Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 29.[1] Synthesis of Rhenium–Tungsten Compounds; *X*-Ray Crystal Structures of $[ReW_2(\mu\text{-}Br)(\mu\text{-}L)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)_2]$ (L = CO or O) *

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The compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) reacts with the rhenium compounds $[Re_2(CO)_{10}]$, $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$ (thf = tetrahydrofuran), and $[ReBr(NCMe)_2(CO)_3]$ to afford, respectively, the cluster complexes $[Re_2W(\mu_3\text{-}CR)(CO)_{10}(\eta\text{-}C_5H_5)]$, $[Re_2W(\mu\text{-}Br)_2(\mu_3\text{-}CR)(CO)_7(\eta\text{-}C_5H_5)]$, and $[ReW_2(\mu\text{-}Br)(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$. The latter compound has been structurally characterised by an *X*-ray diffraction study. A ReW_2 triangle of metal atoms [W–W 2.620(1), Re–W 2.867(1) and 2.912(1) Å] is asymmetrically capped by a CC_6H_4Me-4 ligand [μ_3-C–Re 2.248(12), μ_3-C–W 2.035(14) and 2.050(11) Å], and is edge-bridged by CC_6H_4Me-4, Br, and CO groups, with the latter being asymmetrically bound [W–C–O 155(1)°]. The two tungsten atoms carry cyclopentadienyl ligands, and the rhenium atom three terminally bound CO groups. The compound $[ReW_2(\mu\text{-}Br)(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$ readily oxidises in air to afford the oxo-bridged species $[ReW_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)_2]$ which was also characterised by *X*-ray diffraction. This complex is structurally similar to its precursor but with the significant differences of the μ-CO ligand being replaced by μ-O and the capping CC_6H_4Me-4 being very asymmetrically bound to the metal triangle [μ_3-C–Re 2.515(20), μ_3-C–W 2.017(19) and 2.114(18) Å]. In addition to reacting with oxygen, the compound $[ReW_2(\mu\text{-}Br)(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$ reacts with sulphur. The nature of the product is described, and the n.m.r. spectra (^1H and $^{13}C\text{-}\{^1H\}$) of all the new compounds are reported and discussed in relation to their established or proposed structures.

In a variety of reactions using the tolylmethylidynetungsten compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) we have described the preparation of trimetal cluster complexes with core structures $M_2W(\mu_3\text{-}CR)$ (*closo* with M = Mo, W, Fe, Co, or Rh; butterfly with Pt or Cu), $MM'W(\mu_3\text{-}CR)$ (*closo* with M = Fe, M′ = Co, Rh, or Pt; butterfly with M = Pt, M′ = Cu), $MW_2(\mu\text{-}CR)_2$ (M = Ni, Pd, Pt, Ag, or Au), $MW_2[\mu_3\text{-}(\eta^2\text{-}\perp)RC_2R]$ (M = Fe), and $MW_2[\mu_3\text{-}(\eta^2\text{-}\parallel)\text{-}RC_2R]$ (M = Ru or Os).[1,2] However, we have not as yet described trimetal clusters derived from $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and involving the elements manganese or rhenium. In this paper we report some cluster compounds with rhenium–tungsten bonds and bridging μ-CR and μ_3-CR groups.

Results and Discussion

Based on the isolobal model,[3] and our previous synthesis of the cluster compound $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4),[4] the trimetal complex $[Re_2W(\mu_3\text{-}CR)(CO)_{10}(\eta\text{-}C_5H_5)]$ would be expected to exist because of the relationships (i). Unlike $[Co_2(CO)_8]$, however, decarbonyldirhenium

$$\begin{matrix} \mathrm{Co(CO)_3} & \xleftrightarrow[\circ]{} & \mathrm{CR} & \xleftrightarrow[\circ]{} & \mathrm{Re(CO)_4} \\ \mathrm{ML_3}\ (d^9) & & & & \mathrm{ML_4}\ (d^7) \end{matrix} \qquad \text{(i)}$$

is relatively inert. For example, it does not readily react with alkynes as does the dicobalt species. Since there is a similarity between the reactivity patterns of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $RC\equiv CR$ towards metal carbonyls, we were not surprised to find that no reaction took place between $[Re_2(CO)_{10}]$ and the tolylmethylidynetungsten compound when heated together in toluene. However, a reaction occurred between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Re_2(CO)_{10}]$ at room temperature in the presence of Me_3NO, using tetrahydrofuran as solvent. The ability of the amine oxide to remove CO groups from metal carbonyls is well known. The product proved to be the desired cluster compound (1), data for which are given in Tables 1 and 2. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum the complex has the expected and characteristic [5,6] resonance for the μ_3-C group at δ 311.5 p.p.m. Signals for CO groups occur at δ 216.4 and 199.8 p.p.m., and may be assigned to the $W(CO)_2$ and $Re(CO)_4$ groups, respectively, on the basis of their relative intensities. The observation of one resonance for CO ligands on rhenium implies site exchange at this metal centre for these groups on the n.m.r. time-scale. Compound (1) belongs to the growing class of cluster compound, mentioned earlier, with a *closo* tetrahedrane $\mu_3\text{-}CM_2W$ core.

The investigation was extended to reactions between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and the two dirhenium compounds $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$ (thf = tetrahydrofuran) [7] and $[ReBr(NCMe)_2(CO)_3]$.[8] These species were chosen because they contain labile ligands, thf and MeCN, respectively, and would thus be expected to be more reactive than $[Re_2(CO)_{10}]$.

Refluxing a 1 : 1 mol mixture of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$ in hexane afforded an orange crystalline compound (2) in *ca.* 10% yield. The low yield was due in part to the simultaneous formation of $[Re_2(\mu\text{-}Br)_2(CO)_8]$, probably produced in a side-reaction between $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$ and CO. Data for compound (2) are given in Tables 1 and 2. This species decomposes in solution after several hours. It was not possible to grow crystals for an *X*-ray diffraction study, and hence its structure can only be inferred from the available spectroscopic data, discussed below.

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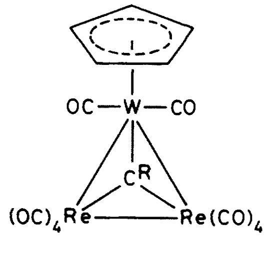
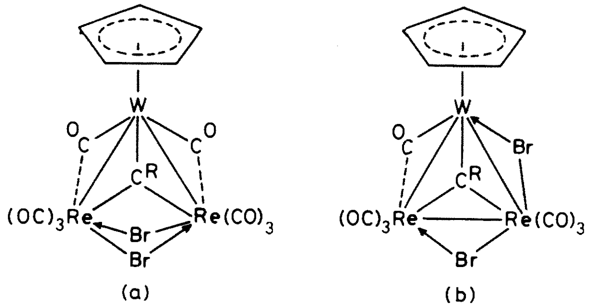
* 1,2-μ-Bromo-1,3-μ-carbonyl- and 1,2-μ-bromo-1,3-μ-oxo-1,1,1-tricarbonyl-2,3-bis(η-cyclopentadienyl)-2,3-μ-*p*-tolylmethylidyne-μ_3-*p*-tolylmethylidyne-*triangulo*-rheniumditungsten.

Supplementary data available (No. SUP 23919, 55 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

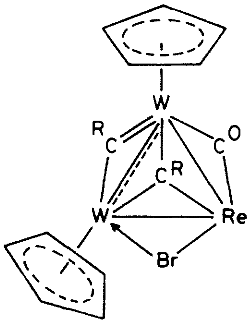


(1)

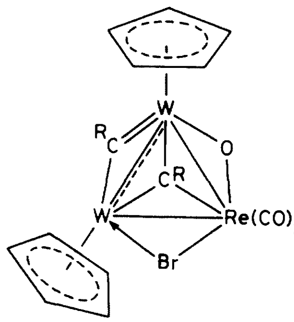


(a) (b)

(2)



(3)



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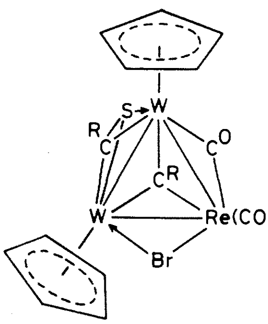


(5)

R = C_6H_4Me-4

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

	M.p. [c]				Analysis (%)		
Complex [b]	(θ_c/°C)	Colour	Yield	$\tilde{\nu}_{max.}$(CO) [d]/cm^{-1}	C	H	Br
(1) $[Re_2W(\mu_3\text{-}CR)(CO)_{10}(\eta\text{-}C_5H_5)]$	110	Purple	12	[e] 2 109w, 2 038w, 2 011s, 2 003s, 1 994w, 1 974m, 1 945w, 1 938(sh), 1 924w	27.1 (27.5)	1.1 (1.2)	
(2b) $[Re_2W(\mu\text{-}Br)_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$	160	Orange	10	2 052m, 2 034s, 1 967(br), 1 929m(br), 1 814(br)	22.9 (22.2)	1.3 (1.1)	14.4 (14.8)
(3) $[ReW_2(\mu\text{-}Br)(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$	226—228	Green	53	2 016s, 1 947m, 1 916m, 1 746w	33.7 (33.3)	2.3 (2.2)	7.5 (7.4)
(4) $[ReW_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)_2]$	240—242	Red	57	2 027vs, 1 949s, 1 912s	32.7 (32.5)	2.3 (2.2)	7.2 (7.5)
(5) $[ReW_2(\mu\text{-}Br)(\mu_3\text{-}CR)(\mu\text{-}SCR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$	272	Brown	28	2 015vs, 1 942s, 1 911s, 1 775m(br)	[f] 32.6 (32.3)	2.3 (2.2)	6.9 (7.2)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] With decomposition. [d] In CH_2Cl_2, unless otherwise stated. [e] In pentane. [f] S, 3.1 (2.9%).

The product of the reaction between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$ might be expected to have structure (2a). The dirhenium precursor does not contain a rhenium–rhenium bond, and is known [7] to react with certain bidentate ligands to give compounds with structures akin to (2a). However, structure (2a) does not accord with the $^{13}C\text{-}\{^1H\}$ n.m.r. data for the product from $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$. Thus, although there is a characteristic signal at δ 312.3 p.p.m. for a triply bridging μ-*C*R group, there are seven peaks due to CO ligands (Table 2), implying a much more asymmetric structure than (2a). For this reason we prefer structure (2b) which has six non-equivalent terminal CO groups and a semi-bridging CO ligand. The resonance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at δ 237.9 p.p.m. is assignable to the semi-bridging carbonyl group, which reveals itself in the i.r. spectrum with a band at 1 814 cm^{-1}. Compound (2b) could form from (2a) by loss of a CO group, with the bromide ligand changing from a Re–Re to a Re–W bridging position.

Based on the reaction of $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$ with bidentate ligands, mentioned above, it seems possible that a species (2a) is the initial product in the reaction with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$. The $ReBr(\mu\text{-}Br)(CO)_3$ fragments present in (2a) are formally ML_5 d^6 species [3] and as such are isolobal with CH_2, which is in turn isolobal with PtL_2 (L = CO or PR_3). A diplatinum complex $[Pt_2W(\mu_3\text{-}CR)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$, isolobal with (2a), has been structurally characterised by *X*-ray crystallography.[9] However, it is not unusual for a product predicted by isolobal considerations to rearrange into a thermodynamically more stable structure.[3,10] Moreover, in (2b) both rhenium fragments are also isolobal with CH, being formally d^7-ML_4 and d^5-ML_5 groups,[3] respectively.

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

Complex [b]	^1H (δ) [c]	^{13}C (δ) [d]
(1)	2.40 (s, 3 H, Me-4), 5.69 (s, 5 H, C_5H_5), 7.11 (m, 4 H, C_6H_4)	311.5 (μ_3-C), 216.4 [WCO, *J*(WC) 175], 199.8 (ReCO), 165.4 [$C^1(C_6H_4)$], 136.7, 128.7, 121.9 (C_6H_4), 92.6 (C_5H_5), 21.4 (Me-4)
(2b)	2.39 (s, 3 H, Me-4), 5.89 (s, 5 H, C_5H_5), 7.16 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[e] 312.3 (μ_3-C), 237.9 (μ-CO), 191.8, 191.4, 191.0, 188.8, 188.7, 188.2 (CO), 158.5 [$C^1(C_6H_4)$], 138.1, 128.8, 121.9 (C_6H_4), 96.7 (C_5H_5), 21.4 (Me-4)
(3)	[e] 2.38 (s, 3 H, Me-4), 2.55 (s, 3 H, Me-4), 5.22 (s, 5 H, C_5H_5), 5.61 (s, 5 H, C_5H_5), 6.87 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 9], 6.87 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7]	[f] 364.9 (μ-C), 305.2 (μ_3-C), 261.1 (μ-CO), 196.5, 194.8, 188.8 (CO), 166.4, 165.4 [$C^1(C_6H_4)$], 135.5, 128.8, 128.0, 122.1 (C_6H_4), 100.6, 97.0 (C_5H_5), 21.1, 20.8 (Me-4)
(4)	2.44 (s, 3 H, Me-4), 2.48 (s, 3 H, Me-4), 5.52 (s, 5 H, C_5H_5), 5.72 (s, 5 H, C_5H_5), 6.78 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 6.91 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7]	341.4 (μ-C), 294.5 (μ_3-CR), 192.7, 188.9, 185.6 (CO), 166.8, 165.8 [$C^1(C_6H_4)$], 135.5, 135.4, 128.7, 128.4, 128.2, 121.7 (C_6H_4), 103.9, 101.6 (C_5H_5), 21.0, 20.7 (Me-4)
(5)	[e] 2.43 (s, 3 H, Me-4), 2.47 (s, 3 H, Me-4), 5.18 (s, 5 H, C_5H_5), 5.60 (s, 5 H, C_5H_5), 6.69—7.25 (m, 8 H, C_6H_4)	[g] 264.6 (μ_3-C), 244.1 (μ-CO), 196.1, 191.3, 190.2 (CO), 166.5, 146.2 [$C^1(C_6H_4)$], 136.1, 133.9 [$C^4(C_6H_4)$], 133.4, 131.4, 129.7 (2 C), 129.2, 128.0, 127.1, 125.1 (C_6H_4), 101.6, 95.9 (C_5H_5), 90.9 (CS), 21.0 (Me-4)

[a] Chemical shifts (δ) in p.p.m., those for ^{13}C to high frequency of $SiMe_4$; coupling constants in Hz. [b] R = C_6H_4Me-4. [c] Measured in CD_2Cl_2 unless otherwise stated. [d] Measured in CD_2Cl_2–CH_2Cl_2 unless otherwise stated. [e] In $CDCl_3$. [f] Spectrum measured at −30 °C. [g] Spectrum measured at −80 °C.

Table 3. Selected internuclear distances (Å) and angles (°) for the complexes [ReW_2(μ-Br)(μ-L)(μ-CC_6H_4Me-4)(μ_3-CC_6H_4Me-4)$(CO)_3$-(η-C_5H_5)$_2$] [L = CO (3) and O (4)]

Complex (3)				Complex (4)			
W(1)–W(2)	2.620(1)	Re–Br	2.643(2)	W(1)–W(2)	2.645(1)	Re–Br	2.644(2)
Re–W(1)	2.867(1)	Re–C(3)	1.934(13)	Re–W(1)	3.004(1)	Re–C(7)	1.877(24)
Re–W(2)	2.912(1)	Re–C(4)	1.905(13)	Re–W(2)	2.871(1)	Re–C(9)	1.916(23)
W(1)–C(1)	2.035(14)	Re–C(5)	1.929(13)	W(1)–C(1)	2.017(19)	Re–C(8)	1.886(24)
W(1)–C(2)	1.954(12)	Re–C(6)	2.424(12)	W(1)–C(2)	1.933(19)	Re–O	2.139(16)
W(1)–Br	2.511(2)	C(3)–O(3)	1.159(16)	W(1)–Br	2.515(3)	C(7)–O(7)	1.161(30)
W(2)–C(1)	2.050(11)	C(4)–O(4)	1.132(17)	W(2)–C(1)	2.114(18)	C(9)–O(9)	1.166(29)
W(2)–C(2)	1.993(12)	C(5)–O(5)	1.155(16)	W(2)–C(2)	2.071(18)	C(8)–O(8)	1.210(29)
W(2)–C(6)	2.034(14)	C(6)–O(6)	1.130(19)	W(2)–O	1.782(13)	C(1) · · · C(2)	2.922
Re–C(1)	2.248(12)	C(1) · · · C(2)	2.907	Re–C(1)	2.515(20)		
Re–W(1)–W(2)	63.9(1)	W(2)–Re–Br	89.1(1)	Re–W(1)–W(2)	60.7(1)	W(2)–Re–Br	86.6(1)
Re–W(1)–Br	58.4(1)	W(1)–Re–C(6)	79.5(3)	Re–W(1)–Br	56.4(1)	W(1)–Re–O	79.0(4)
W(2)–W(1)–Br	89.9(1)	W(2)–Re–C(6)	43.6(3)	W(2)–W(1)–Br	94.4(1)	W(2)–Re–O	38.3(4)
Re–W(1)–C(1)	51.2(3)	Br–Re–C(6)	76.6(4)	Re–W(1)–C(1)	56.0(6)	Br–Re–O	80.9(4)
W(2)–W(1)–C(1)	50.4(3)	W(1)–Re–C(1)	44.9(3)	W(2)–W(1)–C(1)	51.8(5)	W(1)–Re–C(1)	41.7(4)
Re–W(1)–C(2)	108.8(3)	W(2)–Re–C(1)	44.6(3)	Re–W(1)–C(2)	106.0(7)	W(2)–Re–C(1)	45.6(4)
W(2)–W(1)–C(2)	49.1(3)	Br–Re–C(1)	98.9(3)	W(2)–W(1)–C(2)	51.0(5)	Br–Re–C(1)	94.1(4)
Br–W(1)–C(2)	108.0(4)	C(6)–Re–C(1)	88.1(4)	Br–W(1)–C(2)	102.4(8)	O–Re–C(1)	83.9(5)
C(1)–W(1)–C(2)	93.6(5)	Re–C(1)–W(1)	83.9(5)	C(1)–W(1)–C(2)	95.4(7)	Re–C(1)–W(1)	82.3(7)
Re–W(2)–W(1)	62.2(1)	Re–C(1)–W(2)	85.2(4)	Re–W(2)–W(1)	65.9(1)	Re–C(1)–W(2)	76.1(6)
Re–W(2)–C(6)	55.3(3)	W(1)–C(1)–W(2)	79.8(5)	Re–W(2)–O	48.0(5)	W(1)–C(1)–W(2)	79.6(7)
W(1)–W(2)–C(6)	93.0(4)	Re–C(1)–C(31)	127.5(8)	W(1)–W(2)–O	96.0(5)	Re–C(1)–C(31)	122.1(13)
Re–W(2)–C(1)	50.3(3)	W(1)–C(1)–C(31)	130.3(7)	Re–W(2)–C(1)	58.2(5)	W(1)–C(1)–C(31)	136.1(14)
W(1)–W(2)–C(1)	49.8(4)	W(2)–C(1)–C(31)	132.6(9)	W(1)–W(2)–C(1)	48.6(5)	W(2)–C(1)–C(31)	137.8(14)
C(6)–W(2)–C(1)	105.5(5)	W(1)–C(2)–W(2)	83.2(5)	O–W(2)–C(1)	106.3(7)	W(1)–C(2)–W(2)	82.6(7)
Re–W(2)–C(2)	106.0(4)	W(1)–C(2)–C(41)	138.3(8)	Re–W(2)–C(2)	106.8(6)	W(1)–C(2)–C(41)	138.8(13)
W(1)–W(2)–C(2)	47.8(3)	W(2)–C(2)–C(41)	138.1(8)	W(1)–W(2)–C(2)	46.4(5)	W(2)–C(2)–C(41)	138.1(14)
C(6)–W(2)–C(2)	104.2(6)	Re–Br–W(1)	67.5(1)	O–W(2)–C(2)	109.5(8)	Re–Br–W(1)	71.2(1)
C(1)–W(2)–C(2)	91.9(5)	Re–C(6)–W(2)	81.0(5)	C(1)–W(2)–C(2)	88.5(8)	Re–O–W(2)	93.7(6)
W(1)–Re–W(2)	53.9(1)	Re–C(6)–O(6)	123.3(10)	W(1)–Re–W(2)	53.4(1)		
W(1)–Re–Br	54.0(1)	W(2)–C(6)–O(6)	155.3(11)	W(1)–Re–Br	52.4(1)		

If the reaction between [Re_2(μ-Br)$_2$(thf)$_2$(CO)$_6$] and [W(≡CR)$(CO)_2$(η-C_5H_5)] is carried out using an excess of the latter reagent in addition to (2) another complex (3) is produced, albeit in low yield. Experiments established that (3) is not formed by treating (2) with [W(≡CR)$(CO)_2$(η-C_5H_5)]. The nature of compound (3) was clarified when it was found that it could be prepared in good yield by refluxing [ReBr-(NCMe)$_2$(CO)$_3$] with [W(≡CR)$(CO)_2$(η-C_5H_5)] in hexane. Evidently (3) is formed in the reaction between the latter and [Re_2(μ-Br)$_2$(thf)$_2$(CO)$_6$] *via* dissociation of the dirhenium complex.

Compound (3), data for which are given in Tables 1 and 2, was structurally characterized by an *X*-ray diffraction study. The molecule is shown in Figure 1 and selected internuclear separations and angles are listed in Table 3. The structure of (3) is novel in that the ReW_2 metal triangle is edge-bridged by one tolylmethylidyne ligand and triply bridged by another. Although C(2) essentially symmetrically bridges the W(1)–W(2) edge [W(1)–C(2) 1.954(12), W(2)–C(2) 1.993(12) Å], C(1) asymmetrically caps the metal triangle [W(1)–C(1) 2.035(14), W(2)–C(1) 2.050(11), Re–C(1) 2.248(12) Å]. The Re–W(1) edge is bridged by the Br atom [W(1)–Br 2.511(2), Re–Br 2.643(2) Å], whilst the Re–W(2) vector is asymmetrically bridged by a carbonyl ligand [W(2)–C(6)–O(6) 155(1),

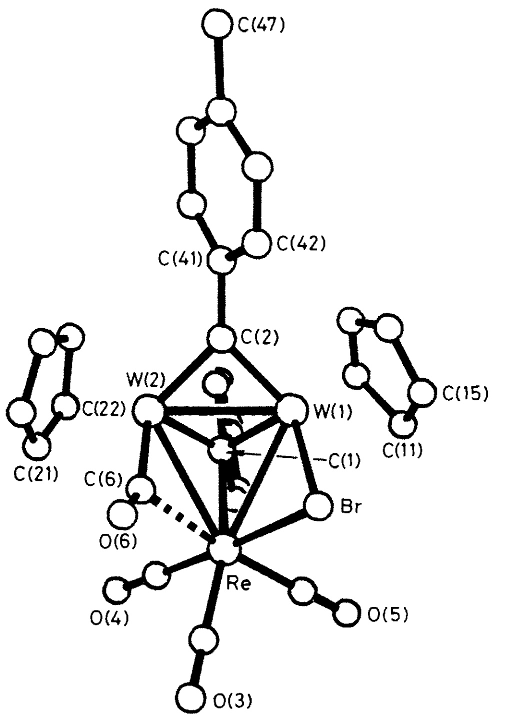
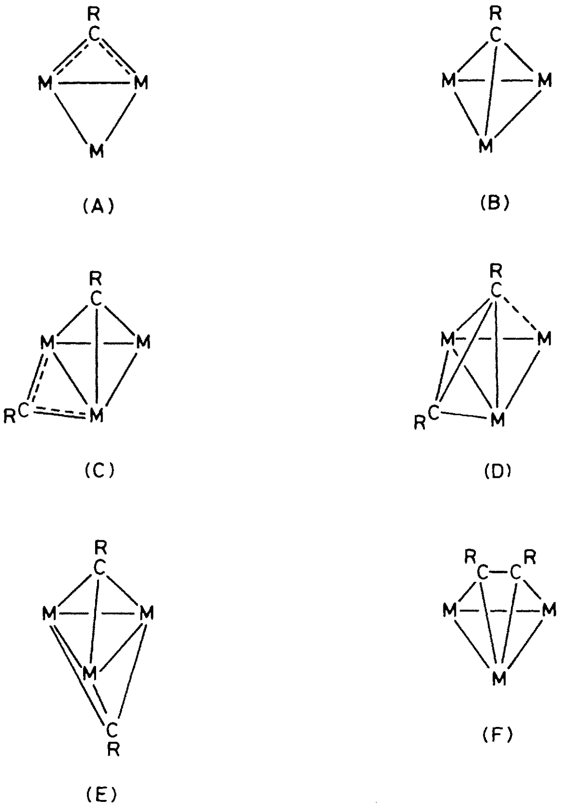


Figure 1. The molecular structure of $[ReW_2(\mu\text{-Br})(\mu\text{-CC}_6H_4Me\text{-}4)(\mu_3\text{-CC}_6H_4Me\text{-}4)(\mu\text{-CO})(CO)_3(\eta\text{-}C_5H_5)_2]$ (3), with the crystallographic numbering scheme



Scheme. Bridging modes of alkylidyne and alkyne ligands in trimetal clusters. Metal atoms are not necessarily of the same element. Representative complexes from recent work are: (A), $[Fe_2W(\mu\text{-CR})(\mu_3\text{-S})(CO)_7(\eta\text{-}C_5H_5)]$;[18] (B) $[Fe_2W(\mu_3\text{-CR})(\mu\text{-CO})(CO)_8(\eta\text{-}C_5H_5)]$;[5] (C) (3) (this work); (D) $[FeW_2(\mu_3\text{-RC}_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$;[5] (E) $[Co_3(\mu_3\text{-CPh})_2(\eta\text{-}C_5H_5)_3]$;[11] (F) $[OsW_2(\mu_3\text{-RC}_2R)(CO)_7(\eta\text{-}C_5H_5)_2]$[16]

Re–C(6)–O(6) 123(1)°]. The rhenium atom carries three terminal CO ligands, and each tungsten is bonded to a cyclopentadienyl ligand.

In the Scheme we have summarised the known bonding modes of alkylidyne and alkyne ligands in trimetal clusters. These clusters may or may not involve metal atoms of the same element. Complex (3) is the first example of a cluster of type (C). In related work we have observed coupling of carbyne groups to give the $\mu_3\text{-}(\eta^2\text{-}\perp)$ and $\mu_3\text{-}(\eta^2\text{-}\|)$ alkynetrimetal clusters (D) and (F), respectively.[2] Vollhardt and co-workers[11] have studied tricobalt complexes with both faces of the metal triangle capped by μ_3-CR ligands [(E) in Scheme]. Evidently skeletal rearrangements occur readily among the core structures (C)—(F), leading to carbon–carbon bond formation or cleavage. These processes may be relevant to the behaviour of carbyne groups on metal surfaces.[11]

The Re–C(1) separation [2.248(12) Å] in compound (3) is *ca.* 0.2 Å longer than the μ_3-C(1)–W separations, suggesting a rather weaker bond. In structures of type (B) and (C) (Scheme) the capping μ_3-CR need not be symmetrically bound to the metal triangle, particularly if different metallic elements comprise the triangle.[12] It is interesting that CO groups can also either symmetrically or asymmetrically bridge metal triangles,[13,14] and as with the carbyne ligands this reflects the mobility of these systems.

Although we have chosen to represent (3) with the edge-bridging μ-CR ligand forming a C=W bond with one tungsten centre, as mentioned above, the C(2)–W distances are essentially the same being similar to those found [1.91(2)—2.025(6) Å] in a range of dimetal compounds having $\overline{W(\mu\text{-CR})M}$ core structures for which carbon–tungsten multiple bonding has been invoked.[15] Complex (3) is a 46-valence-electron cluster, and as such is unsaturated. In accord with this property the W(1)–W(2) distance [2.620(1) Å] is short, perhaps reflecting some multiple-bond character. In the two isomers of the 48-electron clusters $[OsW_2(\mu\text{-RC}_2R)_2(CO)_7(\eta\text{-}C_5H_5)_2]$ the W–W distances are significantly longer at 3.159(2) and 3.017(2) Å.[16] In contrast, in the 46-electron clusters $[FeW_2(\mu_3\text{-RC}_2R)(CO)_5L(\eta\text{-}C_5H_5)_2]$ (L = CO or O) the W–W distances [L = CO, 2.747(1); L = O, 2.848(1) Å] are relatively short,[5] but they are not as short as that in (3).

The Re–W distances [2.867(1) and 2.912(1) Å] in compound (3) are also somewhat short, and may be compared with those we have recently found[17] in the species $[ReW(\mu\text{-CHR})(CO)_9]^-$ [3.033(1) Å] and $[ReW\{\mu\text{-C(O)CH}_2R\}(\mu\text{-CO})(CO)_5(\mu\text{-dppm})\{P(OMe)_3\}]$ [3.155(1) Å] (R = C_6H_4Me-4, dppm = $Ph_2PCH_2PPh_2$). The short Re–W separations in (3) may also have their origin in the electronic unsaturation of the cluster.

The n.m.r. data for compound (3) (Table 2) are readily interpreted in terms of the structure established by *X*-ray crystallography. The $^{13}C\text{-}\{^1H\}$ and ^1H n.m.r. spectra show peaks corresponding to $\eta\text{-}C_5H_5$ and μ-CR groups in different environments. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum the resonances at δ 364.9 and 305.2 p.p.m. may be assigned to the μ-*C*R and μ_3-*C*R groups, respectively. Signals for μ-*C*R groups are always more deshielded than those for μ_3-*C*R ligands.[5,15] The peak at δ 261.1 p.p.m. in the spectrum of (3) may be assigned to the asymmetrically bridging CO ligand, and the signals at 196.5, 194.8, and 188.8 p.p.m. to the non-equivalent CO groups on rhenium.

Compound (3) which is green in colour, turns red on exposure to air with formation of the oxo-bridged complex (4), data for which are summarised in Tables 1 and 2. This compound was also structurally characterised by an *X*-ray

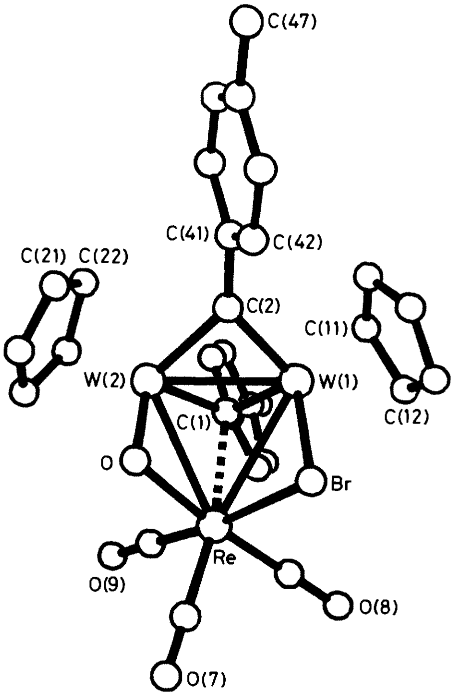


Figure 2. The molecular structure of $[\mathrm{ReW_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)_2}]$ (4), with the crystallographic numbering scheme

diffraction study. The molecule is shown in Figure 2, and selected internuclear separations and angles are listed in Table 3, together with those for (3) for easy comparison.

In compound (4) a bridging oxygen atom [W(2)–O 1.782(13), Re–O 2.139(16) Å] has replaced the CO ligand which asymmetrically bridges the Re–W(2) bond in (3). The gross stereochemical features of (3) and (4) are not greatly changed by substitution of O for CO, except for a substantial increase (*ca.* 0.27 Å) in the length of the μ_3-C(1)–Re bond [2.515(20) Å]. Compound (4), therefore, tends towards a structure in which both μ-CR groups edge-bridge the W(1)–W(2) bond, and thus the core atoms have an arrangement intermediate between that of (C) and (D) in the Scheme. These structures emphasise the potential mobility of the alkylidyne ligands in metal clusters.[11]

The presence of the μ-O ligand in compound (4) evidently strengthens the Re–W(2) bond [2.871(1) Å] compared with (3) [2.912(1) Å], but the two other metal–metal bonds are weaker. The bonds from C(2) to the tungsten atoms in (4) are perceptibly shorter than those in (3).

Since (3) with oxygen afforded (4) it was of interest to study the reaction of the former compound with sulphur. We have previously studied reactions between the cluster compounds $[\mathrm{Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)}]$ (R = $\mathrm{C_6H_4Me}$-4 or Me) and sulphur, and have structurally characterised by *X*-ray diffraction two species $[\mathrm{Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)}]$ and $[\mathrm{Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)}]$.[18] The former complex contains an edge-bridging $\mathrm{CC_6H_4Me}$-4 group and a capping sulphur atom. The latter compound contains a SCMe ligand co-ordinated to the face of the $\mathrm{Fe_2W}$ triangle.

Compound (3) reacts with sulphur in dichloromethane to give a very dark brown, almost black, complex (5) (Table 1). Our attempts to grow crystals for an *X*-ray diffraction study were unsuccessful, hence the structure shown is based on the spectroscopic data. The i.r. spectrum shows three bands in the terminal CO-stretching region, as expected for the $\mathrm{Re(CO)_3}$ group and a bridging carbonyl band at 1 775 cm^{-1}. The ^{13}C-{^{1}H} n.m.r. spectrum (Table 2) is in agreement, having four CO resonances, the peak at δ 244.1 p.p.m. being due to the μ-CO group. The molecule exhibits dynamic behaviour and the data in Table 2 are from the −80 °C spectrum. At room temperature the μ-CO resonance shows ^{183}W satellites [*J*(WC) 104 Hz]. The stereochemical non-rigidity of (5) involves rotation of the $\mathrm{CC_6H_4Me}$-4 groups about the C–C^1($\mathrm{C_6H_4}$) axes. At −80 °C the $\mathrm{C_6H_4}$ groups give eleven signals with one (δ 129.7 p.p.m.) being of double intensity, and thus corresponding to two carbon nuclei. At ambient temperatures the ^{13}C-{^{1}H} n.m.r. spectrum shows six resonances at δ 167.0, 146.5, 136.4, 134.1, 129.5, and 128.7 p.p.m.

As expected for the structure proposed, there are two $\mathrm{C_5H_5}$ resonances in the ^{13}C-{^{1}H} n.m.r. spectrum. Although only one Me-4 peak is seen, this is not surprising since the environments of the methyl groups are not significantly different. In the ^{1}H n.m.r. spectrum the $\mathrm{C_5H_5}$ and Me-4 groups each give rise to two resonances.

The peak in the ^{13}C-{^{1}H} n.m.r. spectrum of (5) at 264.6 p.p.m. is ascribed to the μ_3-*C*R group. Although, this signal is less deshielded than those for the μ_3-C nuclei in compounds (1)—(4), it is similar to that observed (257.7 p.p.m.) for the triply bridging carbon in $[\mathrm{Fe_2W(\mu_3\text{-}CR)(\mu\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)}]$.[19] This di-irontungsten compound has a structure with the alkyne edge-bridging and is thus related to (5), which also has a trimetallatetrahedrane core but with the SCR group edge-bridging. The relative shielding of the μ_3-C resonance in (5) may be due to incipient interaction with the ligated carbon of the SCR group, to which we assign the signal at δ 90.9 p.p.m. in the ^{13}C-{^{1}H} n.m.r. spectrum. The two bridging carbon atoms may well approach bonding distance. In $[\mathrm{Fe_2W(\mu_3\text{-}CR)(\mu\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)}]$ the μ_3-C to C(SiMe$_3$) non-bonding distance is relatively small and in this respect as in (5) only a minor topological change would be needed for C–C bond formation.

As mentioned above, in the compound $[\mathrm{Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)}]$ the thioacyl group bridges a face of the metal triangle and in other structures such as (5) it may well bridge an edge, showing the same versatility in this respect as do alkynes. One may compare the formation of compound (5) from (3) with that of (4). Oxygen oxidises the CO ligand in (3) while sulphur adds to the $\mathrm{W_2(\mu\text{-}CR)}$ system, capping the ditungstacyclopropene ring. It is interesting that the i.r. spectra of compounds (3) and (5) in the CO region (Table 1) show a remarkable similarity in frequency for the three bands of the $\mathrm{Re(CO)_3}$ group, but the bands due to the μ-CO groups are significantly different. This might be expected on the basis of the structure proposed for (5).

Experimental

All experiments were carried out under oxygen-free nitrogen using Schlenk-tube techniques. The instrumentation used has been described previously.[1,12] The light petroleum employed was that fraction of b.p. 40—60 °C. The compounds $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)}]$,[20] $[\mathrm{Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6}]$,[7] and $[\mathrm{ReBr(NCMe)_2(CO)_3}]$[8] were prepared by literature methods. The $\mathrm{Me_3NO}$ was freshly sublimed. Analytical and other data for the new compounds are given in Table 1.

Reaction between $[\mathrm{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)}]$ *and* $[\mathrm{Re_2(CO)_{10}}]$.—A tetrahydrofuran (20 cm^3) solution of $[\mathrm{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)}]$ (0.40 g, 1.0 mmol), $[\mathrm{Re_2(CO)_{10}}]$ (0.65 g, 1.0 mmol), and $\mathrm{Me_3NO}$ (0.30 g, 4.0 mmol) was stirred at room temperature for 5 h. Solvent was removed *in vacuo* and the dark purple residue was dissolved in dichloromethane–light petroleum (1 : 4, *ca.* 5 cm^3), and chromatographed on alumina using the same solvent mixture. A dark red band was collected,

Table 4. Atomic positional (fractional co-ordinates) parameters (× 10^4) with estimated standard deviations in parentheses for $[ReW_2(\mu\text{-}Br)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$ (3)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	2 073(1)	752(1)	4 575(1)	C(21)	5 365(18)	1 848(6)	4 817(18)
W(1)	−487(1)	1 393(1)	3 038(1)	C(22)	4 766(24)	1 926(8)	3 787(18)
W(2)	2 451(1)	1 804(1)	4 114(1)	C(23)	3 841(20)	2 387(9)	3 518(17)
Br	−743(2)	983(1)	4 688(1)	C(24)	3 945(21)	2 554(6)	4 600(21)
C(3)	2 852(16)	426(6)	6 034(10)	C(25)	4 894(21)	2 216(8)	5 367(16)
O(3)	3 332(13)	223(4)	6 901(7)	C(31)	2 121(14)	1 045(4)	2 086(9)
C(4)	4 175(14)	623(4)	4 565(10)	C(32)	2 618(15)	567(5)	1 938(10)
O(4)	5 447(11)	556(4)	4 590(8)	C(33)	2 908(18)	449(6)	979(11)
C(5)	1 085(16)	138(5)	3 785(10)	C(34)	2 725(16)	792(6)	186(11)
O(5)	509(13)	−219(4)	3 261(8)	C(35)	2 227(17)	1 273(5)	332(10)
C(6)	2 724(16)	1 531(4)	5 638(11)	C(36)	1 924(18)	1 403(5)	1 248(11)
O(6)	2 893(15)	1 559(4)	6 543(8)	C(37)	3 107(27)	669(8)	−810(12)
C(1)	1 725(15)	1 201(4)	3 033(9)	C(41)	−632(14)	2 600(4)	3 213(9)
C(2)	165(15)	2 093(4)	3 437(9)	C(42)	−1 785(16)	2 706(4)	3 655(11)
C(11)	−2 452(16)	855(6)	1 668(13)	C(43)	−2 532(16)	3 176(5)	3 485(11)
C(12)	−1 714(15)	1 210(7)	1 145(10)	C(44)	−2 124(16)	3 543(5)	2 923(10)
C(13)	−2 249(18)	1 654(6)	1 266(11)	C(45)	−1 066(16)	3 438(4)	2 453(10)
C(14)	−3 227(16)	1 627(5)	1 836(11)	C(46)	−3 26(15)	2 964(5)	2 616(11)
C(15)	−3 366(16)	1 142(7)	2 078(12)	C(47)	−2 889(21)	4 079(6)	2 801(14)

Table 5. Atomic positional (fractional co-ordinates) parameters (× 10^4) with estimated standard deviations in parentheses for $[ReW_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)_2]$ (4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	−1 036(1)	2 944(1)	5 141(1)	C(23)	896(24)	205(16)	6 119(10)
W(1)	706(1)	2 327(1)	4 045(1)	C(24)	−266(19)	16(21)	6 184(13)
W(2)	0	931(1)	5 016(1)	C(25)	−561(25)	−641(22)	5 591(14)
Br	−1 196(2)	2 915(2)	3 682(1)	C(31)	1 751(16)	2 742(17)	5 672(9)
C(7)	−2 528(19)	3 263(19)	5 293(12)	C(32)	1 767(15)	3 755(14)	5 955(9)
O(7)	−3 441(14)	3 479(20)	5 410(14)	C(33)	2 622(22)	4 134(18)	6 364(12)
C(8)	−650(17)	4 375(19)	5 156(11)	C(34)	3 593(20)	3 538(19)	6 486(10)
O(8)	−465(17)	5 304(13)	5 117(11)	C(35)	3 577(19)	2 497(19)	6 217(13)
C(9)	−746(19)	2 882(21)	6 182(13)	C(36)	2 680(21)	2 138(17)	5 831(11)
O(9)	−623(16)	2 833(51)	6 821(9)	C(37)	4 530(25)	4 000(27)	6 956(17)
C(1)	927(16)	2 320(14)	5 151(10)	C(41)	741(21)	4(13)	3 364(8)
C(2)	606(21)	823(15)	3 947(9)	C(42)	5(24)	−23(19)	2 803(11)
C(11)	2 598(24)	2 923(21)	3 953(14)	C(43)	80(32)	−740(19)	2 213(13)
C(12)	1 934(25)	3 801(20)	3 795(14)	C(44)	847(26)	−1 492(18)	2 207(11)
C(13)	1 398(23)	3 629(18)	3 137(12)	C(45)	1 625(22)	−1 463(17)	2 793(12)
C(14)	1 706(27)	2 610(19)	2 897(13)	C(46)	1 562(20)	−775(16)	3 368(10)
C(15)	2 443(23)	2 177(19)	3 389(14)	C(47)	834(34)	−2 217(19)	1 583(18)
C(21)	309(27)	−891(16)	5 188(11)	O	−1 408(11)	1 321(12)	4 989(7)
C(22)	1 263(20)	−424(20)	5 483(12)				

evaporated to dryness *in vacuo*, and crystallised from dichloromethane–light petroleum to afford purple *crystals* of $[Re_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}(\eta\text{-}C_5H_5)]$ (1) (0.12 g).

Reactions of $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$.—A mixture of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.19 g, 0.47 mmol) and $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$ (0.40 g, 0.47 mmol) in hexane (25 cm^3) was refluxed for 1 h, after which i.r. bands for the reactants, $[Re_2(\mu\text{-}Br)_2(CO)_8]$, and a new compound were observed. Hexane was decanted, and the residue washed with light petroleum (3 × 15 cm^3) and then dissolved in dichloromethane–diethyl ether (1 : 1, 30 cm^3). The solution was passed through an alumina pad (3 cm) and concentrated *in vacuo* to *ca.* 5 cm^3, causing some precipitation of a yellow-orange solid. Further precipitation was produced by addition of light petroleum (20 cm^3). Removal of solvent with a syringe afforded a residue which was crystallised from dichloromethane–hexane (1 : 3) at −20 °C to give orange *crystals* of $[Re_2W(\mu\text{-}Br)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)]$ (2) (0.05 g).

In another reaction, $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.50 g, 1.22 mmol) and $[Re_2(\mu\text{-}Br)_2(thf)_2(CO)_6]$ (0.22 g, 0.26 mmol) were refluxed (5 h) in hexane. Solvent was removed *in vacuo* and the residue was dissolved in dichloromethane–light petroleum (1 : 1, 15 cm^3) and chromatographed on alumina at −20 °C. Elution with the same mixture of solvents, gradually increasing the dichloromethane ratio from 1 : 4 to 1 : 2, separated compound (2) (0.026 g) from (3) (0.056 g), described below.

Synthesis of $[ReW_2(\mu\text{-}Br)(\mu\text{-}L)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)_2]$ (L = CO *or* O).—A suspension of $[ReBr(NCMe)_2(CO)_3]$ (0.30 g, 0.70 mmol) and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.60 g, 1.47 mmol) in hexane (20 cm^3) was refluxed for 96 h in the absence of light. After cooling to room temperature, the solvent was removed with a syringe. The greenish residue was washed with light petroleum (3 × 30 cm^3) and extracted with dichloromethane–diethyl ether (1 : 1, 70 cm^3). The extracts were passed through an alumina pad (3 cm) at −20 °C and solvent was removed *in vacuo*. Crystallisation from dichloromethane–light petroleum afforded green *crystals* of $[ReW_2(\mu\text{-}Br)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$ (3) (0.40 g, 53%).

A suspension of compound (3) (0.20 g, 0.18 mmol) in light petroleum (20 $\mathrm{cm^3}$) was stirred under air (*ca.* 24 h) monitoring the course of the reaction by i.r. spectroscopy. Solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane (10 $\mathrm{cm^3}$) and chromatographed on alumina. Dichloromethane initially eluted a trace of green (3) which was followed by a red fraction. The latter was reduced in volume to *ca.* 1 $\mathrm{cm^3}$ and light petroleum (20 $\mathrm{cm^3}$) was added. Cooling to *ca.* −20 °C gave red *microcrystals* of $[\mathrm{ReW_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)_2}]$ (4) (0.11 g, 57%). Complex (4) may be recrystallised from dichloromethane–diethyl ether mixtures at −15 °C.

Reaction of $[\mathrm{ReW_2(\mu\text{-}Br)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2}]$ *with Sulphur.*—Compound (3) (0.38 g, 0.35 mmol) and sulphur (0.10 g, 3.1 mmol) in dichloromethane (20 $\mathrm{cm^3}$) were stirred (40 h) at room temperature. Solvent was removed *in vacuo* and the residue was vacuum dried (1 h). The solid was dissolved in diethyl ether–light petroleum (3 : 1, 100 $\mathrm{cm^3}$) and the mixture was passed through an alumina pad (4 × 4 cm) at *ca.* −15 °C. The filtrate was reduced in volume to *ca.* 5 $\mathrm{cm^3}$, light petroleum was added (30 $\mathrm{cm^3}$), and the Schlenk tube was cooled giving a black precipitate. The latter was recovered and dissolved in dichloromethane (3 $\mathrm{cm^3}$) to which light petroleum (30 $\mathrm{cm^3}$) was added. Cooling to −20 °C overnight afforded dark brown or black *microcrystals* of $[\mathrm{ReW_2(\mu\text{-}Br)(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}SCC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2}]$ (5) (0.11 g).

The i.r. spectrum of the mixture prior to the isolation of (5) showed a trace of another product [$\nu_{\mathrm{max.}}$(CO) at 2 028vs, 1 959s, 1 917s, and 1 723w(br) $\mathrm{cm^{-1}}$ ($\mathrm{CH_2Cl_2}$)] which was not identified. Compound (5) can also be isolated (*ca.* 40% yield) by chromatography of the crude reaction mixture on alumina. Using this procedure, eluting the column with light petroleum affords a trace of a violet product with $\nu_{\mathrm{max.}}$ (CO) at 2 034w, 2 013s, 1 956vs, 1 920w(br), and 1 878m $\mathrm{cm^{-1}}$ (hexane). It was formed in insufficient quantity for n.m.r. or other studies.

Crystal Structure Determinations.—(*a*) $[\mathrm{ReW_2(\mu\text{-}Br)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2}]$ (3). Crystals of (3) were grown from dichloromethane–light petroleum as green prisms. Intensities were collected at 298 K from a crystal of dimensions *ca.* 0.35 × 0.25 × 0.15 mm in the range $2.9 \leqslant 2\theta \leqslant 50°$. Data were collected ($\omega$ scans) on a Nicolet *P*3*m* four-circle diffractometer. Of the total 4 928 intensities, 3 951 had $I \geqslant 2.5\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, and these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data. $\mathrm{C_{30}H_{24}BrO_4ReW_2}$, M = 1 082.2, monoclinic, a = 8.893(5), b = 26.587(15), c = 13.071(6) Å, β = 115.26(4)°, U = 2 795(3) $\mathrm{Å^3}$, Z = 4, D_c = 2.57 g $\mathrm{cm^{-3}}$, $F(000)$ = 1 976, space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 142.2 $\mathrm{cm^{-1}}$.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and electron-density difference methods. Hydrogen atoms were included in calculated positions (C–H 0.96 Å) and were given isotropic thermal parameters 1.2 times those of their parent carbon atoms. All remaining atoms were refined with anisotropic thermal parameters. Refinement by blocked-cascade least squares led to R 0.042 (R' 0.043) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$ giving a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks > *ca.* 1 e $\mathrm{Å^{-3}}$ except in the immediate vicinity of the tungsten and rhenium atoms where peaks of *ca.* 5 e $\mathrm{Å^{-3}}$ were observed. Scattering factors were from ref. 21. All computations were carried out on an Eclipse (Data General) mini-computer with the SHELXTL system of programs.[22] Atom co-ordinates are listed in Table 4.

(*b*) $[\mathrm{ReW_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)_2}]$ (4). A suitable red crystal of dimensions *ca.* 0.50 × 0.36 × 0.20 mm was grown from dichloromethane–light petroleum solutions.

Crystal data. $\mathrm{C_{29}H_{24}BrO_4ReW_2}$, M = 1 070.2, orthorhombic, a = 12.145(2), b = 12.767(2), c = 18.079(3) Å, U = 2 803(1) $\mathrm{Å^3}$, Z = 4, D_c = 2.54 g $\mathrm{cm^{-3}}$, $F(000)$ = 1 952, space group $P2_1cn$ [non-standard setting of $Pna2_1$ (no. 33)], Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 141.7 $\mathrm{cm^{-1}}$.

Conditions as for (3) except 3 381 reflections to $2\theta = 55°$ gave 2 730 independent intensities [$I \geqslant 2.5\sigma(I)$]; weights $w = [\sigma^2(F_o) + 0.002|F_o|^2]^{-1}$. Final electron density (max.) by difference 1.4 e $\mathrm{Å^{-3}}$; R 0.043 (R' 0.044). Atom co-ordinates are listed in Table 5.

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