

Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 33.¹ Reactions of $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ with the Dimetal Compounds $[MRh(\mu-CO)_2(\eta-C_5Me_5)_2]$ ($M = Co$ or Rh); X-Ray Crystal Structure of $[Rh_2W(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]^*$

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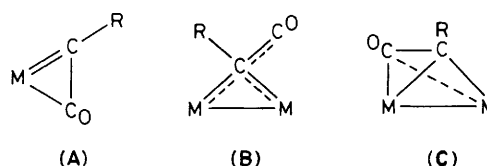
The compound $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ reacts with $[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2]$ in tetrahydrofuran (thf) at room temperature to give two crystalline products, red $[Rh_2W(\mu-CO)(\mu_3-C(O)CMe)(CO)(\eta-C_5H_5)(\eta-C_5Me_5)_2]$ (1) and green $[Rh_2W(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]$ (2a). The structures of both species are assigned on the basis of spectroscopic data (i.r. and n.m.r.), with that of the latter confirmed by a single-crystal X-ray diffraction study. The methylmethylidyne ligand symmetrically bridges the metal atom triangle [μ_3-C-Rh 2.026(7), μ_3-C-W 2.030(12), $Rh-Rh$ 2.639(1), $Rh-W$ 2.836(1) Å]. One CO ligand symmetrically bridges the $Rh-Rh$ vector, while the remaining two CO groups bonded to tungsten asymmetrically bridge the $Rh-W$ edges of the triangle [$W-C-O$ 167.4(9)°]. Compound (1) in solution releases CO irreversibly to give (2a). The $\mu_3-C(O)CMe$ ligand in (1) may be protonated or methylated, affording dirhodiumtungsten salts containing bridging alkyne ligands $[Rh_2W(\mu-CO)\{\mu_3-C(OR)CMe\}(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2][X]$ ($R = H$, $X = BF_4$ or CF_3CO_2 ; $R = Me$, $X = CF_3SO_3$). Treatment of $[CoRh(\mu-CO)_2(\eta-C_5Me_5)_2]$ with $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ in thf at room temperature gives a mixture of the dimetal compound $[RhW(\mu-CMe)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]$ and the trimetal complex $[CoRhW(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]$. Protonation ($HBF_4 \cdot Et_2O$) of the latter affords the salt $[CoRhW(\mu-H)(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2][BF_4]$ (two isomers). The related salts $[Rh_2W(\mu-H)(\mu-CO)(\mu_3-CR)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2][BF_4]$ ($R = Me$ or C_6H_4Me-4) have also been prepared. The 1H and $^{13}C\{-^1H\}$ n.m.r. spectra of the new compounds are reported and discussed.

Heteronuclear di- or tri-metal compounds containing bonds between tungsten and other transition elements are readily obtained as products of reactions between the (tolylmethylidyne)tungsten complex $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ and low-valent metal species.^{2,3} In these cluster compounds the metal-metal bonds are bridged by CC_6H_4Me-4 or $C_2(C_6H_4Me-4)_2$ groups. Related chemistry involving the (methylmethylidyne)tungsten complex $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ has as yet been little studied, and only a few compounds with CMe groups bridging bonds between tungsten and other metallic elements are known. Those derived from $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ are limited to the six species $[PtW(\mu-CMe)(CO)_2(PR_3)_2(\eta-C_5H_5)]$ ($R = Me$ or Et),⁴ $[RhW(\mu-CMe)(CO)_3(\eta-C_5H_5)(\eta-C_9H_7)]$,⁵ $[Co_2W(\mu_3-CMe)(CO)_8(\eta-C_5H_5)]$,⁶ $[Fe_2W(\mu_3-CMe)(\mu-CO)(CO)_8(\eta-C_5H_5)]$,⁷ and $[VW(\mu-CMe)(CO)_2(\eta-C_5H_5)_3]$.³ Further work on complexes in which methylmethylidyne ligands bridge two or three metal centres is merited since preliminary studies indicate that their chemistry is markedly different from that of their tolylmethylidyne analogues.^{4,7} Herein we describe reactions between $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ and the dimetal complexes $[MRh(\mu-CO)_2(\eta-C_5Me_5)_2]$ ($M = Co$ or Rh), as well as protonation and methylation studies on some of the products.

Results and Discussion

In tetrahydrofuran (thf), at room temperature, the compounds $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ and $[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2]$ yield two crystalline complexes (1) and (2a), data for which are given in Table 1. It was also observed that (2a) was formed *via* (1), solutions of the latter in organic solvents releasing CO irreversibly to give the former. The molecular structure of the green compound (2a) was established by an X-ray diffraction study, described below. Despite repeated attempts, no single

crystals of the red complex (1) suitable for X-ray diffraction could be obtained. The structure shown for this species, a triangle of metal atoms triply bridged by a $C(O)CMe$ ligand on one side, and asymmetrically bridged by a CO group on the other, is inferred from the spectroscopic data, discussed below. Several mono- and bi-nuclear metal complexes containing 'ketenyl' ligands have been reported,⁸⁻¹² with these groups adopting bonding modes (A)–(C). Compound (1) appears to be the first example of a complex where the ketenyl group is bridging three metal centres.



The 1H and $^{13}C\{-^1H\}$ n.m.r. spectra of (1) (Table 2) are informative, and support the structure proposed. In both spectra there are the expected resonances for two $\eta-C_5Me_5$ groups in different chemical environments. The $^{13}C\{-^1H\}$ spectrum has four resonances in the range 230–265 p.p.m. The peaks at δ 264.9 and 233.1 p.p.m. are assigned to WCO

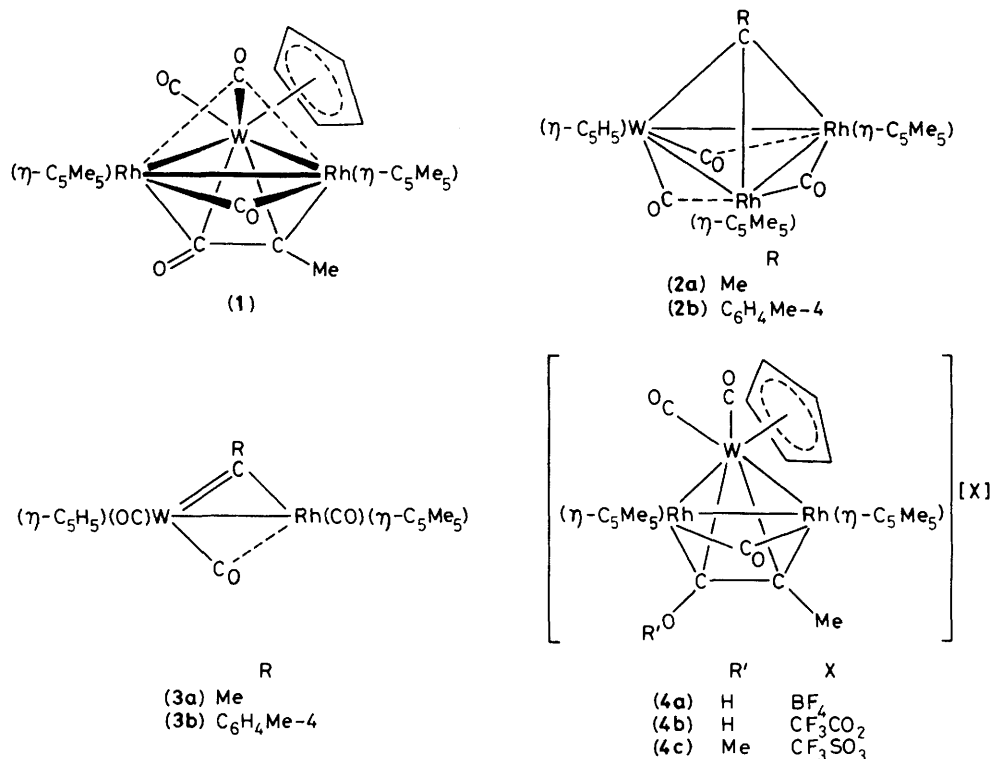
* 1,2- μ -Carbonyl-3,3-dicarbonyl-3- η -cyclopentadienyl- μ_3 -methylmethylidyne-1,2-bis(η -pentamethylcyclopentadienyl)-triangulo-dirhodiumtungsten.

Supplementary data available (No. SUP 56197, 6 pp.); thermal parameters, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Table 1. Analytical^a and physical data for the complexes

Compound	Colour	Yield (%)	$\nu(\text{CO})^b/\text{cm}^{-1}$	Analysis (%)	
				C	H
(1) $[\text{Rh}_2\text{W}(\mu\text{-CO})(\mu_3\text{-CO})\{\mu_3\text{-C}(\text{O})\text{CMe}\}(\text{CO})(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2]$	Red	41	^c 1 805s, 1 772m, 1 672mbr	43.0 (43.0)	4.6 (4.4)
(2a) $[\text{Rh}_2\text{W}(\mu\text{-CO})(\mu_3\text{-CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2]$	Green	35	^c 1 860s, 1 795m, 1 778m	43.0 (43.1)	4.8 (4.5)
(3a) $[\text{RhW}(\mu\text{-CMe})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$	Orange	23	^d 1 974m, 1 916s, 1 828m	40.2 (40.1)	3.8 (3.8)
(4a) $[\text{Rh}_2\text{W}(\mu\text{-CO})(\mu\text{-MeC}_2\text{OH})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2][\text{BF}_4]$	Brown	100	1 969s, 1 874m, 1 810s	39.2 (39.1)	3.9 (4.1)
(4b) $[\text{Rh}_2\text{W}(\mu\text{-CO})(\mu\text{-MeC}_2\text{OH})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2][\text{CF}_3\text{CO}_2]$	Brown	100	1 963s, 1 872m, 1 805s, 1 687mbr	39.7 (40.5)	4.0 (4.0)
(4c) $[\text{Rh}_2\text{W}(\mu\text{-CO})(\mu\text{-MeC}_2\text{OMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2][\text{CF}_3\text{SO}_3]$	Brown	100	1 972s, 1 878m, 1 814s	38.3 (38.5)	4.0 (4.0)
(5a) $[\text{Rh}_2\text{W}(\mu\text{-H})(\mu\text{-CO})(\mu_3\text{-CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2][\text{BF}_4]$	Green-brown	85	2 015s, 1 960s, 1 917wbr, 1 818m	38.0 (38.9)	4.2 (4.2)
(5b) $[\text{Rh}_2\text{W}(\mu\text{-H})(\mu\text{-CO})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2][\text{BF}_4]$	Brown	80	2 020s, 1 966s, 1 917wbr, 1 811m	^e 40.8 (40.9)	4.8 (4.2)
(6) $[\text{CoRhW}(\mu\text{-CO})(\mu_3\text{-CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2]$	Brown	38	1 859s, 1 785mbr, 1 764mbr	45.7 (45.4)	5.0 (4.8)
(7) $[\text{CoRhW}(\mu\text{-H})(\mu\text{-CO})(\mu_3\text{-CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2][\text{BF}_4]^f$	Green	100	2 014s, 1 958s, 1 808m	41.1 (40.9)	4.8 (4.4)

^a Calculated values are given in parentheses. ^b In CH_2Cl_2 unless otherwise stated. ^c In tetrahydrofuran. ^d In pentane. ^e Crystallises with a molecule of CH_2Cl_2 . ^f Isomeric mixture, see text.



groups. The former signal is an apparent triplet [$J(\text{RhC})$ 15 Hz] and this observation, together with the chemical shift, strongly suggests that this relatively deshielded carbonyl group is asymmetrically triply bridging the Rh_2W triangle. The appearance of the signal as a triplet, arising from the overlap of two doublets, is in accord with the chemically inequivalent rhodium centres present in (1). A resonance at 236.7 p.p.m., also a 1:2:1 triplet, is assigned to the

$\text{Rh}(\mu\text{-CO})\text{Rh}$ group. In the $^{13}\text{C}\{-^1\text{H}\}$ spectrum of (2a) the signal for the CO group bridging the Rh-Rh bond occurs at a similar chemical shift (δ 229.2 p.p.m.) appearing as a triplet [$J(\text{RhC})$ 46 Hz] since the rhodium nuclei are equivalent. In the spectrum of (1), the remaining resonance (258.8 p.p.m.) in the 230–265 p.p.m. region is assigned to the ligated oxygen-bound carbon $\text{C}(\text{O})\text{CMe}$ of the ketenyl group, appearing as a doublet [$J(\text{RhC})$ 24 Hz] since it is bonded to one

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

Compound	¹ H ^b (δ)	¹³ C ^c (δ)
(1)	^d 1.45 (s, 15 H, C ₅ Me ₅), 1.60 (s, 15 H, C ₅ Me ₅), 1.80 (s, 3 H, μ-CMe), 5.25 (s, 5 H, C ₅ H ₅)	264.9 [t, μ ₃ -CO, <i>J</i> (RhC) 15], 258.8 [d, μ ₃ -C(O)CMe, <i>J</i> (RhC) 24], 236.7 [t, μ-CO, <i>J</i> (RhC) 43 and 43], 233.1 (WCO), 106.5, 105.0 (C ₅ Me ₅), 95.9 (C ₅ H ₅), 85.6 [d, μ ₃ -C(O)CMe, <i>J</i> (RhC) 24], 16.6 (μ-CMe), 8.9, 8.0 (C ₅ Me ₅)
(2a)	^d 1.66 (s, 30 H, C ₅ Me ₅), 4.07 (s, 3 H, μ ₃ -CMe), 5.20 (s, 5 H, C ₅ H ₅)	299.7 [t, μ ₃ -C, <i>J</i> (RhC) 30], 232.1 [s, 2 WCO, <i>J</i> (WC) 174], 229.2 [t, μ-CO, <i>J</i> (RhC) 46], 101.8 (C ₅ Me ₅), 90.0 (C ₅ H ₅), 53.9 (μ ₃ -CMe), 9.1 (C ₅ Me ₅)
(3a)	^d 1.86 (s, 15 H, C ₅ Me ₅), 2.76 (s, 3 H, μ ₃ -CMe), 5.43 (s, 5 H, C ₅ H ₅)	332.8 [d, μ-CMe, <i>J</i> (RhC) 27], 232.2, 230.0 (WCO), 190.0 [d, RhCO, <i>J</i> (RhC) 89], 103.3 (C ₅ Me ₅), 91.1 (C ₅ H ₅), 50.1 (μ-CMe), 9.9 (C ₅ Me ₅)
(4a)	1.69 (s, 15 H, C ₅ Me ₅), 1.77 (s, 15 H, C ₅ Me ₅), 2.27 (s, 3 H, μ-CMe), 5.49 (s, 5 H, C ₅ H ₅), 7.09 [br, s, 1 H, μ-C(OH)]	226.7, 202.5 (WCO), 190.6 [d, μ-C(OH), <i>J</i> (RhC) 34], 138.5 [d, μ-CMe, <i>J</i> (RhC) 28], 106.1 [d, C ₅ Me ₅ , <i>J</i> (RhC) 6], 104.1 (C ₅ Me ₅), 91.6 (C ₅ H ₅), 23.8 (μ-CMe), 9.8, 9.6 (C ₅ Me ₅)
(4b)	1.68 (s, 15 H, C ₅ Me ₅), 1.76 [d, 15 H, C ₅ Me ₅ , <i>J</i> (RhH) 1], 2.27 (s, 3 H, μ-CMe), 5.49 (s, 5 H, C ₅ H ₅)	^e 227.6 [WCO, <i>J</i> (WC) 167], 216.9 [d of d, μ-CO, <i>J</i> (RhC) 47 and 44], 203.8 [WCO, <i>J</i> (WC) 157], 194.5 [d, μ-C(OH), <i>J</i> (RhC) 32], 160.8 (br, CO ₂ CF ₃), 137.1 [d, μ-CMe, <i>J</i> (RhC) 27, <i>J</i> (WC) 115], 114.7 [q, br, CO ₂ CF ₃ , <i>J</i> (FC) 290], 105.2, 103.4 (C ₅ Me ₅), 91.5 (C ₅ H ₅), 25.2 (μ-CMe), 9.6, 8.7 (C ₅ Me ₅)
(4c)	1.70 [d, 15 H, C ₅ Me ₅ , <i>J</i> (RhH) 0.5], 1.77 [d, 15 H, C ₅ Me ₅ , <i>J</i> (RhH) 1], 2.41 (s, 3 H, μ-CMe), 3.71 (s, 3 H, μ-COMe), 5.52 (s, 5 H, C ₅ H ₅)	^e 224.6 (WCO), 216.3 [d of d, μ-CO, <i>J</i> (RhC) 52 and 43], 199.6 [WCO, <i>J</i> (WC) 160], 194.0 [d, μ-COMe, <i>J</i> (RhC) 31], 148.1 [d, μ-CMe, <i>J</i> (RhC) 28], 120.0 [q, SO ₃ CF ₃ , <i>J</i> (FC) 321], 105.1, 102.9 (C ₅ Me ₅), 90.4 (C ₅ H ₅), 58.5 (μ-COMe), 25.5 (μ-CMe), 8.6, 7.6 (C ₅ Me ₅)
(5a)	^f -18.69 [d, 1 H, Rh(μ-H)W, <i>J</i> (RhH) 26, <i>J</i> (WH) 40], * -17.51 [d, 1 H, Rh(μ-H)W, <i>J</i> (RhH) 26], * 1.73 (s, 15 H, C ₅ Me ₅), 1.80 (s, 15 H, C ₅ Me ₅), 1.81 (s, 15 H, C ₅ Me ₅), * 1.87 (s, 15 H, C ₅ Me ₅), 3.96 (s, 3 H, μ ₃ -CMe), * 4.22 (s, 3 H, μ ₃ -CMe), 5.20 (s, 5 H, C ₅ H ₅), * 5.33 (s, 5 H, C ₅ H ₅)	278.4 [t, μ ₃ -CMe, <i>J</i> (RhC) 29], 222.6 (μ-CO), 211.7, 204.1 (WCO), 105.8 [d, C ₅ Me ₅ , <i>J</i> (RhC) 5], 103.9 (C ₅ Me ₅), 85.4 (C ₅ H ₅), 43.6 (μ ₃ -CMe), 9.6 (2C ₅ Me ₅)
(5b)	^f -18.80 [d, 1 H, Rh(μ-H)W, <i>J</i> (RhH) 26, <i>J</i> (WH) 37], * -17.90 [d, 1 H, Rh(μ-H)W, <i>J</i> (RhH) 26], 1.56 (s, 15 H, C ₅ Me ₅), * 1.60 (s, 15 H, C ₅ Me ₅), 1.68 (s, 15 H, C ₅ Me ₅), 2.39 (s, 3 H, Me-4), * 2.46 (s, 3 H, Me-4), 5.26 (s, 5 H, C ₅ H ₅), * 5.46 (s, 5 H, C ₅ H ₅), 7.32 (m, 4 H, C ₆ H ₄)	275.8 (μ ₃ -C), 223.7 [d of d, μ-CO, <i>J</i> (RhC) 52 and 31], 209.9, 204.4 (WCO), 154.5 [C ¹ (C ₆ H ₄)], 138.9 [C ⁴ (C ₆ H ₄)], 131.7, 129.1 (C ₆ H ₄), 106.7 [d, C ₅ Me ₅ , <i>J</i> (RhC) 6], 104.5 [d, C ₅ Me ₅ , <i>J</i> (RhC) 6], 85.5 (C ₅ H ₅), 21.3 (Me-4), 9.5, 9.3 (C ₅ Me ₅)
(6)	^d 1.57 (s, 15 H, C ₅ Me ₅), 1.65 (s, 15 H, C ₅ Me ₅), 4.49 (s, μ ₃ -CMe), 5.20 (s, 5 H, C ₅ H ₅)	313.5 (μ ₃ -CMe), 242.2 [d, μ-CO, <i>J</i> (RhC) 37], 235.5, 230.5 (WCO), 102.4 [d, Rh(C ₅ Me ₅), <i>J</i> (RhC) 4], 96.2 [Co(C ₅ Me ₅)], 90.1 (C ₅ H ₅), 49.1 (μ ₃ -CMe), 9.34, 9.08 (C ₅ Me ₅)
(7)	^f -22.67 [s, 1 H, Co(μ-H)W, <i>J</i> (WH) 40], * -18.91 [d, 1 H, Rh(μ-H)W, <i>J</i> (RhH) 27], 1.64 (s, 15 H, C ₅ Me ₅), * 1.69 (s, 15 H, C ₅ Me ₅), * 1.73 (s, 15 H, C ₅ Me ₅), 1.80 (s, 15 H, C ₅ Me ₅), 4.16 (μ ₃ -CMe), * 4.27 (μ ₃ -CMe), 5.12 (s, 5 H, C ₅ H ₅), * 5.21 (s, 5 H, C ₅ H ₅)	^f 287.1 [d, μ ₃ -CMe, <i>J</i> (RhC) 34], 235.2 [d, μ-CO, <i>J</i> (RhC) 55], 211.6, 205.6 (WCO), * 106.0, 104.4, 101.1, * 98.0 (C ₅ Me ₅), * 86.1, 85.5 (C ₅ H ₅), * 44.7, 44.2 (μ ₃ -CMe), 9.9, 9.3 (C ₅ Me ₅)

^a Chemical shifts (δ) in p.p.m., coupling constants in Hz; spectra measured at room temperature unless otherwise stated. ^b Measured in CD₂Cl₂ unless otherwise stated. ^c Hydrogen-1 decoupled, to high frequency of SiMe₄; measured in CD₂Cl₂-CH₂Cl₂. ^d Measured in CDCl₃. ^e Measured at -20 °C. ^f Resonances due to minor isomer indicated by an asterisk, see text.

rhodium. The peak at 85.6 p.p.m., also an expected doublet [*J*(RhC) 24 Hz] is assigned to the other ligated carbon atom of the 'ketenyl' ligand.

The i.r. spectrum of (1) has three bands in the carbonyl stretching region. It seems likely that the very broad absorption observed at 1 672 cm⁻¹ corresponds to two overlapping bands due to the μ₃-C(O)CMe and the μ₃-CO groups. In accord with this suggestion, the complex [Rh₃(μ₃-CO)₂(η-C₅Me₅)₃],¹³ which contains an asymmetric triply-bridging carbonyl group, shows a band at 1 682 cm⁻¹, while in the spectra of the complexes [PtW{μ-C(O)C(C₆H₄Me-4)}(CO)(PR₃)(η-C₈H₁₇)(η-C₅H₅)] [PR₃ = PMe₃, PMe₂(CH₂Ph), or PMe₂Ph], which contain a ketenyl group bridging the Pt-W bonds,¹² the ketenyl CO stretch occurs at ca. 1 625 cm⁻¹. The band in the spectrum of

(1) at 1 772 cm⁻¹ may be assigned to the Rh(μ-CO)Rh group, and is comparable with those due to this group seen at 1 795 and 1 733 cm⁻¹ in the spectra of (2a) and (2b),¹⁴ respectively. The remaining band (1 805 cm⁻¹) in the spectrum of (1) may be attributed to a WCO group, but the relatively low frequency suggests that it incipiently bridges a metal-metal bond.

Data from the X-ray diffraction study of (2a) are summarised in Table 3, and the molecular structure is shown in the Figure. The molecule has mirror symmetry, so that the atoms Rh, C(1), and O(1) are related to Rh^a, C(1^a), and O(1^a), respectively; the mirror plane is defined by the atoms W, C(2), O(2), C(3),

C(4), C(31), and by the midpoints of all symmetry-related atom pairs. The three metal atoms form an isosceles triangle [Rh-Rh^a 2.639(1), Rh-W 2.836(1) Å] capped by the CMe group. The ligated μ₃-C carbon is revealed in the ¹³C-{¹H} n.m.r. spectrum by a triplet resonance at 299.7 p.p.m. [*J*(RhC) 30 Hz] (Table 2). The rhodium and tungsten atoms carry η-C₅Me₅ and η-C₅H₅ groups, respectively. The Rh-Rh vector is symmetrically bridged by the carbonyl group C(2)O(2) [Rh-C(2) 1.975(9) Å, Rh-C(2)-Rh^a 83.8(5), Rh-C(2)-O(2) 138.0(2)°], and the tungsten atom has two essentially terminal carbonyl ligands each of which weakly semi-bridges a Rh-W bond [W-C(1) 1.97(1), Rh-C(1) 2.62(1) Å, W-C(1)-O(1) 167.4(9)°], thus accounting for CO stretching bands in the i.r. spectrum (Table 1) at the relatively low frequencies of 1 860 and 1 795 cm⁻¹.

If the pentamethylcyclopentadienyl ligands in (2a) are notionally replaced by bidentate acetylacetonato (acac) ligands then the resulting structure is almost identical with that found¹⁵ for the complex [Rh₂W(μ-CO)(μ₃-CC₆H₄Me-4)(acac)₂(CO)₂(η-C₅H₅)] which has pseudo-mirror symmetry in the solid state. Moreover, in the latter the Rh-Rh separation is 2.613(2) Å, very similar to that found in (2a). The Rh-W distances in (2a) [2.836(1) Å] are, however, longer than those found in other rhodium-tungsten compounds containing bridging CC₆H₄-Me-4 ligands: [RhW(μ-CO)(μ₃-CC₆H₄Me-4)(CO)₂(PMe₃)(η-C₅H₅)(η-C₉H₇)] [2.796(1) Å],¹² [Rh₂W(μ-CO)(μ₃-CC₆H₄Me-4)(acac)₂(CO)₂(η-C₅H₅)] [2.764(2) and 2.809(2) Å],¹⁵ and [FeRhW-

Table 3. Selected bond lengths (Å) and interbond angles (°) for $[\text{Rh}_2\text{W}(\mu\text{-CO})(\mu_3\text{-CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2]$ (**2a**)^{*}

Rh–W	2.836(1)	W–C(1)	1.974(12)	W–C(3)	2.030(12)	Rh ^a –W	2.836(1)
Rh–C(1)	2.624(10)	Rh–C(2)	1.975(9)	Rh–C(3)	2.026(7)	Rh–Rh ^a	2.639(1)
C(1)–O(1)	1.148(15)	C(2)–O(2)	1.176(14)	C(3)–C(4)	1.488(16)		
Rh–W–C(1)	63.2(3)	Rh–W–C(3)	45.6(2)	C(1)–W–C(3)	108.7(4)	Rh–W–Rh ^a	55.4(1)
Rh–W–C(1 ^a)	99.5(3)	C(1)–W–C(1 ^a)	82.9(7)	W–Rh–C(1)	42.2(3)	W–Rh–C(2)	80.5(3)
C(1)–Rh–C(2)	74.6(4)	W–Rh–C(3)	45.7(3)	C(1)–Rh–C(3)	87.8(4)	C(2)–Rh–C(3)	94.8(3)
W–Rh–Rh ^a	62.3(1)	C(1)–Rh–Rh ^a	89.7(3)	C(2)–Rh–Rh ^a	48.1(2)	C(3)–Rh–Rh ^a	49.4(2)
W–C(1)–Rh	74.7(3)	W–C(1)–O(1)	167.4(9)	Rh–C(1)–O(1)	117.7(8)	Rh–C(2)–O(2)	138.0(2)
Rh–C(2)–Rh ^a	83.8(5)	W–C(3)–Rh	88.7(4)	W–C(3)–C(4)	134.5(8)	Rh–C(3)–C(4)	123.8(6)
Rh–C(3)–Rh ^a	81.2(4)						

^{*} C(1), C(1^a) and Rh, Rh^a are symmetry related atoms (see text).

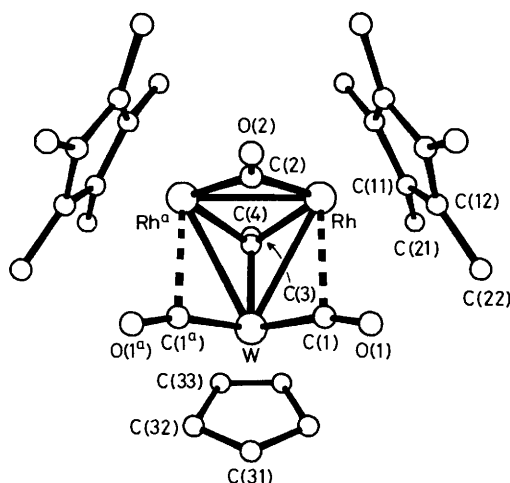


Figure. The molecular structure of $[\text{Rh}_2\text{W}(\mu\text{-CO})(\mu_3\text{-CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)_2]$ (**2a**) showing the atom numbering scheme

$(\mu\text{-CO})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_9\text{H}_7)$ [2.760(1) Å].¹⁴

The methylmethylidyne group in (**2a**) is symmetrically bound to the Rh_2W triangle (Table 3). However, the axis of the CMe group is not normal to the plane of the metal triangle, the W–C(3)–C(4) angle [134.5(8)°] being larger than the Rh–C(3)–C(4) angle [123.8(6)°]. We have observed this bonding feature for $\mu_3\text{-CC}_6\text{H}_4\text{Me-4}$ ligands in related complexes.¹⁴

The synthesis of (**2a**) in thf at room temperature proceeds under milder conditions than those which afford (**2b**). Previously the latter species was prepared by heating $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with $[\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$ in toluene at 60 °C for several hours.¹⁴ We have now found that (**2b**) can be obtained from these reagents in thf, but to bring the synthesis to completion it is necessary to heat the mixture to ca. 50 °C for a period of ca. 15 h. No product analogous to (**1**) is formed in the synthesis of (**2b**).

The preparation of (**2a**) might have been expected to have been accompanied by the formation of the dimetal species (**3a**), since its analogue (**3b**) is simultaneously produced in the synthesis of (**2b**).¹⁴ However, complex (**3a**) was isolated in another reaction described below.

The structure proposed for (**1**), and discussed above, suggested that this complex might be protonated or methylated at the oxygen atom of the bridging ketenyl ligand to give salts with alkyne ligands adopting a $\mu_3(\eta^2\text{-})$ bonding mode.^{16,17} Recently protonation and methylation of the ketenyl complexes $[\text{W}\{\mu\text{-C}(\text{O})\text{CR}\}(\text{CO})(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)]$ (R = Me or $\text{C}_6\text{H}_4\text{-}$

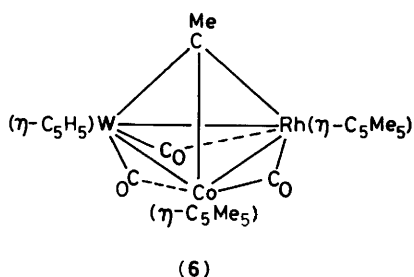
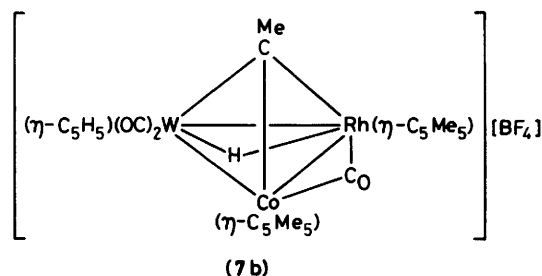
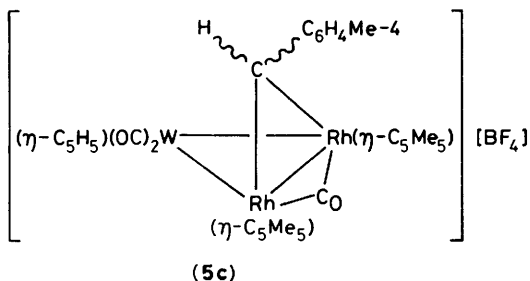
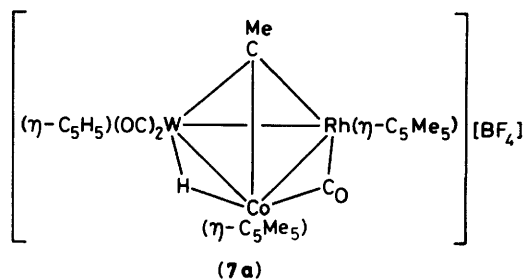
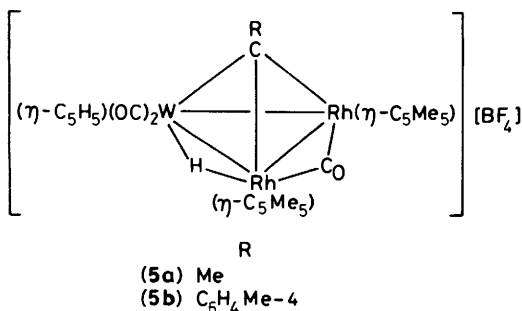
Me-4) to give the salts $[\text{W}(\text{CO})(\text{PMe}_3)(\eta\text{-RC}_2\text{OR}')(\eta\text{-C}_5\text{H}_5)][\text{X}]$ (R' = H, X = BF_4^- ; R' = Me, X = CF_3SO_3^-) has been accomplished.^{18,19}

Treatment of (**1**) with an equivalent amount of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ or $\text{CF}_3\text{CO}_2\text{H}$ affords the brown salts (**4a**) and (**4b**), characterised by microanalysis and by their spectroscopic properties (Tables 1 and 2). Methylation of (**1**) with $\text{CF}_3\text{SO}_3\text{Me}$ similarly affords (**4c**). The i.r. spectra of (**4a**) and (**4c**) show three bands in the CO stretching region at higher frequency than those in the spectrum of (**1**), in accord with the salt-like nature of these products. Moreover, neither (**4a**) nor (**4c**) shows a band near 1680 cm^{-1} attributable to the CO stretch of a $\mu\text{-C}(\text{O})\text{CMe}$ group present in the precursor (**1**). In contrast, the spectrum of (**4b**) shows a peak at 1687 cm^{-1} , but this may be assigned to the anion CF_3CO_2^- .

The n.m.r. data for the salts (**4**) are in agreement with the proposed structures. The presence in the cations of alkyne ligands in which the ligated carbon atoms have different substituents leads to non-equivalent environments at the rhodium centres. Hence the ^1H spectra (Table 2) show for each species two $\eta\text{-C}_5\text{Me}_5$ resonances. The ^1H spectrum of (**4b**) does not show a signal for the hydroxy proton, probably due to hydrogen bonding between it and the CF_3CO_2^- anion. In the $^{13}\text{C}\{^1\text{H}\}$ spectrum of (**4a**), recorded at room temperature, no band due to the $\text{Rh}(\mu\text{-CO})\text{Rh}$ group was observed. However, when the spectra of the related species (**4b**) and (**4c**) were measured at –20 °C, the resonance due to the $\mu\text{-CO}$ ligand in each salt was observed at δ 216.9 and 216.3 p.p.m., respectively. These signals appear as doublets of doublets due to the chemically non-equivalent rhodium atoms. All other bands in the spectra were as expected, and assignments were made accordingly (Table 2).

Protonation ($\text{HBF}_4\cdot\text{Et}_2\text{O}$) of the compounds (**2**) was also investigated as part of our studies. The cluster compound (**5a**) was readily obtained from (**2a**) and fully characterised (Tables 1 and 2). It was formed as a mixture of two isomers, most clearly revealed in the ^1H n.m.r. spectrum [see Table 2 where bands due to the minor isomer (ca. 15%) are marked with an asterisk]. Two signals for the hydrido-ligand were observed at δ –18.69 and –17.51 for the major and minor isomers, respectively. Both signals were doublets [$J(\text{RhH})$ 26 Hz] in accord with the presence of a $\text{Rh}(\mu\text{-H})\text{W}$ rather than a $\text{Rh}(\mu\text{-H})\text{Rh}$ bridge structure in these species. Moreover, the peak due to the major isomer showed $^{183}\text{W}\text{-}^1\text{H}$ coupling (40 Hz). Isomers of (**5a**) are possible¹⁴ corresponding to different rotational orientations of the $\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ group with respect to an axis through the tungsten atom and the centroid of the plane defined by $\mu_3\text{-CRh}_2$.

Previous attempts to protonate (**2b**)¹⁴ were unsuccessful, but in view of the results with (**2a**) these experiments were repeated. Treatment of (**2b**) with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ in dichloromethane afforded, after isolation from the reaction mixture, the salt (**5b**) in good yield (Table 1). On the basis of the n.m.r. data (Table 2)



the compound may be assigned a structure similar to that of (5a). As found for the latter, complex (5b) exists in solution as a mixture of two isomers (4:1, based on relative peak intensities in the ¹H n.m.r. spectrum).

On closer examination of the protonation reaction, it was found that initially a product (5c) was formed, which readily rearranged to (5b) thus preventing its isolation. Moreover, if the protonation of (2b) is carried out at *ca.* -40 °C, the kinetic isomer (5c) is the dominant species (>80%) as deduced from peak intensities in the ¹H n.m.r. spectrum. The spectrum of (5c) showed only one η-C₅Me₅ resonance (δ 1.50) and no signals at high field corresponding to a bridging hydrido-ligand (see Experimental section). The n.m.r. data thus lead us to suggest tentatively that (5c) has the structure shown, in which protonation has occurred at the alkylidyne carbon atom, thereby leading to a symmetrical arrangement of η-C₅Me₅ groups. Interestingly, no intermediate species akin to (5c) was observed in the protonation of (2a) at low temperatures.

The recent discovery¹³ of the mixed-metal unsaturated complex [CoRh(μ-CO)₂(η-C₅Me₅)₂] prompted a study of its reaction with [W(≡CMe)(CO)₂(η-C₅H₅)] with the object of obtaining the trimetal cluster (6). The latter compound was formed under mild conditions (thf, room temperature), but surprisingly the dimetal complex (3a) was also produced. Isolation of the latter implies cleavage of the Co-Rh bond in [CoRh(μ-CO)₂(η-C₅Me₅)₂] during reaction, since there was no evidence for the decomposition of (6) into (3a). Isolation of the latter might have been accompanied by formation of its cobalt analogue [CoW(μ-CMe)(CO)₃(η-C₅H₅)(η-C₅Me₅)], but this

was not so, and its absence may imply that it is unstable, even under the mild reaction conditions.

The two compounds (3a) and (6) were fully characterised (Tables 1 and 2). The presence of bridging methylmethylidyne ligands in both complexes is clearly revealed by the ¹³C-{¹H} n.m.r. spectra with resonances at δ 332.8 [d, J(RhC) 27 Hz] and 313.5 p.p.m. for (3a) and (6), respectively. Shifts for dimetal complexes with bridging alkylidyne ligands are always more downfield than those in which the groups bridge three metal centres.^{5,14} The ¹³C-{¹H} spectrum of (6) shows separate resonances for the Co(η-C₅Me₅) and Rh(η-C₅Me₅) groups, and a doublet signal for the μ-CO ligand (Table 2). Compound (6) joins the growing number of compounds wherein alkylidyne groups bridge a triangle formed by atoms of three different metallic elements.^{14,20}

It was of interest to protonate (6) to determine if possible the preferred location of the hydrido-ligand in the resulting cation. Treatment with the reagent HBF₄·Et₂O afforded the green tetrafluoroborate salt (7) in quantitative yield. Examination of the ¹H and ¹³C-{¹H} n.m.r. spectra (Table 2) revealed that in solution it existed as a mixture of isomers, the relative peak intensities in the ¹H spectrum at room temperature indicating a *ca.* 9:1 ratio, so that not all of the signals due to the minor isomer were observed in the carbon-13 spectrum. The ¹H spectrum was particularly informative. The predominant isomer showed a singlet high-field resonance at δ -22.67 with ¹⁸³W-¹H coupling (40 Hz), but no ¹⁰³Rh-¹H coupling, implying that the hydrido-ligand bridges the Co-W edge of the cluster in this species (7a). The high-field resonance of the minor isomer at δ -18.91 is, however, a doublet [J(RhH) 27 Hz], these indicating a structure (7b) for this complex, in which the hydrido-ligand bridges the Rh-W bond.

The results described in this paper illustrate some differences between the chemistry of the two precursors [W(≡CR)(CO)₂(η-C₅H₅)] (R = Me or C₆H₄Me-4), and compounds derived from them. Formation of (2a) proceeds under milder conditions than that of (2b), and no analogue of (1) with a C₆H₄Me-4 substituent has been isolated in this or in the previous work.¹⁴ Isolation of (1) allowed the preparation of the alkyne complexes (4) to be accomplished. Although both compounds (2) afford stable salts on protonation, in the case of (2b) a kinetically unstable intermediate was observed.

Experimental

Experiments were carried out using Schlenk tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were dried prior to use. Light petroleum refers to that fraction of b.p. 40–60 °C. A Nicolet MX-10 FT spectrophotometer was used to measure i.r. spectra, and JEOL instruments (FX 90Q and FX 200) for the n.m.r. studies. The compounds $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]^{21}$ and $[MRh(\mu-CO)_2(\eta-C_5Me_5)_2]$ ($M = Co^{13}$ or $Rh^{22,23}$) were prepared by previously described methods. Alumina used for column chromatography was Brockman, activity II. The tetrafluoroboric acid–diethyl ether adduct used for protonation studies was from B.D.H. (54% HBF_4). Analytical and other data for the new compounds are given in Table 1.

Reactions of $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$.—(a) A mixture of $[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2]$ (0.52 g, 0.97 mmol) and $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ (0.30 g, 1.0 mmol) in thf (20 cm³) was magnetically stirred at room temperature for 12 h, during which time the colour changed from blue to dark brown, and monitoring (i.r.) of the reaction showed that all the reactants had been consumed. Solvent was removed *in vacuo*, and a light petroleum (10 cm³) slurry of the residue was transferred to the top of an alumina chromatography column (20 × 2 cm). Elution with dichloromethane–light petroleum mixtures (1:9), increasing gradually to pure dichloromethane, afforded a green eluate. Evaporation of solvent *in vacuo* gave dark green microcrystals of $[Rh_2W(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]$ (**2a**) (0.30 g). Elution of the column with methanol gave a dark red solution which on removal of solvent afforded red microcrystals of $[Rh_2W(\mu-CO)(\mu_3-CO)\{\mu_3-C(O)CMe\}(CO)(\eta-C_5H_5)(\eta-C_5Me_5)_2]$ (**1**) (0.36 g). Solutions of the latter at room temperature slowly convert to compound (**2a**) with loss of CO.

(b) A thf (20 cm³) solution of $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ (0.15 g, 0.50 mmol) and $[CoRh(\mu-CO)_2(\eta-C_5Me_5)_2]$ (0.24 g, 0.50 mmol) was stirred at room temperature for 10 h, after which time reaction was complete (i.r.). Solvent was removed *in vacuo*, and the solid residue dissolved in dichloromethane (5 cm³) and adsorbed onto dry alumina (*ca.* 2 g). The latter was transferred to the top of an alumina column. Elution with light petroleum, to which dichloromethane was gradually added, gave initially an orange band followed by a brown band. Continued elution with dichloromethane afforded an orange solution which on removal of solvent *in vacuo* yielded orange crystals of $[RhW(\mu-CMe)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]$ (**3a**) (0.07 g). Subsequently a brown band was recovered from the column which after removal of solvent gave brown crystals of $[CoRhW(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]$ (**6**) (0.15 g).

Protonation and Methylation of Compound (1).—(a) A dichloromethane (10 cm³) solution of (**1**) (0.22 g, 0.25 mmol) was stirred at room temperature for 10 h, after this time no starting materials were present (i.r.), and the original red coloured solution had turned brown. Addition of diethyl ether (40 cm³) produced a brown-black precipitate. Solvent was decanted off, the precipitate washed with diethyl ether (3 × 20 cm³), and recrystallised from dichloromethane–diethyl ether (1:10) to give brown crystals of $[Rh_2W(\mu-CO)(\mu_3-MeC_2OH)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2][BF_4]$ (**4a**) (0.24 g). In a similar reaction the salt (**4b**) (Table 1) was obtained quantitatively using CF_3CO_2H for protonation.

(b) A dichloromethane (10 cm³) solution of (**1**) (0.22 g, 0.25 mmol) was stirred (30 min) with CF_3SO_3Me (0.25 mmol), the mixture turning from red to brown. Addition of diethyl ether (40 cm³) gave a brown-black precipitate. Solvent was removed, the residue washed with diethyl ether (3 × 20 cm³) and crystallised from dichloromethane–diethyl ether (1:10), thereby

affording brown crystals of $[Rh_2W(\mu-CO)(\mu_3-MeC_2OMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2][CF_3SO_3]$ (**4c**) (0.26 g).

Protonation of the Complexes (2) and (6).—(a i) A dichloromethane (10 cm³) solution of (**2a**) (0.21 g, 0.25 mmol) was stirred with $HBF_4 \cdot Et_2O$ (0.25 mmol) for 45 min, after which time all of (**2a**) was consumed (i.r.). Solvent was removed *in vacuo*, and the brown oily residue was washed with diethyl ether (3 × 20 cm³). Crystallisation from dichloromethane–light petroleum (1:10) afforded dark brown-green crystals of $[Rh_2W(\mu-H)(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2][BF_4]$ (**5a**) (0.20 g), as a mixture of isomers (see Results and Discussion section).

(a ii) Similarly a dichloromethane (10 cm³) solution of (**2b**) (0.23 g, 0.25 mmol), after treatment with $HBF_4 \cdot Et_2O$ (0.25 mmol), gave dark brown crystals of $[Rh_2W(\mu-H)(\mu-CO)(\mu_3-CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2][BF_4]$ (**5b**) (0.22 g), formed as a mixture of isomers (see Results and Discussion section).

When the protonation reaction is carried out at low temperatures (–40 °C or below) a pale red product (**5c**) is formed initially, which converts into (**5b**). Complex (**5c**) had an i.r. spectrum with $\nu_{max}(CO)$ at 2 000s, 1 944s, and 1 821 cm^{–1}. The ¹H n.m.r. spectrum (in CD_2Cl_2) had signals at δ 1.50 (s, 30 H, C_5Me_5), 2.14 (s, 3 H, Me-4), 6.30 (s, 5 H, C_5H_5), and 7.32 (m, 4 H, C_6H_4). The resonance due to the presumed μ -CHR group was not observed but may be masked by peaks due to (**5b**) (Table 2).

(b) A dichloromethane (10 cm³) solution of (**6**) (0.39 g, 0.50 mmol) was treated with $HBF_4 \cdot Et_2O$ (0.50 mmol) and stirred for 1 h, during which period the mixture turned from red-brown to green. Addition of diethyl ether (40 cm³) precipitated a green solid. The mother-liquor was decanted off, and the residue washed with diethyl ether (3 × 20 cm³) and crystallised (dichloromethane–diethyl ether, 1:10) to give green crystals of $[CoRhW(\mu-H)(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2][BF_4]$ (**7**) (0.44 g), formed as a mixture of isomers (see Results and Discussion section).

Crystal Structure Determination of $[Rh_2W(\mu-CO)(\mu_3-CMe)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]$ (2a**).**—Crystals of (**2a**) were grown from dichloromethane–light petroleum as dark green prisms. Diffracted intensities were collected at room temperature from a crystal of dimensions *ca.* 0.40 × 0.38 × 0.30 mm, with well developed faces of the type (1 0 1), (–1 0 1), <0 1 0>, <0 0 1>. Data were collected on a Nicolet P3m four-circle diffractometer, according to methods described earlier.²⁴ Of the total 3091 independent intensities collected to $2\theta \leq 50^\circ$, 2 631 had $F \geq 5.0\sigma(F)$, where $\sigma(F)$ is the standard deviation based on statistics and only 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; the last was by a semi-empirical method based on azimuthal scan data.²⁵

Crystal data for (2a). $C_{30}H_{38}O_3Rh_2W$, $M = 836.0$, orthorhombic, $a = 8.551(3)$, $b = 18.186(7)$, $c = 18.249(7)$ Å, $U = 2 838(2)$ Å³, $Z = 4$, $D_c = 1.96$ g cm^{–3}, $F(000) = 1 624$, space group $Pcmm$ (non-standard setting of $Pnma$, no. 62), Mo- K_α X-radiation (graphite monochromator, $\lambda = 0.710 69$ Å), $\mu(Mo-K_\alpha) = 52.9$ cm^{–1}.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. Hydrogen atoms were not included in the refinement and all atoms were given anisotropic thermal parameters. Refinement by blocked-cascade least squares led to $R = 0.064$ ($R' = 0.060$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks ≥ 1 e Å^{–3} except in the immediate vicinity of the W atom where a peak of *ca.* 2 e Å^{–3} occurred. Scattering factors were from ref. 26.

Table 4. Atomic positional parameters (fractional co-ordinates; $\times 10^4$), with estimated standard deviations in parentheses, for (2a)

Atom	x	y	z	Atom	x	y	z
W	9 787(1)	7 500	7 459(1)	C(25)	9 875(22)	6 422(10)	4 451(9)
Rh	11 016(1)	6 774(1)	6 210(1)	C(1)	11 479(13)	6 781(7)	7 631(6)
C(11)	9 795(11)	5 761(7)	5 761(8)	O(1)	12 387(10)	6 380(5)	7 864(4)
C(12)	10 953(14)	5 539(6)	6 276(7)	C(2)	12 697(14)	7 500	6 378(7)
C(13)	12 437(10)	5 743(5)	5 989(5)	O(2)	14 054(9)	7 500	6 481(7)
C(14)	12 219(11)	6 125(5)	5 345(5)	C(3)	9 252(11)	7 500	6 375(7)
C(15)	10 586(13)	6 133(6)	5 165(6)	C(4)	7 769(14)	7 500	5 948(8)
C(21)	8 084(16)	5 566(10)	5 834(15)	C(31)	8 782(18)	7 500	8 647(9)
C(22)	10 549(23)	5 101(8)	6 937(10)	C(32)	8 204(17)	8 120(8)	8 300(8)
C(23)	14 008(14)	5 592(9)	6 338(8)	C(33)	7 174(14)	7 850(10)	7 667(8)
C(24)	13 537(17)	6 400(8)	4 865(8)				

All computations were carried out on an 'Eclipse' (Data General) computer with the SHELXTL system of programs.²⁵

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References

- Part 32, M. Green, J. A. K. Howard, S. J. Porter, F. G. A. Stone, and D. C. Tyler, *J. Chem. Soc., Dalton Trans.*, 1984, 2553.
- F. G. A. Stone, in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, vol. 211, pp. 383—397; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89; in 'Chemistry for the Future,' ed. H. Gr̄unewald, Pergamon Press, Oxford, 1983, pp. 149—154.
- U. Behrens and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1605 and refs. therein.
- M. R. Awang, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 1426.
- J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2075.
- R. Amos and F. G. A. Stone, unpublished work.
- E. Delgado, A. T. Emo, J. C. Jeffery, N. D. Simmons, and F. G. A. Stone, following paper.
- F. R. Kreissl, K. Eberl, and W. Uedelhoven, *Chem. Ber.*, 1977, **110**, 3782.
- J. Martin-Gil, J. A. K. Howard, R. Navarro, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1979, 1168.
- O. Orama, U. Schubert, F. R. Kreissl, and E. O. Fischer, *Z. Naturforsch., Teil B*, 1980, **35**, 82.
- C. P. Casey, P. J. Fagan, and V. W. Day, *J. Am. Chem. Soc.*, 1982, **104**, 7360; C. P. Casey, P. J. Fagan, W. H. Miles, and S. R. Marder, in 'Organometallic Compounds: Synthesis, Structure and Theory,' ed. B. L. Shapiro, Texas A and M University Press, 1983, pp. 86—114.
- J. C. Jeffery, C. Sambale, M. F. Schmidt, and F. G. A. Stone, *Organometallics*, 1982, **1**, 1597.
- M. Green, D. R. Hankey, J. A. K. Howard, P. Louca, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 757.
- M. Green, J. C. Jeffery, S. J. Porter, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1982, 2475.
- M. J. Chetcuti, P. A. M. Chetcuti, J. C. Jeffery, R. M. Mills, P. Mitprachachon, S. J. Pickering, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 699.
- M. G. Thomas, E. L. Muettterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.*, 1976, **98**, 4645.
- L. Busetto, M. Green, B. Hessner, J. A. K. Howard, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 519.
- J. C. Jeffery, J. C. V. Laurie, I. Moore, and F. G. A. Stone, *J. Organomet. Chem.*, 1983, **258**, C37.
- F. R. Kreissl, W. Sieber, and M. Wolfgruber, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 493.
- M. J. Chetcuti, J. A. K. Howard, R. M. Mills, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1757.
- W. Uedelhoven, K. Eberl, and F. R. Kreissl, *Chem. Ber.*, 1979, **112**, 3376.
- A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **166**, C21.
- M. L. Aldridge, M. Green, J. A. K. Howard, G. N. Pain, S. J. Porter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1333.
- A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065; R. Goddard, S. D. Killops, S. A. R. Knox, and P. Woodward, *ibid.*, 1978, 1255.
- G. M. Sheldrick, 'SHELXTL' programs for use with the Nicolet X-ray system, University of Cambridge, 1976; updated at Göttingen, 1981.
- 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

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