Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 50.[1] Synthesis and Crystal Structures of the Complexes $[RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)(\mu\text{-}CPh)_2(\mu_3\text{-}CPh)(CO)_2(\eta\text{-}C_5H_5)_3]$ and $[RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)\{\mu\text{-}C(Ph)C(O)\}(\mu\text{-}CPh)(\mu_3\text{-}CPh)(CO)(PMePh_2)(\eta\text{-}C_5H_5)_3]$ *

Louis J. Farrugia
Department of Chemistry, The University, Glasgow G12 8QQ
John C. Jeffery, Christine Marsden, Paul Sherwood, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The zero-valent ruthenium compounds $[Ru(\eta^6\text{-}C_8H_{10})(cod)]$ (C_8H_{10} = cyclo-octa-1,3,5-triene, cod = cyclo-octa-1,5-diene) or $[Ru(\eta^6\text{-}C_{10}H_8)(cod)]$ ($C_{10}H_8$ = naphthalene) react at room temperature in light petroleum with the alkylidynetungsten complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Ph) to give a chromatographically separable mixture of the cluster compounds $[RuW_2(\mu_3\text{-}C_2R_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ and $[RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3]$. A single-crystal *X*-ray diffraction study established the molecular structure of the rutheniumtritungsten species containing phenylmethylidyne ligands. The metal-atom core consists of a RuW_2 triangle [W–Ru 2.775(2) and 2.847(2), W–W 2.610(1) Å] to which a third tungsten atom is attached *via* the ruthenium [W–Ru 2.735(2) Å]. The '*exo*-ligated' tungsten atom carries a terminal CO ligand and a C_5H_5 group, with the Ru–W bond asymmetrically bridged by CPh and CO groups. The latter is also η-co-ordinated to one of the tungsten atoms in the RuW_2 triangle [W–C 2.43(1), W–O 2.05(1) Å] so that it occupies a triply-bridging site. The tungsten atoms in the triangle are ligated by C_5H_5 groups, and the ruthenium atom carries a terminal CO ligand. A phenylmethylidyne group symmetrically caps the triangle, and a similar fragment edge-bridges the W–W bond. A carbonyl group bridges the Ru–W edge of the triangle. The compounds $[RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3]$ react with tertiary phosphines to afford complexes $[RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)\{\mu\text{-}C(R)C(O)\}(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)(PR'_3)(\eta\text{-}C_5H_5)_3]$ (R = C_6H_4Me-4, PR'_3 = PMe_3; R = Ph, PR'_3 = PMe_3 or $PMePh_2$) containing ketenyl groups. An *X*-ray diffraction study on the complex with R = Ph and PR'_3 = PMe_2Ph established the structure of this class of compound. The core structure of the molecule is remarkably similar to that of its precursor, with the RuW_2 triangle 'spiked' by a tungsten atom, and with bridging μ-CR, μ_3-CR, μ-CO, and μ_3-η-CO groups. The important difference is associated with the *exo*-ligated tungsten which now carries a $PMePh_2$ ligand instead of a terminal CO group, and the W–Ru vector is edge-bridged by a μ-C(Ph)C(O) fragment [W–Ru 2.771(1), μ-C–Ru 2.19(1), μ-C–W 2.15(1), μ-C(O)–W 2.14(1), μ-C–C 1.39(2) Å]. The i.r. and n.m.r. (^1H and $^{13}C\text{-}\{^1H\}$) spectra of the new compounds are discussed in relation to their structures.

Developing our use of the complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (**1a**) as a reagent for the synthesis of heteronuclear metal cluster compounds,[2] we have studied its reactions with the zero-valent ruthenium complexes $[Ru(\eta^6\text{-}C_8H_{10})(cod)]$ (C_8H_{10} = cyclo-octa-1,3,5-triene, cod = cyclo-octa-1,5-diene)[3] and $[Ru(\eta^6\text{-}C_{10}H_8)(cod)]$ ($C_{10}H_8$ = naphthalene).[4] During the investigation it became necessary to extend the study to (**1b**), the phenylmethylidyne analogue of (**1a**), in order to obtain products with crystals suitable for *X*-ray diffraction studies.

Results and Discussion

The reaction between (**1a**) and $[Ru(\eta^6\text{-}C_8H_{10})(cod)]$ in light petroleum at room temperature afforded a chromatographically separable mixture consisting of a trace of the bridged-alkyne complex $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$,[5] appreciable amounts of the known compound $[RuW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (**2a**),[6] and a new cluster complex (**3a**). Complete identification of the latter was not possible on the basis of the microanalysis and spectroscopic data (see below).

The compound $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ is a frequent product of reactions of (**1a**).[5] The ruthenium-ditungsten complex (**2a**) exists as a mixture of two isomers [(**A**) and (**B**)] in solution, and is formed in a reaction involving coupling of *p*-tolylmethylidyne fragments.[6] In both isomers the alkyne adopts the $\mu_3\text{-}(\eta^2\text{-}\|)$ bridge-bonding mode.[7] The related complex (**2b**) with a $\mu_3\text{-}C_2Me_2$ ligand, has also been prepared, and its isomer (**B**) structurally characterised by *X*-ray diffraction.[8]

The reaction between (**1a**) and $[Ru(\eta^6\text{-}C_{10}H_8)(cod)]$ gave the same three products as those obtained with $[Ru(\eta^6\text{-}C_8H_{10})(cod)]$, but since the naphthalene–ruthenium complex

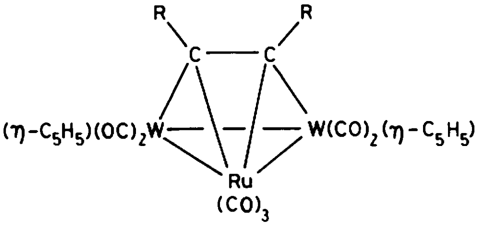
---

* 1,2-μ-Carbonyl-μ_3-[η-carbonyl-*C*(Ru^1,$W^{3,4}$),*O*(W^3)]-1,4-dicarbonyl-2,3,4-tris(η-cyclopentadienyl)-1,4;2,3-di-μ-phenylmethylidyne-1,2,3-μ_3-phenylmethylidyne-*cyclo*-rutheniumtritungsten(3*Ru–W*,*W–W*) and 1,2-μ-carbonyl-μ_3-[η-carbonyl-*C*(Ru^1,$W^{3,4}$),*O*(W^3)]-1-carbonyl-2,3,4-tris(η-cyclopentadienyl)-4-methyldiphenylphosphine-μ-[2-oxo-1-phenylethenyl-C^1(Ru^1,W^4),C^2(W^4)]-2,3-μ-phenylmethylidyne-1,2,3-μ_3-phenylmethylidyne-*cyclo*-rutheniumtritungsten(3*Ru–W*,*W–W*) respectively.

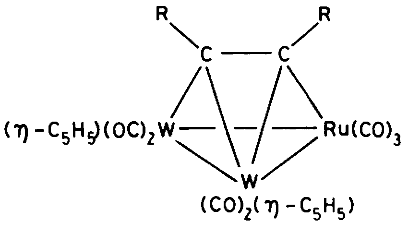
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

$[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$

	R
(**1a**)	$C_6H_4Me\text{-}4$
(**1b**)	Ph

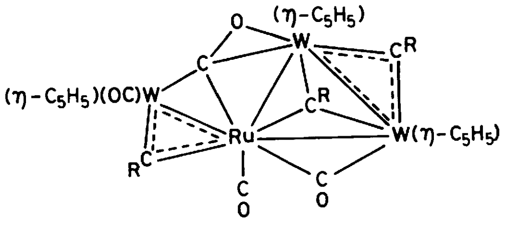


(**A**)



(**B**)

	R
(**2a**)	$C_6H_4Me\text{-}4$
(**2b**)	Me
(**2c**)	Ph



	R
(**3a**)	$C_6H_4Me\text{-}4$
(**3b**)	Ph

was easier to prepare in our laboratory, it became the favoured precursor for this work.

The ^{1}H and $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectra of (**3a**) were informative, but even with these data available it was not possible to resolve fully the structure of the complex. The ^{1}H n.m.r. spectrum showed resonances for C_5H_5 groups in three different environments, and three distinct peaks were observed for Me-4 substituents of *p*-tolylmethylidyne groups. The $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectrum was consistent with the ^{1}H in showing three signals for C_5H_5 ligands, and three for Me-4 groups (see Experimental section). In addition resonances were observed at δ 350.1 and 348.0 p.p.m. characteristic for $\mu\text{-}CC_6H_4Me\text{-}4$ groups edge bridging metal–metal bonds, with a further signal at δ 292.8 suggestive of the presence of a $\mu_3\text{-}CC_6H_4Me\text{-}4$ moiety.[1] An interesting feature of the resonances at δ 350.1 and 292.8 p.p.m. was the observation that two sets of $^{183}W\text{–}^{13}C$ satellite peaks were associated with each signal. This feature provided a clear indication that the two *p*-tolylmethylidyne groups responsible for these signals bridge W–W bonds with the tungsten atoms occupying non-equivalent sites. It was thus evident from the n.m.r. studies that the cluster (**3a**) contained three $CC_6H_4Me\text{-}4$ and three $W(\eta\text{-}C_5H_5)$ groups. Persistent attempts to grow crystals of (**3a**) for an *X*-ray diffraction study were unsuccessful. In view of this result the reaction between (**1b**) and $[Ru(\eta^6\text{-}C_{10}H_8)(cod)]$ was examined.

Treatment of (**1b**) with $[Ru(\eta^6\text{-}C_{10}H_8)(cod)]$ in light petroleum at room temperature afforded a mixture of $[RuW_2(\mu_3\text{-}C_2Ph_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ (**2c**), and a dark green cluster compound (**3b**). The spectroscopic properties (i.r. and n.m.r.) of the latter showed that it was structurally similar to (**3a**). Crystals of (**3b**) were successfully grown, and an *X*-ray diffraction study was carried out with the results described below. Compound (**2c**) was characterised by microanalysis, and by i.r. and n.m.r. spectroscopy (see Experimental section). Like the complexes (**2a**) and (**2b**), compound (**2c**) shows seven absorptions in the CO stretching region of the i.r., with band frequencies virtually identical with those of (**2a**).[6] Similarly, the $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectrum of (**2c**) showed resonances for carbonyl ligands at δ 220.9 [WCO, *J*(WC) 167], 220.7 [WCO, *J*(WC) 157], and 196.5 p.p.m. (RuCO) to be compared with those observed at 221.1, 220.2, and 195.9 p.p.m. in the spectrum of (**2a**). The observation of only three resonances in the spectrum of (**2c**) for the CO ligands indicates that these groups undergo site-exchange on the n.m.r. time-scale, as found for (**2a**).[6] Formation of (**2c**) in the reaction between (**1b**) and $[Ru(\eta^6\text{-}C_{10}H_8)(cod)]$ thus provides a further example of alkylidyne group coupling to form a ligated alkyne at a trimetal centre.

The results of the *X*-ray diffraction study on (**3b**) are summarised in Table 1, and the molecule is shown in Figure 1. The structure has several noteworthy features. The metal-atom framework comprises a triangle of two tungsten atoms, W(1) and W(2), and a ruthenium, to which a third tungsten atom [W(3)] is bonded. Such a metal array, designated by the description[9] 'spiked-metal cluster' or 'metallo-ligated metal cluster,' is relatively uncommon. In tetranuclear metal species it is generally associated with a cluster valence electron (c.v.e.) count of 64, as found, for example, in $[Os_4(CO)_{15}(PMe_3)]$[10] or $[Re_4H(\mu\text{-}H)_3(CO)_{15}]^{2-}$.[11] The *exo*-ligated metal atom may either lie in an equatorial 'ligand' position with respect to the metal triangle to which it is attached, or alternatively be in an axial position. The former arrangement has been found for $[CrReRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_9H_7)_2]$,[1] $[Os_4(CO)_{15}(PMe_3)]$,[10] and $[Re_2Os_3(\mu\text{-}H)_2(CO)_{20}]$ (two Re atoms 'spiking' the Os_3 unit).[9] The latter arrangement occurs in the clusters $[Re_4H(\mu\text{-}H)_3(CO)_{15}]^{2-}$,[11] $[MnOs_3(\mu\text{-}H)(\mu\text{-}CO)\{\mu\text{-}CH{=}CH(Ph)\}(CO)_{11}(\eta\text{-}C_5H_5)]$,[12] and $[Co_2Mo_2(\mu\text{-}CO)_3(\mu_4\text{-}$

Table 1. Comparison of selected bond lengths (Å) and angles (°) for the compounds $[RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)(\mu\text{-}CPh)_2(\mu_3\text{-}CPh)(CO)_2(\eta\text{-}C_5H_5)_3]$ (**3b**) and $[RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)\{\mu\text{-}C(Ph)C(O)\}(\mu\text{-}CPh)(\mu_3\text{-}CPh)(CO)(PMePh_2)(\eta\text{-}C_5H_5)_3]$ (**4c**)

	(**3b**)	(**4c**)		(**3b**)	(**4c**)
W(1)–W(2)	2.610(1)	2.617(1)	W(1)–Ru	2.775(2)	2.789(1)
W(1)–C(2)	2.07(2)	2.06(2)	W(1)–C(46)	1.96(1)	1.97(2)
W(1)–C(66)	2.06(2)	2.08(1)	W(2)–Ru	2.847(2)	2.871(1)
W(2)–C(1)	2.43(1)	2.45(1)	W(2)–O(1)	2.05(1)	2.07(1)
W(2)–C(46)	2.00(1)	2.02(1)	W(2)–C(66)	2.09(1)	2.11(1)
W(3)–Ru	2.735(2)	2.771(1)	W(3)–C(1)	1.93(1)	1.93(1)
W(3)–C(4)	1.93(3)	2.14(1)	W(3)–C(56)	1.88(1)	2.15(1)
W(3)–P		2.462(4)	Ru–C(1)	2.16(1)	2.17(1)
Ru–C(2)	2.03(2)	2.01(2)	Ru–C(3)	1.88(2)	1.89(2)
Ru–C(56)	2.11(1)	2.19(1)	Ru–C(66)	2.13(1)	2.13(1)
C(1)–O(1)	1.30(2)	1.31(2)	C(2)–O(2)	1.19(2)	1.19(2)
C(3)–O(3)	1.15(2)	1.15(2)	C(4)–O(4)	1.21(3)	1.22(2)
C(4)–C(56)		1.39(2)	C(46)–C(40)	1.43(2)	1.48(2)
C(56)–C(50)	1.49(2)	1.49(2)	C(66)–C(60)	1.44(2)	1.46(2)
P–C(70)		1.87(2)	P–C(80)		1.83(1)
P–C(90)		1.86(1)			
W(2)–W(1)–Ru	63.8(1)	64.1(1)	W(2)–W(1)–C(2)	87.7(4)	88.1(4)
Ru–W(1)–C(2)	46.8(5)	46.0(4)	W(2)–W(1)–C(46)	49.3(4)	49.8(4)
Ru–W(1)–C(46)	106.7(4)	108.8(4)	C(2)–W(1)–C(46)	100.4(5)	104.4(6)
W(2)–W(1)–C(66)	51.5(4)	51.8(4)	Ru–W(1)–C(66)	49.6(4)	49.3(4)
C(2)–W(1)–C(66)	96.3(6)	95.1(6)	C(46)–W(1)–C(66)	97.4(6)	97.2(6)
W(1)–W(2)–Ru	60.9(1)	60.9(1)	W(1)–W(2)–C(1)	98.5(4)	97.2(3)
Ru–W(2)–C(1)	47.6(3)	47.3(3)	W(1)–W(2)–O(1)	111.6(3)	109.4(2)
Ru–W(2)–O(1)	77.7(3)	77.2(2)	C(1)–W(2)–O(1)	32.4(4)	32.4(4)
W(1)–W(2)–C(46)	48.1(4)	48.1(5)	Ru–W(2)–C(46)	103.0(4)	104.3(4)
C(1)–W(2)–C(46)	115.9(6)	117.0(5)	O(1)–W(2)–C(46)	101.9(5)	102.2(5)
W(1)–W(2)–C(66)	50.4(4)	50.8(3)	Ru–W(2)–C(66)	48.2(4)	47.7(4)
C(1)–W(2)–C(66)	94.1(5)	93.6(5)	O(1)–W(2)–C(66)	125.7(5)	124.9(4)
C(46)–W(2)–C(66)	95.2(6)	94.8(6)	Ru–W(3)–P		108.0(1)
Ru–W(3)–C(1)	51.8(4)	51.2(4)	P–W(3)–C(1)		92.2(4)
Ru–W(3)–C(4)	85.3(5)	66.0(4)	P–W(3)–C(4)		79.4(4)
C(1)–W(3)–C(4)	86.1(7)	110.0(5)	Ru–W(3)–C(56)	50.5(4)	50.9(4)
P–W(3)–C(56)		116.9(4)	C(1)–W(3)–C(56)	101.6(6)	101.7(5)
C(4)–W(3)–C(56)	96.8(7)	37.8(6)	W(1)–Ru–W(2)	55.3(1)	55.1(1)
W(1)–Ru–W(3)	143.3(1)	139.3(1)	W(2)–Ru–W(3)	98.0(1)	99.0(1)
W(1)–Ru–C(1)	100.5(4)	99.5(4)	W(2)–Ru–C(1)	55.9(4)	56.2(4)
W(3)–Ru–C(1)	44.5(4)	43.9(4)	W(1)–Ru–C(2)	48.1(5)	47.6(5)
W(2)–Ru–C(2)	82.2(4)	82.4(5)	W(3)–Ru–C(2)	109.8(5)	104.0(5)
C(1)–Ru–C(2)	88.9(6)	87.9(6)	W(1)–Ru–C(3)	88.4(5)	88.2(5)
W(2)–Ru–C(3)	131.6(5)	131.9(5)	W(3)–Ru–C(3)	126.7(5)	127.8(5)
C(1)–Ru–C(3)	171.1(6)	171.7(6)	C(2)–Ru–C(3)	96.7(7)	95.0(6)
W(1)–Ru–C(56)	158.1(5)	150.0(4)	W(2)–Ru–C(56)	140.8(4)	148.5(3)
W(3)–Ru–C(56)	43.2(4)	49.7(3)	C(1)–Ru–C(56)	87.1(6)	93.3(5)
C(2)–Ru–C(56)	112.3(6)	106.5(6)	C(3)–Ru–C(56)	84.4(6)	78.4(6)
W(1)–Ru–C(66)	47.4(4)	47.7(3)	W(2)–Ru–C(66)	46.9(4)	47.0(4)
W(3)–Ru–C(66)	134.1(4)	138.3(3)	C(1)–Ru–C(66)	100.9(5)	101.6(5)
C(2)–Ru–C(66)	95.3(6)	95.3(6)	C(3)–Ru–C(66)	85.4(6)	85.9(6)
C(56)–Ru–C(66)	151.6(6)	154.0(5)	W(2)–C(1)–W(3)	150.8(8)	156.2(7)
W(2)–C(1)–Ru	76.5(5)	76.5(4)	W(3)–C(1)–Ru	83.7(5)	84.9(5)
W(2)–C(1)–O(1)	57.5(7)	57.5(7)	W(3)–C(1)–O(1)	148.1(11)	145.4(10)
Ru–C(1)–O(1)	127.7(10)	127.5(9)	W(2)–O(1)–C(1)	90.1(8)	90.1(8)
W(1)–C(2)–Ru	85.1(7)	86.4(6)	W(1)–C(2)–O(2)	145.2(12)	144.5(12)
Ru–C(2)–O(2)	129.5(12)	128.8(12)	Ru–C(3)–O(3)	175.8(18)	179.1(9)
W(3)–C(4)–O(4)	177.8(16)	147.8(11)	W(3)–C(4)–C(56)		71.6(8)
O(4)–C(4)–C(56)		138.4(13)	W(1)–C(46)–W(2)	82.6(5)	82.1(6)
W(1)–C(46)–C(40)	143.3(11)	138.7(10)	W(2)–C(46)–C(40)	134.0(10)	139.2(10)
W(3)–C(56)–Ru	86.4(5)	79.3(4)	W(3)–C(56)–C(4)		70.6(8)
Ru–C(56)–C(4)		96.6(9)	W(3)–C(56)–C(50)	143.6(11)	137.6(9)
Ru–C(56)–C(50)	128.9(10)	126.6(9)	C(4)–C(56)–C(50)		127.7(12)
W(1)–C(66)–W(2)	78.1(5)	77.4(5)	W(1)–C(66)–Ru	83.0(6)	83.0(5)
W(2)–C(66)–Ru	84.9(5)	85.3(5)	W(1)–C(66)–C(60)	138.9(10)	135.1(9)
W(2)–C(66)–C(60)	131.8(11)	132.7(8)	Ru–C(66)–C(60)	121.3(10)	124.9(9)

η-CO)(η-$C_5H_5)_2(\eta$-$C_5Me_5)_2$].[13] The recently reported cluster compound $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$[14] contains a platinum-spiked Os_3 triangle with the Pt–Os vector inclined to it at 75°. The c.v.e. count for this Os_3Pt species is 62; this being rationalised in terms of the presence of the platinum atom in an essentially square-planar 16-electron environment.

Compound (**3b**) contains a carbonyl ligand C(1)O(1) attached to three metal centres [Ru, W(2), and W(3)] in the μ_3-

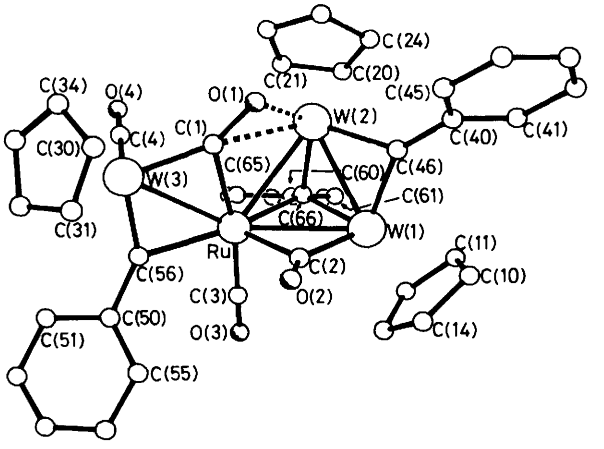


Figure 1. Molecular structure of $[RuW_3(\mu-CO)(\mu_3-\eta-CO)(\mu-CPh)_2(\mu_3-CPh)(CO)_2(\eta-C_5H_5)_3]$ (**3b**), showing the crystallographic numbering

η^2 bonding mode. If it is assumed that this group functions as a four-electron donor, the c.v.e. count for (**3b**) is 60, indicating that it is unsaturated. Consistent with this property, the W(1)–W(2) distance [2.610(1) Å] is relatively short, indicative of some multiplicity in this bond. The 46 c.v.e. complexes $[FeW_2\{\mu_3-C_2(C_6H_4Me-4)_2\}(CO)_6(\eta-C_5H_5)_2]$[15] and $[ReW_2(\mu-Br)(\mu-CC_6H_4Me-4)(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_3-(\eta-C_5H_5)_2]$[16] are also unsaturated and have W–W separations of 2.747(1) and 2.620(1) A, respectively. However, too much reliance should not be placed on correlating these metal–metal distances with the unsaturation of the clusters since these parameters are highly sensitive to other factors. Thus in the anion $[W_2(\mu-H)_2(CO)_8]^{2-}$, with 32 c.v.e. and a formal W=W bond, the metal–metal separation is 2.9945(5) Å.[17]

The ruthenium–tungsten distances in (**3b**) [W(1)–Ru 2.775(2), W(2)–Ru 2.847(2), and W(3)–Ru 2.735(2) Å] are similar to those found in the compounds $[RuW(\mu-Cl)(\mu-CMe)(Cl)(CO)_2(PPh_3)_2(\eta-C_5H_5)]$ [2.769(1) Å] and $[RuW_2(\mu_3-C_2Me_2)(CO)_7(\eta-C_5H_5)_2]$ [2.835(1) and 3.026(1) Å].[8] Because of the considerable variation in Ru–W distances in (**3b**), these parameters do not allow any conclusions to be drawn concerning the site of the electron deficiency.

The *exo*-ligated tungsten atom [W(3)] lies significantly [1.251(1) Å] out of the plane defined by W(1)W(2)Ru, with the W(3)–Ru vector inclined at an angle of 27.2° to this plane. The core metal-atom geometry is thus very approximately that of an equatorial metallo-substituted triangle.

Each tungsten atom bears an $\eta-C_5H_5$ ligand as expected, and the ruthenium atom carries a terminal CO group. The RuW(1)W(2) triangle is capped by a μ_3-CPh ligand in an approximately symmetrical fashion [W(1)–C(66) 2.06(2), W(2)–C(66) 2.09(1), and Ru–C(66) 2.13(1) Å]. The W(1)–W(2) bond is essentially symmetrically bridged by a CPh group [W(1)–C(46) 1.96(1), W(2)–C(46) 2.00(1) Å]. A similar $\mu-CW_2$ ring occurs in $[ReW_2(\mu-Br)(\mu-CC_6H_4Me-4)(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_3(\eta-C_5H_5)_2]$ with μ-C–W distances of 1.99(1) and 1.95(1) Å.[16] These μ-C–W distances all reflect a degree of multiplicity in the bonds to which they refer. Typically μ-C=W bonds in dimetallacyclopropene ring systems occur in the range 1.91—2.03 Å.[18]

The Ru–W(1) vector in (**3b**) is bridged by a carbonyl group [Ru–C(2) 2.03(2), W(1)–C(2) 2.07(2) Å]. Some slight asymmetry is revealed in the bridge by differences in the Ru–C(2)–O(2) and W(1)–C(2)–O(2) angles, 129.5(12) and 145.2(12)° respectively, indicating a stronger attachment to the tungsten atom.

A major feature of interest in the structure is the co-ordination of the C(1)O(1) ligand. This asymmetrically bridges the Ru–W(3) bond [Ru–C(1) 2.16(1), W(3)–C(1) 1.93(1) Å; Ru–C(1)–O(1) 128(1), W(3)–C(1)–O(1) 148(1)°] and is also π bonded to W(2) [W(2)–C(1) 2.43(1), W(2)–O(1) 2.05(1) Å]. The W(3)Ru(1)C(1)O(1) fragment is non-planar with O(1) lying 0.11(1) Å above the mean plane of RuW(3)C(1), and with W(2) being 0.87(1) Å below this plane.

Carbonyl groups co-ordinated to metals in a manner similar to C(1)O(1) have been the subject of a recent review.[19] The overall co-ordination of the μ_3-C(1)O(1) ligand in (**3b**) has features in common with that found for the $\mu_4-\eta$-CO ligand in $[Co_2Mo_2(\mu-CO)_3(\mu_4-\eta-CO)(\eta-C_5H_5)_2(\eta-C_5Me_5)_2]$.[13] The latter, like (**3b**) (60 c.v.e.), is unsaturated, but has a 62 c.v.e. count if the μ_4-CO ligand is regarded as contributing six electrons to the cluster. Horwitz and Shriver[19] have proposed a function, $\Omega = \exp$ (M–C distance/M–O distance), to measure the extent of interaction of a metal M with the C and O ends of a CO ligand to which it is attached in an η^2 manner. For (**3b**) $\Omega = 3.27$, whilst for $[Co_2Mo_2(\mu-CO)_3(\mu_4-\eta-CO)(\eta-C_5H_5)_2(\eta-C_5Me_5)_2]$ $\Omega = 3.16$. Thus in (**3b**) there is a greater interaction between W(2) and O(1) *versus* C(1) than there is between the molybdenum atom in the Co_2Mo_2 species and the oxygen and carbon atoms of the CO group to which it is η^2 bound. Hitherto the largest Ω value for a π CO ligand–metal interaction was that (3.16) for $[Co_2Mo_2(\mu-CO)_3(\mu_4-\eta-CO)(\eta-C_5H_5)_2(\eta-C_5Me_5)_2]$ (see Figure 4 of ref. 19) which, together with that (3.27) for (**3b**), reflects the oxophilic nature of molybdenum and tungsten. The C(1)–O(1) bond length [1.30(2) Å] in (**3b**) is comparable with the C–O bond distance [1.283(3) Å] for the $\mu_4-\eta$-CO ligand in $[Co_2Mo_2(\mu-CO)_3(\mu_4-\eta-CO)(\eta-C_5H_5)_2-(\eta-C_5Me_5)_2]$. Unfortunately the higher estimated standard deviation (e.s.d.) for (**3b**) precludes a precise comparison between the two complexes.

Having established the molecular structure of (**3b**) it was possible to interpret fully the i.r. and n.m.r. data for this complex, and those of (**3a**) also, since the latter must have the same structure, on account of similarities in spectroscopic properties.

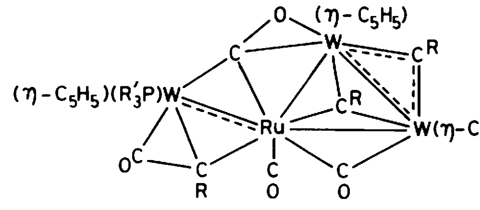
The $\mu_3-\eta$-CO ligand in the complexes (**3**) reveals itself in the i.r. spectra with bands at 1 380 cm^{-1} (**3a**, in CH_2Cl_2) and 1 384 cm^{-1} [**3b**, in tetrahydrofuran (thf)]. When measured in a KBr disc the $\mu_3-\eta$-CO absorption for (**3b**) occurs at 1 375 cm^{-1}. In the complex $[Nb_3(\mu_3-\eta-CO)(CO)_6(\eta-C_5H_5)_3]$ the corresponding peak is at 1 330 cm^{-1},[20] in which the $\mu_3-\eta$-CO ligand formally acts as a six-electron donor. The η-C–O distance is 1.30(1) Å, similar to that found for (**3b**). This suggests that the $\mu_3-\eta$-CO groups present in (**3**) are highly activated, although formally acting as four-electron donors.

The i.r. spectra of (**3a**) and (**3b**) also have bands at 1 734 and 1 745 cm^{-1}, respectively, and these absorptions may be assigned to the μ-CO groups. Moreover, as expected, two i.r. bands corresponding to terminal CO ligands also appear in each spectrum [(**3a**), 1 972 and 1 936; (**3b**) 1 976 and 1 933 cm^{-1}].

We have already mentioned above that the $^{13}C-\{^1H\}$ n.m.r. spectrum of (**3**) showed resonances corresponding to the presence of two edge-bridging and one triply-bridging *p*-tolylmethylidyne groups. For (**3b**), signals for the ligated carbon atoms of the phenylmethylidyne groups occur at δ 349.0, 347.2 (μ-C), and 291.9 p.p.m. (μ_3-C). Resonances in the spectra of (**3a**) and (**3b**) at δ 290.4 [*J*(WC) 187 Hz] and 289.5 p.p.m., respectively, are assigned to the $\mu_3-\eta$-CO ligand, and signals at δ 275.8 (**3a**) and 275.5 p.p.m. (**3b**) to the μ-CO group. The two terminal CO groups present in each complex give rise to resonances at δ 215.3 [WCO, *J*(WC) 201 Hz] and 205.5 (RuCO) (**3a**), and at 214.5 [WCO, *J*(WC) 197 Hz] and 206.3 p.p.m. (RuCO) (**3b**). As for (**3a**), the non-equivalent $\eta-C_5H_5$ groups in (**3b**) are revealed in the ^1H and the $^{13}C-\{^1H\}$ n.m.r. spectra by the appearance of three peaks in each spectrum (see Experimental section).

Since the cluster compounds (**3**) are electronically unsaturated it was of interest to investigate their reactivity towards tertiary phosphines, in order to determine the effect of addition of an electron-pair donor to these molecules. With $\mathrm{PMe_3}$, both (**3a**) and (**3b**) yielded products having similar structures, as inferred from comparison of their spectroscopic properties. However, attempts to grow crystals of these complexes, (**4a**) and (**4b**) respectively, for study by *X*-ray diffraction were unsuccessful. Attention was then directed at using $\mathrm{PMePh_2}$ as a reagent since this tertiary phosphine often affords crystalline products in situations where $\mathrm{PMe_3}$ does not. Treatment of (**3b**) with $\mathrm{PMePh_2}$ in dichloromethane gave a product (**4c**), similar to (**4a**) and (**4b**). Single crystals of (**4c**) could be grown, and an *X*-ray diffraction study was carried out with the results summarised in Table 1, and with the structure shown in Figure 2. This work established that the compounds (**4**) should be formulated as $[\mathrm{RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)\{\mu\text{-}C(R)C(O)\}(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)(PR'_3)(\eta\text{-}C_5H_5)_3}]$ [$\mathrm{R = C_6H_4Me\text{-}4}$, $\mathrm{PR'_3 = PMe_3}$ (**4a**); R = Ph, $\mathrm{PR'_3 = PMe_3}$ (**4b**) or $\mathrm{PMePh_2}$ (**4c**)].

The structure of (**4c**) (Figure 2) is very similar to that of (**3b**), and it is for this reason that the selected internuclear distances and angles for both complexes are presented together in Table 1.



	R	PR'$_3$
(**4a**)	$\mathrm{C_6H_4Me\text{-}4}$	$\mathrm{PMe_3}$
(**4b**)	Ph	$\mathrm{PMe_3}$
(**4c**)	Ph	$\mathrm{PMePh_2}$

In (**4c**) the metal atoms retain the 'spiked triangle' arrangement, and the μ_3-η-CO ligand remains attached to Ru, W(3), and W(2). The major difference occurs at W(3) and its mode of attachment to the ruthenium atom. This is best seen in Figure 3, which compares the core structures of (**3b**) and (**4c**). Thus the result of treatment of the former with $\mathrm{PMePh_2}$ is to replace the CO group on W(3) with the phosphine ligand, and this is accompanied by migration of a CO molecule to the edge-bridging phenylmethylidyne fragment. Hence in (**4c**) the Ru–W(3) bond is bridged by a ketenyl group C(56)(Ph)C(4)-O(4) [Ru–C(56) 2.19(1), W(3)–C(56) 2.15(1), W(3)–C(4) 2.14(1), and C(4)–C(56) 1.39(2) Å]. Apart from this significant change, the molecular parameters for (**4c**) and (**3b**) are remarkably similar.

Complexes in which metal atoms are ligated by ketenyl groups are well established.[21] Formation of (**4c**) is a consequence of coupling of an alkylidyne group with CO to produce a C=C bond. This process has been observed previously in the synthesis of the trinuclear metal species $[\mathrm{PPh_4}]_2[\mathrm{Fe_3\{\mu_3\text{-}\eta\text{-}C(Me)C(O)\}(CO)_9}]$[22] and $[\mathrm{Rh_2W(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}\eta\text{-}C(Me)C(O)\}(CO)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2}]$,[21] which contain ketenyl ligands bridging three rather than two metal atoms. In compound (**4c**) the bonding of the ketenyl group is somewhat similar to that of the related ligand in the dimetal complex $[\mathrm{PtW\{\mu\text{-}\eta\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(cod)(\eta\text{-}C_5H_5)}]$.[23]

The i.r. spectrum of (**4c**) shows a band at 1 976 cm^{-1} due to the terminal CO ligand bonded to ruthenium, while a band at 1 735 cm^{-1} is attributed to the $\overline{\mathrm{Ru(\mu\text{-}CO)W}}$ group. An absorption at 1 341 cm^{-1} can be assigned to the μ_3-η-CO ligand, and compares with that at 1 384 cm^{-1} in the spectrum of the precursor (**3b**). Complex (**4c**) also shows a band at 1 636 cm^{-1} which is attributed to the C=O group of the ketenyl ligand. In $[\mathrm{PtW\{\mu\text{-}\eta\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(cod)(\eta\text{-}C_5H_5)}]$ a similar absorption occurs at 1 625 cm^{-1}.[23] In compounds (**4a**) and (**4b**) bands below 1 600 cm^{-1} are difficult to assign, but both species show characteristic absorptions for the Ru(CO), μ-CO, and μ-C(R)C(O) groups [1 974, 1 735, and 1 623 (**4a**); 1 975, 1 735, and 1 636 cm^{-1} (**4b**)].

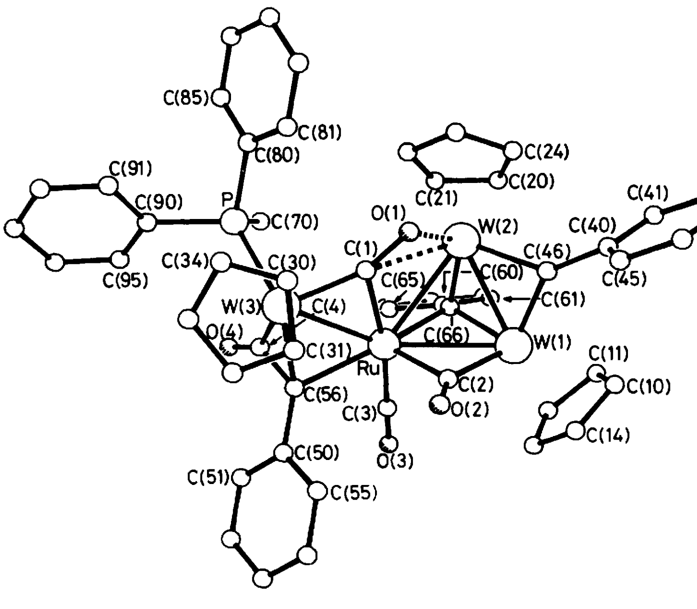
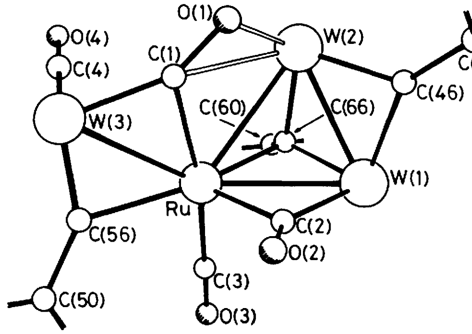
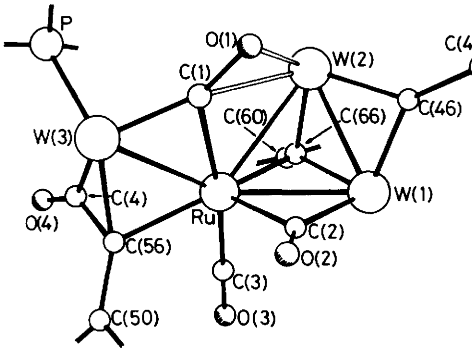


Figure 2. Molecular structure of $[\mathrm{RuW_3(\mu\text{-}CO)(\mu_3\text{-}\eta\text{-}CO)\{\mu\text{-}C(Ph)C(O)\}(\mu\text{-}CPh)(\mu_3\text{-}CPh)(CO)(PMePh_2)(\eta\text{-}C_5H_5)_3}]$ (**4c**), showing the crystallographic numbering



(**3b**)



(**4c**)

Figure 3. The co-ordination environments of the metal atoms and the μ_3-η-CO ligand in compounds (**3b**) and (**4c**)

The n.m.r. spectra (^{1}H and ^{13}C-{^{1}H}) of the compounds (**4**) can be interpreted on the basis of the structure established for (**4c**) by *X*-ray diffraction, and resonances and assignments are listed in the Experimental section. Noteworthy are the two signals for the ligated carbon atoms of the ketenyl group μ-*C*(R)*C*(O). These resonances occur as doublets due to ^{31}P–^{13}C coupling, the signal for the *C*(R)C(O) nucleus being less deshielded than that for C(R)*C*(O) [(**4a**), 114.2 and 222.2; (**4b**) 114.4 and 221.2; and (**4c**) 111.9 and 220.6 p.p.m. respectively]. In their ^{31}P-{^{1}H} n.m.r. spectra the complexes show a singlet signal with strong ^{183}W–^{31}P coupling, as expected for the presence of a W(PR$'_3$) group {(**4a**), 1.31 [*J*(WP) 330]; (**4b**), 1.92 [*J*(WP) 330]; and (**4c**) 25.88 p.p.m. [*J*(WP) 215 Hz]}.

As far as we are aware, formation of the compounds (**4**) from (**3**) provides the first examples of reactions where addition of a donor molecule to a cluster compound forces migration of a CO group onto a co-ordinated alkylidyne ligand. Without labelling experiments it is not possible to be certain of the source of the CO group which forms the ketenyl moiety. There are two possibilities for an associative process. In the simplest, the CO ligand terminally bound to the tungsten atom in (**3**) migrates to the edge-bridging alkylidyne group as the tertiary phosphine approaches the tungsten centre. However, a more complex reaction might occur involving the μ_3-η-CO fragment. The latter might form a C–C bond with the μ-CR ligand, with concomitant transfer of the terminal CO group to the triply-bridging site.

In view of the results with PMe$_3$ and PMePh$_2$, we also investigated reactions of the compounds (**3**) with CO and with H$_2$ (2 atm, *ca.* 20 × 10^4 Pa). No reaction occurred with the latter, and the CO treatment led to decomposition and formation of (**2a**) or (**2c**), respectively.

The compounds (**3**) and (**4**) join a growing number of species having alkylidyne ligands at both edge- and triply-bridging sites. Other tetranuclear metal clusters with both μ-CR and μ_3-CR ligands are the complexes [MPtW$_2$(μ-CR)(μ_3-CR)(CO)$_4$(cod)(η-C$_5$R$'_5$)$_2$] (M = Ni or Pt, R = C$_6$H$_4$Me-4, R$'$ = H; M = Ni or Pt, R = C$_6$H$_4$Me-4, R$'$ = Me; M = Pt, R = R$'$ = Me).[24] Four trimetal compounds are known with both edge- and triply-bridging *p*-tolylmethylidyne groups, *viz.* [ReW$_2$(μ-Br)(μ-L)(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)$_2$] (L = CO or O),[16] [OsW$_2$(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_5$(η-C$_5$H$_5$)$_2$], and [OsW$_2$(H)(μ-H)(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_4$(η-C$_5$H$_5$)$_2$].[25]

Experimental

The experimental techniques used and the instrumentation employed have been described in previous parts of this series.[8,26] Light petroleum refers to that fraction b.p. 40—60 °C. The compounds [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)] (R = Ph or C$_6$H$_4$Me-4),[27] [Ru(η^6-C$_8$H$_{10}$)(cod)],[3,28] and [Ru(η^6-C$_{10}$H$_8$)(cod)][4] were prepared by methods described elsewhere. For n.m.r. data, chemical shifts are given in p.p.m., with coupling constants in Hz. For ^{13}C-{^{1}H} spectra chemical shifts are relative to SiMe$_4$ (0.00 p.p.m.), and for the ^{31}P-{^{1}H} spectra the chemical shifts are relative to 85% H$_3$PO$_4$ (external) with positive values representing shifts to high frequency of the reference.

Synthesis of the Compounds [RuW$_3$(μ-CO)(μ_3-η-CO)(μ-CR)$_2$(μ_3-CR)(CO)$_2$(η-C$_5$H$_5$)$_3$] (R = C$_6$H$_4$Me-4 *or* Ph).—(*i*) A mixture of (**1a**) (0.41 g, 1.0 mmol) and [Ru(η^6-C$_8$H$_{10}$)(cod)] (0.11 g, 0.33 mmol) was stirred in light petroleum (15 cm^3) at room temperature for 24 h. Solvent was removed *in vacuo*, and the residue, as a slurry in CH$_2$Cl$_2$–light petroleum (15 cm^3, 1:9), was transferred to an alumina column (2 × 20 cm) for chromatography. Elution with the same solvent mixture afforded unreacted (**1a**) (0.10 g). Elution with CH$_2$Cl$_2$–light petroleum (1:4, gradually increasing to 1:1) afforded a pink eluate followed by an orange band. The pink eluate gave a trace of the compound [W$_2${μ-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_4$(η-C$_5$H$_5$)$_2$] (identified by i.r.[5]), and the orange eluate yielded the complex [RuW$_2${μ_3-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_7$(η-C$_5$H$_5$)$_2$] (**2a**) (0.07 g) (identified by i.r.[6]). Elution with pure CH$_2$Cl$_2$ afforded, after removal of solvent *in vacuo*, dark green *microcrystals* of [RuW$_3$(μ-CO)(μ_3-η-CO)(μ-CC$_6$H$_4$Me-4)$_2$(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)$_3$] (**3a**) (0.10 g, 24%) (Found: C, 40.8; H, 2.9. C$_{43}$H$_{36}$O$_4$RuW$_3$ requires C, 40.7; H, 2.8%); $\nu_{max.}$(CO) at 1 972s, 1 936s, 1 734m, and 1 380m cm^{-1} (in CH$_2$Cl$_2$). N.m.r.: ^{1}H (CDCl$_3$), δ 2.16 (s, 3 H, Me-4), 2.36 (s, 3 H, Me-4), 2.44 (s, 3 H, Me-4), 4.97 (s, 5 H, C$_5$H$_5$), 5.28 (s, 5 H, C$_5$H$_5$), 5.54 (s, 5 H, C$_5$H$_5$), and 6.0—7.3 (m, 12 H, C$_6$H$_4$); ^{13}C-{^{1}H} (CDCl$_3$), δ 350.1 [μ-C, *J*(WC) 152, 140], 348.0 [μ-C, *J*(WC) 162], 292.8 [μ_3-C, *J*(WC) 98, 92], 290.4 [μ_3-η-CO, *J*(WC) 187], 275.8 (μ-CO), 215.3 [WCO, *J*(WC) 201], 205.5 (RuCO), 166.9, 164.8, 160.6 [C^1(C$_6$H$_4$)], 135.8, 134.0, 133.8 [C^4(C$_6$H$_4$)], 129.0—121.6 (C$_6$H$_4$), 101.7, 96.9, 94.3 (C$_5$H$_5$), 21.3, 21.2, and 20.7 (Me-4).

Compound (**3a**) was also obtained (0.10 g, 24%) from (**1a**) (0.41 g, 1.0 mmol) and [Ru(η^6-C$_{10}$H$_8$)(cod)] (0.11 g, 0.33 mmol), using the same method as described above.

(*ii*) Reaction between (**1b**) (0.39 g, 1.0 mmol) and [Ru(η^6-C$_{10}$H$_8$)(cod)] (0.11 g, 0.33 mmol), using the same procedure as for the synthesis of (**3a**), gave orange *microcrystals* of [RuW$_2$(μ_3-C$_2$Ph$_2$)(CO)$_7$(η-C$_5$H$_5$)$_2$] (**2c**) (0.07 g, 20%) {(Found: C, 38.2; H, 2.1. C$_{31}$H$_{20}$O$_7$RuW$_2$ requires C, 38.2; H, 2.1%); $\nu_{max.}$(CO) at 2 065m, 2 047vs, 2 012m, 1 991vs, 1 983vs, 1 917s, and 1 836w cm^{-1} (pentane); n.m.r.: ^{1}H (CD$_2$Cl$_2$), δ 5.04 (s, 10 H, C$_5$H$_5$) and 6.76—7.25 (m, 10 H, Ph); ^{13}C-{^{1}H} (CD$_2$Cl$_2$–CH$_2$Cl$_2$), δ 220.9 [WCO, *J*(WC) 167], 220.7 [WCO, *J*(WC) 157], 196.5 (RuCO), 159.6—124.6 (CPh), and 92.9 (C$_5$H$_5$)}, and dark green *microcrystals* of [RuW$_3$(μ-CO)(μ_3-η-CO)(μ-CPh)$_2$(μ_3-

Table 2. Atomic positional parameters (fractional co-ordinates × 10^5 for W and Ru and × 10^4 for all other atoms) for complex (**3b**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	65 637(6)	36 856(5)	63 609(4)	C(41)	4 402(14)	799(13)	7 110(11)
W(2)	69 039(6)	46 034(5)	83 418(4)	C(42)	3 238(16)	−168(15)	7 179(11)
W(3)	71 625(6)	82 211(5)	86 080(5)	C(43)	2 286(16)	137(15)	7 609(11)
Ru(1)	75 394(11)	62 666(10)	72 130(8)	C(44)	2 369(18)	1 366(17)	7 983(13)
C(1)	6 545(14)	6 503(12)	8 538(10)	C(45)	3 511(15)	2 294(14)	7 914(11)
C(2)	5 843(15)	5 029(13)	6 364(10)	C(46)	5 610(13)	3 040(12)	7 363(10)
C(3)	8 508(18)	6 332(13)	6 125(12)	C(50)	8 177(14)	8 770(13)	6 610(11)
C(4)	8 701(19)	8 426(14)	9 384(14)	C(51)	9 001(17)	10 063(16)	6 997(13)
C(10)	5 520(16)	1 800(13)	5 027(11)	C(52)	9 250(20)	10 720(20)	6 290(10)
C(11)	6 790(18)	1 907(14)	5 315(11)	C(53)	8 700(20)	10 160(20)	5 360(20)
C(12)	7 676(15)	2 900(17)	5 066(12)	C(54)	7 960(20)	8 960(20)	4 960(20)
C(13)	6 976(18)	3 453(15)	4 648(11)	C(55)	7 721(17)	8 281(16)	5 622(13)
C(14)	5 651(17)	2 766(15)	4 633(11)	C(56)	7 828(14)	8 127(12)	7 370(11)
C(20)	8 196(18)	3 892(19)	9 058(12)	C(60)	9 579(13)	5 120(12)	7 388(10)
C(21)	8 638(17)	5 136(17)	9 573(14)	C(61)	10 042(15)	4 173(14)	7 102(11)
C(22)	7 730(20)	5 370(20)	10 110(10)	C(62)	11 329(16)	4 399(15)	7 182(12)
C(23)	6 648(16)	4 293(18)	9 927(11)	C(63)	12 221(16)	5 590(15)	7 571(12)
C(24)	6 970(18)	3 346(14)	9 304(12)	C(64)	11 813(17)	6 553(15)	7 894(12)
C(30)	5 211(17)	8 428(18)	9 021(17)	C(65)	10 527(16)	6 316(15)	7 805(12)
C(31)	5 550(30)	8 900(20)	8 290(10)	C(66)	8 229(14)	4 889(12)	7 317(10)
C(32)	6 710(30)	9 950(20)	8 700(30)	O(1)	5 815(10)	5 642(8)	8 871(7)
C(33)	6 970(30)	10 010(20)	9 680(20)	O(2)	4 932(12)	5 207(10)	6 125(8)
C(34)	6 050(20)	9 090(20)	9 870(20)	O(3)	9 163(13)	6 382(11)	5 498(10)
C(40)	4 521(13)	2 044(12)	7 470(10)	O(4)	9 640(14)	8 556(12)	9 897(11)

Table 3. Atomic positional parameters (fractional co-ordinates) (× 10^4) for complex (**4c**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	6 840(1)	6 348(1)	8 071(1)	C(43)	9 324	5 011	5 924
W(2)	4 831(1)	6 293(1)	7 149(1)	C(44)	9 393	5 614	5 963
W(3)	4 033(1)	8 119(1)	7 150(1)	C(45)	8 523	5 916	6 369
Ru	5 038(1)	7 275(1)	8 047(1)	C(46)	6 720(14)	5 966(7)	7 172(8)
P	1 646(4)	7 896(2)	6 856(2)	C(50)*	5 438(11)	8 595(4)	8 671(5)
C(1)	4 585(12)	7 338(6)	6 954(6)	C(51)	4 785	8 902	9 169
O(1)	4 954(9)	6 980(4)	6 477(4)	C(52)	5 521	9 267	9 618
C(2)	6 997(15)	7 219(7)	7 850(8)	C(53)	6 911	9 325	9 569
O(2)	7 719(10)	7 584(5)	7 647(6)	C(54)	7 564	9 018	9 071
C(3)	5 355(15)	7 334(6)	9 005(9)	C(55)	6 828	8 653	8 622
O(3)	5 531(12)	7 368(5)	9 591(6)	C(56)	4 626(15)	8 194(6)	8 220(6)
C(4)	3 228(15)	8 156(6)	8 139(7)	C(60)*	3 908(9)	6 122(4)	8 716(4)
O(4)	2 249(10)	8 240(5)	8 476(5)	C(61)	4 136	5 555	8 941
C(10)*	8 798(22)	5 827(12)	8 352(7)	C(62)	3 310	5 310	9 416
C(11)	7 809	5 601	8 775	C(63)	2 256	5 632	9 667
C(12)	7 448	6 045	9 231	C(64)	2 028	6 199	9 442
C(13)	8 213	6 547	9 090	C(65)	2 854	6 444	8 967
C(14)	9 047	6 412	8 546	C(66)	4 782(12)	6 372(6)	8 219(7)
C(20)*	3 704(14)	5 406(5)	7 169(7)	C(70)	884(14)	7 392(7)	7 472(7)
C(21)	2 687	5 832	7 233	C(80)*	1 188(11)	7 559(4)	6 027(4)
C(22)	2 565	6 150	6 612	C(81)	2 180	7 415	5 579
C(23)	3 506	5 921	6 165	C(82)	1 819	7 154	4 953
C(24)	4 211	5 461	6 509	C(83)	466	7 036	4 775
C(30)*	5 145(16)	8 372(5)	6 134(6)	C(84)	−525	7 180	5 223
C(31)	5 937	8 571	6 713	C(85)	−164	7 442	5 848
C(32)	5 170	8 990	7 054	C(90)*	535(9)	8 544(4)	6 809(5)
C(33)	3 904	9 049	6 685	C(91)	215	8 809	6 180
C(34)	3 889	8 667	6 116	C(92)	−557	9 314	6 150
C(40)*	7 584(10)	5 616(5)	6 737(5)	C(93)	−1 010	9 555	6 749
C(41)	7 515	5 013	6 698	C(94)	−689	9 290	7 378
C(42)	8 385	4 711	6 291	C(95)	83	8 785	7 407

* Atom of a rigid group, remaining atoms in the group have identical standard deviations.

CPh)(CO)$_2$(η-C$_5$H$_5$)$_3$] (**3b**) (0.11 g, 27%) {(Found: C, 38.9; H, 2.3. $C_{40}H_{30}O_4RuW_3$ requires C, 39.1, H, 2.4%); $\nu_{max.}$(CO) at 1 976s, 1 933s, 1 745m, and 1 384 cm^{-1} (thf); n.m.r.: ^{1}H (CD$_2$Cl$_2$), δ 5.14 (s, 5 H, C$_5$H$_5$), 5.56 (s, 5 H, C$_5$H$_5$), 5.77 (s, 5 H, C$_5$H$_5$), and 6.38—7.59 (m, 15 H, Ph); ^{13}C-{^{1}H} (CD$_2$Cl$_2$–CH$_2$Cl$_2$, at −40 °C), δ 349.0, 347.2 (μ-C), 291.9 (μ$_3$-C), 289.5 (μ$_3$-η-CO), 275.5 (μ-CO), 214.5 [WCO, *J*(WC) 197], 206.3 (RuCO), 169.5, 167.6, 163.4 [C^1(Ph)], 127.6—122.6 (Ph), 102.0, 97.2, and 94.8 (C$_5$H$_5$)}.

Reactions of the Compounds [RuW$_3$(μ-CO)(μ$_3$-η-CO)(μ-CR)$_2$(μ$_3$-CR)(CO)$_2$(η-C$_5$H$_5$)$_3$] (R = C$_6$H$_4$Me-4 *or* Ph) *with*

Tertiary Phosphines.—(*i*) Compound (**3a**) (0.18 g, 0.14 mmol) in CH_2Cl_2 (5 cm^3) was treated with PMe_3 (0.14 mmol), and the mixture stirred for 30 h, after which the i.r. spectrum showed that little of (**3a**) remained. Solvent was removed *in vacuo*, and the residue was transferred as a slurry in CH_2Cl_2–light petroleum (5 cm^3, 1:1) to an alumina column (2 × 7 cm). Elution with CH_2Cl_2 removed a trace of green (**3a**). Elution with MeOH gave a red solution, from which solvent was removed *in vacuo* to give red *microcrystals* of [RuW$_3$(μ-CO)(μ$_3$-η-CO){μ-C(C$_6$H$_4$Me-4)C(O)}(μ-CC$_6$H$_4$Me-4)(μ$_3$-CC$_6$H$_4$Me-4)(CO)(PMe$_3$)(η-C$_5$H$_5$)$_3$] (**4a**) (0.14 g, 72%) (Found: C, 40.8; H, 3.4. $C_{46}H_{45}O_4PRuW_3$ requires C, 41.0; H, 3.4%); $\nu_{max.}$(CO) at 1 974s, 1 735m, and 1 623m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H ($CDCl_3$), δ 1.58 [d, 9 H, MeP, *J*(PH) 10], 2.30 (s, 3 H, Me-4), 2.36 (s, 3 H, Me-4), 2.57 (s, 3 H, Me-4), 4.98 [d, 5 H, C_5H_5, *J*(PH) 2], 5.04 (s, 5 H, C_5H_5), 5.75 (s, 5 H, C_5H_5), and 6.84—7.74 (m, 12 H, C_6H_4); ^{13}C-{^1H} (CD_2Cl_2–CH_2Cl_2, at −40 °C), δ 346.5 (μ-C), 286.9 [μ$_3$-C, *J*(WC) 98], 278.3 (μ-CO), 276.1 [d, μ$_3$-η-CO, *J*(PC) 10], 222.2 [d, μ-C(C$_6$H$_4$Me-4)*C*(O), *J*(PC) 22], 200.0 (RuCO), 166.4, 164.6, 147.0 [C^1(C$_6$H$_4$)], 134.9—122.8 (C_6H_4), 114.2 [d, μ-*C*(C$_6$H$_4$Me-4)C(O), *J*(PC) 5], 101.8, 97.5, 95.6 (C_5H_5), 21.4, 21.2, 21.0 (Me-4), and 20.4 [d, MeP, *J*(PC) 34]; ^{31}P-{^1H} ($CDCl_3$), δ 1.31 [*J*(WP) 330].

(*ii*) The reaction between (**3b**) (0.16 g, 0.13 mmol) and PMe_3 (0.13 mmol) was carried out in a similar manner, thereby giving red *microcrystals* of [RuW$_3$(μ-CO)(μ$_3$-η-CO){μ-C(Ph)C(O)}-(μ-CPh)(μ$_3$-CPh)(CO)(PMe$_3$)(η-C$_5$H$_5$)$_3$] (**4b**) (0.12 g, 73%) (Found: C, 40.0; H, 3.0. $C_{43}H_{39}O_4PRuW_3$ requires C, 39.6; H, 3.0%); $\nu_{max.}$(CO) at 1 975s, 1 735m, and 1 636m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H ($CDCl_3$), δ 1.59 [d, 9 H, MeP, *J*(PH) 10], 4.99 [d, 5 H, C_5H_5, *J*(PH) 1], 5.06 (s, 5 H, C_5H_5), 5.76 (s, 5 H, C_5H_5), and 6.81—7.88 (m, 15 H, Ph); ^{13}C-{^1H} (CD_2Cl_2–CH_2Cl_2), δ 346.7 (μ-C), 286.8 (μ$_3$-C), 277.2 (μ-CO), 275.7 [d, μ$_3$-η-CO, *J*(PC) 7], 221.2 [d, μ-C(Ph)*C*(O), *J*(PC) 22], 199.9 (RuCO), 170.1, 167.6, 150.6 [C^1(Ph)], 128.6—122.6 (Ph), 114.4 [d, μ-*C*(Ph)C(O), *J*(PC) 7], 102.0, 97.7, 95.7 (C_5H_5), and 20.7 [d, MeP, *J*(PC) 34]; ^{31}P-{^1H} ($CDCl_3$), δ 1.92 [*J*(WP) 330].

(*iii*) Similarly, (**3b**) (0.20 g, 0.16 mmol) with $PMePh_2$ (0.16 mmol) gave red *microcrystals* of [RuW$_3$(μ-CO)(μ$_3$-η-CO){μ-C(Ph)C(O)}(μ-CPh)(μ$_3$-CPh)(CO)(PMePh$_2$)(η-C$_5$H$_5$)$_3$] (**4c**) (0.16 g, 69%) (Found: C, 44.2; H, 3.0. $C_{53}H_{43}O_4PRuW_3$ requires C, 44.2; H, 3.0%); $\nu_{max.}$(CO) at 1 976s, 1 735m, 1 636m, and 1 341m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H, δ 2.27 [d, 3 H, MeP, *J*(PH) 10], 4.65 (s, 5 H, C_5H_5), 4.83 (s, 5 H, C_5H_5), 5.71 (s, 5 H, C_5H_5), and 6.91—7.88 (br m, 25 H, Ph); ^{13}C-{^1H} (CD_2Cl_2–CH_2Cl_2, at −40 °C), δ 347.4 [μ-C, *J*(WC) 141], 288.8 [μ$_3$-C, *J*(WC) 95], 277.6, 277.5 (μ-CO and μ$_3$-η-CO), 220.6 [d, μ-C(Ph)*C*(O), *J*(PC) 18], 199.7 (RuCO), 170.1, 167.1, 150.3 [C^1(Ph)], 136.7—121.9 (Ph), 111.9 [d, μ-*C*(Ph)C(O), *J*(PC) 6], 101.5, 97.7, 97.1 (C_5H_5), and 18.0 [d, MeP, *J*(PC) 40]; ^{31}P-{^1H} ($CDCl_3$), δ 25.88 [*J*(WP) 215].

Crystal Structure Determination of (**3b**).—Crystals of (**3b**) were grown as black prisms from CH_2Cl_2–light petroleum. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.39 × 0.34 × 0.06 mm with well developed faces of the type (1 0 1), $(\bar{1}\,0\,\bar{1})$, $(1\,0\,\bar{1})$, $(\bar{1}\,0\,1)$, (0 1 0), and $(0\,\bar{1}\,0)$. Data were collected on an Enraf-Nonius CAD-4F diffractometer. Of the 3 621 unique data collected (θ—2θ scans, 2θ ≤ 42°), 3 230 had $I \geqslant 2.0\sigma(I)$ and only these were used in structure solution and refinement, after the data had been corrected for Lorentz polarisation and *X*-ray absorption effects. The last was by an analytical method.[29]

Crystal data. $C_{40}H_{30}O_4RuW_3$, *M* = 1 227, triclinic, *a* = 11.244(5), *b* = 12.204(2), *c* = 13.987(2) Å, α = 108.33(2), β = 90.20(3), γ = 110.99(3)°, *U* = 1 686(1) Å^3, *Z* = 2, D_c = 2.42 g cm^{-3}, *F*(000) = 1 136, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 109.10 cm^{-1}.

The metal atoms were located by direct methods, and all remaining non-hydrogen atoms were found by conventional difference-Fourier methods. The aryl carbon atoms, and atoms C(33) and C(46) were refined with isotropic thermal parameters. Attempts to refine the latter two carbon atoms with anisotropic thermal parameters were not successful, probably reflecting our inability to correct adequately the severe absorption effects in this structure. All remaining non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters of 0.05 Å^2. Refinement by full-matrix least squares led to *R* 0.039 (*R′* = 0.046) and a weighting scheme of the form $w^{-1} = \sigma^2(F)$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks ≥1.6 or ≤ −1.7 e Å^{-3}, with the largest peaks lying close to the metal atoms. Scattering factors with corrections for anomalous dispersion were from ref. 30. All computations were carried out on a Gould-SEL 32/27 computer using the GX system of programs.[31]

Crystal Structure Determination of (**4c**).—Crystals of (**4c**) grow from CH_2Cl_2–light petroleum as small black parallelepipeds. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.16 × 0.09 × 0.07 mm with well developed faces of the type (1 0 0), $(\bar{1}\,0\,0)$, (0 1 0), $(0\,\bar{1}\,0)$, (0 0 1), and $(0\,0\,\bar{1})$. Data were collected on a Nicolet *P*3*m* diffractometer. Of the 4 208 unique data (θ—2θ scans, 2θ ≤ 45°), 3 737 had $I \geqslant 1.5\sigma(I)$ and only these were used in structure solution and refinement, after the data had been corrected for Lorentz polarisation and *X*-ray absorption effects. The last was by an empirical method based on azimuthal scan data.[32]

Crystal data. $C_{53}H_{43}O_4PRuW_3$, *M* = 1 427, monoclinic, *a* = 9.928(1), *b* = 23.080(3), *c* = 19.588(2) Å, β = 93.242(9)°, *U* = 4 481.1(9) Å^3, *Z* = 4, D_c = 2.11 g cm^{-3}, *F*(000) = 2 696, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 82.50 cm^{-1}.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference Fourier methods. All atoms were refined with anisotropic thermal parameters but the cyclopentadienyl and phenyl rings were constrained to rigid idealised geometries. Hydrogen atoms were not included. Refinement by blocked-cascade least squares led to *R* = 0.039 (*R′* = 0.038), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,46|F|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks ≥0.7 or ≤ −1.0 e Å^{-3}. Scattering factors and corrections for anomalous dispersion are from ref. 30. All computations were carried out on an Eclipse Data General computer with the SHELXTL system of programs.[32] Atom coordinates for (**3b**) and (**4c**) are given in Tables 2 and 3, respectively.

Acknowledgements

We thank the S.E.R.C. for support and for research studentships (to C. M. and P. S.).

References

1 Part 49, J. A. Abad, E. Delgado, M. E. Garcia, M. J. Grosse-Ophoff, I. J. Hart, J. C. Jeffery, M. S. Simmons, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, preceding paper,
2 F. G. A. Stone, *Pure Appl. Chem.*, 1986, **58**, 529; in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, 383.
3 P. Pertici, G. Vitulli, M. Paci, and L. Porri, *J. Chem. Soc., Dalton Trans.*, 1980, 1961.

4 M. Crocker, Ph.D. Thesis, Bristol University, 1985.

5 M. Green, J. C. Jeffery, S. J. Porter, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1982, 2475; M. Green, S. J. Porter, and F. G. A. Stone, *ibid.*, 1983, 513; M. Green, J. A. K. Howard, S. J. Porter, F. G. A. Stone, and D. C. Tyler, *ibid.*, 1984, 2553.

6 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.

7 M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.*, 1976, **98**, 4645.

8 J. A. K. Howard, J. C. V. Laurie, O. Johnson, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 2017.

9 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1978, **17**, 3546.

10 F. W. B. Einstein, L. R. Martin, R. K. Pomeroy, and P. Rushman, *J. Chem. Soc., Chem. Commun.*, 1985, 345.

11 V. G. Albano, G. Ciani, M. Freni, and P. Romiti, *J. Organomet. Chem.*, 1975, **96**, 259.

12 A. B. Antonova, S. V. Kovalenko, E. D. Korniyets, A. A. Johansson, Yu. T. Struchkov, and A. I. Yanovsky, *J. Organomet. Chem.*, 1984, **267**, 299.

13 P. Brun, G. M. Dawkins, M. Green, A. D. Miles, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1982, 926.

14 L. J. Farrugia, A. D. Miles, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 2437.

15 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.

16 G. A. Carriedo, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1597.

17 M. R. Churchill and S. W. Y. Chang, *Inorg. Chem.*, 1974, **13**, 2413.

18 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.

19 C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, 1984, **23**, 219.

20 W. A. Hermann, H. Biersack, M. L. Ziegler, K. Weidenhammer, R. Siegel, and D. Rehder, *J. Am. Chem. Soc.*, 1981, **103**, 1692.

21 J. C. Jeffery, C. Marsden, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 1315 and refs. therein.

22 F. Dahan and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, 1984, 432.

23 J. C. Jeffery, C. Sambale, M. F. Schmidt, and F. G. A. Stone, *Organometallics*, 1982, **1**, 1597.

24 G. P. Elliott, J. A. K. Howard, T. Mise, I. Moore, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 2091.

25 Yun Chi and J. R. Shapley, *Organometallics*, 1985, **4**, 1900.

26 M. R. Awang, R. D. Barr, M. Green, J. A. K. Howard, T. B. Marder, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 2009.

27 E. O. Fischer, T. Selmayr, F. R. Kreissl, and U. Schubert, *Chem. Ber.*, 1977, **110**, 2574; E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *ibid.*, p. 3397.

28 P. Pertici and G. Vitulli, *Inorg. Synth.*, 1983, **22**, 178.

29 P. Coppens, 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 255.

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

31 P. R. Mallinson and K. W. Muir, *J. Appl. Crystallogr.*, 1985, **18**, 51.

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

Received 23*rd January* 1986; *Paper* 6/170