Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 14.[1] *Triangulo*-metal Complexes containing Tungsten with Iron, Cobalt, Rhodium, or Nickel and a Capping Tolylidyne Ligand; Crystal Structure of the Complex [RhFeW(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_5$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] †

Michael Green, John C. Jeffery, Simon J. Porter, Hayat Razay, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Enneacarbonyldi-iron reacts at room temperature with the compounds [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] (R = C$_6$H$_4$Me-4) and [CoW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] to give the heteronuclear trimetallic complexes [RhFeW(μ_3-CR)(μ-CO)(CO)$_5$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] and [CoFeW(μ_3-CR)(μ-CO)(CO)$_5$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)], respectively. The structure of the rhodiumirontungsten compound was established by an *X*-ray diffraction study. Crystals are monoclinic, space group $P2_1/c$ (no. 14), with $Z = 4$ in a unit cell of dimensions $a = 9.018(2)$, $b = 15.572(4)$, $c = 18.503(6)$ Å, $\beta = 103.69(2)°$. Intensities were measured at room temperature to $2\theta = 50°$, and the structure has been refined to R 0.032 (R' 0.034) for 3 497 unique reflections. The metal triangle has separations Fe–Rh 2.583(1), Fe–W 2.772(1), and Rh–W 2.760(1) Å, and is asymmetrically capped by the CC$_6$H$_4$Me-4 ligand [μ_3-C–Fe 2.029(6), μ_3-C–Rh 2.035(6), μ_3-C–W 2.093(6) Å]. One CO ligand bridges the Fe–Rh bond, while the other five are terminally bonded; two to the tungsten, and three to the iron. The Rh–C(indenyl) distances suggest a tendency for η^3 bonding of the ligand. The compound [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] reacts with [Rh(CO)$_2$(η-C$_9$H$_7$)] in toluene at 60 °C to give [Rh$_2$W(μ_3-CR)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η-C$_9$H$_7$)$_2$], and a related cluster [Rh$_2$W(μ_3-CR)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)$_2$] can be obtained from [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] and [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)]. The latter reaction also affords the dimetal species [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)]. At 60 °C in toluene, [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)] and [Ni$_2$(μ-CO)$_2$(η-C$_5$H$_5$)$_2$] give a mixture of the compounds [Ni$_2$W(μ_3-CR)(CO)$_2$(η-C$_5$H$_5$)$_3$] and [W$_2$(μ-RC$_2$R)(CO)$_4$(η-C$_5$H$_5$)$_2$]. The same products are obtained from [Ni(η-C$_5$H$_5$)$_2$] and [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)], but the latter with [Ni$_2$(μ-Me$_3$SiC$_2$SiMe$_3$)(η-C$_5$H$_5$)$_2$] affords [Ni$_2$W(μ_3-CR)(CO)$_2$(η-C$_5$H$_5$)$_3$] only. Pathways for the formation of some of the complexes, including [W$_2$(μ-RC$_2$R)(CO)$_4$(η-C$_5$H$_5$)$_2$], are proposed, and ^{1}H and ^{13}C n.m.r. data for the various species are reported.

We have previously shown [1] that a family of heteronuclear trimetal complexes [PtFeW(μ_3-CR)(CO)$_{7-n}$(PR'$_3$)$_n$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4, n = 1 or 2) may be obtained from the reaction between [Fe$_2$(CO)$_9$] in thf (tetrahydrofuran) with the compounds [PtW(μ-CR)(CO)$_2$(PR'$_3$)$_2$(η-C$_5$H$_5$)] (PR'$_3$ = PMe$_3$, PMePh$_2$, or PEt$_3$). We have also reported [2] the quantitative synthesis of [Co$_2$W(μ_3-CR)(CO)$_8$(η-C$_5$H$_5$)] by treating [Co$_2$(CO)$_8$] with [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)]. Moreover, the step-wise preparation of [Rh$_2$W(acac)$_2$(μ_3-CR)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)] (acac = acetylacetonate) has been accomplished by reacting [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)] with [Rh(acac)(CO)$_2$] to give [RhW(acac)(μ-CR)(CO)$_3$(η-C$_5$H$_5$)], followed by addition of [Rh(acac)(C$_2$H$_4$)$_2$] to yield the dirhodiumtungsten species.[2] These reactions demonstrate new principles in the synthesis of heteronuclear trimetal clusters, which are further illustrated by the results described herein. Preliminary accounts of some of the work have been given.[3,4]

Results and Discussion

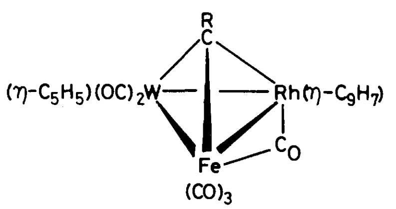
Reaction of [Fe$_2$(CO)$_9$] with [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] [5] in thf at room temperature afforded a purple crystalline trimetal complex [RhFeW(μ_3-CR)(μ-CO)(CO)$_5$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] (1), the formulation of which was initially based on its spectroscopic properties. Thus the i.r. spectrum of (1) showed six bands in the CO stretching region, including one (1 825 cm^{-1}) suggesting a bridging or semi-bridging carbonyl group. The ^{13}C-{^{1}H} n.m.r. spectrum had a doublet resonance at δ 287.3 p.p.m. characteristic of a μ_3-*C*C$_6$H$_4$Me-4 group. As with other species containing a trimetallatetrahedrane structure, the signal for the ligated μ_3-C atom is less deshielded than in the dimetallacyclopropene precursor. In the ^{13}C n.m.r. spectrum of [RhW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)] the resonance for the μ-*C* nucleus is at δ 312.2 p.p.m.[5] The ^{13}C n.m.r. spectrum of (1), measured at room temperature, showed that the CO ligands were undergoing site exchange, since only one resonance for these groups was observed. This behaviour is typical of clusters of this type.[1]

The reaction between [CoW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] [6] and [Fe$_2$(CO)$_9$] at room temperature gave the trimetallatetrahedrane complex [CoFeW(μ_3-CR)(μ-CO)(CO)$_5$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] (2), the i.r. spectrum of which showed a band at 1 745 cm^{-1} ascribable to a bridging CO ligand. In the ^{13}C n.m.r. spectrum the resonance for the μ^3-*C* atom occurs at δ 284.2 p.p.m., whereas in [CoW(μ-CR)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] the signal for μ-*C* is at 341.0 p.p.m. An interesting feature of the ^{13}C n.m.r. spectrum of (2) is that the CO groups give rise to four distinct resonances, including one at δ 260.7 p.p.m. for the μ-CO ligand, indicating that the molecule is not undergoing dynamic behaviour. This is in contrast with (1) and related species, and at present we have no

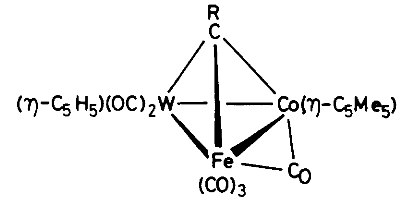
---

† 1,2-μ-Carbonyl-2,2,2,3,3-pentacarbonyl-3-η-cyclopentadienyl-1-η-indenyl-μ_3-(p-tolymethylidyne)-*triangulo*-rhodiumirontungsten.

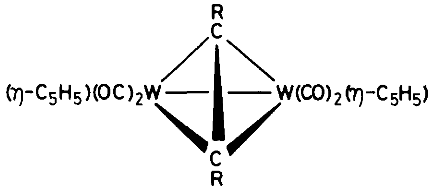
Supplementary data available (No. SUP 23401, 27 pp.): observed and calculated structure factors, hydrogen atom co-ordinates, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



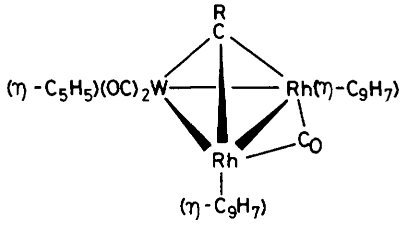
(1)



(2)



(3)



(4)

R = C_6H_4Me-4

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.827 28(3)	0.494 95(1)	0.222 63(1)	C(14)	0.708 3(5)	0.370 5(4)	0.158 8(3)
Rh	0.582 19(5)	0.523 19(3)	0.284 99(3)	C(15)	0.851 9(5)	0.346 4(4)	0.204 5(3)
Fe	0.620 33(10)	0.628 29(5)	0.182 91(5)	C(21)	0.830 0(7)	0.656 5(3)	0.343 5(3)
C(1)	0.486 7(8)	0.523 5(4)	0.180 1(4)	C(22)	0.976 6(7)	0.645 6(4)	0.388 9(4)
O(1)	0.392 1(7)	0.485 4(3)	0.138 0(4)	C(23)	1.032 6(9)	0.700 5(5)	0.448 2(4)
C(2)	0.748 3(7)	0.717 1(4)	0.184 7(4)	C(24)	0.947 7(9)	0.767 7(5)	0.464 7(4)
O(2)	0.828 1(6)	0.773 1(3)	0.184 7(3)	C(25)	0.802 7(9)	0.779 6(4)	0.419 1(4)
C(3)	0.461 6(8)	0.693 0(4)	0.189 8(5)	C(26)	0.745 3(7)	0.725 5(4)	0.359 7(4)
O(3)	0.358 9(7)	0.733 6(3)	0.194 3(5)	C(27)	1.009 5(12)	0.825 2(6)	0.532 8(5)
C(4)	0.590 9(9)	0.613 4(4)	0.084 9(4)	C(31)	0.444 1(7)	0.548 0(4)	0.380 2(4)
O(4)	0.571 1(9)	0.606 5(4)	0.022 2(3)	C(32)	0.369 1(8)	0.491 7(4)	0.321 7(5)
C(5)	0.927 3(8)	0.456 6(4)	0.325 1(4)	C(33)	0.456 9(8)	0.417 2(4)	0.323 4(4)
O(5)	0.983 4(7)	0.429 8(4)	0.382 5(3)	C(34)	0.595 8(8)	0.429 3(4)	0.376 5(4)
C(6)	0.992 1(8)	0.578 2(4)	0.223 9(4)	C(35)	0.585 7(9)	0.509 0(4)	0.415 4(4)
O(6)	1.088 8(6)	0.626 8(3)	0.225 7(3)	C(36)	0.685 4(10)	0.549 3(6)	0.474 9(4)
C(7)	0.764 9(7)	0.598 3(4)	0.281 4(3)	C(37)	0.639 9(13)	0.625 3(7)	0.499 7(5)
C(11)	0.967 2(5)	0.391 0(4)	0.179 0(3)	C(38)	0.500 2(13)	0.663 8(6)	0.465 2(6)
C(12)	0.894 8(5)	0.442 7(4)	0.117 6(3)	C(39)	0.403 5(10)	0.627 8(5)	0.405 6(5)
C(13)	0.734 8(5)	0.430 1(4)	0.105 1(3)				

explanation for the relatively high stereochemical rigidity of (2).

In the reaction between $[Fe_2(CO)_9]$ and $[CoW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ a second product was the bridged-alkyne complex (3), formed by ' apparent ' dimerisation of the mononuclear compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$. We have observed the formation of (3) in a number of reactions of the kind described herein, including others mentioned below, and hence discussion is deferred as to how this product might arise.

The clusters (1) and (2) possess 50 valence electrons, as do the long known species $[Co_3(\mu\text{-}CR)(CO)_9]$.[7-9] All the metal atoms in these complexes obey the 18-electron formalism, and the core atoms provide six skeletal pairs for cluster bonding.[10,11] This situation may be contrasted with the compounds $[PtFeW(\mu_3\text{-}CR)(CO)_{7-n}(PR'_3)_n(\eta\text{-}C_5H_5)]$ ($n = 1$ or 2), mentioned above, which possess five skeletal pairs.[1] An interesting feature of compound (1) is that the core contains metal atoms from the first, the second, and the third series of the transition elements. This property, together with a need to establish the presence of the bridging CO ligand, and its location in the cluster, prompted an *X*-ray diffraction study.

The results are summarised in Tables 1 and 2, and the molecule is shown in Figure 1 with the atom numbering scheme. The triangular RhFeW arrangement with the capping μ_3-CC_6H_4Me-4 ligand is confirmed, the molecule thus being chiral. The Fe–Rh bond is bridged by a CO ligand [Rh–C(1)–Fe 81.6(2)°] which is perceptibly closer (*ca.* 0.09 Å) to the rhodium atom. The remaining five carbonyl ligands occupy terminal sites with M–C–O angles in the range 176.0(6)—179.2(7)°. The $Fe(CO)_3$ and $W(CO)_2$ moieties have inter-axial OC–M–CO angles of 90.9(3)—102.6(4)°, very similar to those observed in the related compound $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$.[12] The plane of the η-C_5H_5 ring is slightly tilted, such that C(11) and C(12) are *ca.* 0.08 Å closer to the tungsten than C(14). A much more pronounced distortion of this kind is observed with the η-C_9H_7 ligand on the rhodium. The unique Rh–C(33) separation [2.210(7) Å] is *ca.* 0.21 Å shorter than Rh–C(31) or Rh–C(35) [average 2.416(8) Å]. A similar feature has been reported [13] for other rhodium indenyl complexes. These distortions towards an η^3-bonding mode for the C_5 ring to the rhodium atoms may be a ground-state manifestation of the η^5 to η^3 ' slippage ' believed to be responsible for the high reactivity of compounds containing Rh-(η-C_9H_7) groups in ligand substitution reactions.[14]

The different metal–metal distances show unexpectedly that the Rh–W separation [2.760(1) Å] is shorter than the Fe–W [2.772(1) Å], a result contrary to that predicted from simple covalent radii considerations. The origins of this phenomenon are obscured by the wide range of Fe–W and Rh–W distances found in metal clusters. Thus the Fe–W separation in (1)

Table 2. Internuclear distances (Å) and angles (°) for [RhFeW(μ-CC_6H_4Me-4)(μ-CO)$(CO)_5$(η-C_5H_5)(η-C_9H_7)] (1), with estimated standard deviations in parentheses

(*a*) Distances

W-Rh	2.760(1)	W-Fe	2.772(1)	C(4)-O(4)	1.136(10)	C(5)-O(5)	1.143(9)
W-C(5)	1.988(7)	W-C(6)	1.968(7)	C(6)-O(6)	1.149(9)	C(7)-C(21)	1.471(8)
W-C(7)	2.093(6)	W-C(11)	2.312(6)	C(11)-C(12)	1.42 *	C(12)-C(13)	1.42 *
W-C(12)	2.318(6)	W-C(13)	2.364(6)	C(13)-C(14)	1.42 *	C(14)-C(15)	1.42 *
W-C(14)	2.388(5)	W-C(15)	2.356(6)	C(15)-C(11)	1.42 *	C(21)-C(22)	1.398(8)
Rh-Fe	2.583(1)	Rh-C(1)	1.928(7)	C(22)-C(23)	1.388(10)	C(23)-C(24)	1.374(11)
Rh-C(7)	2.035(6)	Rh-C(31)	2.417(8)	C(24)-C(25)	1.391(10)	C(25)-C(26)	1.384(9)
Rh-C(32)	2.239(8)	Rh-C(33)	2.210(7)	C(26)-C(21)	1.392(9)	C(24)-C(27)	1.539(11)
Rh-C(34)	2.219(7)	Rh-C(35)	2.415(8)	C(31)-C(32)	1.432(10)	C(32)-C(33)	1.401(9)
Fe-C(1)	2.022(7)	Fe-C(2)	1.796(6)	C(33)-C(34)	1.410(9)	C(34)-C(35)	1.448(10)
Fe-C(3)	1.779(7)	Fe-C(4)	1.784(8)	C(35)-C(36)	1.395(10)	C(36)-C(37)	1.368(14)
Fe-C(7)	2.029(6)	C(1)-O(1)	1.170(8)	C(37)-C(38)	1.405(15)	C(38)-C(39)	1.354(12)
C(2)-O(2)	1.131(8)	C(3)-O(3)	1.141(10)	C(39)-C(31)	1.406(10)	C(31)-C(35)	1.425(9)

(*b*) Angles

Fe-W-Rh	55.7(1)	C(5)-W-Rh	82.9(2)	O(2)-C(2)-Fe	178.9(6)	O(3)-C(3)-Fe	179.2(7)
C(5)-W-Fe	127.0(2)	C(6)-W-Rh	124.6(2)	O(4)-C(4)-Fe	177.9(6)	O(5)-C(5)-W	176.0(6)
C(6)-W-Fe	88.2(2)	C(6)-W-C(5)	90.9(3)	O(6)-C(6)-W	179.0(6)	Rh-C(7)-W	83.9(2)
C(7)-W-Rh	47.1(2)	C(7)-W-Fe	46.8(2)	Fe-C(7)-W	84.5(2)	Fe-C(7)-Rh	78.9(2)
C(7)-W-C(5)	81.5(3)	C(7)-W-C(6)	77.4(3)	C(21)-C(7)-W	140.6(4)	C(21)-C(7)-Rh	120.3(5)
Fe-Rh-W	62.4(1)	C(1)-Rh-W	77.9(2)	C(21)-C(7)-Fe	127.8(4)	C(15)-C(11)-C(12)	108.0 *
C(1)-Rh-Fe	50.8(2)	C(7)-Rh-W	48.9(2)	C(13)-C(12)-C(11)	108.0 *	C(14)-C(13)-C(12)	108.0 *
C(7)-Rh-Fe	50.4(2)	C(7)-Rh-C(1)	97.9(3)	C(15)-C(14)-C(13)	108.0 *	C(14)-C(15)-C(11)	108.0 *
Rh-Fe-W	61.9(1)	C(1)-Fe-W	76.2(2)	C(22)-C(21)-C(7)	122.7(5)	C(26)-C(21)-C(7)	120.3(5)
C(1)-Fe-Rh	47.6(2)	C(2)-Fe-W	100.5(2)	C(26)-C(21)-C(22)	117.0(5)	C(23)-C(22)-C(21)	121.0(6)
C(2)-Fe-Rh	132.1(2)	C(2)-Fe-C(1)	176.5(3)	C(24)-C(23)-C(22)	121.9(6)	C(25)-C(24)-C(23)	117.3(6)
C(3)-Fe-W	155.2(3)	C(3)-Fe-Rh	93.3(3)	C(27)-C(24)-C(23)	120.9(7)	C(27)-C(24)-C(25)	121.8(7)
C(3)-Fe-C(1)	88.5(3)	C(3)-Fe-C(2)	95.0(3)	C(26)-C(25)-C(24)	121.5(7)	C(25)-C(26)-C(21)	119.6(3)
C(4)-Fe-W	95.8(2)	C(4)-Fe-Rh	130.3(2)	C(35)-C(31)-C(32)	107.2(6)	C(39)-C(31)-C(32)	132.8(5)
C(4)-Fe-C(1)	85.7(3)	C(4)-Fe-C(2)	93.4(3)	C(39)-C(31)-C(35)	120.0(6)	C(33)-C(32)-C(31)	109.1(6)
C(4)-Fe-C(3)	102.6(4)	C(7)-Fe-W	48.7(2)	C(34)-C(33)-C(32)	107.9(6)	C(35)-C(34)-C(33)	108.1(6)
C(7)-Fe-Rh	50.6(2)	C(7)-Fe-C(1)	95.2(2)	C(34)-C(35)-C(31)	107.1(6)	C(36)-C(35)-C(31)	120.6(7)
C(7)-Fe-C(2)	83.5(2)	C(7)-Fe-C(3)	115.0(3)	C(36)-C(35)-C(34)	132.3(7)	C(37)-C(36)-C(35)	117.8(8)
C(7)-Fe-C(4)	142.4(3)	Fe-C(1)-Rh	81.6(2)	C(38)-C(37)-C(36)	121.6(8)	C(39)-C(38)-C(37)	121.9(9)
O(1)-C(1)-Rh	138.5(6)	O(1)-C(1)-Fe	139.7(6)	C(38)-C(39)-C(31)	121.3(4)		

* Atoms in rigid groups.

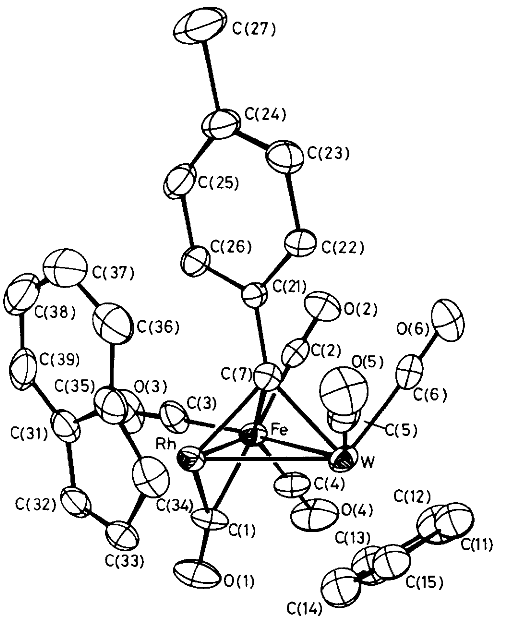
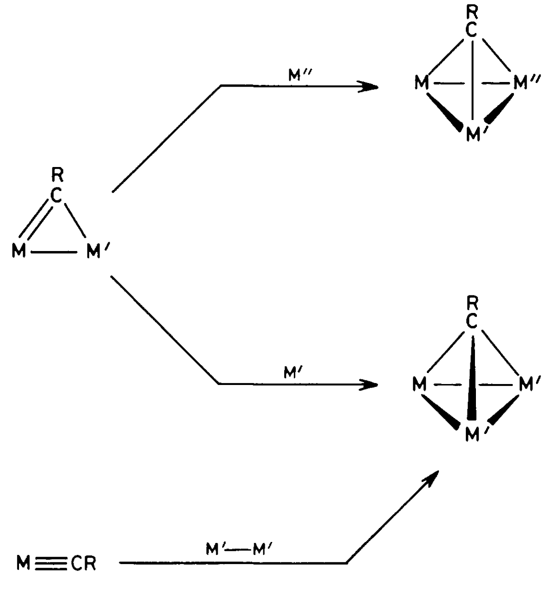


Figure. Molecular structure of the complex [RhFeW(μ_3-CC_6H_4Me-4)(μ-CO)$(CO)_5$(η-C_5H_5)(η-C_9H_7)] (1), showing the atom numbering scheme

[2.772(1) Å] is similar to those in [Fe_2W(μ_3-CR)(μ-CO)$(CO)_8$(η-C_5H_5)] [2.805(2) and 2.756(2) Å] [12] and [PtFeW(μ_3-CR)$(CO)_6$(PEt_3)(η-C_5H_5)] [2.784(3) Å].[1] In [PtFeW(μ_3-CR)$(CO)_5$-$(PMePh_2)_2$(η-C_5H_5)] [2.694(1) Å] [1] and [$PtFeW_2$(μ-CR)(μ_3-CR)$(CO)_7$(η-C_5H_5)$_2$] [2.637(3) Å] [4,15] the Fe–W distances are shorter, perhaps reflecting in the two clusters a degree of unsaturation since these trimetallatetrahedrane species involve 48 valence electrons rather than the 50 of complex (1). The Rh–W distance [2.760 Å] in (1) may be compared with the values found in [Rh_2W(acac)$_2$(μ-CR)(μ-CO)$(CO)_2$(η-C_5H_5)] [2.809(2) and 2.764(2) Å] [2] and in [RhW(μ-CR)$(CO)_2$-(PMe_3)(η-C_5H_5)(η-C_9H_7)] [2.796(1) Å].[16] Data for Fe–Rh distances are comparatively scarce; however, the separation in (1) [2.583(1) Å] is very similar to that previously found in the cluster compounds [$Rh_2Fe_2(CO)_8$(η-C_5H_5)$_2$] [2.570(5) and 2.598(5) Å] and [$RhFe_3(CO)_{11}$(η-C_5H_5)] [2.568(3), 2.615(3), and 2.607(3) Å].[17]

The μ_3-C–metal distances conform to expectation, based on covalent radii, decreasing in the sequence: μ_3-C–W [2.093(6) Å] > μ_3-C–Rh [2.035(6) Å] > μ_3-C–Fe [2.029(6) Å]. The tolylidyne ligand is therefore asymmetrically bound to the metal triangle with μ_3-C–metal separations closely resembling those found in [Fe_2W(μ_3-CR)(μ-CO)$(CO)_8$(η-C_5H_5)] [μ_3-C–W, 2.093(5) Å; μ_3-C–Fe, 1.969(5) and 2.036(5) Å] [12] and [Rh_2W-(acac)$_2$(μ_3-CR)(μ-CO)$(CO)_2$(η-C_5H_5)] [μ_3-C–W, 1.991(8) Å; μ_3-C–Rh, 2.030(8) and 1.994(9) Å].[2] Moreover, the axis of the tolylidyne ligand is not normal to the plane of the metal triangle, principally because of the large W–C(7)–C(21) angle

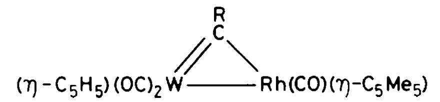


Scheme 1. Ligands on metal atoms omitted for simplification; $R = C_6H_4Me$-4

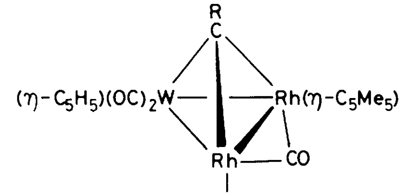
of 140.6(4)°. An almost identical opening out of the corresponding angle [141.7(5)°] occurs in $[Rh_2W(acac)_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$. Both the latter and (1) apparently retain a slight relationship with the structure of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ [W–C–C 176(2)°, W≡C 1.82(2) Å] [18] from which they are derived. The situation in (1) contrasts with that in $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ where the tolylidyne ligand is more symmetrically bridging [W–μ_3-C–C 135.8 (5)°, μ_3-C–W 2.103(7) Å].[2]

The synthesis of (1) and (2) by the method described, as well as the previously reported preparation of the complexes $[PtFeW(\mu_3\text{-}CR)(CO)_{7-n}(PR'_3)_n(\eta\text{-}C_5H_5)]$ (n = 1 or 2), demonstrated an apparently general route to metal clusters having a core structure $MM'M''(\mu_3\text{-}C)$, involving three different transition elements (Scheme 1). In principle, it should be possible to synthesise related trimetallatetrahedrane clusters which contain two different transition elements by addition of a low-valent metal species $M'L_n$ to a dimetallacyclopropene complex containing a $\overline{M(\mu\text{-}CR)M'}$ ring system. We have already reported [2] one example of such a synthesis, in the preparation of $[Rh_2W(acac)_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$ by addition of $[Rh(acac)(C_2H_4)_2]$ to $[RhW(acac)(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)]$. In order to extend the scope of this route to clusters with a $MM'_2(\mu_3\text{-}C)$ core we have investigated the reaction between $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ [15] and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$. Reaction occurs in toluene at *ca.* 50—60 °C to give in virtually quantitative yield the dirhodiumtungsten complex $[Rh_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)_2]$ (4). The mass spectrum shows a parent ion, and the molecular structure is firmly established by the ^1H and ^{13}C n.m.r. spectra, and by appearance in the i.r. spectrum of a CO band at 1 769 cm^{-1} due to the bridging CO ligand. In the ^{13}C n.m.r. spectrum the resonance for the triply bridging carbon atom occurs as a triplet at δ 286.0 p.p.m. [*J*(RhC) 32 Hz]. The bridging CO ligand also gives rise to a triplet signal [δ 227.9 p.p.m., *J*(RhC) 50 Hz], while the signal for the *C*O groups bonded to W occurs at δ 216.0 [*J*(WC) 169 Hz]. Other resonances are as expected for the structure proposed.

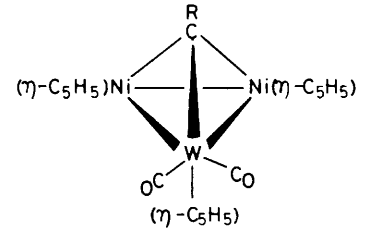
We have earlier mentioned the reaction between $[Co_2(CO)_8]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ which gives the dicobalttungsten compound $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ in quantitative yield. Formally this synthesis involves the addition of a $L_nM\equiv CR$ species across a metal–metal bond to give a cluster with a $MM'_2(\mu_3\text{-}C)$ core (Scheme 1). With a view to extending this route to clusters of this type we have studied reactions between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and the homonuclear dimetal compounds $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ [19] and $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$.[20]



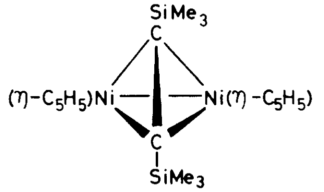
(5)



(6)



(7)



(8)

$R = C_6H_4Me$-4

In toluene at 60 °C, reaction between the carbynetungsten compound and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ occurs to give two products, $[RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (5) and $[Rh_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ (6), in *ca.* 25 and 55% yield, respectively. Formation of the dimetallacompound (5) was unexpected and implies fragmentation of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$. Simple addition of the formal rhodium–rhodium 'double bond' [21] across the carbon–tungsten triple bond is unlikely to occur directly.

Both (5) and (6) have spectroscopic properties in accord with the structures proposed. The i.r. spectrum of (5) shows three bands in the CO stretching region (1 967, 1 911, and 1 833 cm^{-1}), the one at the lower frequency can be ascribed to a semi-bridging carbonyl ligand. The i.r. spectrum of (6) has a band at 1 733 cm^{-1} due to the bridging CO group. The ^{13}C n.m.r. spectrum of (5) has resonances for the μ-C atom at δ 322.9 p.p.m. [d, *J*(RhC) 29 Hz], and for the CO ligands at 232.0, 230.0 (WCO), and 189.6 p.p.m. [d, RhCO, *J*(RhC) 83 Hz]. For (6) the signal for the triply bridging carbon atom occurs as a triplet at δ 271.8 p.p.m. [*J*(RhC) 34 Hz]. The resonance for the bridging CO is also the expected triplet, and occurs at δ 244.0 [*J*(RhC) 44 Hz]. The CO ligands on tungsten give rise to a signal at 218.1 p.p.m., with tungsten satellites [*J*(WC) 161 Hz].

Reaction between $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ in toluene at 60 °C gives the expected trimetal cluster [$Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3$] (7). However, this reaction also produces appreciable amounts of the alkyne-bridged ditungsten compound (3) {50%, based on the reactant [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$]}. The structure of (7) is firmly established by microanalysis, the observation of a molecular ion in the mass spectrum, and the n.m.r. spectra. Thus the ^1H n.m.r. spectrum shows the presence of $\eta\text{-}C_5H_5$ ligands in two environments (relative intensity 1 : 2), and the ^{13}C spectrum shows resonances for the $\mu_3\text{-}C$ nucleus at δ 275.7 p.p.m. [J(WC) 125 Hz], and for the CO ligands at 217.2 p.p.m. [J(WC) 171 Hz]. Signals in the spectrum at 91.5 and 89.5 p.p.m. (relative intensity 1 : 2), may be assigned to the $W(\eta\text{-}C_5H_5)$ and $Ni(\eta\text{-}C_5H_5)$ groups, respectively.

Formation of (3) merits discussion, particularly as the compound [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] does not dimerise when heated alone in toluene. This strongly implies a mechanism for formation of (3) involving the intermediacy of a heteronuclear metal cluster, and, moreover, that the syntheses of species with the core structures $MM'_2(\mu_3\text{-}C)$ by reaction of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] with compounds with metal-metal bonds (Scheme 1) do not proceed as a single step. Herein we discuss various possible pathways in the context of the nickel species [$Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$].

Madach and Vahrenkamp [22] have presented convincing evidence that many carbonyldimetal compounds, including the dinickel complex, afford 17-electron species by rupture of their metal-metal bonds. Thus it is reasonable to suggest that the first step in the reaction of [$Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] with [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] is the formation of the dimetalla-species [$NiW(\mu\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_2$] (Scheme 2). Combination of the dimetallacyclopropene intermediate with a further $Ni(CO)(\eta\text{-}C_5H_5)$ fragment, and concomitant loss of CO would then give the diamagnetic compound (7). It will be noted that there is an isolobal relationship between (7) and the long known alkyne-bridged complexes [$Ni_2(\mu\text{-alkyne})(\eta\text{-}C_5H_5)_2$], which are produced in reactions between [$Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] and alkynes.[23] It is generally assumed that these products are formed by direct addition of the alkyne to the dinickel reactant, although there is no firm evidence for such a mechanism. Direct addition of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] to [$Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] with loss of CO would give (7) directly. However, this path seems unlikely, in view of the ready synthesis of (7) from the mononickel complex [$Ni(\eta\text{-}C_5H_5)_2$], discussed below.

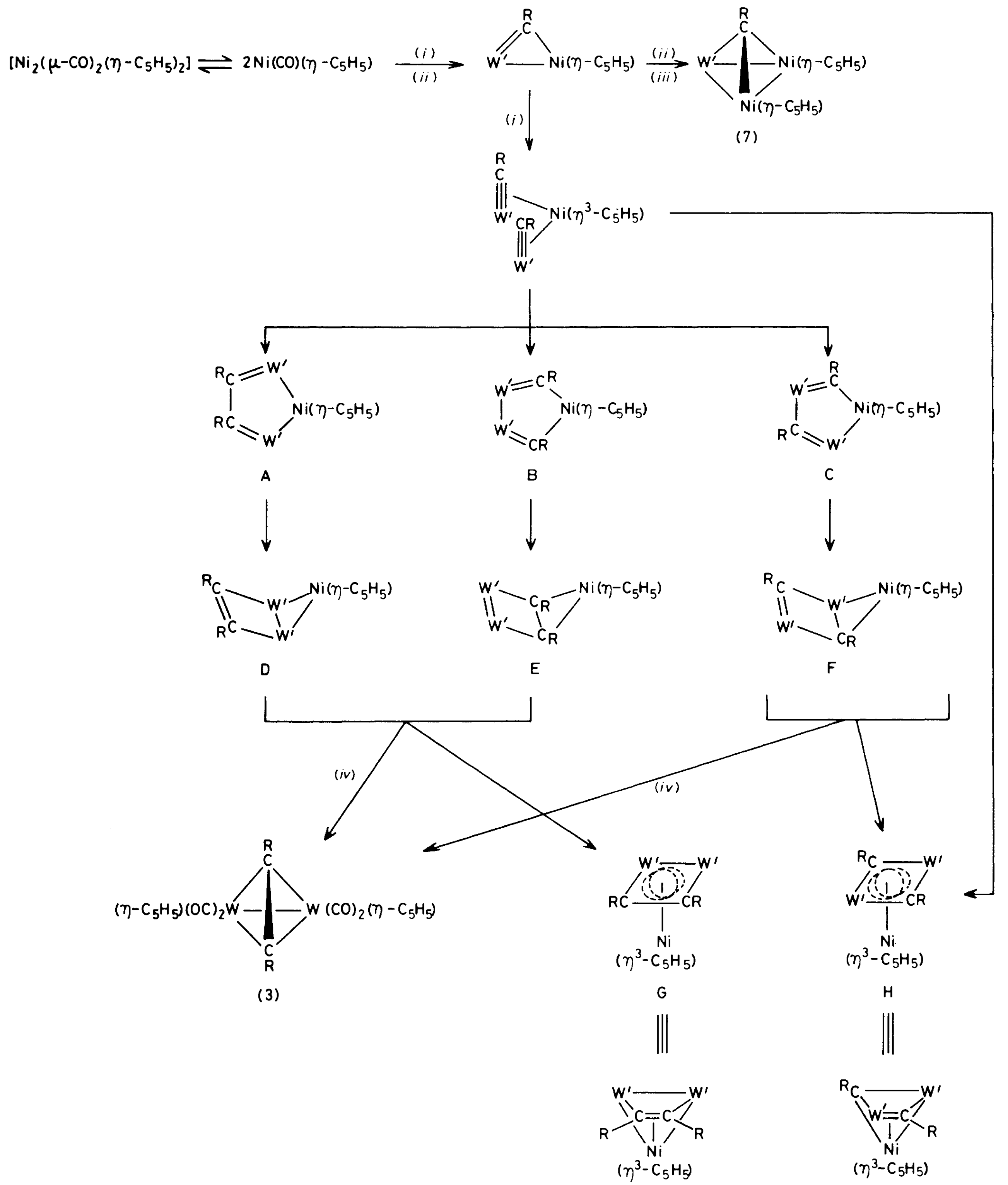
Formation of (3) could occur *via* several pathways, and at this stage of our knowledge the mechanism cannot be established with certainty. However, it is instructive to relate the 'dimerisation' of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] with the synthesis of metallacyclopentadiene and η^4-cyclobutadienemetal complexes from alkynes and low-valent transition-metal complexes. The mechanisms for the syntheses of these two types of organometallic compound have recently been discussed by Vollhardt and co-workers.[24] It is generally assumed that metallacyclopentadiene compounds form in a step-wise manner (Scheme 3),[25] and that from the latter the cyclobutadiene complexes, their valence tautomers, are produced in a reductive step. Hitherto, consideration does not seem to have been given to the manner in which this valence tautomerism might occur. In Scheme 3 we depict an intermediate of reductive coupling which may be viewed as an η^2-cyclobutadiene complex. It should also be noted that evidence has been presented [24] that the η^4-cyclobutadiene complexes might form, directly from the bis(alkyne)metal species, even though this is a symmetry forbidden reaction.

Application of the steps of Scheme 3 to Scheme 2 leads to the proposal that the species [$NiW(\mu\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_2$] would react with a second molecule of reactant [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] to give the pseudo-bis(alkyne)nickel complex shown. This species is formally similar to the trimetal complex [$Pt\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2$],[26] and 'slippage' of the C_5H_5 ring ($\eta^5 \longrightarrow \eta^3$), a common feature of cyclopentadienyl nickel chemistry,[23,27] would limit nickel to an 18-electron shell. The 'bis-alkyne' complex could give one or other, or all, of the trimetallacyclopentadiene species A–C. By analogy with metal alkyne chemistry, and taking into account the isolobal relationship of CR with $W(CO)_2(\eta\text{-}C_5H_5)$ (W, d^5), A–C would be expected to convert to η^4-dimetallacyclobutadiene metal complexes, several examples of which are known.[12] The possible transient existence of the η^2-ditungstacyclobutadiene(cyclopentadienyl)nickel complexes D–F is particularly interesting in the light of a recent theoretical treatment.[28] Structure D (and E and F also, because of the isolobal relationship mentioned above) can also be regarded as a ditungsten (d^4–d^4) complex having a bridging $Ni(\eta\text{-}C_5H_5)$ and a bridging alkyne group, with the latter parallel to the metal–metal bond, and thus formally acting as a $C_2R_2^{2-}$ ligand. Such species can 'twist' such that the alkyne is perpendicular to the metal–metal bond (W–W, d^5–d^5), and this process would probably be assisted by the π-donor properties of the $Ni(\eta\text{-}C_5H_5)$ group.[28] Release of the latter would then provide a pathway to (3).

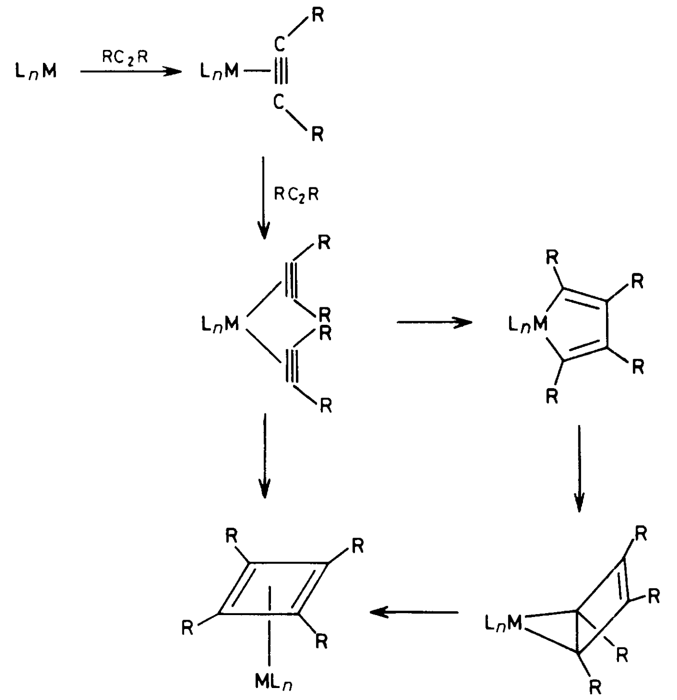
The ditungstacyclobutadiene(η^3-cyclopentadienyl)nickel complexes G and H, if formed, might also provide a route to (3). Release of $Ni(\eta\text{-}C_5H_5)$ fragments would be followed by conversion of the dimetallacyclobutadiene structures produced into the dimetallatetrahedrane (3). However, this transit is symmetry forbidden for the organic counterparts cyclobutadiene and tetrahedrane and, although energetically possible, is probably best regarded as forbidden for the dimetallacyclobutadiene species also. Interestingly, stable complexes are known with dimetallacyclobutadiene structures.[29–32]

The species G and H of Scheme 2 deserve brief comment. They could be directly accessible, following the ideas of Vollhardt and co-workers,[24] from the 'bis-alkyne' intermediate [$Ni(\eta^3\text{-}C_5H_5)\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2$]. Moreover, as indicated in Scheme 2, G, and H can also be regarded as structures in which a *triangulo*-core (NiW_2 or NiWC) is $\mu_3(\eta^2\text{-}||)$ bridged [33] by an 'alkyne'. Such structures undergo several types of ligand site-exchange in solution.[12]

From the 'mono-nickel' centred mechanism of Scheme 2, it is seen that the overall stoicheiometry is such that compounds (3) and (7) form from [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] by reactions of the latter with a source of a $Ni(\eta\text{-}C_5H_5)$ fragment, the additional CO group of $Ni(CO)(\eta\text{-}C_5H_5)$ being unnecessary. Indeed, we have found that reaction of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] with [$Ni(\eta\text{-}C_5H_5)_2$] in toluene gave (3) and (7) in amounts corresponding to equal distribution of the tungsten between these two products. We referred earlier to the formation of (5) as well as (6) in the reaction of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] with [$Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$]. This suggests that in this reaction also, the first stage might involve dissociation of the dimer to give the carbene-like fragment $Rh(CO)(\eta\text{-}C_5Me_5)$ which would be captured by the tungsten carbyne complex to give (5). Subsequent addition of $Rh(CO)(\eta\text{-}C_5Me_5)$, with loss of CO, would yield (6). The last step would be fast since there was no evidence for formation of (3) in this reaction. Interestingly, [$Rh(CO)_2(\eta\text{-}C_5Me_5)$], which is a co-ordinatively saturated 18-electron species, does not react with [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$]. Similar steps to those invoked in Scheme 2 could also occur in the synthesis of [$Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$].[2] Dissociation of [$Co_2(CO)_8$] to give $Co(CO)_4^{\bullet}$ could lead to the species [$CoW(\mu\text{-}CR)(CO)_5(\eta\text{-}C_5H_5)$], which could rapidly add $Co(CO)_4^{\bullet}$, with loss of CO, to give [$Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$]. Again, addition of the second cobalt fragment must be rapid since the dicobalttungsten compound is produced quantitatively and no trace of (3) is observed. In contrast, the



Scheme 2. For clarity W′ = $W(CO)_2(\eta\text{-}C_5H_5)$, R = $C_6H_4Me\text{-}4$; (*i*) $+[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$, (*ii*) $-CO$, (*iii*) $+Ni(CO)(\eta\text{-}C_5H_5)$, (*iv*) $-Ni(\eta\text{-}C_5H_5)$



Scheme 3.

dichromium compound $[Cr_2(CO)_6(\eta-C_5H_5)_2]$ catalyses the quantitative conversion of $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ into (3), a reaction which will be discussed later.[34]

In order to avoid the production of (3) in the synthesis of (7), we considered an alternative route involving alkynedinickel compounds $[Ni_2(\mu-RC_2R)(\eta-C_5H_5)_2]$. Compound (8) was prepared, and found to give (7) in 90% yield on reaction with $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ in toluene at 60 °C. No trace of (3) was observed. It has been previously observed[35] that alkyne exchange occurs with the complexes $[Ni_2(\mu-RC_2R)(cod)_2]$ (cod = cyclo-octa-1,5-diene).

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk tube techniques under a dry oxygen-free nitrogen atmosphere. Chromatography was carried out on columns of alumina (Brockman Activity II). The n.m.r. measurements were made with JEOL PS-100, JNM-FX 90Q, and FX 200 instruments. Chemical shifts, δ (p.p.m.), are relative to $SiMe_4$ for the ^1H and the $^{13}C-\{^1H\}$ spectra; for ^{13}C, positive values represent shifts to high frequency of the standard. A Nicolet MX-1 FT i.r. spectrophotometer was used to record i.r. spectra, and mass spectra for molecular weight measurements were made on an A.E.I. MS 902 instrument. The compounds $[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2]$,[36] $[Rh(C_2H_4)_2(\eta-C_9H_7)]$,[13] $[RhW(\mu-CC_6H_4Me-4)(CO)_3(\eta-C_5H_5)(\eta-C_9H_7)]$,[5] $[CoW(\mu-CC_6H_4Me-4)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]$,[5] and $[Ni_2(\mu-CO)_2(\eta-C_5H_5)_2]$[37] were prepared by methods reported previously.

Synthesis of $[RhFeW(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_5(\eta-C_5H_5)(\eta-C_9H_7)]$.—An excess of solid $[Fe_2(CO)_9]$ (0.7 g, 2.0 mmol) was added to a deep red solution of $[RhW(\mu-CC_6H_4Me-4)(CO)_3(\eta-C_5H_5)(\eta-C_9H_7)]$ (0.5 g, 1.4 mmol) in thf (20 cm³). With stirring (15 h) the mixture became a deep purple-brown colour. Volatile material, including $[Fe(CO)_5]$ (toxic) was removed *in vacuo*, leaving a black residue. The latter was dissolved in dichloromethane–light petroleum (1 : 4) and chromatographed at −10 °C. Elution of the column with the same solvent mixture yielded a deep purple band. Solvent was removed *in vacuo*, and crystallisation of the residue from dichloromethane–light petroleum afforded purple-black *crystals* of $[RhFeW(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_5(\eta-C_5H_5)(\eta-C_9H_7)]$ (1) (0.36 g, 60%) (Found: C, 42.1; H, 2.3. $C_{28}H_{19}FeO_6RhW$ requires C, 42.3; H, 2.4%); $\nu_{max.}(CO)$ (pentane) at 2 033ms, 1 987s, 1 953ms, 1 935m, 1 901w, and 1 825m cm⁻¹. N.m.r. ($[^2H_1]$chloroform): ^1H, δ 2.32 (s, 3 H, Me-4), 5.12 (s, 5 H, C_5H_5), 5.40 and 5.76 (m, 3 H, C_9H_7), 6.3—7.2 (m, 8 H, C_6H_4, C_9H_7); $^{13}C-\{^1H\}$, δ 287.3 [μ_3-C, *J*(RhC) 34 Hz], 212.8 (CO), 156.7 [C^1 (C_6H_4)], 135.4—84.6 (C_6H_4, C_9H_7), 87.8 (C_5H_5), 20.9 p.p.m. (Me-4).

Synthesis of $[CoFeW(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_5(\eta-C_5H_5)(\eta-C_5Me_5)]$.—A purple solution of $[CoW(\mu-CC_6H_4Me-4)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)]$ (0.42 g, 0.66 mmol) in thf (20 cm³) was treated with $[Fe_2(CO)_9]$ (0.7 g, 2.0 mmol). The mixture was stirred (3 d) at room temperature, and solvent and $[Fe(CO)_5]$ were removed *in vacuo*. The brown residue was dissolved in dichloromethane–light petroleum (1 : 3) and chromatographed. Elution with the same solvents, but with increasing proportions of CH_2Cl_2 from 10 to 50%, afforded first a brown band and subsequently a red band. On evaporation of solvent, the latter was identified by i.r. as the alkyne-tungsten complex $[W_2\{\mu-C_2(C_6H_4Me-4)_2\}(CO)_4(\eta-C_5H_5)_2]$ (3). Concentration of the brown solution and cooling to −20 °C gave dark brown *crystals* of the complex $[CoFeW(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_5(\eta-C_5H_5)(\eta-C_5Me_5)]$ (2) (0.16 g, 32%) (Found: C, 42.6; H, 3.6. $C_{29}H_{27}CoFeO_6W\cdot CH_2Cl_2$ requires C, 42.1; H, 3.4%); $\nu_{max.}(CO)$ (hexane) at 2 027vs, 1 981vs, 1 962w, 1 949s, 1 921s, and 1 745w cm⁻¹. N.m.r. ($[^2H_2]$dichloromethane): ^1H, δ 1.40 (s, 15 H, C_5Me_5), 2.40 (s, 3 H, Me-4), 5.08 (s, 5 H, C_5H_5), 7.52 (m, 4 H, C_6H_4); $^{13}C-\{^1H\}$, δ 284.2 (μ_3-C), 260.7 (μ-CO), 216.6 (WCO), 215.8 (FeCO), 212.0 (WCO), 159.3 [C^1 (C_6H_4)], 136.8—128.6 (C_6H_4), 97.9 (*C*$_5$Me$_5$), 88.7 (C_5H_5), 21.4 (Me-4), 8.7 p.p.m. (C$_5$*Me*$_5$).

Synthesis of $[Rh_2W(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_2(\eta-C_5H_5)(\eta-C_9H_7)_2]$.—The compound $[Rh(C_2H_4)_2(\eta-C_9H_7)]$ (0.13 g, 0.5 mmol) in light petroleum (20 cm³) was treated with a stream of CO gas (10 min) to produce $[Rh(CO)_2(\eta-C_9H_7)]$ *in situ*. Solid $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ (204 mg, 0.5 mmol) was added, and the mixture stirred (2 h) to give a brown precipitate of $[RhW(\mu-CC_6H_4Me-4)(CO)_3(\eta-C_5H_5)(\eta-C_9H_7)]$[5] (0.33 g, 100%). The latter was added to a toluene (6 cm³) solution of $[Rh(C_2H_4)_2(\eta-C_9H_7)]$ (0.13 g, 0.5 mmol) through which CO had been bubbled (0.5 h). The mixture was then heated (55 °C) for 10 h in a sealed Schlenk tube fitted with a Young's pressure stopcock (10 mm). Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane–light petroleum (1 : 1) (5 cm³) and chromatographed. Elution with dichloromethane afforded a black band. Evaporation of the solution and cooling (−20 °C) gave purple-black *crystals* of $[Rh_2W(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_2(\eta-C_5H_5)(\eta-C_9H_7)_2]$ (4) (0.043 g, 94%) (Found: C, 46.4; H, 3.0%; *M*, 870. $C_{34}H_{26}O_3Rh_2W$ requires C, 46.8; H, 3.0%; *M*, 870); $\nu_{max.}(CO)$ (CH_2Cl_2) at 1 977 s, 1 917s, and 1 769m cm⁻¹. N.m.r. ($[^2H_1]$chloroform): ^1H δ 2.28 (s, 3 H, Me-4), 5.06 (s, 5 H, C_5H_5), 5.8, 6.4, 6.8 (m, 14 H, C_9H_7), 7.00 (m, 4 H, C_6H_4); $^{13}C-\{^1H\}$, δ 286.0 [t, μ_3-C, *J*(RhC) 32], 227.9 [t, μ-CO, *J*(RhC) 50], 216.0 [WCO, *J*(WC) 169 Hz], 155.6 [C^1 (C_6H_4)], 134—85 (C_6H_4, C_9H_7), 86.6 (C_5H_5), 21.7 p.p.m. (Me-4).

Synthesis of $[Rh_2W(\mu_3-CC_6H_4Me-4)(\mu-CO)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]$.—The compounds $[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2]$ (0.42 g, 0.79 mmol) and $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$

(0.32 g, 0.77 mmol) were dissolved in toluene (10 cm^3) and heated at 60 °C in an evacuated Schlenk tube (Young's stopcock) for 10 h. Volatile material was removed *in vacuo*, and the residue dissolved in dichloromethane–light petroleum (1 : 9) and chromatographed. A red band eluted first, which after evaporation of solvent afforded red *crystals* of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (5) (0.13 g, 24%) (Found: C, 46.4; H, 4.3. $C_{26}H_{27}O_3RhW$ requires C, 46.3; H, 4.0%); $\nu_{max.}$(CO) (pentane) at 1 967s, 1 911vs, and 1 833m cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{1}H, δ 1.75 (s, 15 H, C_5Me_5), 2.30 (s, 3 H, Me-4), 5.40 (s, 5 H, C_5H_5), 7.20 (m, 4 H, C_6H_4); ^{13}C-{^{1}H}, δ 322.9 [d, μ-C, J(RhC) 29], 232.0, 230.0 (WCO), 189.6 [d, RhCO, J(RhC) 83 Hz], 156.8 [C^1 (C_6H_4)], 136.1, 128.8, 128.4 (C_6H_4), 103.4 (C_5Me$_5$), 91.3 (C_5H_5), 22.7 (Me-4), 9.6 p.p.m. (C$_5$*Me*$_5$). Continued elution with dichloromethane–light petroleum (1 : 1) gave a dark purple band which, after concentration of the solution and cooling (−20 °C), afforded purple *crystals* of $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ (6) (0.40 g, 55%) (Found: C, 47.2; H, 4.8%; M, 912. $C_{36}H_{42}O_3Rh_2W$ requires C, 47.4; H, 4.6%; M, 912); $\nu_{max.}$(CO) (CH_2Cl_2) at 1 961s, 1 905s, and 1 733m cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{1}H, δ 1.56 (s, 30 H, C_5Me_5), 2.35 (s, 3 H, Me-4), 4.9 (s, 5 H, C_5H_5), 7.36 (m, 4 H, C_6H_4); ^{13}C-{^{1}H}, δ 271.8 [t, μ$_3$-C, J(RhC) 34], 244.0 [t, μ-CO, J(RhC) 44], 218.1 [WCO, J(WC) 161 Hz], 156.2 [C^1 (C_6H_4)], 135.8, 130.8, 127.5 (C_6H_4), 99.8 (C_5Me$_5$), 85.1 (C_5H_5), 22.8 (Me-4), 9.1 p.p.m. (C$_5$*Me*$_5$).

Synthesis of $[Ni_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)_3]$.—(*a*) A mixture of $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (0.30 g, 1 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.41 g, 1 mmol) in toluene (10 cm^3) was heated (60 °C) for 24 h in an evacuated tube fitted with a Young's stopcock. Solvent was removed *in vacuo* and the residue dissolved in dichloromethane–light petroleum (1 : 4) (5 cm^3) and chromatographed. Light petroleum eluted unreacted starting materials, including $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (0.12 g), and then dichloromethane–light petroleum (1 : 1) eluted a brown solution. The latter was carefully rechromatographed (50 × 2 cm column), elution with light petroleum allowing separation of first a green band and then a red band. Reduction in volume of the former solution, and cooling (−20 °C), gave green *crystals* of $[Ni_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)_3]$ (7) (0.32 g, 50%) (Found: C, 45.7; H, 3.4%; M, 656. $C_{25}H_{22}Ni_2O_2W$ requires C, 45.8; H, 3.4%; M, 656); $\nu_{max.}$(CO) (CH_2Cl_2) at 1 879s and 1 817s cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{1}H, δ 2.28 (s, 3 H, Me-4), 5.24 [s, 10 H, Ni(C_5H_5)], 5.14 [s, 5 H, W(C_5H_5)], 7.3 (m, 4 H, C_6H_4); ^{13}C-{^{1}H}, δ 275.7 [μ$_3$-C, J(WC) 125], 217.2 [WCO, J(WC) 171 Hz], 161.1 [C^1 (C_6H_4)], 137.5, 135.1, 127.5 (C_6H_4), 91.5 (WC_5H_5), 89.5 (NiC_5H_5), 22.5 p.p.m. (Me-4). The red solution afforded *crystals* of $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)\}_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (3) (0.20 g, 50% based on reactant carbyne complex) (Found: C, 44.0; H, 3.0%; M, 816. $C_{30}H_{24}O_4W_2$ requires C, 44.1; H, 2.9%; M, 816); m.p. 210—212 °C; $\nu_{max.}$(CO) (CH_2Cl_2) at 1 969s, 1 911vs, and 1 813m cm^{-1}. N.m.r. ([$^2H_1$]chloroform): ^{1}H, δ 2.37 (s, 6 H, Me-4), 5.23 (s, 10 H, C_5H_5), 6.96 (m, 8 H, C_6H_4); ^{13}C-{^{1}H}, δ 217.5 [WCO, J(WC) 173], 142.6 [C^1 (C_6H_4)], 134.6, 130.0, 128.8 (C_6H_4), 90.9 (C_5H_5), 60.0 p.p.m. [μ-C$_2$, J(WC) 29 Hz].

(*b*) The complex $[Ni_2\{\mu\text{-}C_2(SiMe_3)_2\}(\eta\text{-}C_5H_5)_2]$ (8) was first prepared (0.20 g, 42%) as green *crystals* (Found: C, 50.8; H, 5.9. $C_{18}H_{28}Ni_2Si_2$ requires C, 50.7; H, 5.9%) by heating together $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (0.30 g, 1 mmol) and excess of $Me_3SiC_2SiMe_3$ (1 cm^3) in toluene (10 cm^3) for 3 h. Removal of solvent *in vacuo*, followed by dissolving the residue in dichloromethane–light petroleum (1 : 1) (5 cm^3) and chromatographing, eluting with the same solvent mixture, gave (8). The latter was then reacted with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.40 g, 1 mmol) in toluene (10 cm^3) for 12 h at 60 °C in a Schlenk tube (Young's stopcock). Removal of solvent *in vacuo*, and washing the residue with light petroleum to remove excess carbynetungsten complex, gave a material which was chromatographed on alumina. Elution with dichloromethane afforded a brown solution which gave crystals of (7) (0.30 g, 91%), characterised as above.

Crystal Structure Determination of $[RhFeW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ (1).—Crystals of (1) grow with difficulty from dichloromethane–light petroleum as black plates. Diffracted intensities were collected at room temperature from a crystal of dimensions *ca.* 0.1 × 0.3 × 0.4 mm with well developed faces of the type ⟨0 0 1⟩, ⟨0 1 0⟩, ⟨1 1 0⟩. Data were collected on a Nicolet *P*3*m* four-circle diffractometer, according to methods described earlier.[38,39] Of the total 4 445 independent intensities, recorded to $2\theta \leqslant 50°$, 3 497 had $F > 5.0\sigma(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics and only these were used in the solution and refinement of the structure, after the intensity data had been corrected for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data for (1). $C_{28}H_{19}FeO_6RhW$, M = 793.7, Monoclinic, a = 9.018(2), b = 15.572(4), c = 18.503(6) Å, β = 103.69 (2)°, D_m = 2.05, Z = 4, D_c = 2.09 g cm^{-3}, U = 2 524(1) Å^3, F(000) = 1 520, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 58.90 cm^{-1}.

Structure solution and refinement for (1). The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. Hydrogen atoms were included at calculated positions and chemically related hydrogen atoms were given common refined isotropic temperature factors. The cyclopentadienyl ring was slightly unstable during refinement and it was therefore treated as a rigid group (C–C = 1.420 and C–H = 0.960 Å) with the constituent carbon atoms being given individual isotropic temperature factors. All remaining atoms were refined with anisotropic temperature factors. Refinement by blocked-cascade least squares led to R 0.032 (R' 0.034), and a weighting scheme of the form $w^{-1} = \sigma^2(F_o) + 0.001|F_o|^2$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks > 1.0 e Å^{-3} except in the immediate neighbourhood of the W atom where a peak of *ca.* 1.4 e Å^{-3} occurred. Scattering factors were from refs. 40—42. All computations were carried out on an 'Eclipse' (Data General) Mini-computer with the 'SHELXTL' system of programs.[43]

Acknowledgements

We thank the S.E.R.C. for support, the Syrian Ministry of Higher Education and the University of Aleppo for a Scholarship (to H. R.), and Shell Research Ltd. for a CASE award (to S. J. P.).

References

1 Part 13, M. J. Chetcuti, J. A. K. Howard, R. M. Mills, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1757.

2 M. J. Chetcuti, P. A. M. Chetcuti, J. C. Jeffery, R. M. Mills, P. Mitrprachachon, S. J. Pickering, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 699.

3 M. J. Chetcuti, M. Green, J. A. K. Howard, J. C. Jeffery, R. M. Mills, G. N. Pain, S. J. Porter, F. G. A. Stone, A. A. Wilson, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1980, 1057.

4 T. V. Ashworth, M. J. Chetcuti, L. J. Farrugia, J. A. K. Howard, J. C. Jeffery, R. M. Mills, G. N. Pain, F. G. A. Stone, and P.

Woodward, in 'Reactivity of Metal–Metal Bonds,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 155, 1981, pp. 229—313.
5 M. J. Chetcuti, M. Green, J. C. Jeffery, F. G. A. Stone, and A. A. Wilson, *J. Chem. Soc., Chem. Commun.*, 1980, 948.
6 J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 867.
7 R. Markby, I. Wender, R. A. Friedel, F. A. Cotton, and H. W. Sternberg, *J. Am. Chem. Soc.*, 1958, **80**, 6529.
8 D. Seyferth, *Adv. Organomet. Chem.*, 1976, **14**, 97.
9 B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, 1973, **6**, 73.
10 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
11 J. W. Lauher, *J. Am. Chem. Soc.*, 1978, **100**, 5305.
12 L. Busetto, M. Green, J. A. K. Howard, B. Hessner, J. C. Jeffery, R. M. Mills, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 1101.
13 P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 962.
14 P. Caddy, E. O'Brien, M. Green, L. E. Smart, and P. Woodward, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 648.
15 M. J. Chetcuti, Ph.D. Thesis, Bristol University, 1980.
16 J. C. Jeffery, M. Schmidt, and F. G. A. Stone, unpublished work.
17 M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 1971, 2170, 2995.
18 E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397.
19 A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **166**, C21.
20 E. O. Fischer and C. Palm, *Chem. Ber.*, 1958, **91**, 1725.
21 A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, 1980, **63**, 29.
22 T. Madach and H. Vahrenkamp, *Chem. Ber.*, 1980, **113**, 2675.
23 P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1974, vol. 1, ch. 5.
24 G. Ville, P. C. Vollhardt, and M. J. Winter, *J. Am. Chem. Soc.*, 1981, **103**, 5267.
25 N. M. Boag, G. H. M. Dias, M. Green, J. L. Spencer, F. G. A. Stone, and J. Vicente, *J. Chem. Soc., Dalton Trans.*, 1981, 1981 and refs. therein.
26 T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, F. G. A. Stone, S. J. Wisbey, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 763.
27 D. W. McBride, R. L. Pruett, E. Pitcher, and F. G. A. Stone, *J. Am. Chem. Soc.*, 1962, **84**, 497.
28 D. M. Hoffman, R. Hoffmann, and C. R. Fisel, *J. Am. Chem. Soc.*, 1982, **104**, 3858.
29 F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1971, 1477.
30 M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, 1976, **15**, 2252.
31 M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, 1978, **17**, 696.
32 R. A. Anderson, A. L. Galyer, and G. Wilkinson, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 609.
33 M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.*, 1976, **98**, 4645.
34 S. J. Porter, unpublished work.
35 E. L. Muetterties, W. R. Pretzer, M. G. Thomas, B. F. Beier, D. L. Thorn, V. W. Day, and A. B. Anderson, *J. Am. Chem. Soc.*, 1978, **100**, 2090.
36 M. L. Aldridge, M. Green, J. A. K. Howard, G. N. Pain, S. J. Porter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1333.
37 R. B. King, 'Organometallic Synthesis,' Academic Press, New York, 1965, vol. 1, p. 119.
38 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.
39 R. Goddard, S. D. Killops, S. A. R. Knox, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1978, 1255.
40 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
41 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
42 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
43 SHELXTL programs for use with the Nicolet *X*-ray system, G. M. Sheldrick, University of Cambridge, 1976.

Received 4*th May* 1982; *Paper* 2/725