Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 32.[1] Reactions of the Rhodium–Tungsten Complex $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ with Alkynes; *X*-Ray Crystal Structure of $[RhW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)\}(CO)_2\text{-}(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ *

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The bimetal compound $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ ($R = C_6H_4Me\text{-}4$, C_9H_7 = indenyl) reacts with the alkynes $R^1C{\equiv}CR^2$ ($R^1 = R^2$ = Ph or Me; R^1 = Ph, R^2 = H or Me) in toluene at *ca.* 50—80 °C to give the bridged complexes $[RhW\{\mu\text{-}C(R)C(R^1)C(R^2)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$. The molecular structure of the species obtained from $PhC{\equiv}CPh$ was established by a single-crystal *X*-ray diffraction study. A Rh–W bond [2.754(1) Å] is bridged by a three-carbon chain [mean C–C 1.439(8) Å]. Whereas all the atoms of the chain are bound to the rhodium [2.105(6), 2.135(6), and 2.103(5) Å], only the two end carbons are attached to the tungsten [2.175(5) and 2.196(6) Å]. The tungsten atom carries two essentially orthogonal terminal carbonyl groups, as well as the cyclopentadienyl ring. The indenyl group is asymmetrically attached to the rhodium atom, with three short Rh–C [2.185(7), 2.198(7), and 2.204(7) Å] and two long Rh–C [2.334(7) and 2.330(7) Å] separations to the C_5 ring, implying slippage towards an η^3-bonding mode. Formation of $[RhW\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_2(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_5Me_5)]$ from $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ and $PhC{\equiv}CPh$ requires forcing conditions (100 °C, 5 d in toluene), and side-reactions occur to yield hexaphenylbenzene, $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$, and the tetraphenylcyclopentadienone complex $[Rh(\mu\text{-}C_4Ph_4CO)(\eta\text{-}C_5Me_5)]$. The reaction between $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ and $[W({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$ has also been investigated. With heptane as solvent, the products are the trimetal complex $[Rh_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_9H_7)_2]$, the alkyne-bridged complex $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$, and a compound formulated as $[W_2\{\mu\text{-}C(R)C(O)C(R)\}(CO)_4(\eta\text{-}C_5H_5)_2]$. Spectroscopic data (i.r., ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r.) for the new compounds are reported and discussed.

The compounds $[Fe_2(CO)_9]$,[2] $[Co(CO)_2(\eta\text{-}C_5Me_5)]$,[3] $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[4] and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$[3] ($C_9H_7$ = indenyl) react with the tolylmethylidynetungsten complex $[W({\equiv}CR)\text{-}(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) to afford, respectively, the bimetal species $[FeW(\mu\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$, $[MW(\mu\text{-}CR)\text{-}(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (M = Co or Rh), and $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$. The reactivity of the 'dimetallacyclopropene' rings present in these compounds is of potential interest. The iron–tungsten complex, however, is difficult to study because it readily undergoes further reaction with one or other of the precursors, $[Fe_2(CO)_9]$ or $[W({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$, to give the cluster compounds $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and $[FeW_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$, respectively.[2] In contrast, the cobalt- and rhodium-tungsten compounds are readily isolated, thereby allowing their chemical behaviour to be investigated. Thus, for example, $[CoW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ reacts with alkynes such as diphenylacetylene to give the insertion product $[CoW\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$.[5] However, these reactions only proceed to completion after the reactants have been heated together in toluene to *ca.* 100 °C for several days.

In this paper we describe complexes formed by treating the indenylrhodium–tungsten species $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_9H_7)]$ with various alkynes.[6] It was anticipated that this compound would be more reactive than the aforementioned cobalt-tungsten complex $[CoW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$. It is known that indenylmetal compounds can react with nucleophiles *via* an associative mechanism, which is assisted by the transformation $M(\eta^5\text{-}C_9H_7) \longrightarrow M(\eta^3\text{-}C_9H_7)$ (M = Mo[7] or Rh[8-10]), a process which creates a vacant site on M for attack by a substrate molecule.

Results and Discussion

The compound $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ reacts with $PhC{\equiv}CPh$ in toluene at 80 °C to give a red complex (1) (*ca.* 30%), as well as the previously characterised cluster species (2) (*ca.* 50%).[4] Despite the presence in the precursor of the $Rh(\eta\text{-}C_9H_7)$ group, the process requires 1 or 2 d for completion. Moreover, side-reactions must occur to account for the formation of (2) as the major product. Compound (1) was characterised by microanalysis, and by the observation of a parent ion in the mass spectrum (Table 1). Its ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. data are in accord with the formulation shown, but discussion is deferred until the results of an *X*-ray diffraction study are described.

The molecular structure is shown in the Figure, and the internuclear distances and angles are given in Table 2. The Rh–W bond distance [2.754(1) Å] may be compared with those found in the bimetal complex $[RhW(\mu\text{-}CR)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$[2.796(1) Å],[11] and in the cluster compounds $[Rh_2W(\mu_3\text{-}CR)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$ (acac = acetylacetonate) [2.809(2) Å][12] and (2) [2.760(1) Å].[4] The metal–

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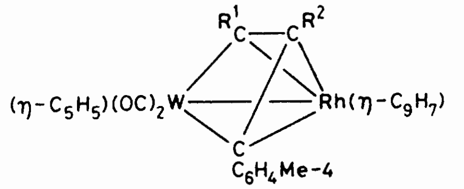
* 2,2-Dicarbonyl-2-η-cyclopentadienyl-μ-[1,2-diphenyl-3-*p*-tolylpropan-2-yl-1,3-diylidene-C^{1-3}(Rh)$C^{1,3}$(W)]-1-η^5-indenylrhodiumtungsten(*Rh–W*).

Supplementary data available (No. SUP 56016, 11 pp.): H-atom co-ordinates, thermal parameters, complete bond parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

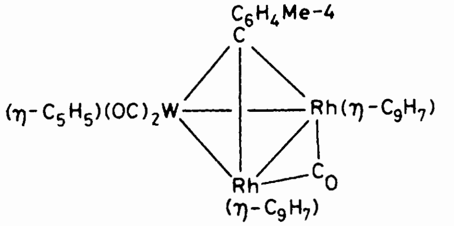
Table 1. Analytical [a] and physical data for the rhodium–tungsten compounds

Compound [b]	M.p.[c] (θ_c/°C)	Colour	$\nu_{max.}$(CO) [d]/ cm^{-1}	Yield (%)	Analysis (%)		M [e]
					C	H	
(1) [RhW{μ-C(R)C(Ph)C(Ph)}(CO)$_2$(η-C$_5$H$_5$)-(η-C$_9$H$_7$)]	178—182	Red	1 966s, 1 905s	33	56.9 (56.7)	3.7 (3.6)	804 (804)
(3) [RhW{μ-C(R)C(Me)C(Me)}(CO)$_2$(η-C$_5$H$_5$)-(η-C$_9$H$_7$)]	168—171	Orange	[f] 1 965, 1 910s	30	49.1 (49.4)	3.6 (3.7)	680 (680)
(4) [RhW{μ-C(R)C(H)C(Ph)}(CO)$_2$(η-C$_5$H$_5$)-(η-C$_9$H$_7$)]	154—157	Orange	1 949s, 1 885s	93	52.2 (52.7)	3.5 (3.5)	728 (728)
(5) [RhW{μ-C(R)C(Me)C(Ph)}(CO)$_2$(η-C$_5$H$_5$)-(η-C$_9$H$_7$)]	162—166	Red	1 953s, 1 890s	98	52.7 (53.4)	3.7 (3.7)	741 (741)
(6) [RhW{μ-C(R)C(Ph)C(Ph)}(CO)$_2$(η-C$_5$H$_5$)-(η-C$_5$Me$_5$)]		Red	1 951s, 1 889s	28	57.1 (56.7)	4.5 (4.5)	822 (824)

[a] Calculated values are given in parentheses. [b] R = C$_6$H$_4$Me-4. [c] With decomposition. [d] In hexane, unless otherwise stated. [e] Mass spectrometry. [f] In dichloromethane.



	R^1	R^2
(1)	Ph	Ph
(3)	Me	Me
(4)	Ph	H
(5)	Ph	Me



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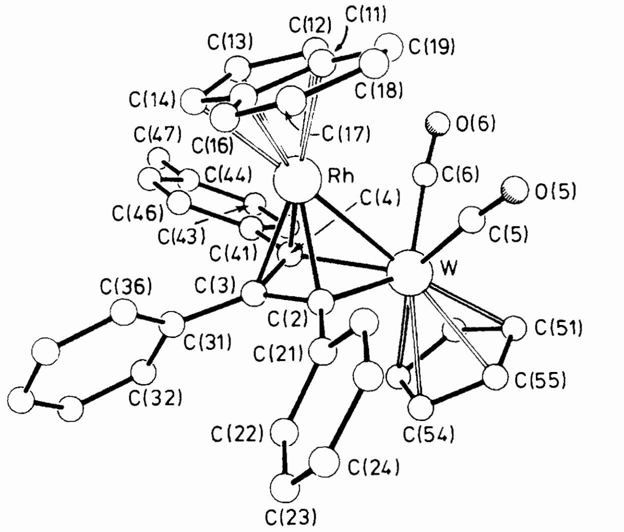


Figure. Molecular structure of the complex [RhW{μ-C(C$_6$H$_4$Me-4)-C(Ph)C(Ph)}(CO)$_2$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] (1), showing the crystallographic numbering

metal bond in complex (1) is bridged by a three-carbon chain [C(2),C(3),C(4)] which may be regarded as an allylic group η^3-bonded to rhodium, and linked to tungsten by two σ bonds [C(2)–W 2.196(6) and C(4)–W 2.175(5) Å]. The C(2)–C(3) [1.441(8) Å] and C(4)–C(3) [1.437(8) Å] distances are very similar, being intermediate between those expected for a single and a double bond. The three μ-C atoms are symmetrically related to the Rh–W vector with Rh–W–C(2) ≈ Rh–W–C(4) (49°) and C(3)–C(4)–W ≈ C(3)–C(2)–W (98°).

Because the groups CR and W(CO)$_2$(η-C$_5$H$_5$) are isolobal,[13] an alternative description of the C(2),C(3),C(4),Rh,W system would be to view it as comprising a Rh(η-C$_9$H$_7$) group η^4-bonded to a tungstacyclobutadiene ring. However, the W,C(2),C(3),C(4) ring is not planar since the Rh–W distance is necessarily longer (*ca.* 0.6 Å) than the three μ-C–Rh separations [C(2)–Rh 2.105(6), C(3)–Rh 2.135(6), and C(4)–Rh 2.103(5) Å]. The dihedral angle between the planes defined by C(2),C(3),C(4) and C(2),W,C(4) is 13°.

Whereas the phenyl ring attached to C(3) is ordered, the rings attached to C(2) and C(4) exhibit a 50 : 50 positional disorder at the *para* site, in that either C(44) or C(24) carry the methyl group originally present in the precursor [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)]. The two rings C(21)—C(26) and C(41)—C(46) are bent away equally from C(3) [C(3)–C(4)–C(41) = C(3)–C(2)–C(21) 126°], whereas the ring C(31)—C(36) is not symmetrically related to the other rings [C(2)–C(3)–C(31) 127° and C(4)–C(3)–C(31) 132°]. In relation to the plane defined by C(2),C(3),C(4), the μ-C–C(aryl) bonds spiral downwards in passing from C(4) to C(2) away from the Rh(η-C$_9$H$_7$) group; *i.e.* the three six-membered rings are oriented in a propeller-like manner.

There is a degree of asymmetry in the attachment of the η-C$_9$H$_7$ group to the rhodium atom, reflecting a tendency towards an η^3-bonding mode, with three of the rhodium-carbon distances being shorter than the other two [Rh–C(12) 2.185(7), Rh–C(13) 2.198(7), Rh–C(14) 2.204(7); and Rh–C(11) 2.334(7), Rh–C(15) 2.330(7) Å]. Moreover, within the indenyl ligand the C$_5$ and C$_6$ rings are not coplanar (interplanar angle 4°). In other indenylrhodium complexes a similar asymmetry in the bonding has been observed, corresponding to an η^5 to η^3 'slippage'.[4,8] The η-C$_5$H$_5$ ring attached to tungsten is planar, but the distances between the metal atom and the ring-carbon atoms vary from 2.296(4) to 2.365(5) Å (Table 2). Both the η-C$_9$H$_7$ and the η-C$_5$H$_5$ ligands incline away from the μ-C$_3$ bridge, while at the same time remaining symmetrically related to the Rh–W vector.

Table 2. Internuclear distances (Å) and angles (°) for $[RhW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (1) with estimated standard deviations in parentheses

Rh–W	2.754(1)	Rh–C(15)	2.330(7)	C(18)–C(17)	1.39(2)	C(5)–O(5)	1.150(9)
Rh–C(2)	2.105(6)	C(11)–C(12)	1.434(10)	C(17)–C(16)	1.377(13)	C(6)–O(6)	1.154(8)
Rh–C(3)	2.135(6)	C(11)–C(15)	1.417(10)	W–C(2)	2.196(6)	W–C(51)	2.296(4)
Rh–C(4)	2.103(5)	C(12)–C(13)	1.413(12)	W–C(4)	2.175(5)	W–C(52)	2.326(5)
C(2)–C(21)	1.480(8)	C(13)–C(14)	1.400(10)	C(2)–C(3)	1.441(8)	W–C(53)	2.365(5)
C(3)–C(31)	1.495(8)	C(14)–C(15)	1.437(10)	C(3)–C(4)	1.437(8)	W–C(54)	2.359(5)
Rh–C(11)	2.334(7)	C(15)–C(16)	1.405(10)	C(4)–C(41)	1.491(8)	W–C(55)	2.317(5)
Rh–C(12)	2.185(7)	C(11)–C(19)	1.415(11)	W–C(5)	1.994(7)	C(44)–C(47) *	1.421(13)
Rh–C(13)	2.198(7)	C(19)–C(18)	1.373(14)	W–C(6)	1.995(6)	C(24)–C(27) *	1.44(3)
Rh–C(14)	2.204(7)						

W–C(2)–C(3)	97.0(4)	Rh–W–C(5)	75.9(2)	C(11)–C(12)–C(13)	108.7(6)
W–C(4)–C(3)	98.0(3)	Rh–W–C(6)	78.7(2)	C(12)–C(13)–C(14)	107.3(6)
C(2)–C(3)–C(4)	101.2(5)	W–C(5)–O(5)	175.6(6)	C(13)–C(14)–C(15)	109.2(6)
Rh–C(4)–C(41)	120.0(4)	W–C(6)–O(6)	174.1(6)	C(14)–C(15)–C(11)	107.1(6)
Rh–C(3)–C(31)	126.3(4)	C(3)–Rh–C(2)	39.7(2)	C(15)–C(11)–C(12)	107.3(6)
Rh–C(2)–C(21)	128.8(4)	C(4)–Rh–C(3)	39.6(2)	C(12)–C(11)–C(19)	133.5(7)
W–C(4)–C(41)	135.0(4)	W–C(2)–C(21)	132.8(4)	C(14)–C(15)–C(16)	131.9(7)

* Disordered Me-4 groups C(27) and C(47), see text.

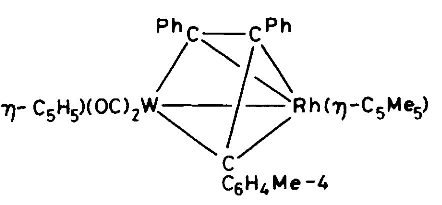
The W(CO) groups are virtually linear (175°), the slight bend placing the oxygen atoms away from the bulky $\eta\text{-}C_9H_7$ ligand. The angle subtended by the CO groups at tungsten is 82.7(3)°. There is no evidence that the carbonyl ligands semi-bridge the metal–metal bond, and this is in accord with the i.r. spectrum (Table 1), there being no C–O stretching bands below 1 900 cm^{-1}.

The $^{13}C\text{-}\{^1H\}$ n.m.r. data are in agreement with the structure established for complex (1) in the solid state. In particular, doublet resonances at δ 118.6, 103.2, and 103.0 p.p.m., with J(RhC) 3, 22, and 22 Hz, respectively, may be assigned to the bridging carbon atoms C(3), C(2), and C(4). The observed $^{103}Rh\text{–}^{13}C$ couplings are consistent with the presence of an allylic group bound to rhodium. Thus, in the cation $[Rh(PPh_3)(\eta^3\text{-}1\text{-}MeC_3H_4)(\eta\text{-}C_5H_5)]^+$ the coupling between rhodium and each of the terminal carbon atoms of the allyl group is greater [J(RhC) 10 Hz] than that with the central carbon atom [J(RhC) 4 Hz].[14] Moreover, the chemical shifts observed for the carbon atoms of the $\mu\text{-}C_3$ group of complex (1) are as expected, with the signal for C(3) being the most deshielded, and with the other two resonances being very similar.[15] In the compound $[CoW\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ peaks for the identical μ-C group are at δ 120.7, 93.5, and 92.7 p.p.m.[5] From the n.m.r. data there was no evidence that (1) was formed in solution as a mixture of two isomers with either μ-C(R)C(Ph)C(Ph) or μ-C(Ph)C(R)-C(Ph) bridging groups. The ^1H n.m.r. spectrum showed only one Me-4 group environment.

The formation of (2) as well as (1) in the reaction of $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ with PhC≡CPh makes it unsafe to assume that (1) is produced directly from the dimetal compound. We have observed earlier[5,6] that iron–tungsten compounds $[FeW\{\mu\text{-}C(R)C(R')C(R')\}(CO)_5(\eta\text{-}C_5H_5)]$, structurally akin to (1), are formed when the trimetal compound $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ is heated with R′C≡CR′ (R′ = Ph, C_6H_4Me-4, or Me), a carbonyliron fragment being displaced. It is possible that complex (1) forms *via* (2), although experiments to test this hypothesis by treating the latter with alkynes have not as yet been carried out.

The compounds $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ and MeC≡CMe react at 50—60 °C in toluene to give a mixture of the insertion product (3) (Table 1), and the complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and (2), together with quantities of insoluble material assumed to be polymers of but-2-yne. The yield of (2) was less than in the corresponding reaction with PhC≡CPh. The n.m.r. data for complex (3) are in accord with the formulation proposed. The ^1H n.m.r. spectrum shows three methyl-group environments [δ 1.48 (μ-CMe), 1.70 (μ-CMe), and 2.28 p.p.m. (Me-4)]. The asymmetry of the molecule is also reflected in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum where two CO signals are seen with significantly different chemical shifts (δ 219.8 and 217.4 p.p.m.). In the more symmetrical molecule (1) the CO resonances are almost coincident (δ 223.2 and 223.0) as expected since the two substituents on the ends of the $\mu\text{-}C_3$ chain are so similar. Resonances in the spectrum of complex (3) at δ 90.3, 106.3, and 108.4 p.p.m., all with J(RhC) *ca.* 5 Hz, are assigned to the three μ-C nuclei. A proton-coupled ^{13}C spectrum led to broadening of these peaks, and no conclusive assignments can be made. On the basis of the chemical shift trends,[15] mentioned above, the most deshielded peak (δ 108.4 p.p.m.) would be assigned to the central μ-CMe group, and the other two peaks at δ 90.3 and 106.3 p.p.m. to the μ-*C*Me and the μ-*C*R fragments, respectively. However, an alternative assignment of δ 90.3 (*C*Me), 106.3 (*C*Me, centre of chain), and 108.4 p.p.m. (*C*R), is perhaps more likely, in view of results described below, which show that the chemical shift of the central carbon of the bridging ligand is very susceptible to the nature of the substituent group on this atom.

The compound $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ reacts smoothly with PhC≡CH in toluene at *ca.* 55 °C to afford complex (4) in nearly quantitative yield. The ^1H n.m.r. spectrum shows a doublet at δ 7.90 p.p.m. [J(RhH) 10 Hz] assigned to the μ-CH group. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum two peaks for the CO ligands are nearly coincident (δ 224.9 and 224.8 p.p.m.), in accord with a symmetrical structure in which the aryl groups are at the terminal positions of the $\mu\text{-}C_3$ chain. The resonances for the latter moiety occur at δ 101.8, 101.6, and 95.4 p.p.m. with J(RhC) 21, 20, and 4 Hz, respectively. The association of the smaller 4 Hz coupling with the doublet at δ 95.4 p.p.m. implies that this signal is due to the central μ-C nucleus, in spite of this resonance being the least deshielded of the three associated with the $\mu\text{-}C_3$ group. In a fully coupled ^{13}C n.m.r. spectrum the peak at 95.4 p.p.m. appears as a doublet of doublets [J(HC) 157, J(RhC) 4 Hz], confirming its assignment to the CH group. The peaks at δ 101.8 and 101.6 p.p.m. are thus due to the μ-*C*R and μ-*C*Ph



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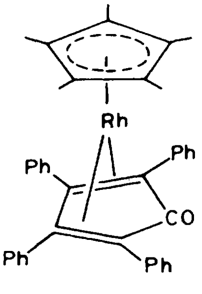

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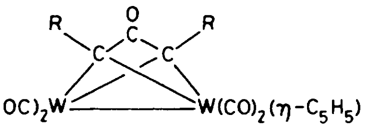

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fragments, but it is not possible to determine which resonance is due to which group.

Compound (5) was also prepared in near-quantitative yield from [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] and PhC≡CMe. The essentially symmetrical bridge structure shown, with the Ph and C$_6$H$_4$Me-4 groups in the terminal positions, is again based on the n.m.r. data. Thus the two CO ligands are apparently in very similar environments since in the ^{13}C-{^{1}H} n.m.r. spectrum they give rise to one broad signal at δ 225.5 p.p.m. [*J*(WC) 137 Hz]. Three resonances, each a doublet, at δ 113.2 [*J*(RhC) 5], 104.1 [*J*(RhC) 22], and 103.9 p.p.m. [*J*(RhC) 22 Hz] are assigned to the μ-C nuclei. The small ^{103}Rh–^{13}C coupling on the resonance at 113.2 p.p.m. implies that it arises from the central carbon of the chain. Moreover, this signal is also the most deshielded of the three. In a ^{13}C n.m.r. spectrum this resonance was observed to be coupled to three equivalent protons [*J*(HC) 5 Hz], showing that it is due to the μ-*C*Me group.

As part of the studies reported herein, the reaction between [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] and PhC≡CPh was also investigated. Forcing conditions (100 °C for 5 d) were required, and a mixture of products was produced, these being the expected 'insertion' product (6) (Table 1), [Rh(CO)$_2$(η-C$_5$Me$_5$)], C$_6$Ph$_6$, and a bright yellow compound (7). Since more vigorous conditions were necessary to produce (6) than compound (1), or the species (3)—(5), it seems that the 'indenyl ligand' effect, mentioned earlier, must operate to some degree in the reactions of [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] with alkynes. The relatively high yields of complexes (4) and (5) compared with (1) may be due to steric effects. Moreover, only one isomer of (4) and of (5) is formed, and for both reactions it is the species with the smaller substituent attached to the central carbon atom of the chain. The absence of any evidence for the cluster compound (2) during the high-yield syntheses of (4) and (5) suggests that the insertion products form directly from [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] and not *via* the trimetal species. The low yield of complex (3) may result from the ready polymerisation of MeC≡CMe observed when this alkyne is employed.

Compound (7) was assigned the structure shown on the basis of microanalytical data, a parent ion in the mass spectrum, and its i.r. and n.m.r. spectra. The i.r. spectrum showed a band at 1 597 cm^{-1} characteristic of the CO group of the cyclopentadienone ring.[16] The ^{1}H n.m.r. spectrum showed resonances for the η-C$_5$Me$_5$ and η-C$_4$Ph$_4$CO ligands, with the correct relative intensities. Cyclopentadienone(cyclopentadienyl)rhodium complexes akin to (7) are formed frequently in reactions between alkynes and dicarbonyl cyclopentadienylrhodium.[16] The formation of (7) and [Rh(CO)$_2$(η-C$_5$Me$_5$)] from the reaction between [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] and PhC≡CPh indicates that the bimetal compound fragments under the reaction conditions, and that (7) probably forms *via* dicarbonyl(η-pentamethylcyclopentadienyl)rhodium.

In view of the observation that PhC≡CPh and [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] afford (1), a study was made of the reaction between the dimetal compound and [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)]. The latter is isolobal with PhC≡CPh. Moreover, as was mentioned earlier, the tolylmethylidynetungsten compound reacts with [FeW(μ-CR)(CO)$_6$(η-C$_5$H$_5$)] to give the ironditungsten compound [FeW$_2$(μ$_3$-RC$_2$R)(CO)$_6$(η-C$_5$H$_5$)$_2$].[2] It was of interest, therefore, to determine whether a RhW$_2$ cluster species could be obtained from [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)]. The latter with [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] in toluene at 55 °C afforded a mixture of the ditungsten alkyne-bridged complex [W$_2$(μ-RC$_2$R)(CO)$_4$(η-C$_5$H$_5$)$_2$][4] and the cluster compound (2). Complex (2) was formed in an amount corresponding to a quantitative conversion of the rhodium in the dimetal precursor. When the same reaction was carried out with heptane as solvent the two species [W$_2$(μ-RC$_2$R)(CO)$_4$(η-C$_5$H$_5$)$_2$] and (2) were again formed, but in addition an orange compound (8) was obtained. The structure proposed for (8) is based on the spectroscopic properties. Although a parent ion is not observed in the mass spectrum, a peak at *m/e* 816 corresponded to the molecular ion minus CO. In the i.r. spectrum, four bands in the terminal carbonyl ligand region are accompanied by an absorption at 1 568 cm^{-1} ascribed to the ketonic carbonyl group. The ^{1}H n.m.r. spectrum shows resonances for the C$_6$H$_4$ and C$_5$H$_5$ groups. The appearance of only one singlet resonance for the Me-4 substituent is in accord with a symmetrical structure. In the ^{13}C-{^{1}H} n.m.r. spectrum a signal at δ 215.3 p.p.m. [*J*(WC) 147 Hz] is characteristic for terminal CO ligands on tungsten. In addition, bands at δ 176.8 [*J*(WC) 169] and δ 236.8 p.p.m. [*J*(WC) 12 Hz] are assigned to the μ-*C*R and ketonic CO groups, respectively. These spectroscopic properties relate to those observed[17] for the diplatinum compounds [Pt$_2${μ-C(Ph)C(O)C(Ph)}L$_4$] (L = CNBu^t or L$_2$ = cod = cyclo-octa-1,5-diene), the i.r. spectra of which show ketonic carbonyl-stretching bands at 1 566 cm^{-1} (L = CNBu^t) and at 1 570 cm^{-1} (L$_2$ = cod). Moreover, in the ^{13}C-{^{1}H} n.m.r. spectrum of [Pt$_2${μ-C(Ph)C(O)C(Ph)}(CNBu^t)$_4$], ^{195}Pt–^{13}C coupling (125 Hz) is observed on the signal (δ 168.5 p.p.m.) due to the μ-CO group, and this together with *X*-ray diffraction results[17] was taken to indicate a degree of direct Pt–μ-CO bonding. The ^{183}W–^{13}C satellite peaks on the resonance of the μ-CO group in the ^{13}C-{^{1}H} n.m.r. spectrum of (8) may reflect μ-η^3 bridge-metal bonding for the C(R)C(O)C(R) ligand in this complex also. The diplatinum compounds [Pt$_2${μ-C(Ph)C(O)C(Ph)}L$_4$] were prepared by treating diphenylcyclopropenone with [Pt(mvk)(cod)] (mvk = methyl vinyl ketone) or [Pt$_3$(CNBu^t)$_6$], reactions which resulted in cleavage of the C=C bond of the organic compound. Accordingly, we investigated the possible synthesis of an analogue of (8), with R = Ph, *via* a reaction between the unsaturated compound $[W_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and diphenylcyclopropenone. However, the only product of this reaction, when carried out in toluene at *ca.* 60 °C, was the alkyne complex $[W_2(\mu\text{-}PhC_2Ph)(CO)_4(\eta\text{-}C_5H_5)_2]$.[18]

A ditungsten compound $[W_2\{\mu\text{-}C(O)C(CO_2Me)C(CO_2Me)\}(CO)_4(\eta\text{-}C_5H_5)_2]$ related to (8), but with an unsymmetrical bridge structure, has been prepared.[19] The μ-CO band in the i.r. spectrum occurs at 1 601 cm^{-1} and the compound readily loses CO on heating to give $[W_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$.

Formation of complex (8) when heptane, rather than toluene, is used in the reaction between $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ may be due to the greater solubility of CO in the former solvent. This would favour CO insertion between two carbyne groups during steps which have been postulated to explain the formation of $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$ from transient heteronuclear trimetal clusters *via* reductive elimination of metal–ligand fragments [*e.g.* $Ni(\eta\text{-}C_5H_5)$ or $Cr(CO)_2(\eta\text{-}C_5H_5)$].[4,20] Hence the reaction between $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ might release CO and afford an unstable cluster $[Rh\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C_9H_7)]$. The latter could lose $Rh(\eta\text{-}C_9H_7)$, which with $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ would afford (2), an observed product. Free carbon monoxide, present in the sealed reaction vessel, could then play a role in the coupling of $W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$ fragments at a rhodium centre yielding (8), rather than the more frequently observed product $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$.[4,19]

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The instrumentation used to obtain spectroscopic information was, for mass spectra an AEI MS 902 spectrometer, for i.r. a Nicolet MX-10 FT spectrophotometer, and for n.m.r. JNM FX 90Q and FX 200 spectrometers. For $^{13}C\text{-}\{^1H\}$ n.m.r. spectra, chemical shifts have positive values representing shifts to high frequency of $SiMe_4$. Hydrogen-1 and $^{13}C\text{-}\{^1H\}$ n.m.r. measurements were all made in $[^2H_1]$chloroform, and i.r. bands were measured in hexane. The compounds $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)L]$ (L = $\eta\text{-}C_9H_7$[3] or $\eta\text{-}C_5Me_5$[4]) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$[21] were prepared by published methods. Analytical and other data for the new compounds are in Table 1.

Reactions between $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ *and Alkynes.*—(*a*) The compounds $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (0.50 g, 0.76 mmol) and $PhC\equiv CPh$ (0.30 g, 1.68 mmol) were heated in toluene (10 cm^3) at 80 °C for 2 d in an evacuated Schlenk tube fitted with a Young's high-pressure stopcock. Solvent was removed *in vacuo*, and the residue extracted with light petroleum (4 × 10 cm^3). The purple residue was identified spectroscopically (i.r. and n.m.r.) as the previously characterised[4] cluster compound $[Rh_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$ (2) (0.16 g, 48%). The light petroleum extracts were reduced in volume to *ca.* 5 cm^3 and chromatographed on alumina. Elution with the same solvent afforded an orange solution. Reduction in volume and cooling to *ca.* −20 °C gave red *crystals* of $[RhW\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (1) (0.20 g, 33%). N.m.r.: ^1H, δ 2.20 (s, 3 H, Me-4), 4.97 (s, 5 H, C_5H_5), 5.19 (m, 1 H, C_9H_7), 5.60 (m, 2 H, C_9H_7), 6.38 (m, 4 H, C_9H_7), and 7.00 (m, 14 H, Ph and C_6H_4); $^{13}C\text{-}\{^1H\}$, δ 223.2 [CO, *J*(WC) 137], 223.0 [CO, *J*(WC) 137], 146.9, 143.9, 136.2, 133.0, 130.6, 127.4, 122.2, 119.7, 119.6 (Ph, C_6H_4, and C_9H_7), 118.6 [d, *C*R^2, *J*(RhC) 3], 105.3, 105.0 (C_9H_7), 103.2 [d, *C*R^1, or *C*R, *J*(RhC) 22], 103.0 [d, *C*R or *C*R^1, *J*(RhC) 22 Hz], 93.3 (C_9H_7), 87.4 (C_5H_5), 81.5 (C_9H_7), and 20.2 p.p.m. (Me-4).

(*b*) The compound $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (0.20 g, 0.30 mmol) and excess of $MeC\equiv CMe$ (*ca.* 0.5 cm^3) were heated in toluene (10 cm^3) at 55 °C for 16 h. Volatile material was removed *in vacuo*, the residue was redissolved in dichloromethane–light petroleum (1 : 5, 5 cm^3), and then chromatographed on alumina. Eluting with the same solvent mixture gave initially a yellow solution, from which $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (0.06 g) was recovered. Changing the composition of the solvent to dichloromethane–light petroleum (1 : 1) eluted compound (2) (0.03 g). Finally, eluting with dichloromethane gave an orange solution which on concentration to *ca.* 2 cm^3 and slow addition of light petroleum (10 cm^3) afforded orange *microcrystals* of $[RhW\{\mu\text{-}C(R)C(Me)C(Me)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (3) (0.06 g). N.m.r.: ^1H, δ 1.48 (s, 3 H, μ-CMe), 1.70 (s, 3 H, μ-CMe), 2.28 (s, 3 H, Me-4), 4.82 (s, 5 H, C_5H_5), 4.92 (m, 1 H, C_9H_7), 5.37 (m, 2 H, C_9H_7), 6.65 (m, 4 H, C_9H_7), and 7.05 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 2]; $^{13}C\text{-}\{^1H\}$, δ 219.8 [CO, *J*(WC) 133], 217.4 [CO, *J*(WC) 133], 151.1, 133.9, 128.4, 126.1 (C_6H_4), 125.6, 124.8, 121.5, 120.1, 111.6, 111.4 (C_9H_7), 108.4 [d, *C*R, *J*(RhC) 5], 106.3 [d, *C*R^2, *J*(RhC) 5], 93.2 (C_9H_7), 90.3 [d, *C*R^1, *J*(RhC) 5 Hz], 89.5 (C_5H_5), 83.7, 83.5 (C_9H_7), 21.1 (Me-4), 15.8 (μ-C*Me*), and 14.9 p.p.m. (μ-C*Me*).

(*c*) Orange *crystals* of $[RhW\{\mu\text{-}C(R)C(H)C(Ph)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (4) (0.21 g) were similarly prepared from $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (0.20 g, 0.30 mmol) and $PhC\equiv CH$ (0.2 cm^3). N.m.r.: ^1H, δ 2.24 (s, 3 H, Me-4), 4.86 (s, 5 H, C_5H_5), 5.50 (m, 2 H, C_9H_7), 6.90 (m, 14 H, C_6H_4, Ph, and C_9H_7), and 7.90 [d, 1 H, μ-CH, *J*(RhH) 10]; $^{13}C\text{-}\{^1H\}$, δ 224.9 [CO, *J*(WC) 155], 224.8 [CO, *J*(WC) 155], 148.7, 145.9, 134.6, 128.5, 127.7, 125.8, 125.2, 125.0, 120.6, 120.4, 105.4, 105.1 (Ph, C_6H_4, and C_9H_7), 101.8 [d, μ-*C*R or μ-*C*R^1, *J*(RhC) 21], 101.6 [d, μ-*C*R^1 or μ-*C*R, *J*(RhC) 20], 95.4 [d, μ-CH, *J*(RhC) 4 Hz], 92.1 (C_9H_7), 87.8 (C_5H_5), 81.4, 80.9 (C_9H_7), and 21.1 p.p.m. (Me-4).

(*d*) Red *crystals* of $[RhW\{\mu\text{-}C(R)C(Me)C(Ph)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (5) (0.22 g) were obtained from $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (0.20 g, 0.30 mmol) and excess of $PhC\equiv CMe$ (0.2 cm^3) by heating the reactants at *ca.* 55 °C for 16 h. N.m.r.: ^1H, δ 1.88 (s, 3 H, μ-CMe), 2.26 (s, 3 H, Me-4), 4.68 (s, 5 H, C_5H_5), 5.08 (m, 1 H, C_9H_7), 5.36 (m, 2 H, C_9H_7), 6.79 (m, 4 H, C_9H_7), and 7.00 (m, 9 H, Ph and C_6H_4); $^{13}C\text{-}\{^1H\}$, δ 225.5 [br, CO, *J*(WC) 137], 149.1, 146.3, 134.0, 128.4, 127.4, 124.9, 124.8, 121.1, 121.0 (Ph, C_6H_4, and C_9H_7), 113.2 [d, μ-*C*R^2, *J*(RhC) 5], 105.9, 105.8 (C_9H_7), 104.1 [d, μ-*C*R^1, *J*(RhC) 22], 103.9 [d, μ-*C*R, *J*(RhC) 22 Hz], 93.3 (C_9H_7), 88.6 (C_5H_5), 82.1, 81.8 (C_9H_7), 21.1 (Me-4), and 20.6 p.p.m. (μ-C*Me*).

Reaction between $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ *and* $PhC\equiv CPh$.—The compounds $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (0.82 g, 1 mmol) and $PhC\equiv CPh$ (0.30 g, 1.68 mmol) were heated at 100 °C in toluene for 5 d. After cooling to room temperature, filtration afforded hexaphenylbenzene (identified by i.r. and analysis: Found, C, 93.7; H, 6.0. Calc. for $C_{42}H_{30}$ C, 94.3; H, 5.6%). Solvent was removed *in vacuo* from the filtrate, and the residue dissolved in light petroleum and chromatographed. Elution with the same solvent gave an orange solution, which on concentration and cooling to −20 °C gave red *microcrystals* of $[RhW\{\mu\text{-}C(R)C(Ph)C(Ph)\}(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (6) (0.23 g). Continued elution of the column with light petroleum gave $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.14 g), identified by i.r. spectroscopy. Elution with dichloro-

Table 3. Atomic positional parameters (fractional co-ordinates), with estimated standard deviations in parentheses, for complex (1)

Atom	*x*	*y*	*z*
W	0.059 75(2)	0.196 11(1)	−0.166 38(1)
Rh	0.182 91(4)	0.080 40(3)	−0.249 17(2)
C(2)	−0.011 0(6)	0.094 4(4)	−0.240 6(4)
C(3)	0.032 4(6)	0.024 1(4)	−0.195 1(4)
C(4)	0.118 5(5)	0.066 0(4)	−0.143 1(3)
C(5)	0.091 5(7)	0.259 1(4)	−0.258 4(4)
O(5)	0.104 8(7)	0.299 6(4)	−0.309 9(4)
C(6)	0.238 0(6)	0.226 1(4)	−0.139 8(4)
O(6)	0.337 4(5)	0.248 1(4)	−0.119 9(4)
C(11)	0.303 0(7)	0.113 7(5)	−0.347 7(4)
C(12)	0.373 0(7)	0.110 2(6)	−0.277 8(5)
C(13)	0.371 6(6)	0.025 8(6)	−0.251 4(5)
C(14)	0.290 8(7)	−0.020 7(5)	−0.299 8(4)
C(15)	0.250 1(7)	0.032 2(5)	−0.361 0(4)
C(16)	0.178 4(8)	0.014 7(6)	−0.426 8(5)
C(17)	0.161 4(10)	0.078 6(8)	−0.478 2(5)
C(18)	0.214 0(12)	0.158 3(8)	−0.465 5(6)
C(19)	0.281 6(9)	0.178 3(5)	−0.401 2(6)
C(21)	−0.112 9(6)	0.091 2(4)	−0.299 5(4)
C(22)	−0.224 1(6)	0.046 4(5)	−0.287 9(5)
C(23)	−0.320 9(7)	0.043 7(5)	−0.343 7(5)
C(24)	−0.308 3(8)	0.082 4(6)	−0.408 6(5)
C(25)	−0.201 3(8)	0.129 2(6)	−0.419 9(5)
C(26)	−0.103 0(7)	0.132 0(5)	−0.365 8(4)
C(27)	−0.418(2)	0.060(2)	−0.454 8(13)
C(31)	−0.010 5(5)	−0.066 1(4)	−0.202 1(4)
C(32)	−0.059 1(7)	−0.105 7(4)	−0.140 9(4)
C(33)	−0.111 3(7)	−0.186 7(5)	−0.147 6(5)
C(34)	−0.116 3(6)	−0.228 1(4)	−0.213 7(5)
C(35)	−0.068 8(6)	−0.190 3(4)	−0.273 4(4)
C(36)	−0.103 5(6)	−0.109 6(4)	−0.268 1(4)
C(41)	0.199 3(6)	0.023 8(4)	−0.084 1(4)
C(42)	0.232 6(7)	0.065 7(5)	−0.018 0(4)
C(43)	0.309 5(7)	0.027 4(5)	0.036 8(4)
C(44)	0.359 7(7)	−0.052 7(5)	0.027 8(4)
C(45)	0.327 8(7)	−0.094 7(5)	−0.038 5(4)
C(46)	0.249 8(6)	−0.057 6(4)	−0.092 4(4)
C(47)	0.439 3(10)	−0.092 3(8)	0.083 2(7)
C(51)	−0.020 6(5)	0.311 9(3)	−0.108 9(3)
C(52)	0.007 9(5)	0.250 2(3)	−0.053 3(3)
C(53)	−0.071 4(5)	0.179 0(3)	−0.067 8(3)
C(54)	−0.149 0(5)	0.196 7(3)	−0.132 3(3)
C(55)	−0.117 6(5)	0.278 9(3)	−0.157 7(3)

methane gave a further orange solution which on evaporation afforded yellow *microcrystals* of [Rh(η-C_4Ph_4CO)(η-C_5Me_5)] (7) (0.14 g, 23%) (Found: C, 74.3; H, 5.4%; *M* 621. $C_{39}H_{35}ORh$ requires C, 75.2; H, 5.6%; *M* 622); $\nu_{max.}$(CO) at 1 597 cm^{-1}; ^1H n.m.r., δ 1.29 (s, 15 H, Me) and 7.2 p.p.m. (m, 20 H, Ph).

Reactions between [RhW(μ-CR)$(CO)_3$(η-C_5H_5)(η-C_9H_7)] *and* [W(≡CR)$(CO)_2$(η-C_5H_5)].—(*a*) The compounds [RhW(μ-CR)$(CO)_3$(η-C_5H_5)(η-C_9H_7)] (0.30 g, 0.44 mmol) and [W(≡CR)-$(CO)_2$(η-C_5H_5)] (0.25 g, 0.61 mmol) were heated in n-heptane (20 cm^3) at 60 °C for 24 h in an evacuated Schlenk tube fitted with a high-pressure stopcock. After cooling to room temperature, solvent was removed *in vacuo*, and the residue redissolved in dichloromethane–light petroleum (1 : 4, 5 cm^3) and chromatographed on alumina. Elution with the same solvent mixture gave orange and brown solutions from which were recovered, respectively, [W(≡CR)$(CO)_2$(η-C_5H_5)] (0.05 g, 20%) and [RhW(μ-CR)$(CO)_3$(η-C_5H_5)(η-C_9H_7)] (0.06 g, 12%). Changing the eluant to dichloromethane–light petroleum (1 : 1) developed red, purple, and green bands, and elution led to the recovery of [W_2(μ-RC_2R)$(CO)_4$(η-C_5H_5)$_2$] (0.12 g, 78% based on tungsten consumed), compound (2) (0.15 g, 77% based on rhodium consumed), and a trace of a species believed to be [Rh_3(μ-CO)$_3$(η-C_9H_7)$_3$] (i.r. spectrum [8]). Elution of the column with pure dichloromethane gave an orange solution which, on concentration to *ca.* 5 cm^3, addition of pentane (2 cm^3), and cooling, gave orange *microcrystals* of [W_2{μ-C_2(C_6H_4Me-4)$_2$-CO}$(CO)_4$(η-C_5H_5)$_2$] (8) (0.07 g, 16%) (Found: C, 44.2; H, 2.9%; *M* − CO 816. $C_{31}H_{24}O_5W_2$ requires C, 44.1; H, 2.9%; *M* 844, *M* − CO 816); $\nu_{max.}$(CO) at 2 019s, 1 977m, 1 933m, 1 917(sh), and 1 568m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H, δ 2.30 (s, 6 H, Me-4), 5.01 (s, 10 H, C_5H_5), and 7.26 [$(AB)_2$, 8 H, C_6H_4, *J*(AB) 13]; ^{13}C-{^1H}, δ 236.8 [μ-CO, *J*(WC) 12], 215.3 [CO, *J*(WC) 147], 176.8 [μ-*C*R, *J*(WC) 169 Hz], 148.5, 133.4, 128.5, 127.9 (C_6H_4), 91.2 (C_5H_5), and 21.0 p.p.m. (Me-4).

(*b*) When [RhW(μ-CR)$(CO)_3$(η-C_5H_5)(η-C_9H_7)] (0.30 g, 0.44 mmol) and [W(≡CR)$(CO)_2$(η-C_5H_5)] (0.25 g, 0.61 mmol) were heated in toluene (10 cm^3) at 55 °C for 24 h the products were the compounds (2) (0.18 g, 94% based on rhodium in reactant) and [W_2(μ-RC_2R)$(CO)_4$(η-C_5H_5)$_2$] (0.17 g, 40%). Some [W(≡CR)$(CO)_2$(η-C_5H_5)] (0.13 g) was recovered.

Crystal Structure Determination of [RhW{μ-C(C_6H_4Me-4)-C(Ph)C(Ph)}$(CO)_2$(η-C_5H_5)(η-C_9H_7)] (1).—Dark red prismatic crystals of complex (1) were grown from hot diethyl ether. Diffracted intensities were collected at room temperature from a crystal of dimensions *ca.* 0.20 × 0.87 × 0.12 mm with faces of the type ⟨0$\bar{1}$1⟩, ⟨011⟩, and ⟨101⟩. Data were collected on a Nicolet *P*3*m* four-circle diffractometer using an ω–2θ scan mode, in the range 2.9 ⩽ 2θ ⩽ 50°. Of the total of 5 361 intensities recorded, 4 184 were deemed both independent and with $I \geqslant 2.5\sigma(I)$, where σ(*I*) is the estimated standard deviation based on counting statistics, and only these were used in the final refinement of the structure, after correction for Lorentz, polarisation, and *X*-ray absorption effects, the last by a semi-empirical method based on azimuthal scan data.[22]

Crystal data. $C_{38}H_{29}O_2RhW$, $M = 804.4$, monoclinic, $a = 10.709(3)$, $b = 15.737(5)$, $c = 18.192(4)$ Å, $\beta = 93.75(2)°$, $U = 3\,059(1)$ Å^3, $D_m = 1.75$ g cm^{-3}, $Z = 4$, $D_c = 1.75$ g cm^{-3}, *F*(000) = 1 568, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 44.0 cm^{-1}.

Structure solution and refinement. The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and Fourier difference methods. Refinement by blocked-cascade least squares, with anisotropic thermal parameters for all non-hydrogen atoms, led to *R* 0.032 (*R'* 0.034), and a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ ($g = 0.000\,37$) gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.4 e Å^{-3}. Scattering factors and corrections for anomalous dispersion were from ref. 23. All computations were carried out with an Eclipse (Data General) computer using the SHELXTL system of programs.[22] Atom co-ordinates for compound (1) are listed in Table 3.

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