Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 38.[1] Ruthenium–Tungsten Compounds: Crystal Structures of [RuW(μ-Cl)(μ-CMe)(Cl)(CO)$_2$(PPh$_3$)$_2$(η-C$_5$H$_5$)] and [RuW$_2$(μ_3-C$_2$Me$_2$)(CO)$_7$(η-C$_5$H$_5$)$_2$] *

Judith A. K. Howard, Jill C. V. Laurie, Owen Johnson, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Purple crystals of the compound [RuW(μ-Cl)(μ-CMe)(Cl)(CO)$_2$(PPh$_3$)$_2$(η-C$_5$H$_5$)] are obtained by placing a diethyl ether solution of [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] above a tetrahydrofuran (thf) solution of [RuCl$_2$(PPh$_3$)$_3$]. The ruthenium–tungsten complex has been characterised by an *X*-ray diffraction study. The Ru–W bond [2.769(1) Å] is spanned by the Cl and CMe ligands [C–W 1.942(11), C–Ru 2.021(9), Ru–Cl 2.447(3), W–Cl 2.497(3) Å]. In addition to the cyclopentadienyl ligand the W atom carries terminal Cl and CO ligands which exhibit a positional disorder between two effectively interchangeable sites in the complementary ratios 3:1. The ruthenium atom is ligated by two PPh$_3$ groups and a CO group. Treatment of the ruthenium–tungsten complex with MeC$\equiv$CMe affords [RuW(μ-Cl)(μ-CMe)(Cl)(CO)$_2$(PPh$_3$)(η-C$_2$Me$_2$)(η-C$_5$H$_5$)], possible structures for which are discussed on the basis of n.m.r. data. The compound [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] reacts with the species [Ru(CO)$_n$(PPh$_3$)$_{5-n}$] (n = 2 or 3) to afford an insoluble trimetal complex [RuW$_2$(μ_3-C$_2$Me$_2$)(CO)$_6$(PPh$_3$)(η-C$_5$H$_5$)$_2$]. The PPh$_3$ group in the latter may be displaced with CO or PEt$_3$ to give the species [RuW$_2$(μ_3-C$_2$Me$_2$)(CO)$_6$(L)(η-C$_5$H$_5$)$_2$] (L = CO or PEt$_3$), but the reaction with CO is reversed unless the PPh$_3$ is removed by complexation. The structure of the heptacarbonyl complex has been established by *X*-ray diffraction. The molecule has a triangular metal core [Ru–W 3.026(1) and 2.835(1), W–W 2.944(1) Å] bridged by the MeC$\equiv$CMe ligand in such a manner that the alkyne lies essentially parallel to one of the Ru–W vectors. Hence this ligand is σ bonded to the ruthenium atom and to one tungsten centre [C–Ru 2.068(9), C–W 2.169(9) Å] while being η^2 co-cordinated to the other tungsten atom [C–W mean 2.281 (9) Å]. The ruthenium atom carries three terminally bound CO ligands, while the tungsten atoms are each ligated by a C$_5$H$_5$ and two CO groups. Three of the four CO ligands bound to tungsten semi-bridge the edges of the metal-atom triangle. The complexes [RuW$_2$(μ_3-C$_2$Me$_2$)(CO)$_6$(L)(η-C$_5$H$_5$)$_2$] undergo dynamic behaviour in solution, as revealed by n.m.r. studies.

The alkylidyne–tungsten complexes [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)] (R = Me or C$_6$H$_4$Me-4) combine with a variety of low-valent metal–ligand species affording cluster compounds with bonds between tungsten and other transition elements.[2,3] The metal–metal bonds in these products are bridged either by CR groups or by alkynes, C$_2$R$_2$, the latter being formed by coupling of alkylidyne fragments. In spite of the large number of characterised compounds, only one ruthenium–tungsten species has so far been identified. Reaction between [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] and [Ru$_3$(CO)$_{12}$] in toluene at *ca.* 80 °C gives the trinuclear metal complex [RuW$_2${μ_3-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_7$(η-C$_5$H$_5$)$_2$], but only in *ca.* 10% yield.[4] In order to extend our knowledge of ruthenium–tungsten compounds we have studied reactions between the alkylidyne–tungsten complexes and the Ru$^{\mathrm{II}}$ species [RuCl$_2$(PPh$_3$)$_3$] and Ru^0 species [Ru(CO)$_2$(PPh$_3$)$_3$], respectively. The compound [RuCl$_2$(PPh$_3$)$_3$] is known to be highly reactive, a property associated with the ready dissociation of a PPh$_3$ ligand in solution.[5] A triphenylphosphine group is also released in solution from the Ru^0 complex [Ru(CO)$_2$(PPh$_3$)$_3$], thereby providing a vacant site for oxidative-addition reactions.[6]

Results and Discussion

When a diethyl ether solution of [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] is placed above a thf (tetrahydrofuran) solution of [RuCl$_2$(PPh$_3$)$_3$] so that diffusion occurs, deep purple crystals of the ruthenium–tungsten compound (**1**) are formed after several hours. The new complex proved to have a very low solubility, even in polar solvents such as thf, acetone, or CH$_2$Cl$_2$. Moreover, these solutions were very air sensitive. Satisfactory ^{1}H and ^{13}C-{^{1}H} n.m.r. data therefore could not be obtained. However, a ^{31}P-{^{1}H} spectrum showed two resonances, at δ 59.0 and 25.9 p.p.m., each a doublet [J(PP) 15 Hz]. The magnitude of the ^{31}P–^{31}P coupling, and the absence of any ^{183}W satellite peaks, indicated the presence in (**1**) of a *cis*-Ru(PPh$_3$)$_2$ group. Microanalytical data were in accord with the complex being a 1:1 adduct of [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] and the species RuCl$_2$(PPh$_3$)$_2$, containing thf of crystallisation. Surprisingly, the tolylmethylidyne complex [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] did not react with [RuCl$_2$(PPh$_3$)$_3$] at room temperature under the same conditions which had afforded (**1**). Moreover, when these species were heated together only the starting materials were recovered.

Fortunately, it was possible to identify (**1**) by an *X*-ray diffraction study. The results are summarised in Table 1, and the

---

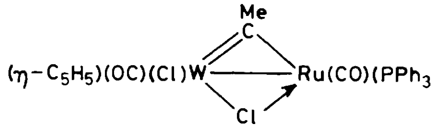
* 1,2-Dicarbonyl-μ-chloro-2-chloro-2-η-cyclopentadienyl-μ-methylmethylidyne-1,1-bis(triphenylphosphine)rutheniumtungsten(*Ru–W*) and 1,1,1,2,2,3,3-heptacarbonyl-2,3-bis(η-cyclopentadienyl)-μ_3-[η^2-dimethylacetylene-C^1(Ru^1,W^2)C^2(W^2,W^3)]-*triangulo*-rutheniumditungsten.

Supplementary data available (No. SUP 56255, 12 pp.): H-atom co-ordinates, thermal parameters, complete bond parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

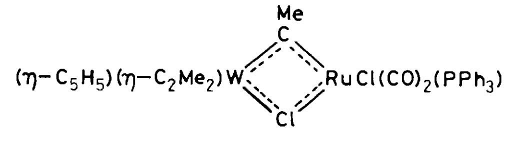
Table 1. Selected bond distances (Å) and interbond angles (°) for $[RuW(\mu\text{-}Cl)(\mu\text{-}CMe)(Cl)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]\cdot 0.67C_4H_8O$ (**1**) (cp = cylopentadienyl)

W-Ru	2.769(1)	W-C(1)	1.987(14)	W-Cl(2)	2.505(4)	W-C(3)	1.942(11)
W-Cl(1)	2.497(3)	Ru-C(2)	1.882(11)	Ru-P(1)	2.360(3)	Ru-P(2)	2.470(3)
Ru-C(3)	2.021(9)	Ru-Cl(1)	2.447(3)	C(1)-O(1)	1.131(17)	C(2)-O(2)	1.072(13)
W-C(cp)*	2.318(8)	P-C(Ph)*	1.834(7)				
C(3)-W-Cl(1)	80.4(3)	Cl(1)-W-Cl(2)	80.5(1)	Cl(2)-W-C(1)	87.9(4)	C(1)-W-C(3)	80.4(3)
Ru-W-C(3)	46.9(3)	Ru-W-Cl(1)	55.1(1)	Ru-W-C(1)	73.7(3)	Ru-W-Cl(2)	93.4(1)
W-C(1)-O(1)	169.1(9)	W-Cl(1)-Ru	68.1(1)	W-C(3)-Ru	88.6(5)	W-C(3)-C(4)	139.3(6)
Ru-C(3)-C(4)	129.0(7)	C(3)-Ru-P(2)	152.4(4)	C(2)-Ru-Cl(1)	170.1(2)	Cl(1)-Ru-P(1)	90.4(1)
C(2)-Ru-P(1)	96.4(4)	C(3)-Ru-Cl(1)	80.2(3)	C(3)-Ru-C(2)	91.7(4)	C(3)-Ru-P(1)	97.9(4)
P(2)-Ru-Cl(1)	97.9(1)	P(2)-Ru-C(2)	86.6(3)	P(2)-Ru-P(1)	109.6(1)	W-Ru-C(2)	113.4(2)
W-Ru-C(3)	44.5(3)	W-Ru-Cl(1)	56.8(1)	W-Ru-P(1)	129.6(1)	W-Ru-P(2)	111.8(1)
Ru-C(2)-O(2)	178.8(5)	Ru-P(1)-C(Ph)*	116.6(3)	Ru-P(2)-C(Ph)*	115.8(3)		

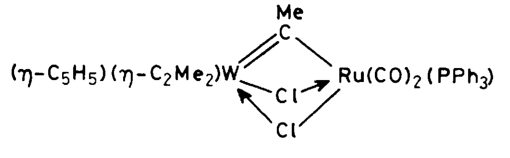
* Mean value.



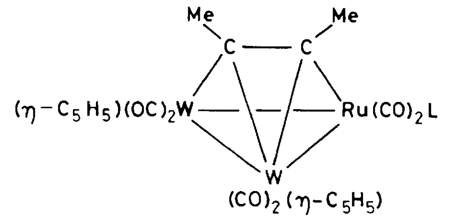
(**1**)



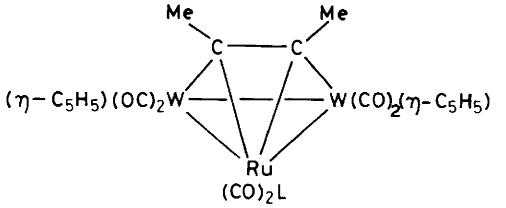
(**2a**)



(**2b**)



L
(**3a**) PPh3
(**4a**) CO
(**5a**) PEt3



L
(**3b**) PPh3
(**4b**) CO
(**5b**) PEt3

molecule is shown in Figure 1. It is immediately apparent that during the course of the reaction, groups have migrated between the two metal centres. Thus the ruthenium and tungsten atoms carry terminally bound carbonyl and chloride ligands, respectively. The metal–metal bond [2.769(1) Å], which is bridged by chloride and by methylidyne groups, appears to be the first example of a Ru–W linkage determined crystallographically, and hence comparisons with separations in other molecules are not possible.

The C(3)–W distance [1.942(11) Å] is within the range found [1.913(7)—2.025(6) Å][7] for several dimetal complexes containing bridging alkylidyne ligands with formal double bonds between carbon and tungsten. The C(3)–Ru separation [2.021(9) Å] is somewhat shorter than the μ-C–Ru distances in the alkylidene compounds $[Ru_2(\mu\text{-}CMe_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ [2.113(4) Å] and $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ [2.079(5) Å][8] in which the hybridisation of the μ-carbon atom differs.

The ruthenium atom is ligated by two mutually *cis* PPh_3 groups and by a terminal CO group [Ru–C(2)–O(2) 178.8(5)°], *transoid* to the bridging Cl(1) atom [C(2)–Ru–Cl(1) 170.1(2)°]. The tungsten atom carries a cyclopentadienyl ligand, a CO group, and a Cl atom. The last two exhibit a positional disorder such that they occupy mutually '*cisoid*' sites in the ratios 3:1 and 1:3. The interchangeability is not exact since W–C and W–Cl separations are not equivalent and indeed the Cl–W–C(O) angles vary between the major and minor site positions (88 and 116°, respectively). For clarity, in Figure 1 each of the two sites shows only the group with the highest (75%) site occupancy.

The W–C(1)–O(1) angle [169.1(9)°] in (**1**) is indicative of a semi-bridging carbonyl group, and this is supported by the observation of a band in the i.r. spectrum at 1 881 cm^{-1}. However, the disorder in the molecule, mentioned above, may effect the reliability with which the atoms of this CO ligand have been located.

A possible pathway for the formation of (**1**) is shown in Scheme 1. Formation of heteronuclear dimetallic complexes with bridging halide or carbonyl ligands has been observed previously in reactions of the ruthenium compounds $[RuCl_2L_n]$ ($L = PMe_3$, $n = 4$; $L = PPh_3$, $n = 3$; $L = Ph_2PCH_2PPh_2$, $n = 2$) with $Na[Mn(CO)_5]$ and $[ZrMe_2(\eta\text{-}C_5H_5)_2]$.[9]

The poor solubility of (**1**) has been mentioned above. It was hoped that the PPh_3 groups in the compound would be replaced by PMe_3 or PEt_3 ligands, leading to derivatives of (**1**) which were more soluble species. With PMe_3 it was found that four equivalents were required (i.r. monitoring) for reaction to be complete, and the products were identified as the mononuclear metal species $[W(\equiv CMe)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$[10] and *cis,mer*-$[RuCl_2(CO)(PMe_3)_3]$. Under similar conditions PEt_3 afforded $[W(\equiv CMe)(CO)(PEt_3)(\eta\text{-}C_5H_5)]$ and *cis,mer*-$[RuCl_2(CO)(PEt_3)_3]$.[11,12] Evidently the trialkylphosphines cleave the bridge system in (**1**), in addition to substituting PPh_3 by PMe_3 or PEt_3. Attempts to produce compounds similar to (**1**) from reactions between $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and $[RuCl_2(PR_3)_4]$ ($PR_3 = PMe_3$ or PMe_2Ph) gave only unreacted starting materials, possibly due to the inability of these tetrakis(phosphine)ruthenium complexes to dissociate PMe_3 or PMe_2Ph groups, and provide vacant sites on the metal.[5]

Treatment of a suspension of (**1**) in CH_2Cl_2 with excess of $MeC\equiv CMe$ afforded a green complex (**2**). Microanalytical data suggested a formulation $[RuW(\mu\text{-}Cl)(\mu\text{-}CMe)(Cl)(CO)_2(PPh_3)(\eta\text{-}C_2Me_2)(\eta\text{-}C_5H_5)]$ for this product. The i.r. spectrum had two bands at 2 018 and 1 996 cm^{-1} in the CO stretching region. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed a single resonance (δ 49.6 p.p.m.) with no ^{183}W satellite peaks, implying that the PPh_3 group was attached to the ruthenium. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum a resonance at 203.9 p.p.m. must be assigned to the CO groups, because of the chemical shift and since in a fully coupled ^{13}C spectrum it was the only signal which did not show $^1H\text{-}^{13}C$ coupling. The CO ligands in (**2**) are chemically non-equivalent, hence the appearance of only one signal indicates that the site-exchange of these groups must be occurring at the temperature of the measurement (−10 °C). Data could not be obtained at lower temperatures due to the insolubility of the compound. Peaks due to C_5H_5, Ph, and Me groups were observed (see Experimental section), but no resonance which could be unambiguously assigned to the $\mu\text{-}C$Me ligated group was seen, even though the spectrum was scanned to 500 p.p.m. The absence of a signal clearly attributable to the alkylidyne carbon nucleus might be a consequence of its loss in the noise resulting from the relative insolubility of the complex. Alternatively a peak observed at 199.2 p.p.m., near the CO resonance, might possibly be due to the μ-C nucleus but it seems more likely that this resonance results from the ligated carbon atoms of an alkyne ligand functioning as a four-electron donor,[13] as implied in formulation (**2a**). In the complex $[W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(\eta\text{-}C_2Me_2)]$, where but-2-yne is acting as a four-electron donor, the C_2Me_2 resonance occurs at 221 p.p.m.[14]

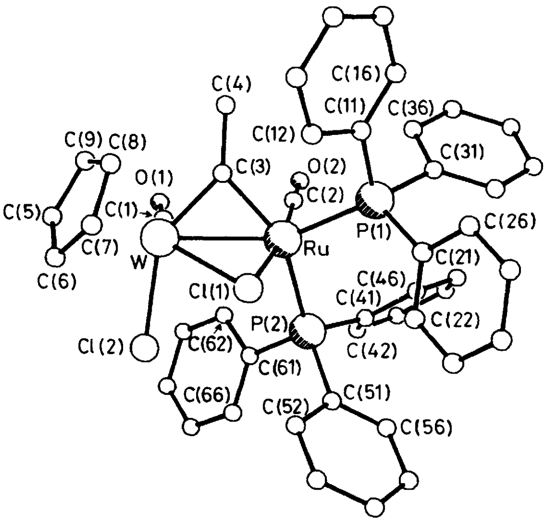
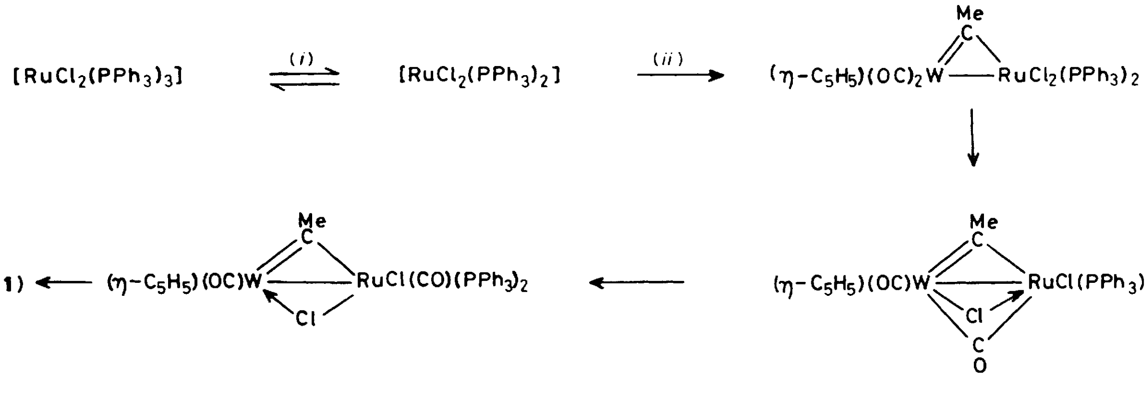


Figure 1. The molecular structure of $[RuW(\mu\text{-}Cl)(\mu\text{-}CMe)(Cl)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ (**1**), with the crystallographic numbering scheme. Only the major occupant (75%) is shown at the Cl(2) and C(1)O(1) sites

An alternative formulation for (**2**) is (**2b**). The signal at 199.2 p.p.m. in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum would then be assigned to the $\mu\text{-}C$Me nucleus rather than to the ligated carbons of the but-2-yne. In (**2b**) the alkyne would be acting as a two-electron donor group, and the resonance for the ligated carbon atoms would be shifted upfield, possibly being hidden under the peaks of the PPh_3 ligand. The signal at 199.2 p.p.m. is, however, at a relatively high field for a $\mu\text{-}CR$ group. When alkylidyne ligands bridge dimetal centres the μ-C resonances generally occur in the range 320—390 p.p.m.,[7] *e.g.* at 359 and 339 p.p.m. in the aforementioned $[W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4(\eta\text{-}C_2Me_2)]$.[14] However, in $[Re_2(\mu\text{-}Br)(\mu\text{-}CPh)(CO)_8]$, which is somewhat analogous to (**2a**) in containing a halide bridge, the μ-C resonance occurs at 201.2 p.p.m.[15] No crystals of (**2**) suitable for *X*-ray diffraction could be obtained, and hence the exact structure of this complex must remain unresolved.

The reaction between $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Ru(CO)_2(PPh_3)_3]$ was next investigated. Layering diethyl ether solutions of the former above dichloromethane solutions of the latter afforded orange crystals of a new compound (**3**) in *ca.* 70% yield. The mother-liquor contained small quantities of $[Ru(CO)_3(PPh_3)_2]$ and $[W\{=C(Me)C=O\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$.

Compound (**3**) could also be prepared, but in lower yield, by



Scheme 1. (*i*) $-PPh_3$; (*ii*) $+[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$

Table 2. Selected bond distances (Å) and interbond angles (°) for $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ (**4a**) (cp = cyclopentadienyl)

W(1)–Ru	3.026(1)	W(2)–Ru	2.835(1)	W(1)–W(2)	2.944(1)	C(7)–C(8)	1.393(13)
C(7)–C(71)	1.519(14)	C(8)–C(81)	1.489(13)	W(1)–C(7)	2.169(9)	Ru–C(8)	2.068(9)
W(2)–C(7)	2.277(9)	W(2)–C(8)	2.284(9)	W(1)–C(1)	1.972(10)	W(1)–C(2)	1.973(9)
Ru–C(3)	1.883(10)	Ru–C(4)	1.989(10)	Ru–C(5)	1.887(10)	W(2)–C(6)	1.926(10)
W(2)–C(9)	1.992(11)	C(1)–O(1)	1.125(12)	C(2)–O(2)	1.149(12)	C(3)–O(3)	1.125(13)
C(4)–O(4)	1.121(13)	C(5)–O(5)	1.129(13)	C(6)–O(6)	1.199(12)	C(9)–O(9)	1.146(13)
W(1)–C(cp)*	2.343(8)	W(2)–C(cp)*	2.334(10)				

Ru–W(1)–W(2)	56.7(1)	W(1)–W(2)–Ru	63.1(1)	W(2)–Ru–W(1)	60.2(1)	C(7)–W(2)–C(8)	35.6(3)
W(1)–C(7)–C(71)	122.0(7)	Ru–C(8)–C(81)	125.1(7)	W(1)–C(7)–C(8)	115.5(6)	Ru–C(8)–C(7)	109.8(6)
C(7)–C(8)–C(81)	123.4(8)	C(8)–C(7)–C(71)	120.7(8)	Ru–W(1)–C(7)	64.3(3)	W(1)–Ru–C(8)	70.5(2)
W(1)–Ru–C(3)	91.1(3)	W(1)–Ru–C(4)	105.1(3)	W(1)–Ru–C(5)	160.8(3)	C(8)–Ru–C(3)	101.3(4)
C(8)–Ru–C(4)	158.9(4)	C(8)–Ru–C(5)	90.5(4)	C(1)–W(1)–C(7)	73.0(4)	C(2)–W(1)–C(7)	124.9(4)
C(1)–W(1)–C(2)	86.9(4)	Ru–W(1)–C(1)	83.3(3)	Ru–W(1)–C(2)	62.7(3)	C(7)–W(2)–C(6)	120.2(4)
C(7)–W(2)–C(9)	110.4(4)	W(1)–W(2)–C(6)	121.0(3)	W(1)–W(2)–C(9)	63.9(3)	C(8)–W(2)–C(6)	85.5(4)
C(8)–W(2)–C(9)	118.7(4)	Ru–W(2)–C(6)	61.4(3)	Ru–W(2)–C(9)	77.4(3)	W(1)–C(1)–O(1)	173.7(9)
W(1)–C(2)–O(2)	166.6(9)	Ru–C(3)–O(3)	178.3(8)	Ru–C(4)–O(4)	174.6(9)	Ru–C(5)–O(5)	177.0(9)
W(2)–C(6)–O(6)	164.4(8)	W(2)–C(9)–O(9)	166.5(8)				

* Mean value.

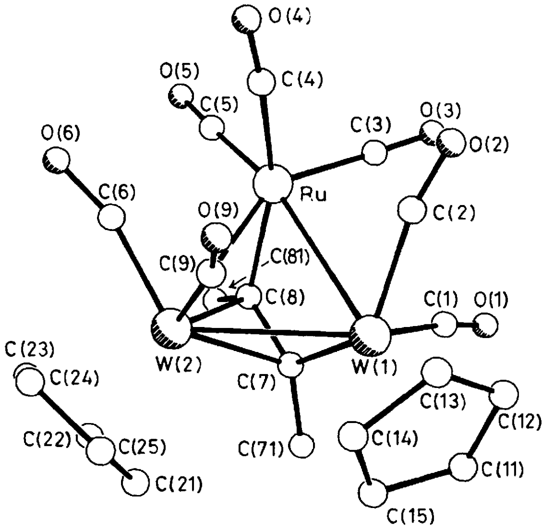


Figure 2. The molecular structure of $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ (**4a**), with the crystallographic numbering scheme

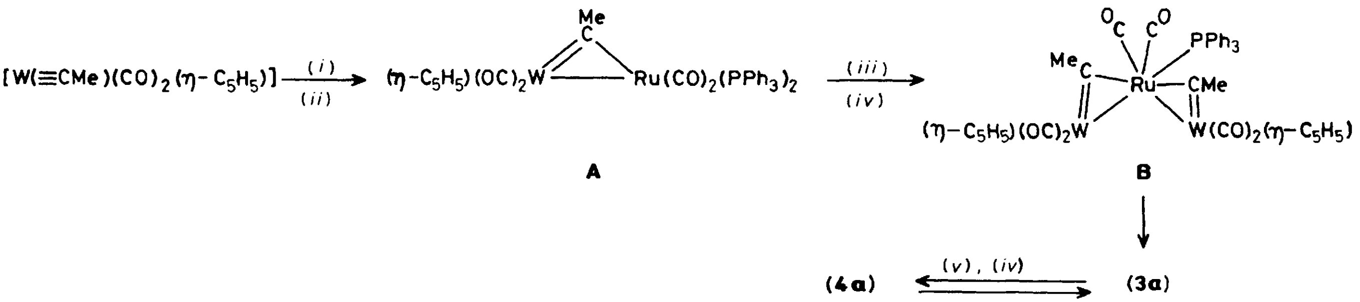
heating a mixture of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Ru(CO)_3(PPh_3)_2]$ in toluene. The very low solubility of the complex in all common organic solvents prevented n.m.r. measurements. The i.r. spectrum (see Experimental section) showed several bands in the CO stretching region, some at relatively low frequencies, indicative of semi-bridging ligands. Analytical data for (**3**) were in accord with it being the trimetal species $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_6(PPh_3)(\eta\text{-}C_5H_5)_2]$. Since no suitable crystals could be obtained for an *X*-ray diffraction study, the complex was treated with CO gas in the hope of displacing the PPh_3 ligand, and producing a more soluble and crystalline derivative amenable to study.

When CO gas was bubbled through an orange suspension of (**3**) in dichloromethane a clear, pale red solution formed. Evaporation of the latter, however, led only to recovery of starting material, even though the i.r. spectrum of the red solution showed none of the bands due to (**3**). This observation suggested that the reaction with CO was reversible in the presence of the displaced PPh_3. In order to remove the latter, a thf solution of $[W(CO)_5(thf)]$ was added to the red solution. In this manner the complex $[W(CO)_5(PPh_3)]$ was obtained and a new red compound (**4**) isolated. Compound (**4**) proved to be moderately soluble in light petroleum and diethyl ether, in contrast with the parent complex (**3**). Analytical and spectroscopic data (see Experimental section) suggested that (**4**) was the complex $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_7(\eta\text{-}C_5H_5)_2]$, an analogue of the previously reported species $[MW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (M = Ru or Os).[4]

Suitable crystals of (**4**) were obtained for an *X*-ray diffraction study and the results are summarised in Table 2, with the molecule shown in Figure 2. It is apparent that the structure corresponds to the formulation (**4a**), rather than its isomer (**4b**). Interestingly, an *X*-ray diffraction study on the complex $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ revealed that the unit cell of this species contained two isomers similar to (**4a**) and (**4b**), but with Os replacing Ru and with $C_2(C_6H_4Me\text{-}2)_2$ instead of C_2Me_2.[4] In solution, both compounds $[MW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ exist as mixtures of the two isomers. In the ruthenium complex, however, the isomer ratio is 1:9 in favour of the form found for (**4**) in the solid state, *i.e.* (**4a**) with the alkyne ligand σ bonded to the Ru and W(1) atoms, and η^2 bonded to W(2). The molecular asymmetry in (**4a**) is reflected in the metal–metal distances, with Ru–W(1) [3.026(1) Å] being longer than Ru–W(2) [2.835(1) Å]. The W(1)–W(2) separation [2.944(1) Å] is close to that found [3.017(2) Å][4] in the corresponding isomer of the related osmiumditungsten compound mentioned above.

As expected, the W(1)–C(7) [2.169(9) Å], W(2)–C(7) [2.277(9) Å], and W(2)–C(8) [2.284(9) Å] distances all differ, but are close to the values previously reported for the analogous isomer of $[OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$. In (**4a**), the W(1)–W(2) and Ru–W vectors are semi-bridged by CO ligands [W(2)–C(9)–O(9) 166.5(8), W(1)–C(2)–O(2) 166.6(9), and W(2)–C(6)–O(6) 164.4(8)°]. This is in agreement with the observation of bands in the i.r. spectrum at 1 868, 1 830, and 1 713 cm^{-1}. Establishment of the structure (**4a**) suggests that the very insoluble precursor (**3**) has been formulated correctly but whether it exists as (**3a**) or (**3b**) or as a mixture of these isomers is not known.

The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**4**) indicate that it undergoes dynamic behaviour in solution, probably involving a (**4a**) $\rightleftharpoons$ (**4b**) interconversion. Thus the ^1H n.m.r. spectrum at room temperature displays only one resonance for the two Me groups (δ 2.60 p.p.m.) and one for the two $\eta\text{-}C_5H_5$ ligands (δ 5.15), a result not in accord with the *X*-ray diffraction study. The



Scheme 2. (*i*) $+[Ru(CO)_{5-n}(PPh_3)_n]$ (*n* = 2 or 3); (*ii*) −CO or $-PPh_3$; (*iii*) $+[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$; (*iv*) $-PPh_3$; (*v*) +CO; (*vi*) −CO, $+PPh_3$

appearance in the ^{13}C-$\{^1H\}$ n.m.r. spectrum of only one C_5H_5 resonance (90.6 p.p.m.) and one Me signal (35.3 p.p.m.) is also consistent with the molecule undergoing dynamic behaviour. On cooling to −25 °C, the resonance at 35.3 p.p.m. is replaced by two peaks of equal intensity at 36.3 and 34.9 p.p.m. The limiting spectrum was not attained, since a mixture of (**4a**) and (**4b**) interconverting slowly on the n.m.r. time-scale, or not at all, would be expected to give rise to four resonances due to the methyl groups, as occurs with compound (**5**) described below. As discussed elsewhere,[4] limiting spectra were observed for the related compounds $[MW_2\{\mu_3-C_2(C_6H_4Me-4)_2\}(CO)_7(\eta-C_5H_5)_2]$ (M = Ru or Os) and these were interpreted in terms of the occurrence of three distinct site-exchange processes, which are presumably occurring in solutions of (**4**).

Formation of (**3a**) and subsequently (**4a**) from the mononuclear metal complexes $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ and $[Ru(CO)_2(PPh_3)_3]$ or $[Ru(CO)_3(PPh_3)_2]$ represents yet a further example of alkylidyne group coupling in reactions involving the species $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ (R = Me or C_6H_4Me-4).[16] A possible pathway is shown in Scheme 2. Intermediate **A** is an analogue of numerous related dimetal compounds,[7] while **B** is similar in structure to the complex $[MoW_2(\mu-CC_6H_4Me-4)_2(CO)_6(\eta-C_5H_5)_2]$, characterised by *X*-ray diffraction.[17]

The PPh_3 ligand in (**3**) could also be displaced with PEt_3, affording a red complex $[RuW_2(\mu_3-C_2Me_2)(CO)_6(PEt_3)(\eta-C_5H_5)_2]$ (**5**). Examination of the n.m.r. spectra of this product in solution (see Experimental section) revealed the existence of two isomers in 1:1 ratio, interconverting on the n.m.r. time-scale. Thus at room temperature the ^{31}P-$\{^1H\}$ n.m.r. spectrum showed one very broad resonance whereas at −80 °C two signals of equal intensity were observed at 28.2 and 33.2 p.p.m. At −80 °C the ^1H n.m.r. spectrum showed four resonances of equal intensity for the Me groups (δ 2.40, 2.46, 2.61, and 2.91), and three peaks for $\eta-C_5H_5$ (δ 5.30, 5.34, and 5.47; relative intensity 1:2:1). Although a mixture of (**5a**) and (**5b**) would be expected to give four C_5H_5 signals, the appearance of three resonances can be ascribed to two of these ligands being in very similar environments. On warming to −60 °C the peaks for the Me groups at δ 2.40 and 2.46 coalesce, and these appear as a singlet (δ 2.44) at room temperature. Similarly, the other two Me resonances afford a singlet (δ 2.70) in the room-temperature spectrum. The C_5H_5 signals at δ 5.30 and 5.47 also form a sharp singlet in the room temperature spectrum, with the peak at δ 5.34 remaining unaltered. It seems likely that in solution (**5**) exists as an equilibrium mixture of (**5a**) and (**5b**), and these species are undergoing fluxional processes similar to (**4**). However, the presence of the bulky PEt_3 group in (**5**) appears to slow down the dynamic behaviour and even alter the relative energies of the three processes so that the high-temperature limiting spectra are no longer observed at ambient temperatures.

Experimental

All reactions were carried out using Schlenk tube techniques under an atmosphere of oxygen-free nitrogen. Solvents were rigorously dried before use. Light petroleum refers to that fraction of b.p. 40—60 °C. The n.m.r. measurements were made with JEOL FX 90Q or FX 200 instruments, and i.r. spectra recorded with Nicolet 5-MX or 10-MX spectrometers. Carbon-13 chemical shifts are in p.p.m. with positive values representing shifts to high frequency of $SiMe_4$. Phosphorus-31 chemical shifts are positive to high frequency of 85% H_3PO_4 (external). Spectra, recorded at room temperature unless otherwise stated, were measured in CD_2Cl_2 (^1H) or CD_2Cl_2–CH_2Cl_2 (^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$). The compounds $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$,[10] $[RuCl_2(PPh_3)_3]$,[18] $[Ru(CO)_2(PPh_3)_3]$,[19] and $[Ru(CO)_3(PPh_3)_2]$[20] were prepared by methods described elsewhere.

Synthesis of $[RuW(\mu-Cl)(\mu-CMe)(Cl)(CO)_2(PPh_3)_2(\eta-C_5H_5)]$.—A thf (20 cm^3) solution of $[RuCl_2(PPh_3)_3]$ (0.57 g, 0.60 mmol) was placed in a rigorously dry Schlenk tube. A diethyl ether (15 cm^3) solution of $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ (0.21 g, 0.61 mmol) was carefully, by means of a syringe, layered upon the top of the thf solution. The mixture was allowed to stand at room temperature without stirring for 28 h. Purple *crystals* of $[RuW(\mu-Cl)(\mu-CMe)(Cl)(CO)_2(PPh_3)_2(\eta-C_5H_5)]\cdot0.67thf$ (**1**) (0.55 g, 86%) were collected, washed with diethyl ether (2 × 15 cm^3), and dried *in vacuo* (Found: C, 52.8; H, 3.9. $C_{45}H_{38}Cl_2O_2P_2RuW\cdot0.67C_4H_8O$ requires C, 53.3; H, 3.8%); m.p. 187—188 °C (decomp.); $\nu_{max.}$(CO) at 1 929s and 1 881m cm^{-1} (Nujol); ^{31}P-$\{^1H\}$ n.m.r., δ 59.0 [d, 1 P, *J*(PP) 15] and 25.9 p.p.m. [d, 1 P, *J*(PP) 15 Hz].

Preparation of $[RuW(\mu-Cl)(\mu-CMe)(Cl)(CO)_2(PPh_3)(\eta-C_2Me_2)(\eta-C_5H_5)]$.—Compound (**1**) (0.40 g, 0.40 mmol), suspended in CH_2Cl_2 (15 cm^3), was placed in a Schlenk tube fitted with a high-pressure stopcock. An excess of MeC≡CMe (*ca.* 0.5 cm^3) was added, and the mixture allowed to stand at room temperature for 2 h. Removal of solvent *in vacuo*, and crystallisation of the residue from CH_2Cl_2–light petroleum (1:3) afforded green *crystals* of $[RuW(\mu-Cl)(\mu-CMe)(Cl)(CO)_2(PPh_3)(\eta-C_2Me_2)(\eta-C_5H_5)]$ (**2**) (0.32 g, 98%) (Found: C, 45.2; H, 3.5. $C_{31}H_{29}Cl_2O_2PRuW$ requires C, 45.4; H, 3.6%); m.p. 142—143 °C (decomp.); $\nu_{max.}$(CO) at 2 018s and 1 996vs cm^{-1} (CH_2Cl_2). N.m.r.: ^1H, δ 1.03 (s, 3 H, μ-CMe), 3.06 (s, 3 H, C_2Me), 3.18 (s, 3 H, C_2Me), 5.49 (s, 5 H, C_5H_5), and 7.45—7.55 (m, 15 H, Ph); ^{13}C-$\{^1H\}$ (at −10 °C), δ 203.9 [d, CO, *J*(PC) 12], 199.2 [d, C_2Me_2, *J*(PC) 11], 134.2—129.1 (Ph), 103.6 (C_5H_5), 30.1 (C_2*Me*$_2$), and 9.4 p.p.m. (μ-C*Me*); ^{13}C, δ 204.0 [d, CO, *J*(PC) 12], 137.8—127.5 (Ph), 104.2 [d, C_5H_5, *J*(HC) 176], 30.4 [q, C_2*Me*$_2$, *J*(HC) 174], and 9.3 p.p.m. [q, μ-C*Me*, *J*(HC) 175 Hz]; ^{31}P-$\{^1H\}$, δ 49.6 p.p.m.

Synthesis of $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_6(PPh_3)(\eta\text{-}C_5H_5)_2]$.—A CH_2Cl_2 (15 cm^3) solution of $[Ru(CO)_2(PPh_3)_3]$ (0.30 g, 0.30 mmol) was treated with an Et_2O (10 cm^3) solution of $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.60 mmol) so that the two layers were able to diffuse without stirring (48 h). This method produced orange crystals and a red mother-liquor. The orange *crystals* of $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_6(PPh_3)(\eta\text{-}C_5H_5)_2]$ (3) (0.21 g, 65%) were collected, washed with diethyl ether (2 × 15 cm^3), and dried *in vacuo* (Found: C, 42.4; H, 2.9. $C_{38}H_{31}O_6PRuW_2$ requires C, 42.0; H, 2.9%); m.p. 224—226 °C; $\nu_{max.}$(CO) at 2 006s, 1 959m, 1 909w, 1 831w, 1 788w, and 1 741w cm^{-1} (Nujol). The mother-liquor was evaporated *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (1 cm^3; 1 : 1) and chromatographed on an alumina column (10 × 1 cm). Elution with the same solvent mixture gave small quantities of the known compounds $[Ru(CO)_3(PPh_3)_2]$ (40 mg) and $[\overline{W\{=C(Me)C}=O\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (80 mg), identified spectroscopically.

Compound (3) could also be prepared, but in lower yield (*ca.* 30%) by heating $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ with $[Ru(CO)_3(PPh_3)_2]$ (70 °C for 16 h) in toluene.

Reactions of $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_6(PPh_3)(\eta\text{-}C_5H_5)_2]$ (3).—(*a*) *With* CO. Compound (3) (0.10 g, 0.10 mmol) was suspended in CH_2Cl_2 (25 cm^3), and CO gas was bubbled through the mixture for 20 min, affording a pale red solution. A thf (20 cm^3) solution of $[W(thf)(CO)_5]$ (*ca.* 5 mmol) was added to remove free PPh_3 as the complex $[W(CO)_5(PPh_3)]$. After 10 min, solvent was removed *in vacuo* giving a red residue. The latter was dissolved in Et_2O–light petroleum (1 cm^3; 1 : 1) and chromatographed on an alumina column (10 × 1 cm) at 0 °C. Elution with the same solvent mixture gave $[W(CO)_6]$ and $[W(CO)_5(PPh_3)]$ (identified by i.r.) in a yellow eluate. Further elution of the column with CH_2Cl_2–Et_2O (3:2) gave a red fraction. Removal of solvent *in vacuo* afforded orange-red *microcrystals* of $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ (4) (0.04 g, 40%) (Found: C, 37.8; H, 2.4. $C_{21}H_{16}O_7RuW_2$ requires C, 37.9; H, 2.4%); m.p. 209—210 °C; $\nu_{max.}$(CO) at 2 060s, 1 994s, 1 975s, 1 889w (br), 1 868m, 1 830m, and 1 713m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H, δ 2.60 (s, 6 H, Me) and 5.15 (s, 10 H, C_5H_5); $^{13}C\text{-}\{^1H\}$, δ 222.3, 221.3 (WCO), 195.5 (RuCO), 90.6 (C_5H_5), and 35.3 p.p.m. (br, $C_2\mathit{Me}_2$); at −25 °C, δ 221.5 (WCO), 193.2 (RuCO), 154.0, 141.4 (C_2Me_2), 90.5 (C_5H_5), 36.3, and 34.9 p.p.m. ($C_2\mathit{Me}_2$).

(*b*) *With* PEt_3. An orange suspension of (3) (0.10 g, 0.10 mmol) in CH_2Cl_2 (10 cm^3) was treated with excess of PEt_3 (*ca.* 0.02 cm^3). The mixture was stirred for 45 min, affording a pale red solution. Solvent was removed *in vacuo*, and the residue crystallised from CH_2Cl_2–light petroleum (1:5) at −20 °C to give red *microcrystals* of $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)_2]$ (5) (0.09, 98%) (Found: C, 33.5; H, 3.5. $C_{26}H_{26}O_6PRuW_2$ requires C, 33.2; H, 3.3%); m.p. 196—197 °C; $\nu_{max.}$(CO) at 1 996s, 1 991 (sh), 1 943s, 1 920s, 1 839m, 1 832 (sh), 1 795m, 1 788 (sh), 1 725m, and 1 714m cm^{-1} (Nujol). N.m.r. (isomeric mixture): ^1H (at −80 °C), δ 0.90—1.20 (m, 18 H, $PCH_2\mathit{Me}$), 1.35—2.10 (m, 12 H, $PC\mathit{H}_2Me$), 2.40 (br, 3 H, Me), 2.46 (br, 3 H, Me), 2.61 (br, 3 H, Me), 2.91 (br, 3 H, Me), 5.30 (s, 5 H, C_5H_5), 5.34 (s, 10 H, C_5H_5), and 5.47 (s, 5 H, C_5H_5); $^{13}C\text{-}\{^1H\}$, δ 222.3 (WCO), 199.6 (RuCO), 150.4, 148.3, 146.0 (C_2Me_2), 93.2 (C_5H_5), 91.0 (C_5H_5), 37.1 ($C_2\mathit{Me}_2$), 20.0 [d, $P\mathit{C}H_2Me$, J(PC) 29 Hz], and 8.3 p.p.m. ($PCH_2\mathit{Me}$); $^{31}P\text{-}\{^1H\}$ (at −80 °C), δ 33.2 and 28.2 p.p.m.

Table 3. Atomic positional parameters (fractional co-ordinates) (× 10^4) for complex (**1**)[a]

Atom	*x*	*y*	*z*
W	2 114(1)	5 202(1)	5 043(1)
Ru	1 617(1)	4 580(1)	4 198(1)
P(1)	1 629(1)	4 075(1)	3 944(2)
C(12)[b]	2 315(1)	4 363(2)	4 418(5)
C(13)	2 643	4 428	4 214
C(14)	2 710	4 276	3 237
C(15)	2 450	4 059	2 464
C(16)	2 122	3 993	2 668
C(11)	2 055	4 146	3 645
C(22)[b]	1 314(2)	3 803(1)	6 176(5)
C(23)	1 220	3 584	7 169
C(24)	1 328	3 349	7 242
C(25)	1 529	3 332	6 323
C(26)	1 623	3 552	5 331
C(21)	1 516	3 787	5 257
C(32)[b]	1 158(1)	3 454(1)	2 830(4)
C(33)	977	3 257	1 837
C(34)	1 028	3 401	679
C(35)	1 260	3 742	516
C(36)	1 442	3 939	1 510
C(31)	1 391	3 795	2 667
P(2)	1 051(1)	4 450(1)	4 885(2)
C(42)[b]	484(2)	4 237(1)	3 324(6)
C(43)	252	4 022	2 460
C(44)	254	3 731	2 104
C(45)	487	3 655	2 611
C(46)	718	3 870	3 475
C(41)	717	4 161	3 831
C(52)[b]	1 101(1)	4 412(1)	7 401(6)
C(53)	1 006	4 259	8 542
C(54)	706	3 953	8 672
C(55)	502	3 801	7 659
C(56)	597	3 954	6 517
C(51)	896	4 260	6 388
C(62)[b]	1 070(2)	5 012(2)	3 857(5)
C(63)	1 020	5 288	3 814
C(64)	877	5 360	4 809
C(65)	785	5 157	5 846
C(66)	835	4 881	5 888
C(61)	978	4 809	4 894
Cl(2a)	2 012(2)	5 137(2)	2 723(9)
C(1a)	1 766(9)	5 244(12)	6 063(44)
O(1a)	1 598(10)	5 219(14)	6 947(44)
Cl(1)	1 879(1)	4 662(1)	6 208(2)
Cl(2)	1 719(1)	5 272(1)	6 427(3)
C(1)	1 895(3)	5 294(3)	3 649(11)
O(1)	1 821(2)	5 378(2)	2 791(8)
C(3)	2 102(2)	4 905(2)	3 753(10)
C(4)	2 290(3)	4 922(3)	2 607(12)
C(2)	1 471(2)	4 596(2)	2 609(10)
O(2)	1 382(2)	4 600(2)	1 709(6)
C(5)[b]	2 493(2)	5 772(2)	5 044(9)
C(6)	2 502	5 664	6 249
C(7)	2 618	5 429	6 189
C(8)	2 681	5 392	4 947
C(9)	2 603	5 604	4 239
O(1′)	9 556(4)	767(4)	2 524(13)
C(2′)	9 844(5)	965(5)	3 236(21)
C(3′)	9 913(5)	1 313(5)	2 999(19)
C(4′)	9 594(5)	1 294(5)	2 703(18)
C(5′)	9 354(5)	922(5)	2 596(18)

[a] Primed atoms belong to the thf molecule of crystallisation. [b] Pivot atom of a rigid group; remaining atoms in the group have identical standard deviations.

Table 4. Atomic positional parameters (fractional co-ordinates) (× 10^4) for complex (**4a**)

Atom	*x*	*y*	*z*
W(1)	2 434(1)	7 343(1)	5 342(1)
W(2)	1 423(1)	6 084(1)	6 732(1)
Ru	3 414(1)	5 852(1)	5 752(1)
C(11)*	1 991(6)	8 566(4)	5 520(11)
C(12)	2 299	8 425	4 040
C(13)	1 586	7 941	3 359
C(14)	836	7 783	4 419
C(15)	1 087	8 169	5 755
C(1)	3 721(7)	7 703(5)	6 207(10)
O(1)	4 411(6)	7 967(5)	6 726(9)
C(2)	3 221(7)	6 959(6)	3 670(10)
O(2)	3 636(6)	6 865(4)	2 573(8)
C(21)*	218(7)	6 682(5)	8 167(13)
C(22)	597	6 085	9 032
C(23)	345	5 423	8 268
C(24)	−189	5 612	6 931
C(25)	−268	6 390	6 869
C(3)	4 705(7)	6 270(6)	5 591(11)
O(3)	5 480(6)	6 508(5)	5 467(10)
C(4)	3 294(8)	5 370(5)	3 762(11)
O(4)	3 197(8)	5 052(5)	2 695(9)
C(5)	3 987(7)	5 015(5)	6 682(12)
O(5)	4 370(7)	4 529(5)	7 235(11)
C(6)	1 862(7)	5 091(6)	6 371(11)
O(6)	1 906(6)	4 436(4)	6 243(10)
C(9)	1 265(7)	6 167(5)	4 520(12)
O(9)	1 034(6)	6 111(4)	3 285(9)
C(7)	2 534(7)	6 940(5)	7 621(11)
C(71)	2 386(10)	7 443(6)	8 953(12)
C(8)	2 983(7)	6 253(5)	7 802(9)
C(81)	3 326(10)	5 956(7)	9 277(11)

* Pivot atom of a rigid group; remaining atoms in the group have identical standard deviations.

Crystal Structure Determinations.—Crystals of (**1**) grow as black rhombs from tetrahydrofuran–diethyl ether, those of (**4a**) as small faceted orange spheres from dichloromethane–light petroleum. Crystals were sealed in Lindemann glass capillaries under dry nitrogen gas, and diffracted intensities were collected using ω–2θ scans in the range $2.9 \leqslant 2\theta \leqslant 50°$ on a Nicolet *P*3*m* four-circle diffractometer at 200 K for (**1**) and at 298 K for (**4a**). For (**1**), of 7 074 intensities, 4 731 had $I \geqslant 5\sigma(I)$, where $\sigma(I)$ is the standard deviation in *I* based on counting statistics. Only these were used in the final refinement of the structure, after all the data had been corrected for Lorentz and polarisation effects, and a numerical correction applied for *X*-ray absorption.[21] Correspondingly for (**4a**), of 3 372 intensities, 3 225 had $I \geqslant 4\sigma(I)$ and only these were used in structure refinement, after similar corrections had been applied.

Crystal data for (**1**). $C_{45}H_{38}Cl_2O_2P_2RuW{\cdot}0.67C_4H_8O$, M = 1 076.7, trigonal, $a = b = 45.833(13)$, $c = 10.969(8)$ Å, U = 19 954(18) Å^3, $D_m = 1.64$ g cm^{-3}, $Z = 18$, $D_c = 1.62$ g cm^{-3}, $F(000)$ = 9 586, space group $R\bar{3}$ (no. 148), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\ 69$ Å, μ(Mo-K_α) = 32.1 cm^{-1}.

Crystal data for (**4a**). $C_{21}H_{16}O_7RuW_2$, M = 849.1, monoclinic, $a = 13.276(3)$, $b = 18.187(8)$, $c = 8.955(3)$ Å, β = 91.28(2)°, U = 2 162(1) Å^3, $Z = 4$, $D_c = 2.62$ g cm^{-3}, $F(000)$ = 1 560, space group $P2_1/n$ (non-standard setting of no. 14), μ(Mo-K_α) = 115.7 cm^{-1}.

The structures were solved by heavy-atom methods, and all non-hydrogen atoms located from difference Fourier calculations. All refinements, by blocked-cascade least-squares techniques, were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[21] All hydrogen atoms were incorporated at calculated 'riding' positions (C–H 0.96 Å) with tied isotropic thermal parameters (1.2 times $U_{eq.}$ for the ligated atom).

Weighting schemes applied were of the form $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$ where g = 0.000 65 for (**1**) and g = 0.000 11 for (**4a**). The final electron-density difference synthesis for (**4a**) showed no peaks > 1 e Å^{-3}, while for (**1**) residual peaks < 2.4 e Å^{-3} were found close to the metal atoms. Scattering factors for W were taken from ref. 22, while those for all other atoms are included in the programs of ref. 21. Refinement led to R = 0.0485 (R' = 0.0526) for (**1**), and R = 0.0331 (R' = 0.0352) for (**4a**).

In (**1**) a positional disorder was observed such that the terminal carbonyl ligand on tungsten occupies two possible sites with a refined occupancy ratio of 3:1. Concurrently Cl(2) occupies its position '*cisoid*' to this carbonyl in the complementary ratio of 3:1. For (**1**) twelve molecules of tetrahydrofuran co-crystallise in each unit cell. Atom co-ordinates for (**1**) and (**4a**) are listed in Tables 3 and 4, respectively.

Acknowledgements

We thank the S.E.R.C. for support and for a research studentship (to J. C. V. L.).

References

1 Part 37, M. R. Awang, R. D. Barr, M. Green, J. A. K. Howard, T. B. Marder, and F. G. A. Stone, preceding paper.

2 J. C. Jeffery, J. C. V. Laurie, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1563; M. R. Awang, G. A. Carriedo, J. A. K. Howard, K. A. Mead, I. Moore, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 964; L. Busetto, J. C. Jeffery, R. M. Mills, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 101.

3 F. G. A. Stone, in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, 383; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89.

4 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.

5 F. H. Jardine, *Prog. Inorg. Chem.*, 1984, **31**, 265.

6 M. A. Bennett, M. I. Bruce, and T. W. Matheson, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 4, sect. 32.3.

7 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.

8 R. E. Colborn, A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2099.

9 S. Sabo, V. Chaudret, and D. Gervais, *J. Organomet. Chem.*, 1983, **258**, C19; S. Sabo, B. Chaudret, D. Gervais, and R. Poilblanc, *Nouv. J. Chim.*, 1981, **5**, 597.

10 W. Uedelhoven, K. Eberl, and F. R. Kreissl, *Chem. Ber.*, 1979, **112**, 3376; 1977, **110**, 3782.

11 W. Hieber and P. John, *Chem. Ber.*, 1970, **103**, 2161.

12 C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 953.

13 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 3288.

14 M. H. Chisholm, J. A. Heppert, and J. C. Huffman, *J. Am. Chem. Soc.*, 1984, **106**, 1151.

15 E. O. Fischer, G. Huttner, T. L. Lindner, A. Frank, and F. R. Kreissl, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 231.

16 M. Green, S. J. Porter, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 513; M. Green, J. C. Jeffery, S. J. Porter, H. Razay, and F. G. A. Stone, *ibid.*, 1982, 2475.

17 G. A. Carriedo, J. A. K. Howard, K. Marsden, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 1589.

18 P. S. Hallmann, T. A. Stephenson, and G. Wilkinson, *Inorg. Synth.*, 1970, **12**, 237.

19 B. E. Cavit, K. R. Grundy, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1972, 60.

20 N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 45.

21 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *P*3*m* *X*-ray system, Cambridge, 1976; updated at Göttingen, 1981.

22 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

Received 20*th November* 1984; *Paper* 4/1980