Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 54.[1] Compounds derived from $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ with Bonds between Tungsten and Iron, Cobalt, or Nickel; Crystal Structure of $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)O\}(CO)_5(\eta\text{-}C_5Me_5)]$ *

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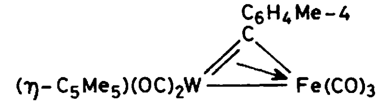
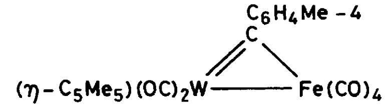
The compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ (**1**) reacts with $[Fe(CO)_3(\eta\text{-}C_8H_{14})_2]$ in hexane at *ca.* −50 °C to give predominantly the electronically unsaturated dimetal complex $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)]$ (**2**). With $[Fe_2(CO)_9]$ in Et_2O at *ca.* 10 °C, compound (**1**) yields a chromatographically separable mixture of (**2**), the saturated dimetal species $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5Me_5)]$, and the trimetal compound $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)]$. The latter is best obtained by treating (**1**) with excess of $[Fe_2(CO)_9]$ in Et_2O at ambient temperatures. Complex (**2**) reacts with oxygen and with sulphur to afford $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)O\}(CO)_5(\eta\text{-}C_5Me_5)]$ (**5**) and $[FeW(\mu\text{-}SCC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)]$, respectively. The structure of (**5**) has been established by *X*-ray diffraction. The Fe–W bond [2.605(1) Å] is bridged by the $C(C_6H_4Me\text{-}4)C(O)O$ fragment [Fe–O 2.007(3), W–O 2.128(3), Fe–$C(C_6H_4Me\text{-}4)$ 2.054(4), and W–$C(C_6H_4Me\text{-}4)$ 2.171(4) Å], with the C=O group interacting weakly if at all with the iron or tungsten centres [Fe ··· C(O) 2.380(3) and W ··· C(O) 2.609(3) Å]. The iron atom carries three CO groups, and the tungsten two CO groups and the $\eta\text{-}C_5Me_5$ ligand. Treatment of (**2**) with an excess of CH_2N_2 gives $[FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)=CH_2\}(\mu\text{-}CH_2)(CO)_5(\eta\text{-}C_5Me_5)]$. However, with one equivalent of CH_2N_2, the major product is $[FeW\{\mu\text{-}trans\text{-}CH=C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5Me_5)]$, together with spectroscopically identified $[FeW\{\mu\text{-}trans\text{-}CH=C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CH_2)(CO)_5(\eta\text{-}C_5Me_5)]$. Compound (**1**) reacts with $[Co_2(CO)_8]$ to give $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5Me_5)]$, and with $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ to give a mixture of $[Ni_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$ and $[NiW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$.

In previous papers of this series we have shown that the compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) is a useful reagent for preparing complexes wherein tungsten is bonded to other transition elements. The C≡W group present in the alkylidynetungsten species acts as a 'ligand' towards a variety of low-valent metal fragments isolobal with methylene.[2] Replacement of $\eta\text{-}C_5H_5$ in $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ by electronically equivalent groups should significantly extend this area of chemistry. This idea has been substantiated by recent studies involving the ligands $HB(pz)_3$ [hydrotris(pyrazol-1-yl)-borate] and $7,8\text{-}C_2B_9H_9Me_2$ in place of C_5H_5. The compounds $[W(\equiv CR)(CO)_2\{HB(pz)_3\}]$[3] and $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$[4] have been successfully employed as precursors to dimetal and metal cluster compounds. Extending this strategy for synthesising compounds with heteronuclear metal–metal bonds we report the preparation of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5Me_5)]$, and describe some of its reactions. It is well known that the $\eta\text{-}C_5Me_5$ ligand often affords metal complexes with significantly different properties from those of their $\eta\text{-}C_5H_5$ analogues. A preliminary account has been given of the iron–tungsten compounds described in this paper.[5]



(**2**)



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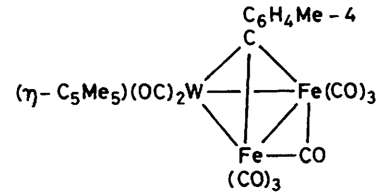

(**4**)

Results and Discussion

Treatment of $[W(\equiv CR)Br(CO)_4]$ with $K(C_5Me_5)$ in thf (tetrahydrofuran) afforded the red complex $[W(\equiv CR)(CO)_2(\eta\text{-}C_5Me_5)]$ (**1**), data for which are given in Tables 1 and 2. Treatment of (**1**) with $[Fe(CO)_3(\eta\text{-}C_8H_{14})_2]$[6] in hexane at −50 °C affords predominantly the purple crystalline compound $[FeW(\mu\text{-}CR)(CO)_5(\eta\text{-}C_5Me_5)]$ (**2**). In contrast, the reaction between (**1**) and $[Fe_2(CO)_9]$ in Et_2O at *ca.* 10 °C gives a *ca.* 1 : 1 mixture of (**2**) and $[FeW(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5Me_5)]$ (**3**), together

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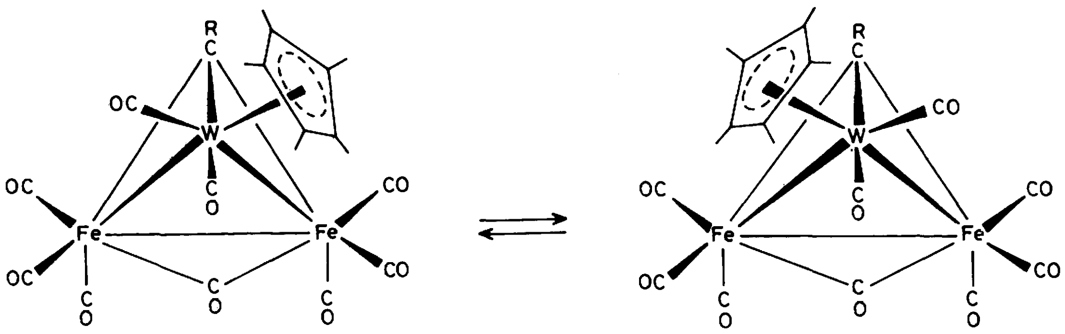
* 1,1,1,2,2-Pentacarbonyl-2-(η-pentamethylcyclopentadienyl)-μ-[carboxy(*p*-tolyl)methylene-*C*(Fe¹,W²),*O*(Fe¹,W²)]irontungsten (*Fe–W*).

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

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

Compound[b]	Colour	Yield (%)	$\nu_{max.}$(CO)[c]/cm^{-1}	Analysis (%)	
				C	H
(1) $[W(\equiv CR)(CO)_2(\eta\text{-}C_5Me_5)]$[d]	Red	90	1 981s, 1 910s	49.9 (50.2)	4.9 (4.7)
(2) $[FeW(\mu\text{-}CR)(CO)_5(\eta\text{-}C_5Me_5)]$	Purple	28	2 045s, 1 987s, 1 970s, 1 873w, 1 851wbr	42.4 (43.5)	3.3 (3.4)
(3) $[FeW(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5Me_5)]$	Brown	21	2 068s, 2 014m, 1 991s, 1 935m, 1 873w		
(4) $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)]$	Black	54	[e]2 058m, 2 018s, 2 006s, 1 965m, 1 942(sh), 1 902wbr, 1 769wbr	41.4 (41.3)	2.9 (2.8)
(5) $[FeW\{\mu\text{-}C(R)C(O)O\}(CO)_5(\eta\text{-}C_5Me_5)]$	Yellow-orange	21	[f]2 056s, 1 998s, 1 983m, 1 923w, 1 705w, 1 685w	42.2 (43.5)	3.5 (3.4)
(6) $[FeW(\mu\text{-}SCR)(CO)_5(\eta\text{-}C_5Me_5)]$	Orange	30	[f]2 039vs, 1 975s, 1 964m, 1 900wbr	[g]40.4 (39.2)	3.2 (3.3)
(7) $[FeW\{\mu\text{-}C(R)=CH_2\}(\mu\text{-}CH_2)(CO)_5(\eta\text{-}C_5Me_5)]$	Dark green	48	2 039s, 1 991s, 1 977m, 1 921w	46.6 (46.5)	4.5 (4.1)
(8) $[FeW\{\mu\text{-}CH{=}C(H)R\}(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5Me_5)]$	Green-brown	49	2 045m, 1 993s, 1 977m, 1 939w, 1 742m	45.5 (45.5)	4.3 (3.7)
(10) $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5Me_5)]$	Green	76	2 077m, 2 066w, 2 037m, 2 027s, 2 010w, 2 000m, 1 965w, 1 939w, 1 859w	39.1 (40.7)	3.2 (2.9)
(11) $[Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$	Black	20	[e]1 909s, 1 846s	49.2 (49.6)	5.0 (4.6)

[a] Calculated values are given in parentheses. [b] R = $C_6H_4Me\text{-}4$. [c] In hexane, unless otherwise stated. [d] Molecular ion at *m/z* = 478 in mass spectrum. [e] In CH_2Cl_2. [f] In thf. [g] Contains a CH_2Cl_2 molecule of crystallisation (see ^1H n.m.r. data, Table 2).



Scheme 1. Dynamic behaviour in solution for complex (4) involving rotation of the $W(CO)_2(\eta\text{-}C_5Me_5)$ group about an axis through W and the mid-point of the $\mu_3\text{-}CFe_2$ triangle

with a small amount of the trimetal compound $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)]$ (4). Data for (2)—(4) are given in Tables 1 and 2.

Since purple (2) may be readily separated from brown (3) by column chromatography, it is perhaps more convenient to prepare the former from $[Fe_2(CO)_9]$ than from $[Fe(CO)_3(\eta\text{-}C_8H_{14})_2]$. Moreover, (2) with CO gives (3), and the latter *in vacuo* tends to reform (2) through loss of CO. The trimetal compound (4) can be obtained in good yield from the reaction between (1) and $[Fe_2(CO)_9]$ in 1:3 ratio in Et_2O at room temperature. Complex (4) undergoes dynamic behaviour in solution as revealed by examination of the $^{13}C\text{-}\{^1H\}$ spectrum. When measured at ambient temperatures only one sharp CO resonance at δ 216.8 p.p.m. is observed. However, when the spectrum is recorded at −90 °C (Table 2) two resonances are observed at δ 225.2 [*J*(WC) 161] and 203.3 p.p.m. [*J*(WC) 149 Hz] and these may be assigned to the inequivalent tungsten-ligated CO groups, whilst another signal at δ 245.9 p.p.m. is characteristic for the μ-CO moiety. In addition, the observation of three overlapping resonances in the $Fe(CO)_3$ region (of relative intensity *ca.* 1 : 1 : 4) suggests that rotation of the $Fe(CO)_3$ group adjacent to the bulky pentamethylcyclopentadienyl ligand has become slow on the n.m.r. time-scale. This may be readily explained if a dynamic process of the type shown in Scheme 1 is accompanied by CO site exchange between the iron and tungsten atoms.

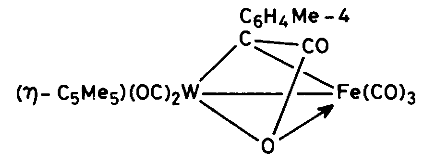
The synthesis of (2) is of considerable interest, since in this compound the $Fe(CO)_3$ fragment (isolobal with CH^+) is stabilised by 'complexation' with (1); the latter evidently functioning formally as a four-electron donor. It is noteworthy that in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (2) the resonance for the μ-C nucleus (δ 395.4 p.p.m.) is *ca.* 54 p.p.m. more deshielded than the signal for the μ-C group in (3) (δ 341.8 p.p.m.). A similar trend in μ-C chemical shifts is observed in the spectra of the related complexes $[FeW(\mu\text{-}CR)(CO)_n(\eta\text{-}C_5H_5)]$ (*n* = 5, δ 392.5; *n* = 6, δ 331.3 p.p.m.),[3b] with the resonance for the alkylidyne carbon nucleus being significantly more deshielded in the compound with the $Fe(CO)_3$ group. We have drawn attention to an analogy between these results [3b] and the $^{13}C\text{-}\{^1H\}$ n.m.r. data for alkyne–metal complexes. With the latter compounds the signals for the ligated carbon nuclei are *ca.* 80 p.p.m. more deshielded when the alkynes donate four electrons to a metal centre than when these ligands act as two-electron donors.[7]

The compounds (2) and (3) are significantly more stable than the previously described complexes $[FeW(\mu\text{-}CR)(CO)_n(\eta\text{-}$

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

Compound	^{1}H(δ)[c]	^{13}C(δ)[d]
(1)	1.72 (s, 15 H, C_5Me_5), 2.07 (s, 3 H, Me-4), 7.21 (m, 4 H, C_6H_4)	301.3 [C≡W, *J*(WC) 211], 225.4 [CO, *J*(WC) 193], 148.3 [C^1 (C_6H_4)], 137.2 [C^4(C_6H_4)], 128.0, 127.6 [$C^{2,3}$ and $C^{5,6}$ (C_6H_4)], 104.0 (*C*$_5$Me$_5$), 20.7 (Me-4), 10.3 (C$_5$*Me*$_5$)
(2)	2.14 (s, 15 H, C_5Me_5), 2.38 (s, 3 H, Me-4), 7.28 (m, 4 H, C_6H_4)	[e] 395.4 [μ-C, *J*(WC) 156], 228.9 [2 × CO, *J*(WC) 175], 216.3 (3 × CO), 159.2 [C^1(C_6H_4)], 136.4, 128.2, 120.5 (C_6H_4), 106.7 (*C*$_5$Me$_5$), 21.6 (Me-4), 10.7 (C$_5$*Me*$_5$)
(3)	1.91 (s, 15 H, C_5Me_5), 2.25 (s, 3 H, Me-4), 6.58—7.25 (m, 4 H, C_6H_4)	341.8 (br, μ-C), 242.9 (br, 2 × CO), 216.6 (br, 4 × CO), 161.5 [C^1(C_6H_4)] 139.3, 128.2, 127.3 (C_6H_4), 107.3 (*C*$_5$Me$_5$), 21.1 (Me-4), 10.5 (C$_5$*Me*$_5$)
(4)	2.03 (s, 15 H, C_5Me_5), 2.44 (s, 3 H, Me-4), 7.23, 7.46 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[f] 274.9 (μ_3-C), 245.9 (μ-CO), 225.2 [CO, *J*(WC) 161], 214.6, 214.2, 213.4 [2 × $Fe(CO)_3$], 203.3 [CO, *J*(WC) 149], 157.6 [C^1(C_6H_4)], 137.3, 130.8, 128.5 (C_6H_4), 107.2 (*C*$_5$Me$_5$), 21.5 (Me-4), 10.7 (C$_5$*Me*$_5$)
(5)	[f] 2.02 (s, 15 H, C_5Me_5), 2.28 (s, 3 H, Me-4), 7.26—7.62 (m, 4 H, C_6H_4)	[g] 223.6, 223.2 (WCO), 208.2 (3 × CO), 163.4 (C=O), 140.3 [C^1(C_6H_4)], 134.5, 128.5, 128.2 (C_6H_4), 103.6 (*C*$_5$Me$_5$), 82.0 (*C*C_6H_4Me-4), 20.1 (Me-4), 8.9 (C$_5$*Me*$_5$)
(6)	[f] 1.95 (s, 15 H, C_5Me_5), 2.28 (s, 3 H, Me-4), 5.30 (s, CH_2Cl_2), 7.00—7.26 (m, 4 H, C_6H_4)	220.5, 218.9 (WCO), 212.2 (3 × CO), 144.2 [C^1(C_6H_4)], 135.1, 129.3, 128.9 (C_6H_4), 102.5 (*C*$_5$Me$_5$), 95.6 (*C*C_6H_4Me-4), 21.3 (Me-4), 10.8 (C$_5$*Me*$_5$)
(7)	1.34 [d, 1 H, μ-CH_2, *J*(HH) 4], 1.87 (s, 15 H, C_5Me_5), 1.87 (s, 1 H, μ-CR=CH_2), 2.29 (s, 3 H, Me-4), 3.55 (s, 1 H, μ-CR=CH_2), 4.04 [d, 1 H, μ-CH_2, *J*(HH) 4], 7.01, 7.16 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[h] 225.3 [CO, *J*(WC) 129], 220.8 [CO, *J*(WC) 134], 214.6 (br, 3 × CO), 181.4 [μ-*C*R=CH_2, *J*(WC) 67], 156.8 [C^1(C_6H_4)], 136.3, 129.6, 127.6 (C_6H_4), 97.7 (*C*$_5$Me$_5$), 89.9 [μ-CH_2, *J*(WC) 58], 74.2 (μ-CR=*C*H$_2$), 21.2 (Me-4), 10.5 (C$_5$*Me*$_5$)
(8)	1.99 (s, 15 H, C_5Me_5), 2.27 (s, 3 H, Me-4), 3.85 [d, 1 H, μ-CH=C*H*R, *J*(HH) 13], 7.06, 7.14 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 8.14 [d, 1 H, μ-C*H*=CHR, *J*(HH) 13]	[i] 281.6 (μ-CO), 223.0 [CO, *J*(WC) 129], 220.5 [CO, *J*(WC) 148], 213.0 (br, 3 × CO), 139.8 [C^1(C_6H_4)], 137.7, 127.0, 125.8 (C_6H_4), 120.4 [μ-*C*H=CHR, *J*(WC) 58], 101.4 (μ-CH=*C*HR), 99.2 (*C*$_5$Me$_5$), 21.4 (Me-4), 10.5 (C$_5$*Me*$_5$)
(9)	1.99 (s, 15 H, C_5Me_5), 1.87 [d, 1 H, μ-CH_2, *J*(HH) 4], 2.29 (s, 3 H, Me-4), 4.17 [d, 1 H, μ-CH=C*H*R, *J*(HH) 14], 4.18 [d, 1 H, μ-CH_2, *J*(HH) 4], 7.09, 7.19 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 8.30 [d, 1 H, μ-C*H*=CHR, *J*(HH) 14]	225.5, 222.3 (br, WCO), 214.0 (br, 3 × CO), 139.6 [C^1(C_6H_4)], 137.5 [C^4(C_6H_4)], 134.8 [μ-*C*H=CHR, *J*(WC) 62], 129.9, 126.1 (C_6H_4), 99.6 (br, μ-CH=*C*HR), 98.8 (*C*$_5$Me$_5$), 88.2 [μ-CH_2, *J*(WC) 61], 21.0 (Me-4), 11.5 (C$_5$*Me*$_5$)
(10)	1.95 (s, 15 H, C_5Me_5), 2.28 (s, 3 H, Me-4), 6.05 (m, 4 H, C_6H_4)	[j] 254.0 (μ_3-C), 211.6 [2 × CO, *J*(WC) 167], 203.2 (6 × CO), 156.6 [C^1(C_6H_4)], 135.4, 127.2, 127.0 (C_6H_4), 100.7 (*C*$_5$Me$_5$), 20.3 (Me-4), 10.6 (C$_5$*Me*$_5$)
(11)	1.80 (s, 15 H, C_5Me_5), 2.39 (s, 3 H, Me-4), 5.16 (s, 10 H, C_5H_5), 7.27 (m, 4 H, C_6H_4)	280.1 (μ_3-C), 223.0 (CO), 159.4 [C^1(C_6H_4)], 134.8, 128.6, 127.1 (C_6H_4), 102.5 (*C*$_5$Me$_5$), 91.9 (*C*$_5$H$_5$), 21.0 (Me-4), 10.3 (C$_5$*Me*$_5$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures unless otherwise stated. [b] R = C_6H_4Me-4. [c] Measured in CD_2Cl_2 unless otherwise stated. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2. [e] Spectrum measured at −70 °C. [f] Spectrum measured at −90 °C. [g] Measured in $CDCl_3$. [h] Spectrum measured at −60 °C. [i] Spectrum measured at −40 °C. [j] Spectrum measured at −80 °C; peaks for major isomer only, see text.



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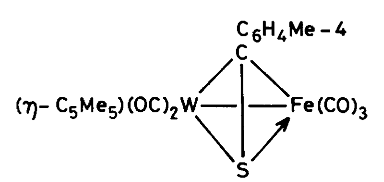


(6)

C_5H_5)] (n = 5[3b] or 6[8]). Indeed [FeW(μ-CR)$(CO)_5$(η-C_5H_5)], the cyclopentadienyl analogue of (**2**), decomposes in solution above *ca.* −20 °C. It is thus evident that the η-C_5Me_5 ligand has a significant effect on stability, thus allowing reactions between the unsaturated 32-valence electron complex (**2**) and a variety of compounds to be explored.

During preliminary work with the iron–tungsten compound (**4**), formation of small amounts of a yellow-orange complex was observed. The nature of this product, [FeW{μ-C(R)C(O)O}$(CO)_5$(η-C_5Me_5)] (**5**), only became apparent after an *X*-ray diffraction study (see below), and discovery that it was readily prepared by treating (**2**) with oxygen. Its initial isolation as a by-product of the synthesis of (**4**) was thus explained by the presence of traces of oxygen among the reactants.

The results of the *X*-ray diffraction study are summarised in Table 3, and the structure of (**5**) is shown in the Figure. The metal–metal bond is bridged by the C(C_6H_4Me-4)C(O)O group. Three CO ligands are terminally attached to the iron and two to the tungsten, with Fe(W)–C–O angles in the range 174.0(4)—179.8(4)°. As anticipated, the tungsten atom carries the η-C_5Me_5 group. The Fe–W distance [2.605(1) Å] is somewhat shorter than that in [FeW{μ-C(C_6H_4Me-4)C(Me)C(Me)}$(CO)_5$(η-C_5H_5)] [2.720(1) Å][9] with which it is perhaps best compared, because of a degree of similarity in the bridge systems. An *X*-ray diffraction study has not been carried out on (**2**), and hence the Fe–W separation for this species cannot be compared with that of (**5**). However, in the 32-valence electron complex [FeW(μ-CR)$(CO)_5${HB$(pz)_3$}][3b] the Fe–W distance is 2.612(2) Å, somewhat longer than in (**5**). Nevertheless, in the latter both metal centres attain 18-electron shells (*i.e.* it is a 34-

Table 3. Selected internuclear distances (Å) and angles (°) for $[\mathrm{FeW}\{\mu\text{-C}(\mathrm{C_6H_4Me\text{-}4})\mathrm{C(O)O}\}(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5Me_5})]$ (**5**)

W–Fe	2.605(1)	W–C(7)	2.171(4)	Fe–C(7)	2.054(4)	C(6)–O(6)	1.216(5)
W–C(1)	1.982(4)	Fe–C(3)	1.812(5)	Fe–O(7)	2.007(3)	C(7)–C(111)	1.488(5)
W–C(2)	2.018(4)	Fe–C(4)	1.743(5)	C(6)–O(7)	1.429(5)	Fe $\cdots$ C(6)	2.380(3)
W–O(7)	2.128(3)	Fe–C(5)	1.828(3)	C(6)–C(7)	1.433(5)	W $\cdots$ C(6)	2.609(3)
C≡O(av.)	1.138	W–η-$\mathrm{C_5Me_5}$(av.)	2.337				
Fe–C(7)–W	76.1(2)	C(7)–C(6)–O(7)	100.1(3)	C(6)–O(7)–W	92.2(2)	Fe–C(7)–C(111)	129.3(3)
Fe–C(7)–C(6)	84.0(2)	C(7)–C(6)–O(6)	139.5(4)	C(6)–O(7)–Fe	85.9(2)	W–C(7)–C(111)	136.7(3)
C(6)–C(7)–W	90.4(2)	O(7)–C(6)–O(6)	120.4(4)	W–O(7)–Fe	78.0(1)	C(6)–C(7)–C(111)	122.8(5)
Fe–W–O(7)	48.9(1)	Fe–W–C(1)	85.6(2)	W–Fe–O(7)	53.1(1)	W–Fe–C(4)	105.6(2)
Fe–W–C(7)	49.9(1)	Fe–W–C(2)	79.7(2)	W–Fe–C(7)	54.0(1)	W–Fe–C(5)	108.3(2)

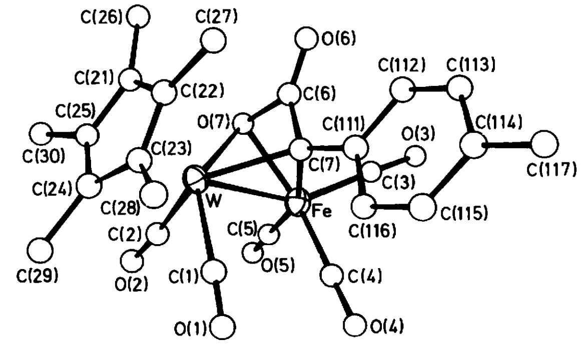


Figure. The molecular structure of $[\mathrm{FeW}\{\mu\text{-C}(\mathrm{C_6H_4Me\text{-}4})\mathrm{C(O)O}\}(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5Me_5})]$ (**5**) with the crystallographic numbering scheme

valence-electron species), assuming the oxo bridge acts as a three-electron donor to the FeW system.

The bridging ligand in (**5**) results from a coupling of alkylidyne, CO, and O groups, a process not previously observed. Formation of (**5**) from (**2**) is not stoicheiometric. However, as mentioned earlier, compound (**2**) scavenges CO to give (**3**), which might then react with oxygen. Moreover, we have recently found[10] that $[\mathrm{FeMo}(\mu\text{-CR})(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})]$, a complex related to (**3**), readily reacts stoicheiometrically with oxygen to give $[\mathrm{FeMo}\{\mu\text{-C}(\mathrm{C_6H_4Me\text{-}4})\mathrm{C(O)O}\}(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$, a species structurally analogous to (**5**).

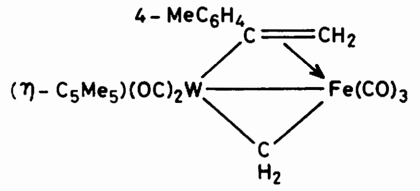
The C(7)C(6)O(6)O(7) fragment in (**5**) is essentially planar [maximum deviation is 0.012(3) Å for C(6)]. The C(6) atom is in a distorted trigonal planar environment with C(7)–C(6)–O(6) 139.5(4), O(7)–C(6)–O(6) 120.4(4), and O(7)–C(6)–C(7) 100.1(3)°. The C(6)–O(6) distance [1.216(5) Å] is typically 'ketonic', and in accord with this result the i.r. spectrum of (**5**) shows bands at 1 705 and 1 685 $\mathrm{cm^{-1}}$. The oxygen atom O(7) asymmetrically bridges the Fe–W bond [Fe–O(7) 2.007(3) and W–O(7) 2.128(3) Å], which is not surprising in view of the different radii of iron and tungsten, 1.17 and 1.30 Å, respectively. The Fe–W vector lies at an angle of 94.3° to the mean plane of C(7)C(6)O(6)O(7), *i.e.* is essentially perpendicular to this plane. The Fe $\cdots$ C(6) and W $\cdots$ C(6) contact distances are 2.380(3) and 2.609(3) Å, respectively, and this may reflect weak interactions.

In view of the reaction of (**2**) with oxygen, the reaction with sulphur was next investigated. Treatment of (**2**) with sulphur in light petroleum at low temperatures afforded the orange complex $[\mathrm{FeW}(\mu\text{-SCR})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5Me_5})]$ (**6**), characterised by the data given in Tables 1 and 2. Compound (**6**) is structurally similar to $[\mathrm{FeMo}(\mu\text{-SCR})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$ which has been shown by *X*-ray diffraction to contain the tranversely bridging thioacyl ligand $\mathrm{SCC_6H_4Me\text{-}4}$.[10] The spectroscopic data for the two compounds are similar. The compound $[\mathrm{FeMo}(\mu\text{-SCR})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$ was prepared by treating $[\mathrm{FeMo}(\mu\text{-CR})(\mathrm{CO})_6(\eta\text{-}\mathrm{C_5H_5})]$ with sulphur, but the complex $[\mathrm{FeMo}\{\mu\text{-C(R)C(O)S}\}(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$ is also formed in this reaction. The latter is structurally akin to (**5**), but nevertheless in the reaction of (**2**) with sulphur there was no evidence for formation of the sulphur-containing compound $[\mathrm{FeW}\{\mu\text{-C(R)C(O)S}\}(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5Me_5})]$.

We have also studied the reaction of (**2**) with diazomethane in the expectation that this reagent would provide a source of $\mathrm{CH_2}$ groups for coupling with the μ-CR ligand in the iron–tungsten compound. Carbon–carbon bond formation *via* coupling of μ-CR (R = $\mathrm{C_6H_4Me\text{-}4}$ or Me) and $\mathrm{CH_2}$ groups in heteronuclear dimetal compounds has been demonstrated previously with the species $[\mathrm{TiW}(\mu\text{-CR})(\mu\text{-CO})(\mathrm{CO})(\eta\text{-}\mathrm{C_5H_5})_3]$ (R = $\mathrm{C_6H_4Me\text{-}4}$) and $[\mathrm{PtW}(\mu\text{-CR})(\mathrm{CO})_2(\mathrm{PMe_3})_2(\eta\text{-}\mathrm{C_5H_5})]$ (R = $\mathrm{C_6H_4Me\text{-}4}$ or Me) and the reagent $[\overline{\mathrm{Ti}\{\mathrm{Cl(AlMe_2)}}\mathrm{CH_2}\}(\eta\text{-}\mathrm{C_5H_5})_2]$.[11] The products of these reactions are dimetal compounds with μ-σ:η-$\mathrm{C(R){=}CH_2}$ ligands σ bonded to titanium or platinum, and π bonded to tungsten.

It was found that the nature of the products obtained by treating (**2**) with $\mathrm{CH_2N_2}$ depends markedly on the reaction conditions. Reactions involving excess of $\mathrm{CH_2N_2}$ with (**2**) in $\mathrm{Et_2O}$ at *ca.* −20 °C give the dark green complex $[\mathrm{FeW}\{\mu\text{-C(R)}{=}\mathrm{CH_2}\}(\mu\text{-CH_2})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5Me_5})]$ (**7**). This product, data for which are given in Tables 1 and 2, is structurally similar to $[\mathrm{FeMo}\{\mu\text{-C(R)}{=}\mathrm{CH_2}\}(\mu\text{-CH_2})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5H_5})]$ which has been characterised by an *X*-ray diffraction study.[10] The n.m.r. data for (**7**) are in accord with the structure shown. In the ^{1}H n.m.r. spectrum peaks for the μ-$\mathrm{CH_2}$ group occur at δ 1.34 [d, 1 H, *J*(HH) 4] and 4.04 [d, 1 H, *J*(HH) 4 Hz], and signals for the geminal hydrogens of the μ-$\mathrm{C(R)}{=}\mathrm{CH_2}$ fragment are seen as singlets at δ 1.87 and 3.55. The absence of H–H coupling on the $\mathrm{C{=}CH_2}$ resonances is as expected.[12] In the ^{13}C-{^{1}H} n.m.r. spectrum of (**7**) the resonance for μ-*C*(R)=$\mathrm{CH_2}$ (δ 181.4 p.p.m.) shows ^{183}W–^{13}C coupling (67 Hz), as expected for this nucleus being σ bonded to the tungsten. Moreover, the μ-$\mathrm{CH_2}$ resonance at 89.9 p.p.m. also shows ^{183}W satellite peaks [*J*(WC) 58 Hz], but that for the μ-C(R)=*C*$\mathrm{H_2}$ group (δ 74.2 p.p.m.) does not. A ^{13}C spectrum (measured at −30 °C) confirmed these assignments. The signals at δ 74.2 and 89.9 p.p.m. were apparent triplets with *J*(HC) 156 and 143 Hz, respectively, while that at 181.4 p.p.m. remained a singlet.

If the reaction between (**2**) and $\mathrm{CH_2N_2}$ is carried out under conditions whereby the reactants are mixed slowly at −20 °C and only one equivalent of diazomethane is used, the major product is $[\mathrm{FeW}\{\mu\text{-}trans\text{-}\mathrm{CH{=}C(H)R}\}(\mu\text{-CO})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5Me_5})]$ (**8**), together with an inseparable mixture of (**7**) and $[\mathrm{FeW}\{\mu\text{-}trans\text{-}\mathrm{CH{=}C(H)R}\}(\mu\text{-CH_2})(\mathrm{CO})_5(\eta\text{-}\mathrm{C_5Me_5})]$ (**9**). As expected for the structure proposed, the i.r. spectrum of (**8**) shows a band at 1 742 $\mathrm{cm^{-1}}$, attributable to the μ-CO group. The latter in the ^{13}C-{^{1}H} n.m.r. spectrum (Table 2) shows a characteristic peak at δ 281.6 p.p.m. The remaining CO ligands



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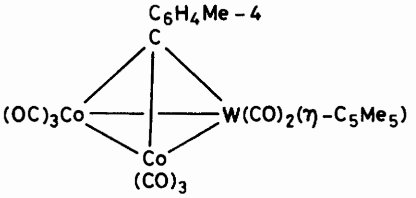

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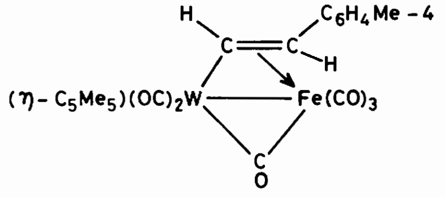

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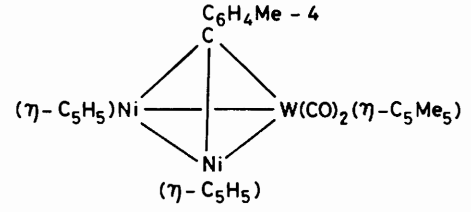

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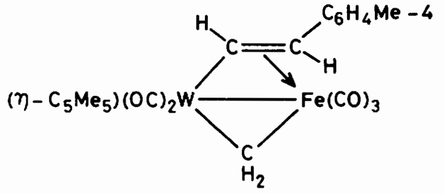

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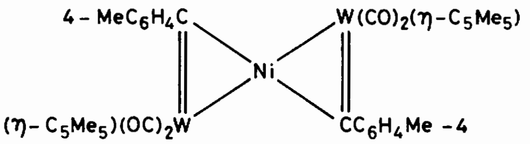


(12)

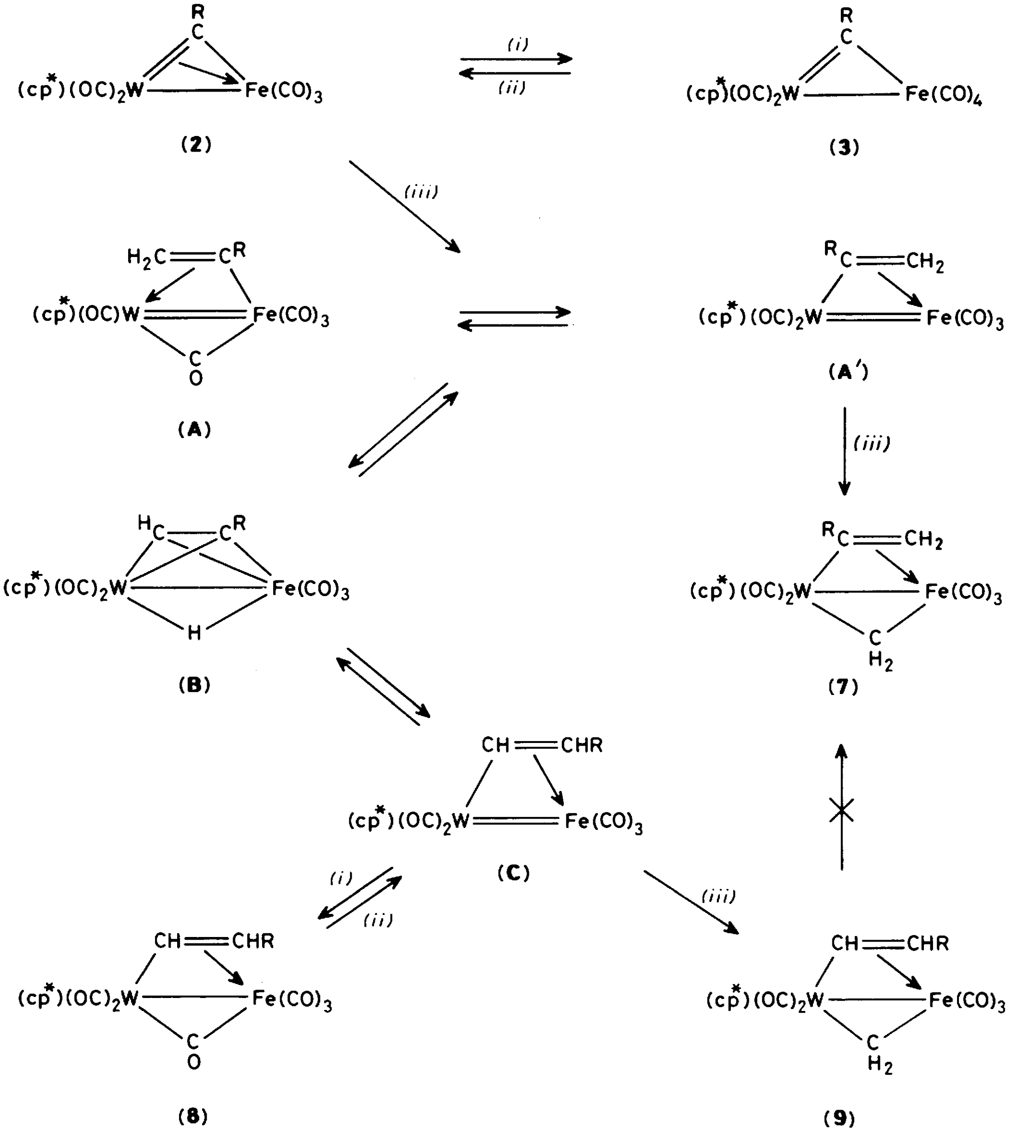
give rise to resonances at 223.0, 220.5 (WCO) and 213.0 [br, $Fe(CO)_3$]. Signals at δ 120.4 [*J*(WC) 58 Hz] and 101.4 p.p.m. may be assigned to the μ-*C*H=C(H)R and μ-CH=*C*(H)R groups, respectively. The ^1H n.m.r. spectrum of (**8**) was especially informative in that the two resonances for the μ-CH=CH fragment at δ 3.85 and 8.14 were doublets with *J*(HH) = 13 Hz, a value diagnostic for the two protons being *trans* to one another.[12]

The n.m.r. spectra of (**9**) are also in excellent agreement with the structure proposed. In the ^1H n.m.r. spectrum the *trans*-CH=C(H)R group reveals itself with two signals at δ 4.17 and 8.30, both doublets with *J*(HH) 14 Hz. The inequivalent protons of the μ-CH_2 ligand occur as doublets [*J*(HH) 4 Hz] at δ 1.87 and 4.18. In the ^{13}C-{^1H} n.m.r. spectrum there are signals at δ 134.8 [μ-*C*H=C(H)R, *J*(WC) 62], 99.6 [μ-CH=*C*(H)R], and 88.2 p.p.m. [μ-CH_2, *J*(WC) 61 Hz], as expected for the bridge systems. In a fully coupled ^{13}C spectrum (400 MHz), the resonances at δ 134.8 and 99.6 p.p.m. are doublets with *J*(HC) 140 and *ca.* 150 Hz, respectively. The resonance at 88.2 p.p.m. is an apparent triplet [*J*(HC) 139 Hz] in the coupled spectrum.

The mode of formation of compounds (**7**)—(**9**) is of interest. It was found possible to reverse the pathway to (**8**) since treatment of the latter with excess of CH_2N_2 slowly afforded a mixture (*ca.* 1:4) of (**7**) and (**9**). It was also observed that solutions containing (**9**) do not isomerise to (**7**). Possible pathways to (**7**)—(**9**) are indicated in Scheme 2. The addition of CH_2 to (**2**) to give the intermediate (**A**) has precedent in our earlier work with μ-CR bridged Ti–W and Pt–W species.[11] The interconversion between (**A**) and (**A′**) involving pivoting of a vinyl group at a dimetal centre is well established,[12] and would be facilitated in 32-valence electron dimetal species. In reactions involving rapid addition of excess of CH_2N_2 to (**2**), formation of (**7**) *via* (**A′**) would be expected to be favoured as found experimentally. With very slow addition of only one equivalent of CH_2N_2 to (**2**) it is possible that intermediates (**A**) or (**A′**) proceed to (**8**) *via* (**B**) and (**C**). The final step (**C**) $\longrightarrow$ (**8**) requires capture of a CO molecule which is likely in the absence of CH_2. In the presence of the latter, compound (**9**) might form. As mentioned earlier, the synthesis of (**8**) is accompanied by the appearance of small amounts of (**7**) and (**9**). In Scheme 2 the transformation of (**A**) or (**A′**) into (**8**) or (**9**) invokes the intermediacy of a hydrido- and alkyne-bridged Fe–W species (**B**), a step for which there is also precedent.[13]

In order to extend the use of (**1**) as a building block for the synthesis of compounds with heteronuclear metal–metal bonds we have studied its reactions with the compounds $[Co_2(CO)_8]$ and $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$. Mixtures of (**1**) and $[Co_2(CO)_8]$ react rapidly in light petroleum at room temperature to give the green trimetal compound $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5Me_5)]$ (**10**) in high yield. Examination of the spectroscopic properties of this compound revealed that it was formed as a mixture of two isomers in *ca.* 5:1 proportions, based on peak intensities in the n.m.r. spectra. In Table 2 resonances measured at −80 °C for the major isomer are listed, from which it will be seen that the ^{13}C-{^1H} n.m.r. spectrum shows the characteristic signal for the μ_3-C nucleus at δ 254.0 p.p.m. For the minor isomer, also at −80 °C, this peak is at 270.2 p.p.m., with other resonances at 211.6 [2 × CO, *J*(WC) 167 Hz], 203.2 (6 × CO), 156.6, 135.4, 127.2, 127.0 (C_6H_4), 100.7 (C_5Me_5, *C*), 20.3 (Me-4), and 10.6 p.p.m. (C_5*Me*$_5$). When measured at room temperature some signals become broad, coalesce, or disappear, indicating a rapid interconversion between the isomers on the n.m.r. time-scale.

The two isomers of (**10**) probably involve alternative orientations of the $W(CO)_2(\eta\text{-}C_5Me_5)$ fragment with respect to an axis through the tungsten and the mid-point of the triangle formed by $\mu_3\text{-}CCo_2$.[14] We have previously prepared related dicobalttungsten compounds $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$[14] and $[Co_2W(\mu_3\text{-}CR)(CO)_8\{HB(pz)_3\}]$,[3a] as well as the dicobaltmolybdenum complex $[Co_2Mo(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$.[15] Although the n.m.r. data for these species did not reveal the existence of isomers, the i.r. spectra of the three complexes show more than the expected number of CO stretching bands for the



Scheme 2. cp* = η-C_5Me_5, R = C_6H_4Me-4; (*i*) +CO, (*ii*) −CO, (*iii*) CH_2N_2

presence in solution of a single species. Hence for these compounds their rotational isomers must be interconverting rapidly on the n.m.r. time-scale. It is noteworthy that the i.r. spectrum of (**10**) (Table 1) shows nine bands in the CO stretching region, more absorptions than expected based on the symmetrical structure established for $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ by *X*-ray diffraction.[14] The observation of isomers for (**10**) *via* measurement of a limiting low-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum is probably a consequence of the presence of the more sterically demanding η-C_5Me_5 group.

We have previously shown that reactions between the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ afford the dinickeltungsten compound $[Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3]$, together with the alkyne-bridged ditungsten complex $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$. The latter results from a nickel-catalysed dimerisation of the *p*-tolylmethylidyne tungsten compound.[16] It was therefore of interest to investigate the reaction between (**1**) and $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$. In toluene at 70 °C, these reactants afford a chromatographically separable mixture of $[Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$ (**11**) and the previously reported compound $[NiW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (**12**).[17] Reactions between (**1**) and $[Ni(\eta\text{-}C_5H_5)_2]$ afford the same two products. Data for (**11**) are given in Tables 1 and 2, and are in agreement with the structure proposed. Formation of (**12**) was unexpected, since it involves displacement of C_5H_5 and CO groups from $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ or C_5H_5 from $[Ni(\eta\text{-}C_5H_5)_2]$. However, loss of C_5H_5 ligands from cyclopentadienylnickel compounds is not without precedent,[18] and in the present work evidently reflects the more powerful bonding properties of (**1**). Interestingly, in the reaction between (**1**) and $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ there was no evidence for the formation of $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5Me_5)_2]$, contrasting with the analogous reaction involving $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ which affords $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$.[16]

The results described in this paper show that compound (**1**) is likely to be a useful precursor to many other complexes. Formation of the unsaturated complex (**2**) is of considerable interest, as are its reactions with oxygen, sulphur, and diazomethane. The syntheses of (**5**) and (**6**) demonstrate new

C–C, C–O, and C–S bond-forming reactions at a dimetal centre of a kind recently observed also with $[\mathrm{FeMo(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)}]$.[10] Formation of complexes (**7**) and (**9**) involve addition of two methylene groups to a dimetal centre for which there are very few previous examples.[19] Similar chemistry seems unlikely to be developed with $[\mathrm{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)}]$ in view of the thermal instability of the $\eta\text{-}\mathrm{C_5H_5}$ analogues of (**2**) and (**3**).[3b,8] However, both (**1**) and $[\mathrm{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)}]$ are useful precursors to trimetal compounds with capping tolylmethylidyne ligands as illustrated for (**1**) in the synthesis of (**10**) and (**11**), and the recently reported $[\mathrm{Rh_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2(\eta\text{-}C_5Me_5)}]$.[15]

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free atmosphere. Chromatographic separations were carried out on 3 × 20 cm columns, packed with Brockman activity II alumina, unless otherwise stated. The reagent $\mathrm{K(C_5Me_5)}$ was prepared by treating KH, suspended in thf, with $\mathrm{C_5Me_5H}$ at room temperature. The compounds $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4}]$[20] and $[\mathrm{Fe(CO)_3(\eta\text{-}C_8H_{14})_2}]$[6] were prepared as described elsewhere. The instrumentation used has been described in previous papers in this series. Analytical data for the new compounds are given in Table 1.

Synthesis of $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)}]$.—The compound $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4}]$ (9.13 g, 23 mmol) in thf (200 cm^3) at −20 °C was treated with solid $\mathrm{K(C_5Me_5)}$ (3.95 g, 23 mmol), and the mixture was stirred for 15 min. An i.r. spectrum of a sample revealed bands at 2 033, 1 971, and 1 896 cm^{-1}. The absorption at 2 033 cm^{-1} corresponded to the presence of some unreacted $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4}]$ and so a suspension of $\mathrm{K(C_5Me_5)}$ in thf was added slowly until the band disappeared. The total amount of $\mathrm{K(C_5Me_5)}$ used in the reaction was 4.7 g (1.2 equivalents). Solvent was removed *in vacuo* at 0 °C, and the dark red solid was extracted with light petroleum–$\mathrm{CH_2Cl_2}$ (*ca.* 3 × 200 cm^3, 4:1), and the extracts passed through an alumina column (3 × 10 cm). Reduction in volume *in vacuo*, with cooling to *ca.* −20 °C, produced deep red crystals which were isolated and dried after removal of solvent with a syringe. Further reduction in volume of the mother-liquor and cooling produced a second batch of red *crystals* of $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)}]$ (**1**) (total yield 9.8 g).

Preparation of the Complexes $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)}]$, $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5Me_5)}]$, and $[\mathrm{Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)}]$.—(*i*) A suspension of $[\mathrm{Fe(CO)_3(\eta\text{-}C_8H_{14})_2}]$ (0.55 g, 1.5 mmol) in hexane (10 cm^3) at −50 °C was treated with (**1**) (0.65 g, 1.36 mmol), dissolved in the same solvent (20 cm^3). The mixing of these reagents was done slowly, so as to maintain the temperature of *ca.* −50 °C. The reactants were warmed to *ca.* −40 °C and stirred for 15 h. Solvent was reduced *in vacuo* to *ca.* 3 cm^3, and this residue was chromatographed at −20 °C on a Florisil column (2 × 20 cm). Elution with light petroleum–$\mathrm{Et_2O}$ (2:1) gave a purple eluate which afforded, after removal of solvent *in vacuo*, purple *crystals* of $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)}]$ (**2**) (0.20 g). Elution with $\mathrm{Et_2O}$ removed a black band from which $[\mathrm{Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)}]$ (**4**) (0.04 g) was recovered.

(*ii*) A mixture of $[\mathrm{Fe_2(CO)_9}]$ (0.55 g, 1.50 mmol) and (**1**) (0.73 g, 1.53 mmol) in $\mathrm{Et_2O}$ (25 cm^3) at 10 °C was stirred for 22 h. Solvent was removed *in vacuo*, and the black residue dissolved in the minimum amount of light petroleum–$\mathrm{Et_2O}$ (4:1), and chromatographed on a Florisil column (2 × 40 cm) at 10 °C. Elution with the same solvent mixture gave a trace of unreacted (**1**) followed by brown, purple, and dark brown eluates. Removal of solvent *in vacuo* from these fractions gave *microcrystals* of brown $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5Me_5)}]$ (**3**) (0.19 g), purple $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)}]$ (**2**) (0.24 g), and black $[\mathrm{Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)}]$ (**4**) (0.05 g).

(*iii*) A mixture of $[\mathrm{Fe_2(CO)_9}]$ (2.18 g, 6.0 mmol) and (**1**) (0.96 g, 2.0 mmol) in $\mathrm{Et_2O}$ (25 cm^3) was stirred (15 h) at room temperature. Solvent was removed *in vacuo*, and the residue dissolved in $\mathrm{CH_2Cl_2}$ (10 cm^3) and filtered through an alumina pad (5 cm). The solution was concentrated to *ca.* 2 cm^3 and light petroleum (*ca.* 15 cm^3) added slowly at −30 °C to give black-brown *microcrystals* of $[\mathrm{Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5Me_5)}]$ (**4**) (0.91 g), recrystallised from $\mathrm{CH_2Cl_2}$–light petroleum (1:10).

Reactions of $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)}]$.—(*i*) *With oxygen.* Complex (**2**) was prepared *in situ* in hexane (30 cm^3) at −40 °C, from (**1**) (0.26 g, 0.54 mmol) and $[\mathrm{Fe(CO)_3(\eta\text{-}C_8H_{14})_2}]$ (0.20 g, 0.54 mmol). After warming to −20 °C, the nitrogen atmosphere was replaced by oxygen causing a change in colour from purple to brown in *ca.* 2 min. Solvent was removed *in vacuo* at −20 °C, and the residue dissolved in $\mathrm{CH_2Cl_2}$–light petroleum (5 cm^3, 1:5) and chromatographed. Elution with thf–$\mathrm{CH_2Cl_2}$ (1:10) produced a yellow eluate. Removal of solvent *in vacuo* gave yellow *microcrystals* of $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)O\}(CO)_5(\eta\text{-}C_5Me_5)}]$ (**5**) (0.075 g).

(*ii*) *With sulphur.* A similar procedure involving (**1**) (0.48 g, 0.77 mmol) and excess sulphur (0.032 g, 1 mmol) in light petroleum (30 cm^3) for 24 h gave orange *microcrystals* of $[\mathrm{FeW(\mu\text{-}SCC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)}]\cdot\mathrm{CH_2Cl_2}$ (**6**) (0.17 g), after chromatography with light petroleum–$\mathrm{CH_2Cl_2}$ (4:1) as eluant.

Reactions of $[\mathrm{FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)}]$ *with Diazomethane.*—(*i*) An excess of $\mathrm{CH_2N_2}$ was added (*ca.* 15 min) to an $\mathrm{Et_2O}$ (25 cm^3) solution of (**2**) (0.52 g, 0.84 mmol) at −20 °C, containing CuCl (0.2 g) as catalyst. The mixture changed quickly in colour from purple to green-brown, and after stirring for 2 h removal of solvent *in vacuo* gave a brown residue. The latter was dissolved in the minimum amount (*ca.* 5 cm^3) of light petroleum–$\mathrm{CH_2Cl_2}$ (3:2) and chromatographed at −20 °C. Elution with the same solvent mixture afforded a green eluate. Removal of solvent *in vacuo*, and crystallisation of the residue from $\mathrm{CH_2Cl_2}$–light petroleum (1:6) at *ca.* −78 °C, gave dark green *microcrystals* of $[\mathrm{FeW\{\mu\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(\mu\text{-}CH_2)(CO)_5(\eta\text{-}C_5Me_5)}]$ (**7**) (0.26 g). The ^{1}H n.m.r. spectrum of the latter revealed the presence of traces of (**9**).

(*ii*) Approximately 1 equivalent of an $\mathrm{Et_2O}$ solution of $\mathrm{CH_2N_2}$ was added slowly (*ca.* 1 h) in small portions to an $\mathrm{Et_2O}$ (25 cm^3 at −20 °C) solution of (**2**) (0.48 g, 0.78 mmol), with CuCl (0.2 g) as catalyst. The reaction was monitored by i.r., and addition of $\mathrm{CH_2N_2}$ was stopped as soon as all CO absorptions attributable to (**2**) had disappeared. At this stage CO stretching bands due to (**7**) and (**9**) were seen. Solvent was removed *in vacuo*, and the green-brown residue dissolved in light petroleum–$\mathrm{CH_2Cl_2}$ (*ca.* 5 cm^3, 3:2) and chromatographed at −20 °C. Elution with the same solvent mixture gave a small amount of a light green band followed by a larger quantity of a darker green eluate. Solvent was removed *in vacuo* from both fractions. The minor fraction was shown by n.m.r. spectroscopy to be a *ca.* 2:3 mixture of (**7**) and (**9**). The latter gave, after crystallisation from $\mathrm{CH_2Cl_2}$–light petroleum (1:10), *microcrystals* of green-brown $[\mathrm{FeW\{\mu\text{-}}\mathit{trans}\text{-}\mathrm{CH{=}C(H)C_6H_4Me\text{-}4\}(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5Me_5)}]$ (**8**) (0.25 g).

Preparation of Tungsten–Cobalt and -Nickel Complexes.—(*i*) The compound $[\mathrm{Co_2(CO)_8}]$ (0.33 g, 0.94 mmol) in light petroleum (15 cm^3) was added to (**1**) (0.41 g, 0.85 mmol) in the same solvent (5 cm^3). After stirring for *ca.* 1 h, the solvent was reduced in volume *in vacuo* to *ca.* 10 cm^3, and the mixture cooled to −20 °C, thereby giving green *microcrystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5Me_5)]$ (**10**) (0.50 g).

(*ii*) A mixture of (**1**) (0.50 g, 1.0 mmol) and $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (0.32 g, 1.0 mmol) in toluene (20 cm^3) was heated at 70 °C for 20 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (5 cm^3, 1:5) and chromatographed. Elution with light petroleum gave a green band shown to be $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ by i.r., followed by a green-black eluate. Reduction of solvent volume *in vacuo* to *ca.* 2 cm^3, and cooling to −20 °C gave green-black *crystals* of $[Ni_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)]$ (**11**) (0.15 g). Elution of the column with CH_2Cl_2–light petroleum (1:1) gave a red solution, which on concentration *in vacuo* to *ca.* 2 cm^3 and cooling to −20 °C afforded red *crystals* of the known compound $[NiW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (**12**) (0.30 g, 28%), identified spectroscopically.[17]

Crystal Structure Determination of Compound (**5**).—Data were collected at ambient temperature on an orange prism (*ca.* 0.18 × 0.44 × 0.42 mm), using an Enraf-Nonius CAD-4F diffractometer in the range $3 \leqslant 2\theta \leqslant 60°$, with a θ—2θ scan mode. Three reflections ($\overline{17}$ 1 $\bar{4}$, 10 2 $\bar{7}$, $\bar{5}$ 5 2) were used as checks, and were measured every 2 h during data collection. These showed no significant decay. Of the 6 869 independent reflections measured, 5 569 satisfied the criterion $I \geqslant 2.5\sigma(I)$, and only these were used in the final stages of refinement. Intensities were corrected for Lorentz and polarisation effects. A Gaussian grid analytical absorption correction was applied,[21] with 1 056 grid points and a crystal volume of 0.043 4 mm^3, defined by the zones ⟨1 0 1⟩, ⟨1 1 $\bar{1}$⟩, ⟨0 1 0⟩, and ⟨1 0 0⟩. Maximum and minimum transmission coefficients were 0.395 and 0.154, respectively.

Table 4. Atomic positional parameters (fractional co-ordinates $\times 10^5$) for (**5**)

Atom	*x*	*y*	*z*
W	14 821(1)	7 379(1)	38 457(1)
Fe	17 781(2)	27 618(5)	30 375(3)
O(1)	19 669(12)	21 709(37)	54 909(20)
O(2)	24 257(11)	−4 981(35)	37 573(26)
O(3)	15 474(14)	49 889(37)	18 122(23)
O(4)	22 102(12)	46 343(36)	43 296(24)
O(5)	26 018(12)	18 501(42)	24 956(25)
O(6)	7 084(10)	21 378(30)	20 181(17)
O(7)	13 899(8)	11 928(24	25 391(15)
C(1)	17 932(13)	16 648(41)	48 758(25)
C(2)	20 918(13)	158(40)	37 700(26)
C(3)	16 292(16)	41 101(39)	22 617(27)
C(4)	20 398(13)	38 904(42)	38 090(27)
C(5)	22 890(15)	21 938(45)	27 027(28)
C(6)	10 256(11)	20 948(34)	25 881(21)
C(7)	11 699(11)	26 802(32)	34 046(19)
C(21)	9 260(13)	−9 688(34)	4 711(23)
C(22)	7 682(12)	−140(37)	40 229(23)
C(23)	10 616(13)	−645(39)	48 019(21)
C(24)	14 046(14)	−10 798(40)	47 288(24)
C(25)	13 151(13)	−16 013(35)	39 091(25)
C(26)	6 900(17)	−12 983(48)	25 932(27)
C(27)	3 401(15)	7 781(42)	38 520(35)
C(28)	9 758(20)	6 085(51)	55 985(28)
C(29)	17 366(19)	−16 376(59)	54 432 34)
C(30)	15 410(17)	−28 006(40)	35 587(38)
C(111)	9 209(11)	37 947(34)	37 536(21)
C(112)	5 441(15)	44 048(39)	32 786(26)
C(113)	3 199(14)	54 377(40)	36 252(26)
C(114)	4 516(13)	59 074(33)	44 358(26)
C(115)	8 230(15)	53 097(43)	49 076(25)
C(116)	10 545(14)	42 613(37)	45 858(25)
C(117)	1 992(16)	70 275(42)	47 992(31)

Crystal data. $C_{24}H_{22}FeO_7W$, $M = 662.1$, monoclinic, $a = 30.624(6)$, $b = 9.675(2)$, $c = 16.174(3)$ Å, $\beta = 100.20(2)°$, $Z = 8$, $U = 4\,716(3)$ Å^3, $D_c = 1.86$ g cm^{-3}, $F(000) = 2\,576$, space group $C2/c$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 56.35$ cm^{-1}.

The tungsten atom was located from a Patterson synthesis, with subsequent non-hydrogen atoms located from successive electron-density difference Fourier syntheses. Hydrogen atoms were included at idealised positions (methyl C–H 1.084 and aryl C–H 1.073 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters, with hydrogen atoms being assigned a fixed isotropic thermal parameter of 0.05 Å^2. Initial refinement was by blocked-diagonal least squares, with a final three cycles of full-matrix least squares. This procedure resulted in convergence at *R* 0.027 (*R′* 0.040), where $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R' = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, and $|\Delta F| = ||F_o| - |F_c||$. A weighting scheme of the form $w = [\sigma^2(F_o)]^{-1}$, where $\sigma(F_o)$ is the estimated error in $|F_o|$ based on counting statistics only, was used and judged satisfactory (maximum shift/e.s.d. for last cycle 0.423, average shift/e.s.d. for last cycle 0.0545). A final electron-density difference synthesis showed no peaks > 2.15 or < -1.46 e Å^{-3}. Scattering factors and corrections for anomalous dispersion were from ref. 22. All calculations were performed on a GOULD-SEL 32/27 computer with the GX system of programs.[21] The atomic co-ordinates for (**5**) are given in Table 4.

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