Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 95.[1] Synthesis and Crystal Structures of $[W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)(\eta\text{-}C_5H_5)_2]$ and $[W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_9(\eta\text{-}C_5H_5)_2]$ *

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Treatment of $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in thf (tetrahydrofuran) with $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ in light petroleum affords the tetranuclear metal cluster compound $[W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$. The latter with 1 equivalent of PMe_2Ph gives $[W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)(\eta\text{-}C_5H_5)_2]$, the structure of which has been established by *X*-ray diffraction. One *p*-tolylmethylidyne group caps three metal atoms WRuPt [W–Ru 2.743(1), W–Pt 2.729(1), and Ru–Pt 2.875(1) Å] in an essentially symmetrical manner. The ruthenium atom carries two carbonyl groups and the phosphine ligand [Ru–P 2.271(4) Å]. The tungsten atom is co-ordinated by a C_5H_5 ring and two CO ligands, but the latter asymmetrically bridge the W–Pt and W–Ru bonds [W–C–O 160(1) and 157(1)°, respectively]. The WRuPt triangle is linked through the Pt atom to a $W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)$ fragment *via* a W–Pt bond [2.733(1) Å] and a bridging $\mu\text{-}CC_6H_4Me\text{-}4$ ligand [μ-C–W 1.92(1), μ-C–Pt 2.03(1) Å]. One of the CO groups attached to the W atom weakly semi-bridges the W–Pt bond [W–C–O 170(1)°]. The reaction between $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ and $[W_2Pt_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(cod)(\eta\text{-}C_5H_5)_2]$ (cod = cyclo-octa-1,5-diene) gives a hexanuclear metal cluster $[W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_9(\eta\text{-}C_5H_5)_2]$, the structure of which has also been determined by *X*-ray diffraction. For descriptive purposes, five of the metal atoms [W(2)Ru(1)Ru(2)Pt(1)Pt(2)] may be regarded as occupying vertices of a 'trigonal bipyramid' but one in which two of the metal–metal bonds [Pt(1) ··· Pt(2) 3.064(4), Ru(1) ··· Pt(2) 3.259(2) Å] are absent. Allowing for this, the ruthenium atoms occupy the apical sites, and the two platinum atoms and the tungsten atom occupy equatorial sites. The Pt(1) atom, in addition to being part of the open metal framework, is attached *via* a W=Pt bond [2.663(3) Å] to an external $W(CO)_3(\eta\text{-}C_5H_5)$ fragment. One of the CO ligands on this W(1) atom asymmetrically bridges the W(1)=Pt(1) linkage [W(1)–C–O 156(3), Pt(1)–C–O 122(2)°]. Both ruthenium atoms carry three terminal CO groups. The Pt(2) atom, ligated only by two of the metal atoms [W(2) and Ru(2)] in the framework, carries a terminal CO group, and the Pt(2)–Ru(2) bond is bridged by a CO ligand [Ru(2)–C–O 136(3), Pt(2)–C–O 143(4)°]. The W(2) atom carries a C_5H_5 ring. Both *p*-tolylmethylidyne groups occupy triply bridging sites. These are on the same side of the Pt(1)W(2)Pt(2) plane, one ligand caps the W(2)Ru(1)Pt(1) triangle, the other spans the atoms Pt(2), W(2), Ru(1). The n.m.r. spectra of the new mixed-metal clusters are reported and discussed.

Because of their unsaturated nature, the trimetal complexes $[M_2M'(\mu\text{-}CR)_2(CO)_4L_2]$ (M = W or Mo, M′ = Pt or Ni, R = alkyl or aryl, L = $\eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$), in which the M–M′–M spines are bridged by alkylidyne groups, are excellent precursors for the preparation of polynuclear metal compounds.[2] For example, starting from $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1**), and with a sequential use of the reagents $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, molecules having chain-type structures based on W–Pt bonds may be obtained, as illustrated in the accompanying Scheme. Nickel or molybdenum atoms may be incorporated into these structures by using the compounds $[Ni(cod)_2]$ or $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = alkyl or aryl) at various stages in the syntheses. In this manner numerous species with W–Pt, Mo–Pt, W–Ni, or Mo–Ni bonds bridged by alkylidyne groups have been obtained. Interestingly, attempts to prepare chain-like structures based on eight metal atoms led instead to the formation of metallacycles.[2c,d] However, recently procedures have been developed which avoid cyclisation reactions and afford molecules with back-bones consisting of nine, ten, or eleven metal atoms.[2e]

The methodology illustrated in the Scheme is in principle extendable to other metal–ligand systems, thereby allowing the synthesis of numerous polynuclear metal compounds with bonds between dissimilar transition elements. In this paper we describe studies using the reagent $[Ru(CO)_4(\eta\text{-}C_2H_4)]$.[3] The latter is potentially a source of the $Ru(CO)_4$ fragment, isolobal[4] with the Pt(cod) group. It was anticipated that the compound $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ would readily react with the unsaturated complex (**1**) since it is known to react with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, affording tri- and tetra-nuclear metal cluster compounds.[5]

Results and Discussion

Treatment of a thf (tetrahydrofuran) solution of (**1**) with $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ in light petroleum gave the green crystalline complex $[W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)\text{-}$

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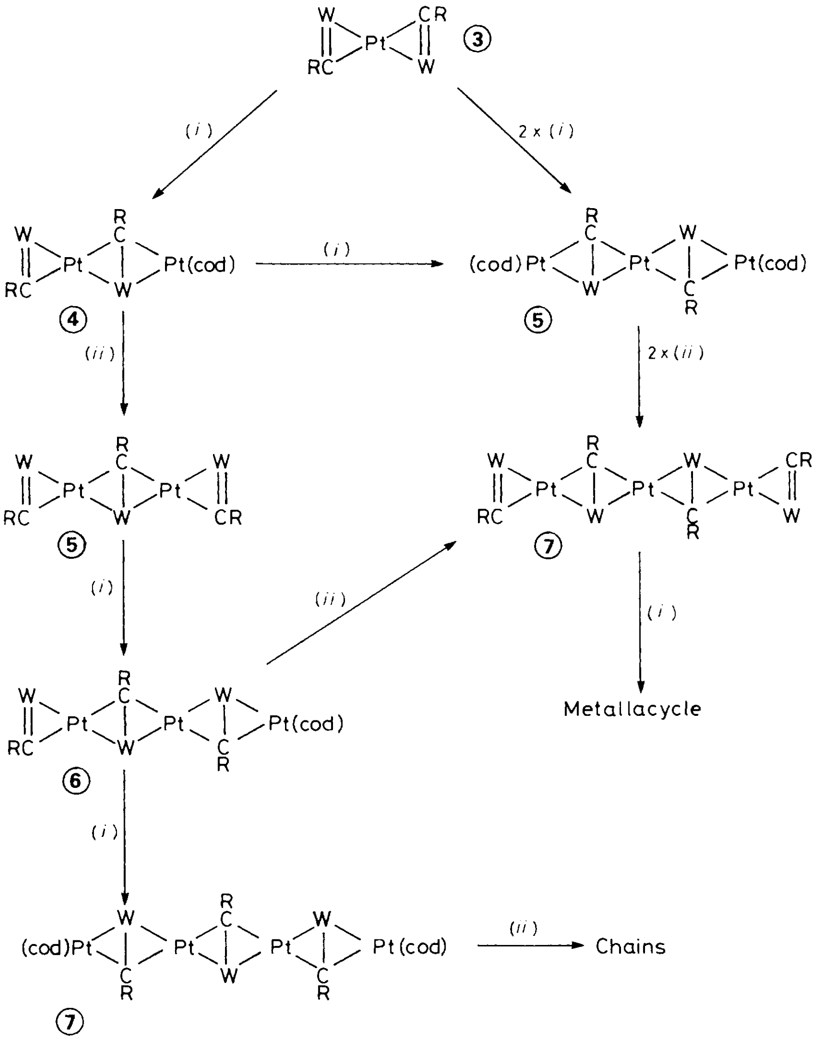
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

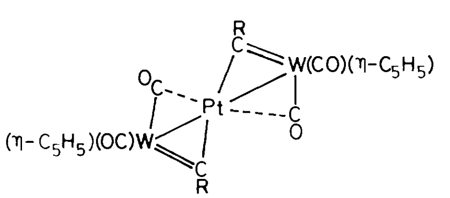


Scheme. Stepwise synthesis of polynuclear tungsten–platinum complexes. Numbers in circles refer to metal atoms in chains. (*i*) [Pt(cod)$_2$]–C$_2$H$_4$; (*ii*) [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)]

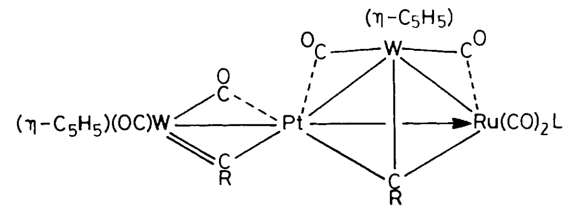
(CO)$_7$(η-C$_5$H$_5$)$_2$] (**2a**). The i.r. spectrum showed (see Experimental section) seven bands in the CO stretching region. Two of these absorptions were at frequencies (1 856 and 1 824 cm^{-1}) which suggested the presence of semi-bridging carbonyl ligands. Examination of the ^{13}C-{^{1}H} n.m.r. spectrum of the complex revealed that the CO ligands undergo site exchange on the n.m.r. time-scale. Even at −40 °C, a limit set by the solubility of the complex, only four CO signals (δ 232.7, 232.4, 228.1, and 214.3 p.p.m.) were observed, and on the basis of the chemical shifts these resonances are assigned to carbonyl groups ligating tungsten rather than ruthenium.[5] The ^{13}C-{^{1}H} n.m.r. spectrum showed characteristic signals at δ 312.4 and 282.3 p.p.m. for μ-C and μ$_3$-C nuclei, respectively. Both the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra showed resonances (see Experimental section) indicating the presence of two non-equivalent C$_5$H$_5$ and two non-equivalent Me-4 groups. The spectroscopic data for (**2a**) were thus insufficiently definitive to establish the structure. Attempts to grow crystals for an *X*-ray diffraction study were unsuccessful, and it was observed that the complex was somewhat unstable in solution, particularly in chlorinated solvents.

In order to define the structure of (**2a**), a derivative was prepared by treating the compound with 1 equivalent of PMe$_2$Ph in the expectation that the phosphine would displace a CO group attached to the ruthenium atom. In this manner the dark green crystalline compound [W$_2$RuPt(μ-CC$_6$H$_4$Me-4)(μ$_3$-CC$_6$H$_4$Me-4)(CO)$_6$(PMe$_2$Ph)(η-C$_5$H$_5$)$_2$] (**2b**) was obtained. As expected, the i.r. spectrum showed one less CO stretching band than (**2a**), but discussion of the spectroscopic properties is deferred until the results of the *X*-ray diffraction study are described.

The molecular structure is shown in Figure 1, and selected interatomic distances and angles are listed in Table 1. The *X*-ray analysis establishes the formulation and shows that (**2b**) may be regarded as derived from (**1**) by the addition of an Ru(CO)$_2$(PMe$_2$Ph) fragment. Similarities in the spectroscopic properties of (**2a**) and (**2b**), as well as the mode of synthesis of the latter, strongly imply that the former species contains an Ru(CO)$_3$ rather than an Ru(CO)$_4$ group. This result was somewhat unexpected for the following reason. As mentioned earlier, the groups Ru(CO)$_4$ and Pt(cod) are isolobal. Since addition of a Pt(cod) fragment to (**1**) gives the ditungstendiplatinum compound [W$_2$Pt$_2$(μ-CC$_6$H$_4$Me-4)(μ$_3$-CC$_6$H$_4$Me-4)(CO)$_4$(cod)(η-C$_5$H$_5$)$_2$] (**3**), reaction of (**1**) with [Ru(CO)$_4$(η-C$_2$H$_4$)] might have afforded a product structurally related to (**3**) but with an Ru(CO)$_4$ instead of a Pt(cod) group attached to one of the C=W bonds of the trimetal precursor. Interestingly, it was shown earlier[6] that treatment of (**1**) with [Fe$_2$(CO)$_9$] gave



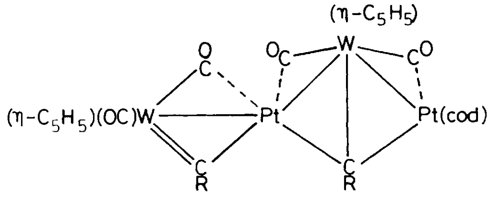
(1)



L

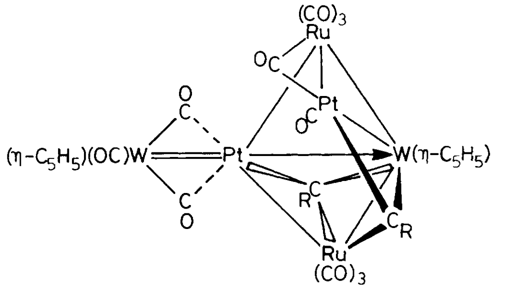
(2a) CO

(2b) PMe_2Ph



(3)

R = C_6H_4Me-4



(4)

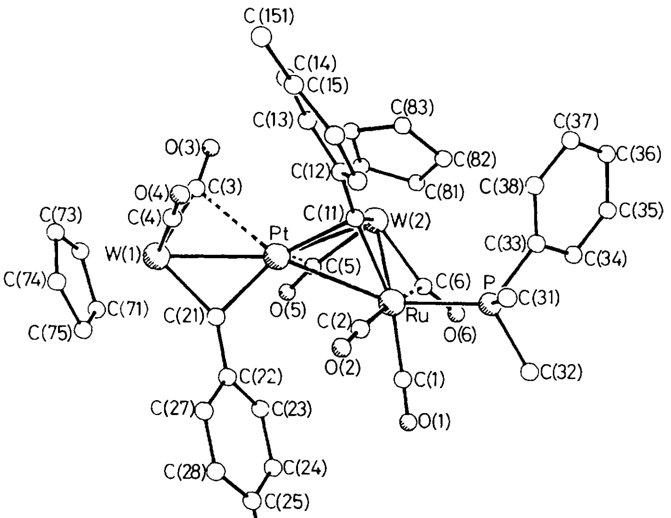


Figure 1. The molecular structure of $[W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)(\eta\text{-}C_5H_5)_2]$ (**2b**), showing the atom-labelling scheme

$[W_2FePt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)_2]$. This product is an analogue of (**2a**) and an *X*-ray diffraction study confirmed the presence of an $Fe(CO)_3$ rather than an $Fe(CO)_4$ group.

The principal feature of interest in the structure of (**2b**) is the Ru–Pt separation [2.875(1) Å]. Several metal cluster compounds containing ruthenium and platinum have been studied by *X*-ray crystallography and the Ru–Pt bond distances vary from 2.707 to 2.858 Å.[7–9] As expected, Ru–Pt bonds with bridging CO ligands tend to lie at the lower end of the range, while those with bridging hydrido groups are among the longest. Probably the best comparison to be made with (**2b**) is that found [2.803(1) Å] for the non-hydrido bridged Ru–Pt bond in $[Ru_2Pt_2(\mu\text{-}H)(\mu_4\text{-}CH)(\mu\text{-}CO)(CO)_2(PPr^i_3)_2(\eta\text{-}C_5H_5)_2]$.[9] Thus although the Ru–Pt separation in (**2b**) [2.875(1) Å] is, as far as we are aware, the longest yet reported, it would appear to indicate the presence of a weak metal–metal bond. We suggest that there might be a Pt→Ru donor interaction which enables the ruthenium atom to attain an 18-electron shell. However, as in other metal cluster compounds which are formally electronically unsaturated, in the sense that not all the metal centres can have filled 18-electron shells, it is possible to assign alternative electron distributions within the core structure. Thus if in (**2b**) there is a Pt–Ru single bond and the C(5)O(5) and C(6)O(6) groups are regarded as fully bridging (see below) then the ruthenium and platinum centres would have 18- and 16-electron shells, respectively, and the W(2) atom would have a 16-electron configuration.

The Ru–W(2) distance [2.743(1) Å] lies at the shorter end of the range of those observed (2.735—3.026 Å) in a variety of metal cluster compounds containing these metals.[10] The Pt–W(2) bond [2.729(1) Å] is somewhat shorter than those found in the compounds $[WFePt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ [2.883(1) Å] and $[WFePt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ [2.775(1) Å].[11] These species, like (**2b**), have a metal triangle capped by a *p*-tolylmethylidyne group, and both contain $Fe(CO)_3$ fragments isolobal with the $Ru(CO)_2(PMe_2Ph)$ group. The $\mu_3\text{-}CC_6H_4Me\text{-}4$ ligand in (**2b**) caps the W(2)PtRu triangle in an essentially symmetrical manner [C(11)–Pt 2.10(1), C(11)–Ru 2.06(1), and C(11)–W(2) 2.06(1) Å]. The ruthenium atom carries the PMe_2Ph group [Ru–P 2.271(4) Å], and two terminal CO groups. The tungsten atom W(2) is ligated by the C_5H_5 ring and two CO groups. The latter, however, asymmetrically bridge the W(2)–Pt [W(2)–C(5)–O(5) 160(1)°] and W(2)–Ru [W(2)–C(6)–O(6) 157(1)°] bonds.

The Pt–W(1) bond [2.733(1) Å] in complex (**2b**) is very simi-

Table 1. Selected internuclear distances (Å) and angles (°) for $[W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)(\eta\text{-}C_5H_5)_2]$ (**2b**) with estimated standard deviations in parentheses

Pt-W(1)	2.733(1)	Pt-W(2)	2.729(1)	Pt-Ru	2.875(1)	W(2)-Ru	2.743(1)
Ru-P	2.271(4)	Pt-C(11)	2.10(1)	Pt-C(21)	2.03(1)	Pt ··· C(3)	2.47(2)
Pt-C(5)	2.22(2)	W(1)-C(21)	1.92(1)	W(1)-C(3)	2.01(2)	W(1)-C(4)	1.99(2)
W(2)-C(11)	2.06(1)	W(2)-C(5)	2.00(1)	W(2)-C(6)	1.96(2)	Ru-C(11)	2.06(1)
Ru-C(1)	1.92(2)	Ru-C(2)	1.90(2)	Ru-C(6)	2.41(2)	C(1)-O(1)	1.12(2)
C(2)-O(2)	1.11(2)	C(3)-O(3)	1.15(2)	C(4)-O(4)	1.15(2)	C(5)-O(5)	1.20(2)
C(6)-O(6)	1.18(2)						
W(1)-Pt-W(2)	154.7(1)	W(1)-Pt-Ru	146.6(1)	W(2)-Pt-C(21)	156.2(4)	Ru-Pt-C(21)	105.6(4)
W(2)-Pt-Ru	58.5(1)	W(1)-Pt-C(3)	45.1(4)	Pt-W(1)-C(3)	60.6(5)	Pt-W(1)-C(4)	85.1(5)
W(2)-Pt-C(3)	110.4(4)	Ru-Pt-C(3)	161.2(4)	Pt-W(1)-C(21)	47.8(4)	Pt-W(2)-Ru	63.4(1)
W(1)-Pt-C(5)	122.2(4)	W(2)-Pt-C(5)	46.3(4)	Pt-W(2)-C(5)	53.2(5)	Ru-W(2)-C(5)	89.8(4)
W(1)-Pt-C(11)	139.1(4)	W(2)-Pt-C(11)	48.3(4)	Pt-W(2)-C(6)	107.6(5)	Ru-W(2)-C(6)	59.0(5)
Ru-Pt-C(11)	45.7(4)	W(1)-Pt-C(21)	44.6(4)	Pt-W(2)-C(11)	49.6(3)	Ru-W(2)-C(11)	48.3(4)
Pt-Ru-W(2)	58.1(1)	Pt-Ru-P	158.7(1)	Ru-C(1)-O(1)	178(1)	W(1)-C(3)-O(3)	170(1)
W(2)-Ru-P	111.4(1)	Pt-Ru-C(1)	112.8(4)	Pt-C(3)-O(3)	115(1)	Pt-C(5)-O(5)	119(1)
W(2)-Ru-C(1)	114.8(5)	Pt-Ru-C(2)	88.4(4)	W(1)-C(4)-O(4)	177(2)	W(2)-C(6)-O(6)	157(1)
W(2)-Ru-C(2)	140.9(4)	Pt-Ru-C(6)	91.8(4)	W(2)-C(5)-O(5)	160(1)	Pt-C(11)-Ru	87.5(5)
W(2)-Ru-C(6)	44.1(4)	W(2)-Ru-C(11)	48.2(4)	Pt-C(11)-W(2)	82.1(5)	W(2)-C(11)-Ru	83.5(5)
Pt-Ru-C(11)	46.8(3)	Ru-C(2)-O(2)	177(1)				

lar in length to those found in (**1**) [2.715(1) and 2.711(1) Å],[12] and to the two Pt-W bonds in $[W_3Pt_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ [2.718(2) and 2.713(2) Å][2a] which are edge-bridged by *p*-tolylmethylidyne groups. The C(21)-W(1) distance [1.92(1) Å] is similar to the corresponding μ-C-W distances in $[W_3Pt_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu_3\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ [1.94(3) and 1.98(2) Å][2a] and in (**1**) [1.91(1) Å].[12] Similarly, the C(21)-Pt separation [2.03(1) Å] is essentially the same as the μ-C-Pt distances in (**1**) [2.02(1) Å]. Evidently addition of an $Ru(CO)_2(PMe_2Ph)$ group to one of the C=W linkages in complex (**1**) has little effect on the dimensions of the remaining three-membered μ-CWPt ring. The W(1) atom is co-ordinated by the C_5H_5 group and two CO ligands. However, C(3)O(3) semi-bridges the W(1)-Pt bond [170(1)°], but only weakly so. A similar structural feature is observed with (**1**) where one CO ligand on each tungsten atom deviates from linearity [W-C-O 167(1)°], adopting a weakly semi-bridging mode to the platinum.

Having established the structure of complex (**2b**) the spectroscopic properties are readily interpreted. The observation of six carbonyl stretching absorptions in the i.r. spectrum (see Experimental section) is as expected. The three bands at lowest frequency (1 843, 1 799, and 1 746 cm^{-1}) may be ascribed to the C(3)O(3), C(5)O(5), and C(6)O(6) groups. However, the relatively low frequencies associated with the two peaks at 1 799 and 1 746 cm^{-1} may imply that the two CO ligands which asymmetrically bridge the W(2)-Ru and W(2)-Pt bonds in the solid state become fully bridging when the complex is in solution.

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**2b**) shows diagnostic peaks[2] for the μ-C and μ_3-C nuclei at δ 311.5 and 286.6 p.p.m., respectively. As with (**2a**), only four CO resonances were observed (δ 229.8, 228.5, 219.0, and 215.0 p.p.m., with relative intensity 1 : 1 : 1 : 1), and these signals are attributed to carbonyl groups attached to the tungsten atoms. The absence of peaks due to the $Ru(CO)_2$ fragment must be due to dynamic behaviour. This may involve rotation of the $Ru(CO)_2(PMe_2Ph)$ group about an axis through the ruthenium and the midpoint of the C(11)WPt triangle, a process of a kind previously observed and requiring little energy.[13,14] Both the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra showed resonances indicating two non-equivalent C_5H_5 and two non-equivalent Me-4 groups. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed a single resonance at δ 16.1 p.p.m. The absence of any $^{183}W\text{-}^{31}P$ coupling is in accord with the PMe_2Ph group being bonded to the ruthenium. Interestingly, ^{195}Pt satellite peaks were not observed, even though the phosphine ligand is transoid to the platinum atom [P-Ru-Pt 158.7(1)°]. The absence of $^{195}Pt\text{-}^{31}P$ coupling may reflect the weakness of the Ru-Pt bond, discussed above.

The reaction between $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ and complex (**3**) was next investigated. In view of the formation of (**2a**) from the reaction between (**1**) and $[Ru(CO)_4(\eta\text{-}C_2H_4)]$, it might be anticipated that the ruthenium reagent would react by adding an $Ru(CO)_3$ fragment to the C=W bond of (**3**). However, since cod ligands attached to platinum are very labile in the presence of metal carbonyl fragments,[15] the reaction could well follow a more complicated pathway and this in fact occurred.

Treatment of a light petroleum solution of $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ with a solution of (**3**) in thf, employing 3 equivalents of the former reagent to one of the latter, gave a dark grey crystalline complex (**4**). This product was obtained irrespective of the stoicheiometry employed. It was identified as the hexanuclear metal cluster complex $[W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4\text{-}Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_9(\eta\text{-}C_5H_5)_2]$ by a single-crystal *X*-ray diffraction study. The structure is shown in Figure 2, and selected internuclear distances are listed in Table 2. It is evident that as a result of the reaction the cod ligand present in (**3**) has been lost, and migration of a *p*-tolylmethylidyne ligand from one tungsten centre to the other has occurred.

In compound (**4**) the five metal atoms W(2)Ru(1)Ru(2)Pt(1)-Pt(2) may to a first approximation be regarded as occupying the vertices of a trigonal bipyramid. However, the Pt(1) ··· Pt(2) [3.064(4) Å] and Ru(1) ··· Pt(2) [3.259(2) Å] separations are non-bonding. Within this group of metal atoms the other metal-metal connectivities are in general within the ranges expected (see above) for W-Ru, W-Pt, and Ru-Pt separations in clusters. However, the Pt(1)-Ru(2) [2.672(4) Å] and Pt(2)-Ru(2) [2.677(5) Å] distances are somewhat shorter than usual. The latter linkage is probably constrained by the bridging carbonyl group [Ru(2)-C(7)-O(7) 136(3), Pt(2)-C(7)-O(7) 143(4)°], but the former connectivity has no bridging ligand and the relative shortness of this bond may indicate a site of unsaturation within the cluster. The three CO ligands attached to Ru(1) are essentially linear, but the C(4)O(4), C(5)O(5), and C(6)O(6) groups bonded to Ru(2) all deviate by *ca.* 10° from the linear bonding mode (Table 2). The ligand C(8)O(8) co-ordinated to Pt(2) is also attached to this metal centre in a

Table 2. Selected internuclear distances (Å) and angles (°) for $[W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_9(\eta\text{-}C_5H_5)_2]$ (**4**) with estimated standard deviations in parentheses

W(1)–Pt(1)	2.663(3)	Pt(1)–Ru(1)	2.788(4)	Pt(1)–Ru(2)	2.672(4)	W(2)–Pt(1)	2.766(3)
W(2)–Ru(1)	2.758(4)	W(2)–Ru(2)	2.843(5)	W(2)–Pt(2)	2.739(3)	Pt(2)–Ru(2)	2.677(5)
Pt(2) ··· Ru(1)	3.259(2)	Pt(1) ··· Pt(2)	3.064(4)	Pt(1)–C(20)	2.11(3)	W(2)–C(20)	1.95(3)
Ru(1)–C(20)	2.11(3)	W(2)–C(30)	2.01(3)	Pt(2)–C(30)	2.14(3)	Ru(1)–C(30)	2.21(3)
W(1)–C(1)	1.99(4)	W(1)–C(2)	1.89(4)	W(1)–C(3)	1.97(3)	Pt(1)–C(3)	2.12(3)
C(1)–O(1)	1.12(4)	C(2)–O(2)	1.25(4)	C(3)–O(3)	1.24(4)	Pt(2)–C(7)	1.93(5)
Ru(2)–C(7)	2.21(5)	Ru(2)–C(4)	1.86(6)	Ru(2)–C(5)	1.95(6)	Ru(2)–C(6)	1.87(5)
C(7)–O(7)	1.20(5)	C(4)–O(4)	1.17(6)	C(5)–O(5)	1.17(6)	C(6)–O(6)	1.13(5)
Pt(2)–C(8)	1.78(5)	Ru(1)–C(9)	1.92(3)	Ru(1)–C(10)	2.08(4)	Ru(1)–C(11)	1.79(4)
C(8)–O(8)	1.19(5)	C(9)–O(9)	1.11(4)	C(10)–O(10)	1.06(4)	C(11)–O(11)	1.19(4)
W(1)–Pt(1)–W(2)	164.5(1)	Pt(1)–Ru(1)–W(2)	59.8(1)	Pt(1)–Ru(2)–W(2)	60.1(1)	Pt(1)–W(2)–Ru(1)	60.6(1)
W(1)–Pt(1)–Ru(1)	134.7(1)	Pt(1)–Ru(1)–C(20)	48.8(8)	Pt(1)–Ru(2)–Pt(2)	69.9(1)	Pt(1)–W(2)–Ru(2)	56.9(1)
W(1)–Pt(1)–Ru(2)	101.8(1)	Pt(1)–Ru(1)–C(30)	91.4(8)	W(2)–Ru(2)–C(7)	105(1)	Pt(1)–W(2)–Pt(1)	67.6(1)
W(1)–Pt(1)–C(20)	146.3(8)	Pt(1)–C(20)–W(2)	86(1)	Pt(2)–Ru(2)–C(7)	45(1)	Pt(1)–W(2)–C(20)	49.7(8)
Ru(1)–Pt(1)–Ru(2)	114.3(1)	Pt(1)–C(20)–Ru(1)	83(1)	Ru(2)–C(4)–O(4)	168(1)	Ru(1)–W(2)–C(20)	49.6(8)
W(1)–C(1)–O(1)	180(2)	Ru(1)–C(20)–W(2)	86(1)	Ru(2)–C(5)–O(5)	172(1)	Pt(2)–W(2)–Ru(1)	72.7(1)
W(1)–C(2)–O(2)	171(3)	Ru(1)–C(9)–O(9)	177(3)	Ru(2)–C(6)–O(6)	171(1)	Pt(2)–W(2)–Ru(2)	57.3(1)
W(1)–C(3)–O(3)	156(3)	Ru(1)–C(10)–O(10)	176(4)	Ru(2)–Pt(2)–C(8)	155(1)	W(2)–C(30)–Ru(1)	82(1)
Pt(1)–C(3)–O(3)	122(2)	Ru(1)–C(11)–O(11)	180(3)	Ru(2)–Pt(2)–W(2)	63.3(1)	W(2)–C(30)–Pt(2)	83(1)
Pt(2)–C(7)–O(7)	143(4)	Ru(2)–C(7)–O(7)	136(3)	Pt(2)–C(8)–O(8)	169(4)	Ru(1)–C(30)–Pt(2)	97(1)

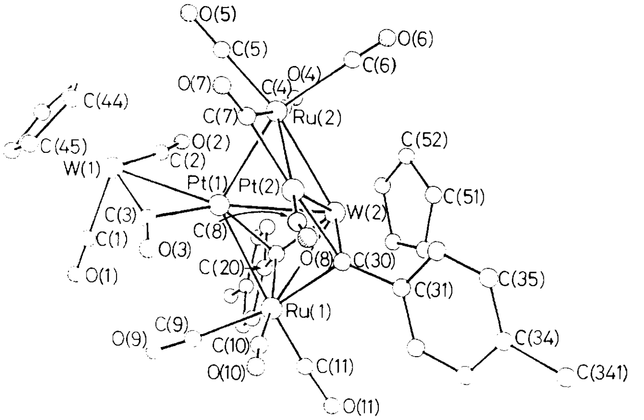


Figure 2. The molecular structure of $[W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_9(\eta\text{-}C_5H_5)_2]$ (**4**), showing the atom-labelling scheme

somewhat non-linear manner [Pt(2)–C(8)–O(8) 169(4)°]. There are two triply bridging *p*-tolylmethylidyne groups, one spanning the metal triangle W(2)Ru(1)Pt(1) and the other ligating W(2), Ru(1), and Pt(2).

The mode of attachment of W(1) to Pt(1) is of interest. The W(1)–Pt(1) [2.663(3) Å] distance is sufficiently short to suggest a W=Pt double bond. It may be compared with the tungsten–platinum distance of 2.602(1) Å found in the complexes $[WPt(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$[16a] and $[WPt(\mu\text{-}CO)_2(PEt_3)_2\{\eta^6\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)\text{-}Me_2\}]$,[16b] species for which W=Pt linkages have been invoked. The C(2)O(2) group shows a slight tendency to semi-bridge the W(1)–Pt(1) bond [W(1)–C(2)–O(2) 171(3)°]. However, C(3)O(3) asymmetrically bridges the metal–metal bond [W(1)–C(3)–O(3) 156(3), Pt(1)–C(3)–O(3) 122(2)°; W(1)–C(3) 1.97(3), Pt(1)–C(3) 2.12(3) Å]. Attempts to assign electron counts to the individual metal centres in complex (**4**) are somewhat unsatisfactory, but that depicted in the structural formula shown, with W=Pt and Pt→W bonds, has the merit of conferring 18 electrons at the tungsten and ruthenium centres and 16 electrons at the platinum atoms.

Having established the structure of compound (**4**) the spectroscopic data (Experimental section) are interpretable. Broad bands in the i.r. spectrum at 1 850 and 1 765 cm^{-1} are attributed to the μ-CO groups. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum revealed 11 CO resonances in accord with the asymmetry of the molecule. Moreover, this observation indicates that the compound does not undergo dynamic behaviour involving site exchange of carbonyl ligands, as do the species (**2**). There are two μ_3-C resonances at δ 269.1 and 254.3 p.p.m. There are also two peaks for the C_5H_5 rings, and two for the Me-4 groups. The ^1H n.m.r. spectrum also shows signals indicating the presence of two non-equivalent C_5H_5 and two non-equivalent Me-4 groups. The $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum has resonances for the non-equivalent platinum atoms at δ 1 273 and 893 p.p.m. [*J*(PtPt) 1 787 Hz].

The results described herein indicate that many mixed-metal cluster compounds are likely to be accessible by treating metal-chain complexes of the type shown in the Scheme with metal carbonyl fragments, derived from reagents like $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ having readily displaceable ligands. However, the composition and structures of the products isolated may well be unpredictable in most instances.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. Light petroleum refers to that fraction of b.p. 40—60 °C. Alumina used in chromatography columns (*ca.* 20 cm in length and 3.5 cm in diameter) was BDH aluminium oxide (Brockman Activity II). The compound $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ was prepared as described previously and used *in situ*.[5] The synthesis of the complexes (**1**)[12] and (**3**)[2a] has been reported earlier. The n.m.r. spectra were recorded with JEOL JNM FX90Q, GX270, and GX400 spectrometers. Chemical shifts are listed in p.p.m., and are relative to $SiMe_4$ for $^{13}C\text{-}\{^1H\}$, 85% H_3PO_4 (external) for $^{31}P\text{-}\{^1H\}$, and $\Xi(^{195}Pt)$ = 21.4 MHz for $^{195}Pt\text{-}\{^1H\}$. All δ values are positive to high frequency of the reference, and coupling constants are in Hz. Measurements, at room temperature unless otherwise stated, were in CD_2Cl_2 for ^1H spectra, and in CD_2Cl_2–CH_2Cl_2 for the other nuclei. The i.r. spectra were recorded in CH_2Cl_2 with Nicolet MX5 and MX10 spectrometers.

Synthesis of the Complexes $[W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(L)(\eta\text{-}C_5H_5)_2]$ (L = CO *or* PMe_2Ph).—(*i*)

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (**2b**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	9 042(1)	9 381(1)	8 881(1)	C(24)	12 916(18)	8 565(10)	7 826(8)
W(1)	8 855(1)	7 747(1)	9 248(1)	C(25)	13 946(17)	8 223(10)	8 063(7)
W(2)	8 069(1)	10 890(1)	8 509(1)	C(251)	15 336(16)	8 189(12)	7 808(9)
Ru	10 737(1)	10 813(1)	8 690(1)	C(26)	13 774(16)	7 910(10)	8 624(7)
P	11 615(4)	12 126(2)	8 803(2)	C(27)	12 582(15)	7 948(10)	8 868(7)
C(1)	11 785(16)	10 695(9)	8 036(7)	C(31)	12 578(20)	12 296(11)	9 431(10)
O(1)	12 389(13)	10 608(7)	7 651(5)	C(32)	12 746(19)	12 439(11)	8 255(10)
C(2)	11 992(15)	10 307(9)	9 173(6)	C(34)	10 215(11)	13 522(6)	8 385(4)
O(2)	12 762(12)	10 017(7)	9 438(5)	C(35)	9 327	14 195	8 426
C(3)	7 242(18)	8 489(8)	9 251(7)	C(36)	8 649	14 334	8 919
O(3)	6 235(11)	8 816(7)	9 287(6)	C(37)	8 859	13 802	9 371
C(4)	9 345(18)	8 225(11)	9 982(7)	C(38)	9 748	13 130	9 330
O(4)	9 641(15)	8 470(7)	10 414(5)	C(33)	10 426	12 990	8 836
C(5)	8 160(15)	9 800(9)	8 089(7)	C(71)	8 739(15)	6 596(9)	8 618(4)
O(5)	8 056(12)	9 298(6)	7 716(4)	C(72)	7 579	6 572	8 947
C(6)	9 320(18)	11 340(10)	7 966(8)	C(73)	7 963	6 437	9 504
O(6)	9 670(12)	11 726(8)	7 573(5)	C(74)	9 360	6 377	9 520
C(11)	9 150(13)	10 612(7)	9 206(5)	C(75)	9 840	6 476	8 973
C(12)	8 962(14)	10 583(8)	9 818(5)	C(81)	6 436(13)	11 660(7)	8 056(4)
C(13)	7 788(14)	10 321(9)	10 056(6)	C(82)	6 832	12 117	8 534
C(14)	7 626(16)	10 202(9)	10 611(6)	C(83)	6 476	11 634	9 005
C(15)	8 645(18)	10 294(9)	10 955(7)	C(84)	5 859	10 878	8 820
C(151)	8 550(26)	10 069(13)	11 581(7)	C(85)	5 834	10 894	8 233
C(16)	9 823(20)	10 633(10)	10 748(8)	C(71A)	8 727(30)	6 352(18)	9 633(8)
C(17)	10 026(16)	10 770(10)	10 183(6)	C(72A)	9 883	6 401	9 303
C(21)	10 246(15)	8 356(7)	8 884(6)	C(73A)	9 490	6 554	8 749
C(22)	11 461(14)	8 308(7)	8 614(6)	C(74A)	8 092	6 599	8 736
C(23)	11 660(14)	8 590(9)	8 060(6)	C(75A)	7 620	6 474	9 282

Table 4. Fractional atomic co-ordinates (× 10^4) for complex (**4**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	181(1)	923(1)	−513(1)	O(11)	−906(34)	1 321(7)	−3 191(17)
Pt(2)	1 155(2)	1 544(1)	−325(1)	C(20)	−1 364(30)	1 028(6)	−1 293(14)
W(1)	1 645(2)	506(1)	125(1)	C(22)	−3 392(23)	676(5)	−1 095(8)
W(2)	−1 533(2)	1 392(1)	−804(1)	C(23)	−4 297	453	−1 305
Ru(1)	449(3)	1 210(1)	−1 793(1)	C(24)	−4 148	334	−1 975
Ru(2)	−539(4)	1 256(1)	574(2)	C(25)	−3 094	438	−2 435
C(1)	1 590(41)	257(9)	−728(20)	C(26)	−2 189	660	−2 225
O(1)	1 561(32)	117(6)	−1 204(15)	C(21)	−2 338	780	−1 555
C(2)	−395(43)	485(8)	177(20)	C(241)	−5 021(39)	75(8)	−2 176(18)
O(2)	−1 709(34)	434(7)	254(15)	C(30)	11(37)	1 624(7)	−1 282(17)
C(3)	2 408(36)	816(7)	−471(16)	C(32)	63(34)	2 156(8)	−1 171(13)
O(3)	3 352(27)	967(6)	−744(13)	C(33)	235	2 425	−1 477
C(4)	−2 289(69)	1 060(13)	549(30)	C(34)	343	2 452	−2 207
O(4)	−3 411(37)	951(8)	657(17)	C(35)	279	2 209	−2 633
C(5)	123(62)	1 086(12)	1 457(31)	C(36)	107	1 940	−2 327
O(5)	666(40)	972(8)	1 937(19)	C(31)	−1	1 913	−1 597
C(6)	−1 137(54)	1 592(11)	1 017(26)	C(341)	556(83)	2 767(16)	−2 457(47)
O(6)	−1 664(43)	1 775(9)	1 307(20)	C(41)	3 350(29)	150(5)	528(14)
C(7)	1 714(50)	1 415(10)	601(24)	C(42)	2 084	145	952
O(7)	2 636(38)	1 440(7)	1 040(17)	C(43)	1 956	415	1 289
C(8)	2 662(54)	1 757(10)	−568(22)	C(44)	3 142	587	1 074
O(8)	3 538(42)	1 938(9)	−678(19)	C(45)	4 003	423	603
C(9)	1 222(36)	847(8)	−2 079(17)	C(51)	−3 027(34)	1 795(6)	−747(17)
O(9)	1 611(28)	631(6)	−2 228(14)	C(52)	−3 599	1 598	−251
C(10)	2 411(42)	1 404(8)	−2 041(19)	C(53)	−4 090	1 354	−627
O(10)	3 369(32)	1 517(7)	−2 176(15)	C(54)	−3 823	1 401	−1 354
C(11)	−365(38)	1 275(8)	−2 632(20)	C(55)	−3 166	1 673	−1 429

A thf (50 cm^3) solution of complex (**1**) (0.40 g, 0.40 mmol) was treated with $[Ru(CO)_4(\eta-C_2H_4)]$ {generated from 0.13 mmol of $[Ru_3(CO)_{12}]$} dissolved in light petroleum (80 cm^3). A cannula [flexible stainless-steel tubing 50 cm × 1 mm (internal diameter)] and ethylene pressure were used to effect transfer of the ruthenium compound. The mixture was stirred for 30 min, and then solvent was removed *in vacuo*. The residue was dissolved in toluene–light petroleum (5 cm^3, 1:1), and chromatographed at −20 °C. Elution with the same solvent mixture gave a green fraction from which solvent was removed *in vacuo* to afford green *microcrystals* of $[W_2RuPt(\mu-CC_6H_4-Me-4)(\mu_3-CC_6H_4Me-4)(CO)_7(\eta-C_5H_5)_2]$ (**2a**) (0.30 g, 63%) (Found: C, 33.1; H, 2.2. $C_{33}H_{24}O_7PtRuW_2$ requires C, 33.1; H, 2.0%), crystallised from toluene–light petroleum (*ca.* 1:1) at −78 °C. For (**2a**), $\nu_{max.}$(CO) at 2 055vs, 2 030w, 2 001vs, 1 986s, 1 922(sh), 1 856m, and 1 824m cm^{-1}. N.m.r.: ^1H, δ 2.22 (s, 3

H, Me-4), 2.41 (s, 3 H, Me-4), 5.35 (s, 5 H, C_5H_5), 5.46 (s, 5 H, C_5H_5), 6.84, 7.05 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], and 7.15, 7.48 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 5]; $^{13}C-\{^1H\}$ (at −40 °C), δ 312.4 (μ-C), 282.3 (μ_3-C), 232.7, 232.4, 228.1, 214.3 (WCO), 156.0—124.7 (C_6H_4), 92.6, 92.0 (C_5H_5), 22.0, and 21.3 p.p.m. (Me-4); $^{195}Pt-\{^1H\}$, δ 1 057 p.p.m. [*J*(PtW) 75 Hz].

(*ii*) A thf (50 cm^3) solution of complex (**2a**) (0.10 g, 0.10 mmol) was treated with PMe_2Ph (0.014 g, 0.10 mmol) in light petroleum (2 cm^3). The mixture was stirred for 24 h, and then the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–light petroleum (3 cm^3, 1:1) and chromatographed. Elution with the same solvent mixture yielded a green eluate. Solvent was removed *in vacuo*, and the residue was crystallised from toluene at −78 °C to give dark green *crystals* of $[W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)(\eta\text{-}C_5H_5)_2]$ (**2b**) (0.09 g, 69%) (Found: C, 36.6; H, 3.0. $C_{40}H_{35}O_6PPtRuW_2$ requires C, 36.8; H, 2.7%); $\nu_{max.}$(CO) at 1 998s, 1 951vs, 1 898m, 1 843m, 1 799m, and 1 746m cm^{-1}. N.m.r.: ^1H, δ 1.57 [d, 6 H, PMe_2, *J*(PH) 0.5], 2.21 (s, 3 H, Me-4), 2.39 (s, 3 H, Me-4), 5.20 (s, 5 H, C_5H_5), 5.43 (s, 5 H, C_5H_5), and 6.89—7.29 (m, 13 H, C_6H_4 and Ph); $^{13}C-\{^1H\}$, δ 311.5 (μ-C), 286.6 (μ_3-C), 229.8, 228.5, 219.0, 215.0 (WCO), 155.8—129.1 (C_6H_4 and Ph), 92.5, 91.5 (C_5H_5), 21.8, 21.0 (Me-4), 19.4, and 19.0 p.p.m. (P*Me*$_2$Ph); $^{31}P-\{^1H\}$, δ 16.1 p.p.m.

Synthesis of the Complex $[W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_9(\eta\text{-}C_5H_5)_2]$.—A light petroleum (100 cm^3) solution of $[Ru(CO)_4(\eta\text{-}C_2H_4)]$ (0.47 mmol) was treated with a thf (25 cm^3) solution of complex (**3**) (0.20 g, 0.15 mmol). The mixture was then stirred for 18 h at room temperature. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed. Elution with the same solvent mixture removed a trace of $[Ru_3(CO)_{12}]$ followed by a grey band. This second eluate was collected, and the solvent was removed *in vacuo*. Crystallisation of the residue at −20 °C from CH_2Cl_2–EtOH (10 cm^3, 1:5) afforded dark grey *crystals* of $[W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_9(\eta\text{-}C_5H_5)_2]$ (**4**) (0.11 g, 46%) (Found: C, 37.2; H, 2.6. $C_{37}H_{24}O_{11}Pt_2Ru_2W_2$ requires C, 36.6, H, 2.4%); $\nu_{max.}$(CO) at 2 082m, 2 050s, 2 038vs, 1 980m, 1 892m, 1 850w br, and 1 765w br cm^{-1}. N.m.r.: ^1H, δ 2.37 (s, 3 H, Me-4), 2.40 (s, 3 H, Me-4), 5.22 (s, 5 H, C_5H_5), 5.32 (s, 5 H, C_5H_5), and 7.08—7.29 (m, 8 H, C_6H_4); $^{13}C-\{^1H\}$, δ 269.1, 254.3 (μ_3-C), 235.4, 228.1, 206.5, 199.7, 199.0, 194.6, 193.7, 192.5, 190.8, 190.7, 190.3 (CO), 160.2, 153.1 [$C^1(C_6H_4)$], 137.1—126.0 (C_6H_4), 95.5, 89.0 (C_5H_5), 21.0, and 20.9 p.p.m. (Me-4); $^{195}Pt-\{^1H\}$, δ 1 273 [*J*(PtPt) 1 787] and 893 p.p.m. [*J*(PtPt) 1 787 Hz].

Crystal Structure Determinations.—Crystals of complexes (**2b**) and (**4**) grow as dark-green and black prisms from toluene (−78 °C) and CH_2Cl_2–ethanol (−20 °C), respectively. Crystals of suitable dimensions [*ca.* 0.30 × 0.33 × 0.15 mm for (**2b**) and *ca.* 0.30 × 0.40 × 0.70 mm for (**4**)] were sealed under nitrogen in Lindemann glass capillaries. Diffracted intensities were collected (θ—2θ scans) at 298 K, in the range $2.9 \leqslant 2\theta \leqslant 50°$, on a Nicolet *P*3*m* four-circle diffractometer. Of 4 235 unique reflections for (**2b**), 3 479 had $F \geqslant 3\sigma(F)$; and of 7 121 unique reflections for (**4**), 3 846 had $F \geqslant 6\sigma(F)$. Only these data were used in the solution and refinement of the structures, after corrections for Lorentz, polarisation, and *X*-ray absorption effects. The latter was by an empirical method based on azimuthal scan data.[17]

Crystal data for complex (**2b**). $C_{40}H_{35}O_6PPtRuW_2$, M = 1 306, orthorhombic, a = 10.137(2), b = 15.778(4), c = 24.200(5) Å, U = 3 871(1) Å^3, Z = 4, D_c = 2.25 g cm^{-3}, F(000) 2 431, space group $P2_12_12_1$ (no. 19), Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 101.5 cm^{-1}.

Crystal data for complex (**4**). $C_{37}H_{24}O_{11}Pt_2Ru_2W_2$, M = 1 604, orthorhombic, a = 9.246(4), b = 46.799(8), c = 18.972(5) Å, U = 8 209(4) Å^3, Z = 8, D_c = 2.61 g cm^{-3}, F(000) 5 806, space group *Pbnb* (non-standard setting of no. 56, *Pccn*), μ(Mo-K_α) = 133.0 cm^{-1}.

The structures were solved, and all non-hydrogen atoms located, by conventional heavy-atom and Fourier difference methods. Refinements were performed by blocked-cascade least squares on a Data General S230 'Eclipse' computer for complex (**2b**), and on a Digital μ-Vax computer for (**4**).[17] For (**2b**) all non-hydrogen atoms, apart from the carbon atoms of the C_5H_5 rings, were refined anisotropically, while for (**4**) only the metal atoms were refined anisotropically. The C_5H_5 group ligating W(1) in (**2b**) was disordered with 66:33 site occupancy [C(71)—C(75), C(71a)—C(75a)]. The C_6H_4Me-4 and C_5H_5 groups in (**4**), and all C_5H_5 groups in (**2b**), were constrained to ideal geometries, and refined as rigid groups. All hydrogen atoms were included at calculated positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for the methyl hydrogen atoms and fixed isotropic thermal parameters (*ca.* 1.2 $U_{equiv.}$ of the parent carbon atom) for all other hydrogen atoms. Refinements, with weighting schemes $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ [with g = 0.000 135 for (**2b**) and 0.003 for (**4**)], converged at R = 0.039 (R' = 0.032) (**2b**) and R = 0.066 (R' = 0.072) (**4**). The enantiomer test for complex (**2b**) showed that the given co-ordinates correspond to the correct isomer. At an earlier stage of isotropic refinement $R(-)$ 0.059 compared with $R(+)$ 0.044 for the given isomer. The final electron-density difference syntheses showed no residual peaks $\geqslant 0.87$ or $\leqslant -1.02$ e Å^{-3} for (**2b**), and $\geqslant 2.0$ or $\leqslant -1.30$ e Å^{-3} for (**4**), close to the metal atoms. Scattering factors and corrections for anomalous dispersion were taken from ref. 18. The atomic co-ordinates for (**2b**) and (**4**) are listed in Tables 3 and 4, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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