (**8**). Crystals were grown from CH_2Cl_2–Et_2O–light petroleum (1:1:2) as red blocks. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.20 × 0.30 × 0.35 mm, on a Nicolet *P*3*m* diffractometer. Of the 4 191 unique data (ω–2θ scans, $2\theta \leqslant 50°$), 2 874 had $I \geqslant 2.0\sigma(I)$ and only these were used in the refinement of the structure, after correction for Lorentz, polarisation, and *X*-ray absorption by an empirical method based on azimuthal scan data.[29]

Crystal data. $C_{25}H_{24}FeMoO_5P$, $M = 590.3$, orthorhombic, $a = 22.701(8)$, $b = 14.917(4)$, $c = 14.690(4)$ Å, $U = 4\,974(3)$ Å^3, $Z = 8$, $D_c = 1.58$ g cm^{-3}, $F(000) = 2\,400$, space group *Pba*2$_1$ (no. 33), $\mu(\text{Mo-}K_\alpha) = 11.70$ cm^{-1}.

The structure was solved and all non-hydrogen atoms located by conventional heavy-atom and difference-Fourier methods. The asymmetric unit consists of two independent molecules of (**8**), these being related by a pseudo-centre of inversion, of fractional co-ordinates (0.125, 0.50, 0.50). All attempts to resolve the structure in the centric space group *Pnam* (non-standard setting of *Pnma*, no. 62) failed, as did attempts to translate one molecule from the original solution to give a solution in *Pnam*. Only one molecule is shown in Figure 4.

The molybdenum, iron, and phosphorus atoms were refined with anisotropic thermal parameters. The remaining non-hydrogen atoms were refined with isotropic thermal parameters, and hydrogen atoms were not included. The C_5H_5 and C_6H_4 rings were constrained to rigid idealised geometries. Refinements by blocked-cascade least squares led to $R = 0.087$ ($R' = 0.086$), using a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.004|F|^2]$. However, for reasons that are still unclear, this refinement is not entirely satisfactory. In particular, the final electron-density difference Fourier synthesis showed two large

Table 6. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**4**)

Atom	*x*	*y*	*z*
Mo	3 197(1)	1 625(1)	1 066(1)
Fe	2 807(1)	4 287(1)	237(1)
C(1)	2 186(2)	3 505(3)	1 042(1)
C(2)	1 264(3)	−528(4)	1 320(3)
C(3)	1 726(3)	1 041(4)	1 395(2)
C(4)	1 645(2)	2 138(3)	817(2)
C(5)	1 238(2)	1 968(4)	19(2)
C(6)	1 624(3)	2 720(5)	−1 219(2)
C(7)	2 002(2)	2 474(4)	−407(2)
C(8)	2 963(2)	2 072(3)	−103(2)
C(9)	3 679(3)	1 658(5)	−588(2)
C(10)	2 827(3)	−164(4)	437(2)
O(10)	2 690(2)	−1 220(3)	62(2)
C(11)	3 651(3)	5 480(4)	803(2)
O(11)	4 210(2)	6 305(3)	1 128(2)
C(12)	1 747(2)	5 425(4)	53(2)
O(12)	1 038(2)	6 093(3)	−47(2)
C(13)	3 356(3)	4 958(4)	−494(2)
O(13)	3 690(3)	5 474(4)	−952(2)
C(21)	1 997(2)	4 432(3)	1 672(2)
C(22)	2 693(2)	5 194(4)	2 174(2)
C(23)	2 452(3)	6 093(4)	2 722(2)
C(24)	1 508(3)	6 282(4)	2 798(2)
C(25)	814(2)	5 541(4)	2 302(2)
C(26)	1 044(2)	4 637(4)	1 749(2)
C(27)	1 251(3)	7 282(6)	3 397(2)
C(31)	4 057(3)	1 926(6)	2 271(2)
C(32)	4 607(3)	2 570(5)	1 826(2)
C(33)	4 888(3)	1 481(5)	1 388(2)
C(34)	4 528(3)	119(5)	1 551(2)
C(35)	3 994(3)	336(6)	2 094(3)

Table 7. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**5a**)

Atom	*x*	*y*	*z*
Mo	3 937(1)	1 874(1)	2 107(1)
Fe	6 000(1)	521(1)	3 219(1)
C(1)	5 204(5)	1 157(2)	1 856(4)
C(2)	8 031(6)	1 032(2)	3 128(5)
C(3)	6 885(5)	947(2)	1 901(4)
C(4)	6 919(6)	462(2)	1 309(5)
C(5)	8 531(7)	166(2)	1 225(7)
C(6)	6 181(6)	2 077(2)	1 778(4)
O(6)	7 488(4)	2 205(2)	1 544(3)
C(7)	3 471(5)	2 285(2)	453(5)
O(7)	3 236(5)	2 551(2)	−480(4)
C(8)	4 060(6)	182(2)	2 667(5)
O(8)	2 844(5)	−36(2)	2 308(4)
C(9)	7 313(6)	6(2)	3 960(5)
O(9)	8 143(5)	−320(2)	4 419(4)
C(10)	5 649(6)	779(2)	4 822(5)
O(10)	5 548(5)	933(1)	5 881(3)
C(11)	3 888(5)	1 153(2)	649(4)
C(12)	2 171(6)	1 181(2)	837(4)
C(13)	843(6)	1 252(2)	−309(5)
C(14)	1 194(7)	1 290(2)	−1 604(5)
C(15)	2 903(7)	1 267(2)	−1 787(5)
C(16)	4 186(6)	1 211(2)	−712(5)
C(17)	−211(7)	1 340(3)	−2 831(6)
C(21)	2 816(6)	1 673(2)	4 095(4)
C(22)	4 276(6)	1 978(2)	4 463(4)
C(23)	3 927(6)	2 455(2)	3 856(5)
C(24)	2 256(7)	2 449(2)	3 149(5)
C(25)	1 572(6)	1 972(2)	3 285(5)

Table 8. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**6b**)

Atom	*x*	*y*	*z*
Mo	3 588(1)	4 506(1)	1 134(1)
Fe	4 392(1)	3 583(2)	2 244(1)
P	3 397(2)	−168(4)	2 343(2)
C(1)	3 822(5)	2 625(12)	1 522(7)
C(2)	3 980(5)	868(12)	2 427(7)
C(3)	3 835(5)	2 188(13)	2 218(7)
C(4)	3 743(6)	3 087(14)	2 720(7)
C(5)	3 787(7)	2 777(16)	3 505(8)
C(6)	2 917(7)	3 764(15)	1 184(8)
O(6)	2 493(5)	3 284(11)	1 210(6)
C(7)	3 287(6)	5 490(16)	1 762(7)
O(7)	3 061(5)	6 106(11)	2 132(6)
C(8)	4 884(7)	3 630(16)	1 732(9)
O(8)	5 215(5)	3 663(12)	1 390(7)
C(9)	4 345(7)	5 149(15)	2 429(9)
O(9)	4 350(5)	6 167(12)	2 642(6)
C(10)	4 854(7)	3 135(16)	2 942(9)
O(10)	5 180(5)	2 831(12)	3 463(7)
C(12)	4 374(3)	1 091(10)	958(5)
C(13)	4 404	178	458
C(14)	3 942	−141	−34
C(15)	3 450	452	−27
C(16)	3 420	1 365	473
C(11)	3 882	1 685	965
C(17)	3 964(9)	−1 134(21)	−626(12)
C(21)	4 246(4)	5 463(11)	520(5)
C(22)	4 086	4 314	186
C(23)	3 521	4 372	−97
C(24)	3 331	5 556	63
C(25)	3 779	6 230	444
C(31)	3 431(7)	−1 241(18)	1 670(9)
C(32)	2 780(6)	681(15)	2 130(8)
C(33)	3 402(7)	−1 008(15)	3 129(8)

pairs of residual peaks, each associated with one of the independent Mo–Fe units. The interpeak separation (*ca.* 2.8 Å) and relative heights (3.6 and 2.1 e Å^{-3}) indicated that they were probably weak images or 'ghosts' of the Mo–Fe dimetal units. They are approximately related to the Mo–Fe dimers by a mirror plane (coincident with the *a*-glide of $Pna2_1$) perpendicular to the *b* axis. This, together with the fact that determination of the chirality of the lattice was not possible, indicates that the crystal may have been an enantiomeric twin. The enantiomeric η parameter suggested by Rogers[30] refined to a value of 0.1(3). In the light of these problems, we believe that detailed discussion of the geometric parameters is not justified. However, the gross geometry, as illustrated in Figure 4, is almost certainly correct and is fully supported by the spectroscopic data.

All calculations were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs,[29] except for the structure solution of (**6b**) which was performed on a Digital μ-Vax computer with the SHELXPLUS crystallographic package.[29] Scattering factors with corrections for anomalous dispersion were taken from ref. 31. The atomic co-ordinates for (**4**), (**5a**), and (**6b**) are listed in Tables 6—8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, remaining bond lengths and angles together with atomic co-ordinates, thermal parameters, and bond lengths and angles for (**8**).

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