Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 20.[1] Complexation of Carbon–Metal Triple Bonds with Low-valent Metal Species; Crystal Structures of the Bimetal Complexes $[CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)]$ and $[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ *

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A series of bimetal complexes $[MW(\mu\text{-}CR)(CO)_2(L_n)(\eta\text{-}C_5H_5)]$ [R = C_6H_4Me-4; ML_n = $Cr(CO)_2(\eta\text{-}C_6Me_6)$, $Mn(CO)_2(\eta\text{-}C_5H_4Me)$, $Re(CO)_2(\eta\text{-}C_5H_5)$, $Co(CO)(\eta\text{-}C_5Me_5)$, $Rh(CO)(\eta\text{-}C_9H_7)$ (C_9H_7 = indenyl), $Ir(CO)(\eta\text{-}C_9H_7)$, and $Ir(CO)(acac)$ (acac = acetylacetonate)] have been prepared from $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Cr(CO)_2(thf)(\eta\text{-}C_6Me_6)]$ (thf = tetrahydrofuran), $[M(CO)_2(thf)(C_5H_4R')]$ (M = Mn, R' = Me; M = Re, R' = H), $[Co(CO)_2(\eta\text{-}C_5Me_5)]$, $[M(CO)_2(\eta\text{-}C_9H_7)]$ (M = Rh or Ir), and $[Ir(acac)(CO)_2]$, respectively. The compounds $[RhW(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ and $[MoRh(acac)(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)]$ have also been obtained from related reactions. The spectroscopic data (i.r. and n.m.r.) for the new compounds are reported and discussed. The structures of the species $[CrW(\mu\text{-}CR)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)]$, (1) and $[CoW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (4) have been established by *X*-ray diffraction, and reveal an interesting distinction between (1) and (4). For both structures the metal–metal bond is bridged by a CC_6H_4Me-4 group and is semi-bridged by a CO ligand, but whereas in (4) it is one of the CO ligands on the W atom which semi-bridges to Co, in (1) it is a CO ligand on the Cr atom which semi-bridges to W. Reasons for this are discussed. In both structures the cyclic ligands bonded to the metal atoms are in a *trans* configuration with respect to the $M(\mu\text{-}C)W$ plane.

The discovery of the carbyne–tungsten complexes $[W(\equiv CR)Br(CO)_4]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = alkyl or aryl) represented a major advance in organometallic chemistry,[2] but with hindsight their existence follows from the isolobal mapping [3] shown below. An appreciation of these isolobal

$$CR \longleftrightarrow WBr(CO)_4 \longleftrightarrow W(CO)_2(\eta\text{-}C_5H_5)$$

relationships prompted synthesis of the compounds $[PtW(\mu\text{-}CR)Br(CO)_4(PMe_3)_2]$ and $[PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4),[4] and the development of a general route to complexes with alkylidyne ligands bridging bonds between tungsten and other transition metals.[5] Herein we give details of the syntheses and properties of several dinuclear bimetal compounds derived from the model 'ligand' $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4). The new species described, as well as those reported earlier,[1,4,6,7] arise from bonding between a carbon–metal triple-bond system and a low-valent metal–ligand fragment ML_n (see below). The dimetallacyclopropene structures so obtained are isolobally related to metal–alkyne complexes where the alkyne substituents are electron withdrawing, and hence can be formulated as having metallacyclopropene rings.[8,9] A preliminary account has been given of some of the results described in this paper.[10]

Results and Discussion

Formation of $[Pt\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}(PMe_2Ph)_2]$ from $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(C_2H_4)(PMe_2Ph)_2]$ is accompanied by release of ethylene.[4] This suggested that other low-valent metal species would form complexes with the *p*-tolylmethylidyne–tungsten compound, given that the reactant contained an easily displaceable ligand.

Studies commenced with the complexes $[Cr(CO)_2(thf)(\eta\text{-}C_6Me_6)]$ (thf = tetrahydrofuran) and $[M(CO)_2(thf)(\eta\text{-}C_5H_4R')]$ (M = Mn, R' = Me; M = Re, R' = H), generated photochemically *in situ*. It is known that the thf molecules in these species are weakly co-ordinated and are readily replaced by other ligands.[11,12] Addition of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ to a solution of $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$ in thf, which had been irradiated with u.v. light, afforded dark green crystals of compound (1), characterised by microanalysis and by i.r. and n.m.r. spectroscopy (Tables 1 and 2). Similar manganese– and rhenium–tungsten complexes, (2) and (3), were prepared *via* $[Mn(CO)_2(thf)(\eta\text{-}C_5H_4Me)]$ and $[Re(CO)_2(thf)(\eta\text{-}C_5H_5)]$, respectively. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of compounds (1)—(3) were revealing, each spectrum (Table 2) showing a resonance characteristic [4] of a μ-*C*R group [δ 430.9 (1), 395.5 (2), and 343.5 p.p.m. (3)]. These signals are all more deshielded than that found (δ 300 p.p.m.) for the ligated alkylidyne carbon atom in $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$.[2] The spectra also show peaks assignable to the other groups present in the compounds.

Reaction of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with $[Co(CO)_2(\eta\text{-}C_5Me_5)]$ in toluene (120 °C, sealed evacuated vessel) gave a

* 1,1,2,2-Tetracarbonyl-2-(η-cyclopentadienyl)-1-(η-hexamethylbenzene)-μ-*p*-tolylmethylidyne-chromiumtungsten (*Cr–W*) and 1,2,2-tricarbonyl-2-(η-cyclopentadienyl)-1-(η-pentamethylcyclopentadienyl)-μ-*p*-tolylmethylidyne-cobalttungsten (*Co–W*).

Supplementary data available (No. SUP 23661, 72 pp.): for (1) and (4), observed and calculated structure factors, positional parameters for all atoms including hydrogen and disordered solvent, thermal parameters, full tables of bond lengths and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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

Complex	Colour	Yield (%)	ν(CO) [b]/cm [-1]	Analysis (%) C	H
(1) [CrW(μ-CC_6H_4Me-4)(CO)$_4$(η-C_5H_5)(η-C_6Me_6)]	Green	68	1 921s, 1 861s 1 837s, 1 785vw,br	[c] 46.5 (47.2)	3.4 (4.2)
(2) [MnW(μ-CC_6H_4Me-4)(CO)$_4$(η-C_5H_5)(η-C_5H_4Me)]	Violet	60	1 958s, 1 914s, 1 877s, 1 865 (sh)	[c] 42.7 (42.2)	3.3 (3.1)
(3) [ReW(μ-CC_6H_4Me-4)(CO)$_4$(η-C_5H_5)$_2$]	Black	22	1 961m, 1 921s, 1 885m		
(4) [CoW(μ-CC_6H_4Me-4)(CO)$_3$(η-C_5H_5)(η-C_5Me_5)]	Purple	37	[d] 1 965s, 1 913vs, 1 833s	49.5 (49.5)	4.2 (4.3)
(5) [RhW(μ-CC_6H_4Me-4)(CO)$_3$(η-C_5H_5)(η-C_9H_7)]	Brown	100	1 985m, 1 917s, 1 837m	45.5 (45.9)	3.0 (2.9)
(6) [IrW(μ-CC_6H_4Me-4)(CO)$_3$(η-C_5H_5)(η-C_9H_7)]	Black	62	1 968m, 1 914s, 1 844m	40.0 (40.4)	2.6 (2.6)
(7) [RhW(μ-CMe)(CO)$_3$(η-C_5H_5)(η-C_9H_7)]	Brown	91	1 995m, 1 919s, 1 834m	39.3 (39.5)	2.6 (2.6)
(8) [IrW(acac)(μ-CC_6H_4Me-4)(CO)$_3$(η-C_5H_5)]	Brown	67	1 988m, 1 938vs, 1 862m	34.9 (34.7)	2.6 (2.6)
(9) [RhMo(acac)(μ-CMe)(CO)$_3$(η-C_5H_5)]	Purple	95	2 009m, 1 957s, 1 871m	38.6 (38.0)	3.2 (3.2)

[a] Calculated values are given in parentheses. [b] In dichloromethane unless otherwise stated. [c] Crystallised with a molecule of CH_2Cl_2. [d] In hexane.

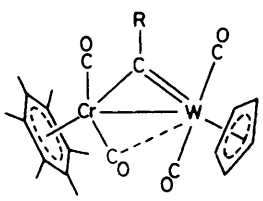
Table 2. Hydrogen-1 and carbon-13 n.m.r. data [a] for the bimetal complexes

Compound	^{1}H (δ) [b]	^{13}C [c]
(1)	2.01 (s, 18 H, C_6Me_6), 2.31 (s, 3 H, Me-4), 5.25 (s, 5 H, C_5H_5), 7.25 [$(AB)_2$ system, 4 H, J(AB) 8]	430.9 (μ-C), 249.3, 244.9, 236.6, 222.0 (CO), 164.8 [C^1(C_6H_4)], 136.3 [C^4(C_6H_4)], 128.9, 121.4 (C_6H_4), 113.9 (C_6Me_6), 93.5 (C_5H_5), 21.3 (Me-4), 16.7 (C_6Me_6)
(2)	1.82 (s, 3 H, C_5H_4Me), 2.32 (s, 3 H, Me-4), 4.46 (m,br, C_6H_4), 5.39 (s, 5 H, C_5H_5), 7.34 [$(AB)_2$ system, 4 H, J(AB) 8]	395.5 (μ-C), 234.3, 231.0, 226.3, 213.1 (CO), 160.9 [C^1(C_6H_4)], 138.6 [C^4(C_6H_4)], 128.9, 127.6 (C_6H_4), 105.4 [C^1(C_5H_4Me)], 93.1 (C_5H_5), 89.3—88.0 [C$^{2-5}$(C_5H_4Me)], 21.5 (Me-4), 13.2 (C_5H_4Me)
(3)	[d] 2.20 (s, 3 H, Me-4), 5.20 (s,br, 10 H, C_5H_5), 7.25 (m, 4 H, C_6H_4)	343.5 [μ-C, J(WC) 123], 205.1, 201.6, 194.7 (CO), 161.0 [C^1(C_6H_4)], 139.5 [C^4(C_6H_4)], 131.9, 129.7 (C_6H_4), 93.2, 90.1 (C_5H_5), 21.7 (Me-4)
(4)	1.60 (s, 15 H, C_5Me_5), 2.32 (s, 3 H, Me-4), 5.42 (s, 5 H, C_5H_5), 7.14 (m, 4 H, C_6H_4)	[e] 341.0 (μ-C), 233.8, 233.5 (WCO), 207.9 (CoCO), 160.3 [C^1(C_6H_4)], 135.1 [C^4(C_6H_4)], 128.6, 123.1 (C_6H_4), 98.8 (C_5Me_5), 91.7 (C_5H_5), 21.6 (Me-4), 9.2 (C_5Me_5)
(5)	2.22 (s, 3 H, Me-4), 5.44 (s, 5 H, C_5H_5), 5.86 (s, 3 H, C_9H_7), 6.8—7.5 (m, 8 H, C_6H_4, C_9H_7)	312.4 [d, μ-C, J(RhC) 30], 226.2, 222.6 (WCO), 188.7 [d, RhCO, J(RhC) 88], 154.5 [C^1(C_6H_4)], 136.4 [C^4(C_6H_4)], 128.0 (C_6H_4), 124.8—81.0 (C_9H_7), 90.6 (C_5H_5), 21.0 (Me-4)
(6)	2.17 (s, 3 H, Me-4), 5.40 (s, 5 H, C_5H_5), 5.85 (m, 3 H, C_9H_7), 6.9—7.3 (m, 8 H, C_6H_4, C_9H_7)	[e] 301.3 (μ-C), 228.0, 220.3 (WCO), 170.7 (IrCO), 156.5 [C^1(C_6H_4)], 136.9 [C^4(C_6H_4)], 137—78 (C_6H_4, C_9H_7), 91.4 (C_5H_5), 21.7 (Me-4)
(7)	1.92 (s, 3 H, μ-CMe), 5.40 (s, 5 H, C_5H_5), 5.85 (m, 3 H, C_9H_7), 7.1 (m, 4 H, C_9H_7)	323.4 [d, μ-C, J(RhC) 27], 225.8 (WCO), 190.6 [d, RhCO, J(RhC) 90], 125—82 (C_9H_7), 91.4 (C_5H_5), 48.8 (μ-CMe)
(8)	1.86 (s, 3 H, CMe), 2.22 and 2.25 (s, 6 H, CMe, Me-4), 5.66 (s,br, 6 H, C_5H_5, CH)	300.4 [μ-C, J(WC) 142], 223.8 [WCO, J(WC) 204], 221.6 [W(CO), J(WC) 215], 188.1, 187.0 [C(Me)O], 168.1 (IrCO), 156.6 [C^1(C_6H_4)], 139.3 [C^4(C_6H_4)], 129.9, 129.2 (C_6H_4), 102.6 (CH), 92.7 (C_5H_5), 27.4, 26.6 [C(Me)O], 22.1 (Me-4)
(9)	1.84, 2.14 (s, 6 H, CMe), 3.23 [d, 3 H, μ-CMe, J(RhC) 1], 5.51 (s, 1 H, CH), 5.56 (s, 5 H, C_5H_5)	348.2 [d, μ-C, J(RhC) 27], 231.1 (MoCO), 187.5 [C(Me)O], 184.3 [d, RhCO, J(RhC) 73], 100.4 (CH), 93.8 (C_5H_5), 47.9 (μ-CMe), 27.4, 27.1 [C(Me)O]

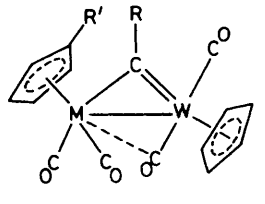
[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in [$^2H_1$]chloroform, unless otherwise stated. [c] Hydrogen-1 decoupled to high frequency of $SiMe_4$, measured in [$^2H_2$]dichloromethane–CH_2Cl_2, unless otherwise stated. [d] Measured in [$^2H_2$]dichloromethane. [e] Measured in [$^2H_1$]chloroform.

trace of the compound [W_2(μ-C_2R_2)(CO)$_4$(η-C_5H_5)$_2$],[13] but the new cobalt–tungsten complex (4) was the main product. The indenyl–rhodium and –iridium compounds [M(CO)$_2$(η-C_9H_7)] (M = Rh or Ir) are more reactive than [Co(CO)$_2$(η-C_5Me_5)]. They were generated *in situ* from [M(C_2H_4)$_2$(η-C_9H_7)] and CO, and with [W(≡CR)(CO)$_2$(η-C_5H_5)] at room temperature in light petroleum afforded the heteronuclear bimetallic complexes (5) and (6).

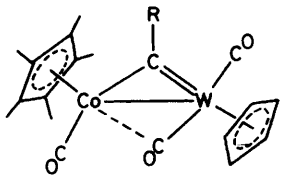
There seems little difference in the co-ordinating abilities of *p*-tolylmethylidyne–tungsten or ethylidyne–tungsten species, as demonstrated by the synthesis of (7) from [W(≡CMe)(CO)$_2$-(η-C_5H_5)] and [Rh(CO)$_2$(η-C_9H_7)]. Compounds (4)—(7) were fully characterised (Tables 1 and 2) by the usual methods. As found with (1)—(3), the ^{13}C-{^{1}H} n.m.r. spectra of compounds (4)—(7) showed the characteristic deshielded resonances of ligated carbon atoms of bridging alkylidyne groups



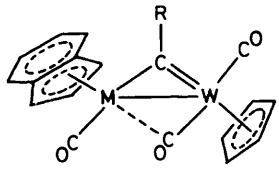
(1) R = C_6H_4Me-4



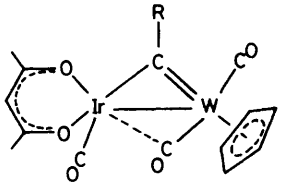
	M	R′	R
(2)	Mn	Me	C_6H_4Me-4
(3)	Re	H	C_6H_4Me-4



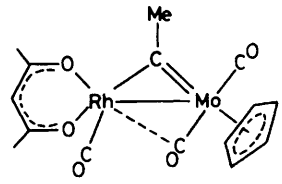
(4) R = C_6H_4Me-4



	M	R
(5)	Rh	C_6H_4Me-4
(6)	Ir	C_6H_4Me-4
(7)	Rh	Me



(8) R = C_6H_4Me-4



(9)

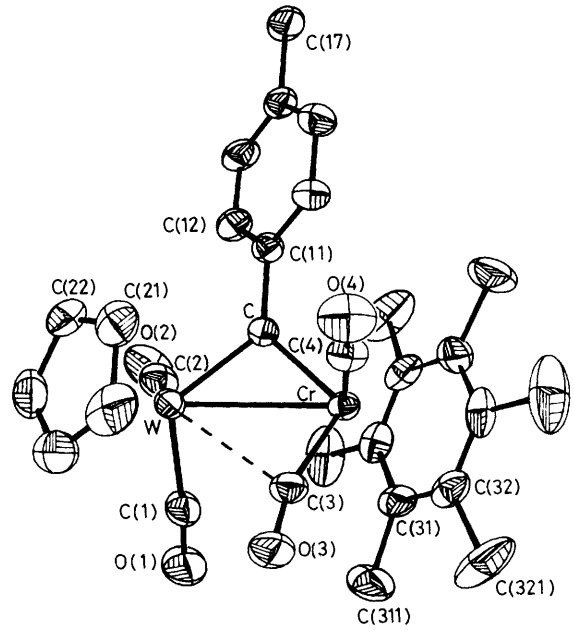


Figure 1. Molecular structure of [CrW(μ-CC_6H_4Me-4)$(CO)_4(\eta$-$C_5H_5)(\eta$-$C_6Me_6)$], (1), showing the crystallographic numbering

(Table 2). The ^1H n.m.r. spectra are in accord with the structures proposed.

Compounds (8) and (9), containing acetylacetonate ligands, were prepared from the reactions between [Ir(acac)$(CO)_2$] and [W(≡CC_6H_4Me-4)$(CO)_2(\eta$-$C_5H_5)$], and between [Rh(acac)$(CO)_2$] and [Mo(≡CMe)$(CO)_2(\eta$-$C_5H_5)$], respectively. The rhodium analogue of (8) has been previously reported.[6] The n.m.r. spectra (Table 2) of compounds (8) and (9) are as expected. The resonance for the μ-C nucleus in (9) at δ 348.2 p.p.m. appears as a doublet [J(RhC) 27 Hz]. The synthesis of (9) from the alkylidyne–molybdenum compound suggests that the species [Mo(≡CR)$(CO)_2(\eta$-$C_5H_5)$] (R = Me or C_6H_4Me-4) are likely to be useful precursors to a variety of heteronuclear metal–metal bonded complexes containing molybdenum, thus extending the scope of this chemistry.

The i.r. spectra of compounds (3)—(9) in the CO stretching region all show a band below 1 900 cm^{-1}, characteristic of a semi-bridging carbonyl ligand. The spectrum of (2) has a shoulder on the absorption at 1 877 cm^{-1} which may be due to asymmetry introduced by the η-C_5H_4Me group. The spectrum of (1) is somewhat different from those of the other complexes in having a weak band at 1 785 cm^{-1} in the bridging CO region, as well as a band at 1 837 cm^{-1} indicative of a semi-bridging carbonyl group.

The synthesis of (1)—(8), together with the previous preparations of [TiW(μ-CR)$(CO)_2(\eta$-$C_5H_5)_3$],[1b] [FeW(μ-CR)$(CO_6)(\eta$-$C_5H_5)$],[7] and [PtW(μ-CR)$(CO)_2(PMe_2Ph)_2(\eta$-$C_5H_5)$],[4] demonstrates that the compound [W(≡CC_6H_4Me-4)$(CO)_2(\eta$-$C_5H_5)$] will form 'complexes' with a broad spectrum of transition elements, thereby providing a versatile route to species with bonds between tungsten and these metals.

Compounds of the type described herein are proving to be useful reagents in further syntheses.[5] Moreover, their formulations with dimetallacyclopropene rings are novel in relation to those of metal–alkyne complexes. These and other factors have prompted rigorous establishment of structures by single-crystal X-ray diffraction studies. We have already reported the crystal structures of [PtW(μ-CR)$(CO)_2(PMe_2$-$Ph)_2(\eta$-$C_5H_5)$],[4] [TiW(μ-CR)$(CO)_2(\eta$-$C_5H_5)_3$],[1b] and [RhW(μ-CR)$(CO)_2(PMe_3)(\eta$-$C_5H_5)(\eta$-$C_9H_7)$].[1a] Here we describe the results for compounds (1) and (4) which merited X-ray diffraction studies for the following reasons. Compound (1), as discussed above, had a somewhat different i.r. spectrum in the CO region from those of the other complexes listed in Table 1. Moreover, in (1) the heteronuclear metal–metal bond involves two elements from the same periodic group. Crystallographic examination of (4) was undertaken in order to correlate the parameters for the Co(μ-C)W ring with those of the three-membered rings in the other compounds studied, and to establish the type of CO bridging present. The previous results revealed that in [TiW(μ-CR)$(CO)_2(\eta$-$C_5H_5)_3$] one of the CO ligands on tungsten is η^2 co-ordinated to the titanium, and that in [PtW(μ-CR)$(CO)_2(PMe_2Ph)_2(\eta$-$C_5H_5)$] there is incipient η^2 bonding by the CO groups to platinum. Thus in both these species the CO ligands function to transfer charge away from tungsten, indicating that this metal centre is relatively electron rich. In contrast, the semi-bridging CO in [RhW(μ-CR)$(CO)_2(PMe_3)(\eta$-$C_5H_5)(\eta$-$C_9H_7)$] [W–C–O 164(2)°] is of the type [14] which reflects charge transfer from a relatively electron-rich rhodium to tungsten. It seems likely that the character of the CO bridging adopted in the bimetal compounds is determined by the net charge transfer produced on complexation of [W(≡CR)$(CO)_2(\eta$-$C_5H_5)$] with the metal-ligand fragments ML_n.

The results of the studies on compounds (1) and (4) are summarised in Tables 3 and 4, and views of the two structures are given in Figures 1 and 2, respectively. In (4) the Co–W bond is bridged by the CC_6H_4Me-4 group and semi-bridged

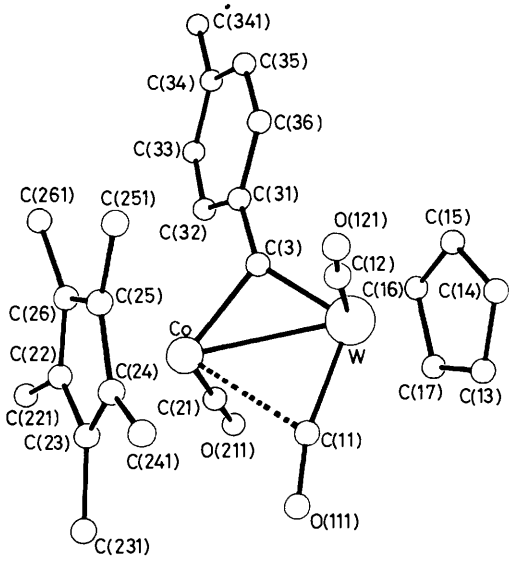


Figure 2. Molecular structure of $[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$, (4), showing the crystallographic numbering

Table 3. Selected bond lengths (Å) and angles (°) for $[CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)]$ (1)

W–Cr	2.941(1)	W–C	2.025(6)
W–C(21)	2.367(6)	W–C(22)	2.325(6)
W–C(23)	2.328(5)	W–C(24)	2.372(6)
W–C(25)	2.395(6)	W–C(1)	1.997(8)
W–C(2)	1.936(8)	W–C(3)	2.688(8)
Cr–C	1.928(6)	Cr–C(31)	2.287(4)
Cr–C(32)	2.258(4)	Cr–C(33)	2.264(4)
Cr–C(34)	2.297(4)	Cr–C(35)	2.324(5)
Cr–C(36)	2.319(5)	Cr–C(3)	1.840(6)
Cr–C(4)	1.798(6)	C–C(11)	1.513(7)
C(1)–O(1)	1.13(1)	C(2)–O(2)	1.17(1)
C(3)–O(3)	1.173(8)	C(4)–O(4)	1.171(9)
Cr–W–C	40.7(2)	Cr–W–C(1)	86.5(2)
Cr–W–C(2)	106.1(2)	Cr–W–C(3)	37.8(2)
W–Cr–C	43.2(2)	W–Cr–C(3)	63.6(2)
W–Cr–C(4)	94.3(2)	W–C–Cr	96.1(3)
W–C–C(11)	131.7(4)	Cr–C–C(11)	131.5(4)
Cr–C(3)–O(3)	163.1(6)		

by a CO ligand [W–C(11)–O(111) 167.0(7)°, Co–C(11) 2.487(8) Å]. This semi-bridging is similar to that in $[RhW(\mu\text{-}CR)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$,[1a] with one of the CO groups on tungsten being bent while the other remains essentially linear.

In (1) the metal–metal bond is again bridged by the CC_6H_4Me-4 group and semi-bridged by a CO ligand. However, in this case the tungsten atom retains its two terminal CO ligands and the semi-bridging involves a ligand terminally bonded to chromium [Cr–C(3)–O(3) 163.1(6), W–C(3) 2.688(8) Å], implying that it is the tungsten centre which needs to dissipate excess of electronic charge by back bonding with the π^* orbitals of C(3)–O(3).[14]

In both compounds (1) and (4) the C_5H_5 and C_6Me_6, and the C_5H_5 and C_5Me_5, groups are *trans* to the M(μ-C)W (M = Cr or Co) planes. In contrast, a *cis* configuration is adopted by the C_5H_5 and C_9H_7 ligands in $[RhW(\mu\text{-}CR)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$.

Table 4. Bond lengths (Å) and selected angles (°) for $[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (4)

W–Co	2.758(1)	W–C(11)	1.981(9)
W–C(12)	1.974(12)	W–C(3)	1.913(7)
W–C(13)	2.364(10)	W–C(14)	2.374(12)
W–C(15)	2.352(10)	W–C(16)	2.324(12)
W–C(17)	2.325(13)	Co–C(11)	2.487(8)
Co–C(21)	1.724(11)	Co–C(3)	1.939(8)
Co–C(22)	2.075(9)	Co–C(23)	2.097(9)
Co–C(24)	2.189(10)	Co–C(25)	2.157(10)
Co–C(26)	2.130(9)	C(11)–O(111)	1.167(12)
C(21)–O(211)	1.160(15)	C(12)–O(121)	1.14(2)
C(3)–C(31)	1.466(11)	C(31)–C(32)	1.385(13)
C(31)–C(36)	1.405(14)	C(32)–C(33)	1.393(14)
C(33)–C(34)	1.39(2)	C(34)–C(35)	1.38(2)
C(34)–C(341)	1.515(13)	C(36)–C(35)	1.386(13)
C(22)–C(23)	1.436(13)	C(22)–C(26)	1.40(2)
C(22)–C(221)	1.53(2)	C(23)–C(24)	1.43(2)
C(23)–C(231)	1.52(2)	C(24)–C(25)	1.419(13)
C(24)–C(241)	1.478(15)	C(25)–C(26)	1.418(14)
C(25)–C(251)	1.51(2)	C(26)–C(261)	1.534(14)
C(13)–C(14)	1.41(2)	C(13)–C(17)	1.35(2)
C(14)–C(15)	1.38(2)	C(15)–C(16)	1.36(3)
C(16)–C(17)	1.42(2)		
W–C(3)–Co	91.4(3)	W–C(11)–Co	75.3(3)
C(3)–Co–W	43.9(2)	C(11)–Co–W	44.0(2)
C(3)–W–Co	44.7(2)	C(11)–W–Co	60.7(2)
Co–C(3)–C(31)	124.7(5)	Co–C(11)–O(111)	117.0(6)
W–C(3)–C(31)	142.1(6)	W–C(11)–O(111)	167.0(7)
Co–C(21)–O(211)	178.9(8)	W–C(12)–O(121)	175.3(9)

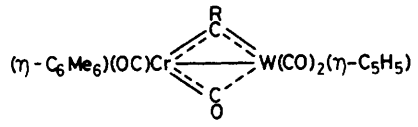
The observed metal–metal separations in (1) and (4) are 2.941(1) and 2.758(1) Å, respectively. There are few data for comparison. However, the Co–W distance in (4) is significantly longer than those found in cobalt–tungsten complexes $[W(\eta\text{-}C_5H_5)\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}(CO)_2\{Co(CO)_2\}]$ [2.664(1) Å][15] or $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ [2.672(1) Å].[6]

Table 5 compares structural data for the three-membered rings in several μ-CR bridged bimetal complexes. For (4) the data closely resemble those for $[RhW(\mu\text{-}CR)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$, and, as previously discussed,[1a,4] the relatively short μ-C–W distances must reflect considerable C=W bond character. In contrast, the μ-C–Co distance is typical of those found for $C(sp^2)$–Co σ bonds (1.86—1.96 Å), implying little or no C=Co bonding in (4). Thus in the latter, in $[RhW(\mu\text{-}CR)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$, and presumably also in compounds (2), (3), and (5)—(9), a dimetallacyclopropene ring formulation for the molecules is a reasonable approximation. For (1), however, both the μ-C–W [2.025(6) Å] and μ-C–Cr [1.928(6) Å] separations are significantly shorter than C=W or C=Cr bonds, *cf.* $[W(=CPh_2)(CO)_5]$ [2.14(2) Å][16] and $[Cr\{=C(OMe)Ph\}(CO)_5]$ [2.04(3) Å].[17] Evidently in compound (1) both μ-C–M bonds have appreciable multiple-bond character. Moreover, as discussed above, in the chromium–tungsten species the semi-bridging CO ligand is terminally bonded to the chromium rather than to the tungsten. Accordingly, complex (1) is probably best represented by the delocalised structure (1a), which is associated with a very symmetrically disposed $\mu\text{-}CC_6H_4Me$-4 ligand [W–C–C(11) 131.7(4)°, Cr–C–C(11) 131.5(4)°]. In contrast, in (4) and in $[RhW(\mu\text{-}CR)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ the ligand is asymmetric, with the W–μ-C–R angles *ca.* 20° larger than the M–μ-C–R angles (Table 5). The *p*-tolylmethylidyne groups in the Pt–W and Ti–W complexes evi-

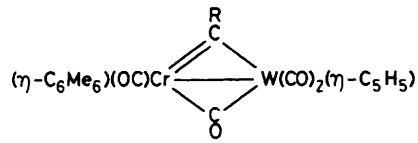
Table 5. Some interatomic separations (Å) and angles (°) for dimetallacyclopropene rings in complexes formed by $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ [a]

Compound	M–W	μ-C–W	W–μ-C–R	M–μ-C–R	M–μ-C–W
$[RhW(\mu\text{-}CR)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ [b]	2.796(1)	1.913(14)	146(1)	124.2(9)	89.7(6)
$[CoW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (4)	2.758(1)	1.913(7)	142.1(6)	124.7(5)	91.4(3)
$[TiW(\mu\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3]$ [c]	2.977(4)	1.91(2)	138(2)	129(1)	92.7(8)
$[PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [d]	2.751(1)	1.967(6)	137.9(7)	134.2(6)	87.9(3)
$[CrW(\mu\text{-}CR)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)]$ (1)	2.941(1)	2.025(6)	131.7(4)	131.5(4)	96.1(3)

[a] R = C_6H_4Me-4. [b] Ref. 1*a*. [c] Ref. 1*b*. [d] Ref. 4.



(1a)



(1b)

dently lie between these extremes, but as yet we have insufficient information to identify the factors causing the effects observed.

The *X*-ray diffraction results for compound (1) do not account for the observation of bands in the i.r. spectrum (Table 1) in the bridging (1 785 cm^{-1}) and semi-bridging (1 837 cm^{-1}) carbonyl region. A possible explanation for this is that in solution (1) exists as a mixture of two tautomers (1a) and (1b).

Experimental

The techniques used have been described previously.[1] Analytical data for the new compounds are given in Table 1. Light petroleum refers to that fraction of b.p. 40—60 °C. I.r. measurements were made with a Nicolet MX-1 FT spectrometer. The n.m.r. spectra were recorded using JEOL FX 90Q or FX 200 spectrometers. Spectroscopic data are summarised in Table 2. The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me), $[Mo(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$,[2,18] $[Co(CO)_2(\eta\text{-}C_5Me_5)]$,[19] $[M(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (M = Rh or Ir),[20] and $[M(acac)(C_2H_4)_2]$ (M = Rh or Ir) [21,22] were made by methods previously reported.

Synthesis of the Complexes.—(*a*) A thf (150 cm^3) solution of $[Cr(CO)_3(\eta\text{-}C_6Me_6)]$ (1.19 g, 4.0 mmol) at −10 to −15 °C, under argon, was irradiated with u.v. light (500-W medium-pressure Hanovia mercury-vapour lamp). After 3 h the lamp was turned off and solid $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.82 g, 2.0 mmol) added. The solution was stirred (3 h) at 0 °C and allowed to warm slowly to room temperature. Solvent was removed *in vacuo*, and the dark green residue was dissolved in the minimum volume of CH_2Cl_2–light petroleum (1 : 1) and chromatographed on an alumina column at 0 °C. Elution with the same solvent mixture, followed by evaporation, gave a green solid. The latter was recrystallised from CH_2Cl_2–light petroleum (1 : 20) to yield dark green *crystals* of $[CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)]\cdot CH_2Cl_2$ (0.9 g). The crystals readily release CH_2Cl_2 *in vacuo*.

(*b*) Similarly, $[Mn(CO)_3(\eta\text{-}C_5H_4Me)]$ (0.87 g, 4.0 mmol) in thf (150 cm^3) was irradiated for 3 h, and then $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.82 g, 2.0 mmol) was added to the purple solution. The mixture was allowed to warm to room temperature, and was stirred overnight. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (1 : 1) and chromatographed on alumina, using the same solvent mixture. Evaporation of the deep purple eluate afforded a residue, which was crystallised from CH_2Cl_2–dichloromethane (1 : 20) to give violet-black *crystals* of $[MnW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (2) (0.7 g).

(*c*) Black *microcrystals* of $[ReW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2]$ (3) (0.16 g), characterised spectroscopically, were obtained from $[Re(CO)_3(\eta\text{-}C_5H_5)]$ (0.34 g, 1.0 mmol) and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.41 g, 1.0 mmol) using the same method as employed for the synthesis of (2).

(*d*) A toluene (20 cm^3) solution of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (1 g, 2.5 mmol) and $[Co(CO)_2(\eta\text{-}C_5Me_5)]$ (0.62 g, 2.5 mmol) was heated (120 °C) for 3 d in an evacuated Schlenk tube fitted with a Young's high-pressure stopcock. Volatile material was removed *in vacuo*, the brown oil remaining was absorbed on alumina and the latter transferred to a column of alumina in light petroleum for chromatography. Elution with light petroleum gave minor amounts of the reactants. Elution with CH_2Cl_2–light petroleum (1 : 3) gave a purple band which after evaporation of solvent afforded purple *needles* of $[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (4) (0.36 g). Elution of the column with CH_2Cl_2–light petroleum (1 : 1) gave dark red $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$, identified spectroscopically.[13]

(*e*) Carbon monoxide was bubbled through a light petroleum (50 cm^3) solution of $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.13 g, 0.5 mmol) for 10 min to generate $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ *in situ*. Solid $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.5 mmol) was added, and the mixture stirred for 4 h. The brown precipitate was collected, washed with cold (0 °C) light petroleum (2 × 5 cm^3), and dried *in vacuo* affording brown *microcrystals* of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (5) (0.33 g).

(*f*) Dark green almost black *crystals* of $[IrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (6) (0.47 g), purified by chromatography using Et_2O–light petroleum (1 : 1) as eluant, were obtained from $[Ir(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.37 g, 1.0 mmol), CO, and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.41 g, 1.0 mmol), using the same method as for (5). The reaction also gave traces of a red complex believed to be $[Ir_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$ [$\nu_{max.}$(CO) at 1 983vs, 1 921vs, and 1 710m cm^{-1} (CH_2Cl_2)], eluted from the chromatography column with CH_2Cl_2. The analogous dirhodiumtungsten compound has been previously prepared.[23]

(*g*) The compound $[RhW(\mu\text{-}CMe)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (7) (0.52 g) was obtained from $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.33 g, 1.0 mmol) and $[Rh(C_2H_4)_2(\eta\text{-}C_9H_7)]$ (0.26 g, 1.0 mmol) treated with CO gas, as described for the synthesis of (5).

(*h*) The compound $[Ir(acac)(C_2H_4)_2]$ (0.15 g, 0.43 mmol) in light petroleum (15 cm^3) was treated with a stream of CO gas for 30 min to give $[Ir(acac)(CO)_2]$. Solvent was removed

Table 6. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for [CrW(μ-CC_6H_4Me-4)$(CO)_4$(η-C_5H_5)(η-C_6Me_6)] (1)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.215 51(3)	0.144 31(2)	0.413 97(1)	C(34)	0.015 1(4)	0.148 2(3)	0.155 1(2)
Cr	0.065 89(10)	0.103 96(6)	0.273 40(5)	C(35)	0.002 1(4)	0.214 9(3)	0.201 1(2)
C	0.232 3(6)	0.161 3(3)	0.304 3(3)	C(36)	−0.086 2(4)	0.211 5(3)	0.259 2(2)
C(11)	0.347 8(4)	0.195 5(2)	0.261 0(2)	C(311)	−0.267 6(10)	0.137 9(7)	0.332 8(5)
C(12)	0.396 5(4)	0.273 2(2)	0.276 3(2)	C(321)	−0.238 4(11)	0.000 1(6)	0.235 3(7)
C(13)	0.499 1(4)	0.306 4(2)	0.234 6(2)	C(331)	−0.048 3(14)	0.003 3(7)	0.115 7(6)
C(14)	0.552 9(4)	0.262 0(2)	0.177 6(2)	C(341)	0.103 9(12)	0.153 2(8)	0.087 1(5)
C(15)	0.504 2(4)	0.184 4(2)	0.162 2(2)	C(351)	0.077 4(11)	0.293 1(6)	0.181 0(7)
C(16)	0.401 7(4)	0.151 1(2)	0.203 9(2)	C(361)	−0.099 5(12)	0.286 7(6)	0.310 1(6)
C(17)	0.669 3(9)	0.297 8(6)	0.131 7(4)	C(1)	0.029 8(8)	0.160 3(5)	0.454 4(4)
C(21)	0.410 8(6)	0.058 7(4)	0.412 1(3)	O(1)	−0.069 9(6)	0.169 3(5)	0.482 6(3)
C(22)	0.446 0(6)	0.128 5(4)	0.454 3(3)	C(2)	0.217 9(8)	0.260 8(5)	0.419 7(4)
C(23)	0.365 9(6)	0.128 3(4)	0.517 5(3)	O(2)	0.223 7(8)	0.330 6(4)	0.426 1(3)
C(24)	0.281 0(6)	0.058 5(4)	0.514 4(3)	C(3)	0.027 9(7)	0.041 1(4)	0.353 3(4)
C(25)	0.308 8(6)	0.015 4(4)	0.449 2(3)	O(3)	−0.017 3(6)	−0.008 7(3)	0.391 1(3)
C(31)	−0.161 5(4)	0.141 6(3)	0.271 4(2)	C(4)	0.180 5(7)	0.022 9(4)	0.252 2(4)
C(32)	−0.148 5(4)	0.074 9(3)	0.225 4(2)	O(4)	0.255 6(7)	−0.030 5(3)	0.241 3(4)
C(33)	−0.060 3(4)	0.078 3(3)	0.167 3(2)				

Table 7. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for [CoW(μ-CC_6H_4Me-4)$(CO)_3$(η-C_5H_5)(η-C_5Me_5)] (4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.368 79(2)	−0.158 82(3)	−0.122 54(2)	C(22)	0.121 5(7)	0.103 3(11)	−0.304 8(7)
Co	0.223 43(8)	−0.013 06(11)	−0.223 38(7)	C(23)	0.181 6(9)	0.193 0(10)	−0.244 5(7)
C(11)	0.338 9(7)	0.022 9(10)	−0.084 0(6)	C(24)	0.268 1(7)	0.187 0(9)	−0.256 3(6)
O(111)	0.331 1(6)	0.120 9(7)	−0.046 3(5)	C(25)	0.260 7(7)	0.090 3(10)	−0.321 8(6)
C(21)	0.158 2(7)	−0.074 8(10)	−0.165 0(7)	C(26)	0.170 6(8)	0.042 4(10)	−0.352 7(6)
O(211)	0.114 0(6)	−0.118 2(9)	−0.126 5(6)	C(221)	0.020 4(8)	0.086(2)	−0.320 1(11)
C(12)	0.457 9(7)	−0.076 3(12)	−0.169 9(7)	C(231)	0.155 9(12)	0.289 5(13)	−0.184 3(9)
O(121)	0.513 7(6)	−0.033 5(11)	−0.193 1(7)	C(241)	0.347 8(9)	0.271 2(12)	−0.212 1(8)
C(3)	0.279 0(6)	−0.190 2(8)	−0.228 7(6)	C(251)	0.334 2(8)	0.052 2(14)	−0.359 1(8)
C(31)	0.238 4(6)	−0.299 7(9)	−0.289 1(6)	C(261)	0.133 5(9)	−0.052 6(12)	−0.429 0(7)
C(32)	0.148 3(7)	−0.336 0(10)	−0.310 8(7)	C(13)	0.429 6(10)	−0.243 0(11)	0.016 3(7)
C(33)	0.112 9(7)	−0.445 5(12)	−0.365 0(7)	C(14)	0.477 2(9)	−0.307 7(13)	−0.032 2(8)
C(34)	0.166 1(8)	−0.517 4(10)	−0.403 4(6)	C(15)	0.416 8(10)	−0.388 1(11)	−0.091 3(8)
C(35)	0.255 9(8)	−0.480 6(11)	−0.384 0(6)	C(16)	0.334 1(11)	−0.374 9(12)	−0.080 9(9)
C(36)	0.291 6(7)	−0.374 6(10)	−0.327 8(6)	C(17)	0.342 2(10)	−0.281 7(12)	−0.013 3(7)
C(341)	0.126 0(10)	−0.634 3(11)	−0.463 6(7)				

in vacuo, and the residue was treated with a CH_2Cl_2 (20 cm^3) solution of [W(≡CR)$(CO)_2$(η-C_5H_5)] (0.19 g, 0.47 mmol). The mixture was refluxed until the i.r. showed the absence of [Ir(acac)$(CO)_2$]. Solvent was then removed *in vacuo*, and the residue was washed with light petroleum (5 × 5 cm^3) at −20 °C, yielding, after drying, dark red-brown *microcrystals* of [IrW(acac)(μ-CC_6H_4Me-4)$(CO)_3$(η-C_5H_5)] (8) (0.21 g).

(*i*) A light petroleum (15 cm^3) solution of [Rh(acac)$(C_2H_4)_2$] (0.26 g, 1 mmol) was treated with a stream of CO gas to generate [Rh(acac)$(CO)_2$]. Solid [Mo(≡CMe)$(CO)_2$(η-C_5H_5)] (0.24 g, 1.0 mmol) was added to the suspension, which rapidly evolved CO. The mixture was stirred for 1 h affording a purple precipitate, which was collected and washed with light petroleum (2 × 2 cm^3) at 0 °C, and dried *in vacuo* to give purple *crystals* of [RhMo(acac)(μ-CMe)$(CO)_3$(η-C_5H_5)] (9) (0.45 g).

Crystal Structure Determination of Complex (1).—The large dark green crystals of (1) obtained from CH_2Cl_2–light petroleum contain one molecule of CH_2Cl_2 per molecule of complex. During preliminary Weissenberg and precession photography it was evident that solvent loss caused significant deterioration of the crystals. This was satisfactorily prevented by coating the crystal (0.14 × 0.40 × 0.45 mm) used for data collection with a thin film of Araldite, and then sealing it in a thin glass capillary tube. Intensities were collected on a Nicolet $P2_1m$ four-circle diffractometer and were corrected for Lorentz, polarisation, and absorption effects.

Crystal data. $C_{29}H_{30}CrO_4W{\cdot}CH_2Cl_2$, M = 678.1, Monoclinic, a = 9.680(4), b = 16.595(4), c = 18.151(5) Å, β = 93.16(3)°, U = 2 911(2) Å^3, D_m = 1.74, Z = 4, D_c = 1.74 g cm^{-3}, $F(000)$ = 1 504, space group $P2_1/c$ (no. 14), Mo-K_α X-radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 46.2 cm^{-1}. Number of measured intensities 7 003. Final R 0.041 (R' 0.043) for 4 653 intensities [295 K, $2\theta \leq 55°$, $I \geq 3\sigma(I)$].

The structure was solved by conventional heavy-atom methods. The cyclopentadienyl and aryl ring systems were treated as rigid groups [C–C(C_5H_5) 1.420, C–C(C_6H_4 and C_6Me_6) 1.395 Å]; hydrogen atoms were not included in the refinement. Refinement by blocked-cascade least squares converged at R 0.041 (R' 0.043) with weights applied according to the scheme $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$. Atom co-ordinates for complex (1) are in Table 6.

Crystal Structure Determination for Complex (4).—Crystals of (4) grow as dark purple prisms. Intensities were collected as for (1) from a crystal of dimensions 0.45 × 0.25 × 0.15 mm.

Crystal data. $C_{26}H_{27}CoO_3W$, $M = 630.3$, Monoclinic, $a = 15.617(3)$, $b = 9.693(1)$, $c = 16.732(2)$ Å, $\beta = 108.19(1)°$, $U = 2\,406(1)$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.74$ g cm^{-3}, $F(000) = 1\,232$, space group $P2_1/c$ (no. 14), Mo-K_α X-radiation, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 55.9 cm^{-1}. Number of measured intensities 6 335. Final R 0.050 (R' 0.049) for 3 507 intensities [292 K, $2\theta \leqslant 55°$, $I \geqslant 4\sigma(I)$].

The metal atoms were located from a sharpened Patterson synthesis, and all non-hydrogen atoms from successive electron-density difference syntheses. All non-hydrogen atoms were allowed anisotropic thermal parameters, and hydrogen atoms were included at calculated positions (C–H 0.96 Å). The methyl groups were refined as rigid groups, being allowed to pivot about the carbon atom, with the aromatic hydrogen atoms in a riding mode. Chemically equivalent hydrogen atoms were given a common isotropic thermal parameter which was allowed to refine; the final values were $U_{iso} = 0.10(2)$ Å^2 for the cyclopentadienyl hydrogens, $U_{iso} = 0.119(13)$ Å^2 for the pentamethylcyclopentadienyl hydrogens, $U_{iso} = 0.14(3)$ Å^2 for the tolyl methyl hydrogens, and $U_{iso} = 0.067(15)$ Å^2 for the aromatic hydrogen atoms. Refinement converged at R 0.050 (R' 0.049) and the final electron-density difference synthesis showed no peaks >2.5 or < -2.7 e Å^{-3}, the largest peaks lying in close proximity to the metal atoms. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$ gave a satisfactory weight analysis.

All computations were carried out within the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[24] Scattering factors, with corrections for anomalous dispersion, were from ref. 25. Atom co-ordinates for complex (4) are in Table 7.

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