Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 28.[1] Synthesis and *X*-Ray Crystal Structures of the Compounds $[MoW_2(\mu\text{-}CR)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[AuW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ ($R = C_6H_4Me\text{-}4$) *

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The compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) reacts readily with the complexes $[M(CO)_3(NCMe)_3]$ (M = Mo or W) in hexane at reflux to afford the trimetal compounds $[MW_2(\mu\text{-}CR)_2(\mu\text{-}\sigma{:}\eta^2\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$, n.m.r. and i.r. data for which are reported. The molybdenum–ditungsten compound was fully characterised structurally by a single-crystal *X*-ray diffraction study. It comprises a bent W–Mo–W spine [148.2(2)°] with the Mo–W bonds [2.938(1) Å] bridged by $CC_6H_4Me\text{-}4$ groups. The Mo atom carries two terminal carbonyl ligands; the bisector of the angle between these is an approximate axis of two-fold symmetry for the molecule as a whole. The two molybdenum–tungsten–carbene ring systems are not coplanar, but are twisted relative to one another so that the two planes are nearly orthogonal. The Mo–W and Mo–C(carbene) bonds do not form a pseudo-tetrahedral group, however, because of the presence of two *cis* carbonyl ligands on the central Mo atom. An especially interesting feature is that, of the two terminal carbonyl ligands on each tungsten atom, one is η^2-bonded to the central molybdenum atom. The significance of this is discussed. Crystals are triclinic, space group $P\bar{1}$ (no. 2), and the structure has been refined to $R = 0.038$ for 3 711 intensities measured to $2\theta = 55°$ at 210 K. Treatment of chloro(tetrahydrothiophene)gold(I) with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ in tetrahydrofuran in the presence of $TlPF_6$ affords the salt $[AuW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$, while $[Ag(NCMe)_4][BF_4]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ give $[AgW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$. The spectroscopic data (i.r. and n.m.r.) for these gold and silver compounds are discussed, and the structure of the former has been established by *X*-ray diffraction. The cation has a bent W–Au–W spine [162.8(1)°] with the Au–W bonds [2.752(1) Å] bridged by the $CC_6H_4Me\text{-}4$ groups. The dihedral angle between the two dimetallacyclopropene rings is 62°. The tungsten atoms carry $\eta\text{-}C_5H_5$ groups and two terminally bound CO ligands. Crystals are orthorhombic, space group *Pnna* (no. 52), and the structure has been refined to $R = 0.050$ for 1 654 reflections measured to $2\theta = 50°$ at 200 K.

The tolylmethylidynetungsten compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ has proved to be a useful reagent for preparing a wide range of heteronuclear di- and tri-metal complexes *via* its reactions with low-valent metal species.[2] The Scheme summarises for the trimetal species the core structures so far identified. Four general classes (A—D) have been observed. In class A a μ-CR ($R = C_6H_4Me\text{-}4$) ligand triply bridges the groups WM_2 or WMM′, in which direct M–M or M–M′ bonding may or may not occur. Examples of class A compounds are: (i) $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$,[3] (ii) $[Pt_2W(\mu_3\text{-}CR)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$,[4] (iii) $[CuPtW(\mu_3\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$,[5] and (iv) $[FeRhW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$.[6] In compounds of class B two carbyne groups couple to form an alkyne ligand which co-ordinates to the metal triangle in either a $\mu_3\text{-}(\eta^2\text{-}\perp)$ or a $\mu_3\text{-}(\eta^2\text{-}\parallel)$ bonding mode, *e.g.* (i) $[FeW_2(\mu_3\text{-}RC_2R)(CO)_6(\eta\text{-}C_5H_5)_2]$,[7] and (ii) or (iii) $[OsW_2(\mu_3\text{-}RC_2R)(CO)_7(\eta\text{-}C_5H_5)_2]$.[8] The class C core structure contains both μ_2- and μ_3-CR groups, a situation found recently in the compound $[ReW_2(\mu\text{-}Br)(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$.[9] Class C species may be intermediates in the formation of type B compounds. The final class D {*e.g.* $[PtW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [10]} is especially interesting since the two dimetallacyclopropene rings joined at M are unsaturated, and are capable of adding other metal–ligand fragments.[11] In this paper we describe the results of a search for further examples of trimetal compounds with structures of type D.[11,12]

Results and Discussion

The isolobal [13] relationship between the species RC≡CR and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ provided the impetus for the synthesis of the compounds $[MW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Ni, Pd, or Pt).[10] However, in these complexes, as in the structurally related compounds $[Pt(RC_2R)_2]$,[14] the formal electron count at the d^{10}-metal centre is a matter of conjecture. Nevertheless, the nature of the bonding at platinum, palladium, or nickel has to be considered, since it may be relevant to the existence of other complexes of type D (Scheme). Platinum(0) compounds are known in which the metal has 14-, 16-, or 18-electron configurations as found in $[Pt\{P(cyclo\text{-}C_6H_{11})_3\}_2]$, $[Pt(C_2H_4)_3]$, and $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene), respectively. If the carbyne ligands in $[PtW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ act as two-electron donors there would be only a 14-electron count at platinum, unless the two CO ligands semi-bridging the Pt–W bonds serve to increase the electron density at the platinum. However, the bonding mode of these CO groups [10] suggests, on the basis of earlier arguments,[15] that the platinum centre is electron rich

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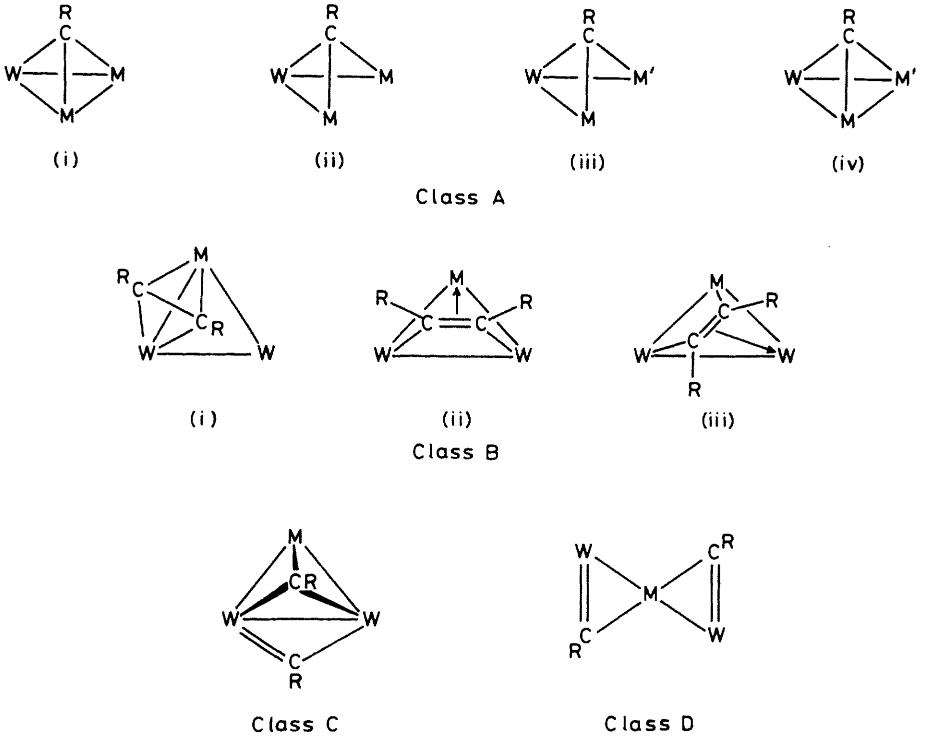
* 1,2;2,3-Di-μ-σ:η-carbonyl-*C*(W)*CO*(Mo)-1,2,2,3-tetracarbonyl-1,3-di-η-cyclopentadienyl-1,2;2,3-di-μ-*p*-tolylmethylidyne-molybdenumditungsten(2 *Mo–W*) and 1,1,3,3-tetracarbonyl-1,3-di-η-cyclopentadienyl-1,2;2,3-di-μ-*p*-tolylmethylidyne-gold-ditungsten-(1+)(2 *Au–W*) hexafluorophosphate.

Supplementary data available (No. SUP 23916, 51 pp.): atom co-ordinates, all thermal parameters, full bond length and angle data, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme. Core structures of trimetal compounds derived from $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$. W = $W(CO)_2(\eta\text{-}C_5H_5)$, ligands on M and M′ omitted for clarity. Class A, (i) M = Mo, W, Fe, Co, Rh, or Ni; (ii) M = Cu or Pt; (iii) M = Cu, M′ = Pt; (iv) M = Fe, M′ = Co, Rh, or Pt. Class B, (i) M = Fe; (ii) and (iii) M = Ru or Os. Class C, M = Re. Class D, M = Ni, Pd, or Pt

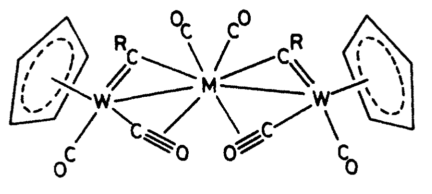
rather than electron deficient. If this is the case it would imply that the C≡W fragments function as four-electron donors giving platinum an 18-electron shell. This is not unreasonable since alkynes in certain complexes contribute four electrons to a transition element.[16,17] However, somewhat against this possibility is the observation that in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the isolobal compounds $[Pt(RC_2R)_2]$ the chemical shifts of the ligated carbon atoms (*ca.* 125 p.p.m.) fall in the range expected [18] for species in which the alkynes function as two-electron donors.

Whereas an electron count less than 18 at platinum (*viz.* 14 or 16) is acceptable in $[PtW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$, based on the known chemistry of this element, other metals have a preference for 18-electron configurations in their low-valent compounds. This is true for Mo and W, and in envisaging the syntheses of other core structures akin to D (Scheme) we were led to Hoffmann's [13] parallel between ML_n and EL_n fragments (M = transition metal, E = main group element, L = electron-pair donor group). This relates a free Pt (d^{10}) atom with C^{4+}, and with $M(CO)_2$ (M = Mo or W, d^6), in the sense that all three species possess four vacant and similar orbitals which can accept eight electrons. Hence, if in compounds of class D an $Mo(CO)_2$ or $W(CO)_2$ group occupies the position M, the W≡C moieties may be forced into functioning as four-electron donors because of the aforementioned preference of Mo or W for an 18-electron shell.

The kinetic inertness of tungsten or molybdenum hexacarbonyls made it unlikely that compounds of formulation $[MW(\mu\text{-}CR)_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) could be prepared by heating the hexacarbonyls with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$. Hence the reagents $[M(CO)_3(NCMe)_3]$ with their labile acetonitrile ligands seemed more promising precursors.[19]

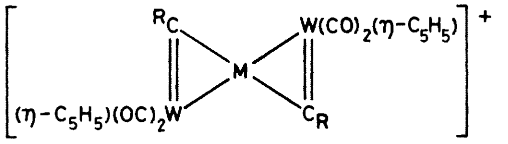
Refluxing mixtures of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[M(CO)_3(NCMe)_3]$ (M = Mo or W) in hexane afforded deep red-violet crystalline compounds (1) and (2), respectively. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of both complexes showed characteristic resonances for μ-*C*R groups [(1), δ 360.1; (2), δ 376.2 p.p.m.]. In the cluster compound $[ReW_2(\mu\text{-}Br)(\mu\text{-}CR)(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$ the W–W edge-bridging *C*R group gives a signal at δ 364.9.[9] An interesting feature of the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (1) and (2), however, was the observation of peaks corresponding to CO ligands in three chemically different environments, with relative intensity 2 : 2 : 2. In the spectrum of (1) two of the signals showed $^{183}W\text{-}^{13}C$ coupling, implying that the resonance which did not was due to an $Mo(CO)_2$ group. The i.r. spectra of (1) and (2) in the carbonyl-stretching region were also informative. Both spectra (in Nujol) showed six bands, one of which [(1), 1 696; (2), 1 728 cm^{-1}] was of sufficiently low frequency to suggest the presence of a CO ligand adopting a σ:η^2-bridge-bonding mode.[20] Clearly, to establish the molecular structures of these compounds an *X*-ray diffraction study on one or other was essential. Fortunately, suitable crystals of (1) were grown.

The results of the *X*-ray diffraction study are summarised in Table 1 and the structure is shown in Figure 1 with the crystallographic numbering scheme. It can be seen at once that the molecule possesses approximate two-fold rotational symmetry (not required crystallographically), the direction of the axis being the bisector of the angle between the two terminal carbonyl ligands on the central molybdenum atom. The W–Mo–W spine of the molecule is bent to give an angle at the Mo atom of 148.2(2)°, and each Mo–W bond is bridged by a $CC_6H_4Me\text{-}4$ ligand. As would be expected because of the molecular symmetry, the two Mo–W bonds are equal [2.938(1) Å], but the geometry is inevitably somewhat different from that [10] in the trimetal compounds $[MW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Ni, Pd, or Pt) because of the



	M
(1)	Mo
(2)	W

R = C_6H_4Me-4



	M	R	X
(3)	Au	C_6H_4Me-4	PF_6
(4)	Ag	C_6H_4Me-4	BF_4

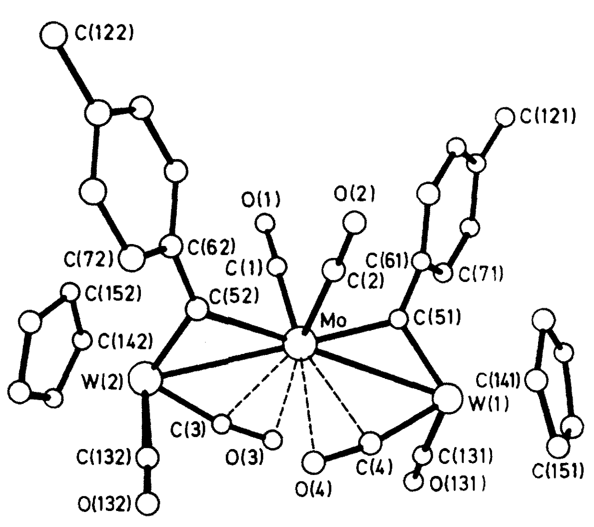


Figure 1. Molecular structure of [MoW_2(μ-CC_6H_4Me-4)$_2$(μ-CO)$_2$(CO)$_4$(η-C_5H_5)$_2$] (1) showing the crystallographic numbering

additional presence in the title compound of two *cis* terminal carbonyl ligands on the central molybdenum atom. It is not, therefore, unexpected that the angle of bend in the metal atom chain for (1) is substantially less than was found[10] for [NiW_2(μ-CR)$_2$(CO)$_4$(η-C_5H_5)$_2$] (175°) and for [PtW_2(μ-CR)$_2$(CO)$_4$(η-C_5H_5)$_2$] (165°). For both of the last two mentioned compounds a pseudo-tetrahedral geometry prevails, though of course the bond angles around the central metal atom suffer severe distortion because of the constraints imposed by the dimetallacyclopropene rings. Similar considerations to those discussed in ref. 10 will, however, apply to (1) and need not be repeated here. The bond distances in (1) again imply that the μ-C–W bonds have an order of *ca.* 2, and that there is considerable delocalisation of the bonding in the dimetallacyclopropene rings. The W=C distances in (1) are actually slightly longer [mean 1.944(12) Å] than those found in [PtW_2(μ-CR)$_2$(CO)$_4$(η-C_5H_5)$_2$], where a mean value of 1.907(13) Å was measured.[10]

In the nickel and platinum pseudo-tetrahedral complexes it was found that one of the carbonyl ligands on each tungsten atom adopted a semi-bridging relationship to the platinum atom, this carbonyl bridge being coplanar with the dimetallacyclopropene ring. In (1) an extremely interesting situation arises in that one of the carbonyl ligands on each tungsten atom is here η^2-bonded to the central molybdenum atom. The tungsten–carbon–oxygen bonds remaining virtually linear (Table 1). Again, the tungsten–carbonyl bonds lie in the plane of the dimetallacyclopropene rings but on the opposite side of the Mo–W bond. Because the two CO ligands adopt a σ:η^2-bonding mode, the central Mo atom acquires a filled shell without the two C≡W groups functioning as four-electron donors (see above discussion). The second, terminal, carbonyl ligand on each W atom lies approximately perpendicular to the dimetallacyclopropene planes: torsion angles Mo–C(51)–W(1)–C(131) 93.8(1), Mo–C(52)–W(2)–C(132) 93.0(1)°.

The two *cis* terminal carbonyl ligands on the central Mo atom are at an interaxial angle [C(1)–Mo–C(2)] of 88.7(5)°, and each lies approximately perpendicular to one of the dimetallacyclopropene rings. This angle is therefore also an approximate measure of the dihedral angle between the two dimetallacyclopropene rings; however, care should be exercised in comparing this value with that for the pseudo-tetrahedral Ni and Pt complexes because of the extra distortion introduced by the terminal CO ligands on the central Mo atom. The non-linearity of the W–Ni–W and W–Pt–W spines was ascribed[10] to the bulkiness of the tolyl ligands which occupy the convex side of the spine. In (1) the terminal carbonyl ligands on the Mo atom also occupy the centre of the convex side of the spine, so the distortions are correspondingly larger.

Finally, the tolyl groups of the bridging carbene ligands are twisted symmetrically relative to the planes of the dimetallacyclopropene rings by *ca.* 72° [torsion angles: W(1)–C(51)–C(61)–C(71) 72.1(2), W(2)–C(52)–C(62)–C(72) 71.0(2)°].

Some reactions of compounds (1) and (2) have been investigated. Both complexes in dichloromethane react with CO readily at room temperature and at atmospheric pressure, with the reaction involving (1) (minutes) proceeding more rapidly than that of (2) (hours). Chromatography of the products from the latter reaction led to the identification (i.r.) of [$W(CO)_6$], [W(≡CR)(CO)$_2$(η-C_5H_5)], and a compound with a spectrum (hexane solution) with CO-stretching bands at 2 072w, 2 005m, 1 953s, and 1 936s cm^{-1}. These frequencies correspond very closely to those reported[21] for the compound [W_2(≡CPh)(CO)$_7$(η-C_5H_5)] in which the carbyne ligand is terminally bound to one of the tungsten atoms. It is reasonable to suppose that treatment of (2) with CO would displace [W(≡CR)(CO)$_2$(η-C_5H_5)] affording an intermediate, [W_2(≡CR)(CO)$_7$(η-C_5H_5)], which with additional CO would give [$W(CO)_6$] and a second equivalent of [W(≡CR)(CO)$_2$(η-C_5H_5)]. In our original communication[12] we formulated the intermediate as [W_2(μ-CR)(CO)$_7$(η-C_5H_5)], with a dimetallacyclopropene structure. However, in view of the results of Fischer *et al.*,[21] in which [W_2(≡CPh)(CO)$_7$(η-C_5H_5)] was synthesised from [W(≡CPh)Br(CO)$_4$] and Na[W(CO)$_3$(η-C_5H_5)], it seems likely that the labile species observed in the CO treatment of (2) is a compound with a *trans*-W–W≡CC_6H_4Me-4 structure. From the mixture obtained by passing CO through a CH_2Cl_2 solution of (1) the compounds [$Mo(CO)_6$] and [W(≡CR)(CO)$_2$(η-C_5H_5)] were identified as the only products.

An attempt was made to displace two of the CO ligands in

Table 1. Selected bond distances (Å) and angles (°) for $[MoW_2(\mu-CC_6H_4Me-4)_2(\mu-CO)_2(CO)_4(\eta-C_5H_5)_2]$ (1)

(*a*) Distances

Mo–W(1)	2.938(1)	Mo–W(2)	2.938(1)	Mo–O(4)	2.522(8)	Mo–O(3)	2.525(10)
Mo–C(51)	2.202(11)	Mo–C(52)	2.189(14)	Mo–C(1)	1.973(13)	Mo–C(2)	1.986(13)
W(1)–C(51)	1.940(13)	W(2)–C(52)	1.949(11)	C(1)–O(1)	1.15(2)	C(2)–O(2)	1.13(2)
C(51)–C(61)	1.459(12)	C(52)–C(62)	1.45(3)	W(1)–C(131)	1.994(14)	W(2)–C(132)	1.979(12)
W(1)–C(4)	1.923(10)	W(2)–C(3)	1.918(15)	C(131)–O(131)	1.12(2)	C(132)–O(132)	1.153(15)
C(4)–O(4)	1.197(13)	C(3)–O(3)	1.19(2)				
Mo–C(4)	2.348(14)	Mo–C(3)	2.355(12)	W(1)–C (cp, mean) *	2.35(2)	W(2)–C (cp, mean) *	2.34(2)

(*b*) Angles

W(1)–Mo–W(2)	148.2(2)	C(1)–Mo–C(2)	88.7(5)	W(1)–C(131)–O(131)	174.2(9)	W(2)–C(132)–O(132)	174.2(14)
C(51)–Mo–W(2)	153.7(3)	C(52)–Mo–W(1)	152.9(3)	W(1)–C(4)–O(4)	170.2(12)	W(2)–C(3)–O(3)	169.7(10)
Mo–C(51)–W(1)	90.1(3)	Mo–C(52)–W(2)	90.3(5)	Mo–C(1)–O(1)	178.2(13)	Mo–C(2)–O(2)	178.1(10)
C(51)–W(1)–C(131)	89.5(6)	C(52)–W(2)–C(132)	89.7(5)	C(51)–Mo–C(2)	82.8(5)	C(52)–Mo–C(1)	83.5(5)
C(51)–W(1)–C(4)	101.4(5)	C(52)–W(2)–C(3)	101.2(5)	W(1)–Mo–C(2)	86.4(4)	W(2)–Mo–C(1)	87.3(4)
C(131)–W(1)–C(4)	91.3(5)	C(132)–W(2)–C(3)	90.4(6)				

* cp = $\eta-C_5H_5$.

(2) with $Ph_2PCH_2PPh_2$ (dppm). No reaction occurred at room temperature in the absence of CO. However, in the presence of the latter the products were $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ and the known compound $[W(CO)_4(dppm)]$.[22] The reaction between (2) and $[Co_2(CO)_8]$ was also studied in an attempt to add $Co(CO)_3$ fragments [3] to the dimetallacyclopropene rings of the tritungsten compound. However, the only products of this reaction, carried out at room temperature, were $[W(CO)_6]$, $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$, $[Co_4(CO)_{12}]$, and unreacted (2). Evidently $[Co_2(CO)_8]$ merely acted as a source of CO, thereby producing the tetracobalt dodecacarbonyl.

In extending the range of compounds with core structures of type D (Scheme), the possibility arises of preparing a gold–tungsten salt $[AuW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2][PF_6]$ (3), isoelectronic with $[PtW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$. With this objective, the compound [AuCl(tht)] (tht = tetrahydrothiophene) was added to a mixture of $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ and $TlPF_6$ in tetrahydrofuran (thf). Reaction occurred to produce (3) in high yield. The $^{13}C-\{^1H\}$ n.m.r. spectrum of (3) showed a characteristic resonance for the ligated carbons of the carbyne groups at δ 295.8 [*J*(WC) 153 Hz]. The i.r. spectrum had two CO-stretching bands at 2 024 and 1 969 cm^{-1}. Not unexpectedly, in view of the salt-like nature of (3), these peaks occur at higher frequencies than the three observed (1 965, 1 942, and 1 828 cm^{-1}) in the spectrum of $[PtW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$. The band at 1 828 cm^{-1} in the spectrum of the latter is ascribed to the semi-bridging CO groups. Hence, it would appear that the gold–ditungsten cation differs in structure from $[PtW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$ in not containing semi-bridging carbonyl ligands, a point discussed further below.

Solutions of (3) are instantly decomposed by exposure to CO, the only product isolated being $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$. The latter is also formed readily on treating (3) with PPh_3, but in this reaction the gold is captured as the salt $[Au(PPh_3)_2][PF_6]$. In contrast, the compound $[PtW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$ reacts only very slowly with PPh_3, releasing $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ and forming $[PtW(\mu-CR)(CO)_2(PPh_3)_2(\eta-C_5H_5)]$.

We have also prepared the silver–ditungsten compound (4) by treating $[Ag(NCMe)_4][BF_4]$, generated *in situ*, with $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ in dichloromethane. Like (3), compound (4) also showed an i.r. spectrum with two CO bands (2 020 and 1 956 cm^{-1}) at relatively high frequency. In the $^{13}C-\{^1H\}$ n.m.r. spectrum of (4), measured at −90 °C, the peak for the μ-*C*R groups occurs at 294.2 p.p.m. as a doublet with ^{183}W satellites [*J*(AgC) 37, *J*(WC) 174 Hz]. However, it became apparent by measuring the $^{13}C-\{^1H\}$ n.m.r. spectrum of (4) at ambient temperatures both in the absence and in the presence of free $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ that the salt was unstable, with respect to dissociation of the ‘carbyne–tungsten’ ligand. Thus in the presence of $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ (δ 300.1 p.p.m. for μ-*C*R), the $^{13}C-\{^1H\}$ n.m.r. spectrum of (4) at room temperature shows broad peaks for the μ-*C*R and CO groups, the signal for the former (δ 298.4) showing no $^{107,109}Ag-^{13}C$ coupling. In the absence of free $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$, the room-temperature spectrum shows a singlet peak for the ligated alkylidyne carbon nuclei at δ 293.7 [*J*(WC) 174 Hz]. The dissociative behaviour of (4) in solution is reminiscent of tertiary-phosphine and -phosphite dissociation from the silver(I) salts $[Ag(PR_3)_4]X$ (R = C_6H_4Me-4 or OEt; X = halide, CN^-, *etc*.).[23]

Solutions of (4) are only moderately stable, decomposing after several hours, particularly in the presence of light, air, or $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$. Compound (4) is evidently less stable than (3), and the latter less so than $[PtW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$. Attempts to prepare (4) using $AgBF_4$ rather than $[Ag(NCMe)_4][BF_4]$ afforded an impure product, and less stable materials which may be oligomeric in nature with chains of Ag–W atoms.[11]

The i.r. spectra of (3) and (4) in the CO region mentioned above, and the earlier discussion of the valence-electron count at the metal centre M in compounds D (Scheme) made an *X*-ray crystallographic study of the more stable gold compound imperative, particularly with a view to comparing the results with those obtained in the structural studies of $[MW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$ (M = Ni or Pt)[10] and (1). The data obtained are summarised in Table 2 and the cation is shown in Figure 2, with the crystallographic numbering scheme. The most striking difference between (3) and the closely analogous pseudo-tetrahedral complexes $[MW_2(\mu-CC_6H_4Me-4)_2(CO)_4(\eta-C_5H_5)_2]$ (M = Ni, Pd, or Pt) is the absence of any semi-bridging carbonyl ligand as inferred from the i.r. spectra, discussed above. In (3) we have a truly pseudo-tetrahedral molecule which in this instance is constrained crystallographically to two-fold rotational symmetry. Remarkably, however, the two dimetallacyclopropene rings are not even approximately orthogonal to one another: the dihedral angle between them is 62°. The metal atom spine of the molecule is also non-linear, with W–Au–W′ 163°. However, a considerable steric effect could be expected from the presence of the bulky tolyl ligands, and predictably these are

Table 2. Selected bond distances (Å) and angles (°) for $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ (3) *

(*a*) Distances			
Au–W	2.752(1)	Au–C	2.119(17)
W–C	1.832(16)	C–C(01)	1.522(24)
W–C(1)	1.995(19)	W–C(2)	1.982(17)
C(1)–O(1)	1.157(24)	C(2)–O(2)	1.175(23)
W–C (cp, mean)	2.36(2)	P–F (mean)	1.575(15)
(*b*) Angles			
		C–Au–C′	155.4(10)
W–Au–C	41.7(4)	W–Au–W′	162.8(1)
W–Au–C′	144.2(4)	Au–C–W	88.0(7)
C–W–C(1)	85.4(8)	C–W–C(2)	104.2(8)
C(1)–W–C(2)	90.7(8)	Au–C–C(01)	110.7(11)
Au–W–C(1)	126.4(6)	Au–W–C(2)	76.0(5)
W–C(1)–O(1)	177.5(17)	W–C(2)–O(2)	178.2(13)

* cp = η-C_5H_5. Primes are used to denote atoms related by the (crystallographically required) two-fold axis.

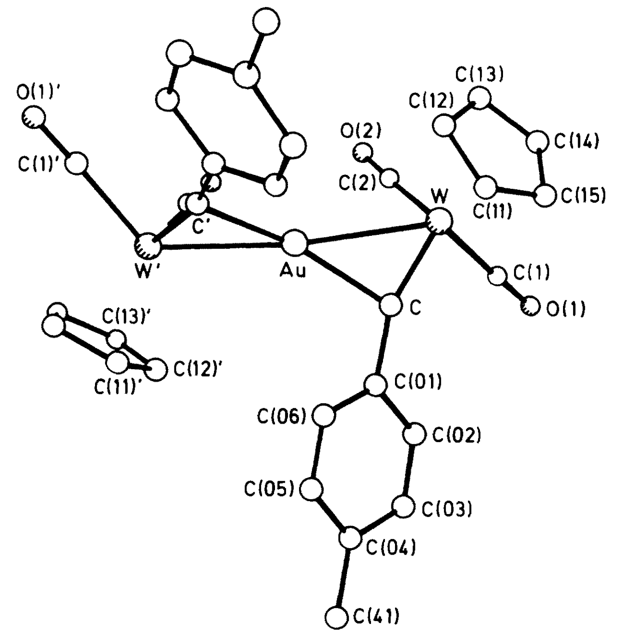


Figure 2. Molecular structure of the cation of $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ (3), showing the crystallographic numbering. Primes are used to denote atoms related by the crystallographic C_2 axis

sited on the convex side of the spine.* The $W(CO)_2(\eta\text{-}C_5H_5)$ moiety has the two terminal carbonyl ligands orthogonal to one another, and both are linear, while the plane defined by $W(CO)_2$ is itself at a dihedral angle of 99° to the corresponding dimetallacyclopropene ring.

Comparison with $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is inevitable, and if it were naively assumed that the gold complex (3) could be derived from the Pt complex by substitution of isoelectronic Au^+ for Pt^0, then closely similar stereochemistry might be expected. In fact the bend in the spine is almost unchanged [W–Pt–W 165, W–Au–W 163°], but whereas in the Pt compound the dihedral angle between the two dimetallacyclopropene rings was 83°, in the Au compound it is 62°. The bond lengths also are interestingly different: Pt–W 2.713(1), Au–W 2.752(1); Pt–C 2.01(1), Au–C 2.12(2); W–C(Pt) 1.91(1), W–C(Au) 1.83(2) Å, suggesting a more than marginal redistribution of electron density. It is of course possible that the counter ion $[PF_6]^-$ in the gold compound also plays a significant part in determining the steric configuration of the cation, but the only contact between anion and cation <3 Å is between a tolyl hydrogen atom and a PF_6 fluorine atom at 2.8 Å. As in other complexes containing bridging CC_6H_4Me-4 ligands, the tolyl groups are twisted relative to the plane of the attached dimetallacyclopropene ring; in (3) the dihedral angle is 34°. The counter anion in the crystal structure is, like the cation, constrained to C_2 symmetry by reason of the phosphorus atom occupying a special position. The mean P–F distance is 1.575(15) Å and there is no departure from O_h symmetry.

Experimental

The techniques used and the instrumentation employed in this work have been described previously.[4] Light petroleum refers to that fraction of b.p. 40—60 °C. Hydrogen-1 n.m.r. spectra were measured in $CDCl_3$, carbon-13 spectra in CD_2Cl_2–CH_2Cl_2 mixtures. The compounds $[M(CO)_3(NCMe)_3]$ (M = Mo or W),[18] [AuCl(tht)],[24] and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ [25] were prepared by literature methods.

Synthesis of the Trimetal Compounds $[MW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W).—A mixture of freshly prepared $[Mo(CO)_3(NCMe)_3]$ (0.50 g, 1.65 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (1.20 g, 2.94 mmol) in hexane (30 cm^3) was refluxed for 75 min. After cooling to room temperature, solvent was decanted and the residue was washed with light petroleum (4 × 20 cm^3). The residue was then extracted with diethyl ether (7 × 40 cm^3) and the extracts filtered through an alumina pad (*ca.* 2.5 × 4 cm). Solvent was removed *in vacuo* and the product washed with light petroleum (3 × 20 cm^3) to afford deep red-violet *microcrystals* of $[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (1) (0.5 g, 31%) (Found: C, 39.5; H, 2.7. $C_{32}H_{24}MoO_6W_2$ requires C, 39.7; H, 2.5%); $\nu_{max.}$(CO) at 1 997w, 1 967s, 1 936m, 1 852w br, and 1 687vw br cm^{-1} (CH_2Cl_2); 1 996m, 1 975vs, 1 951vs, 1 920vs, 1 899s, and 1 696 cm^{-1} (Nujol). N.m.r.: ^{1}H, δ 6.98 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 9 Hz], 5.54 (s, 5 H, C_5H_5), and 2.38 (s, 3 H, Me-4); ^{13}C-{^{1}H}, δ 360.1 [μ-*C*, *J*(WC) 144], 233.0 (2 CO), 228.7 [2 CO, *J*(WC) 178], 218.4 [2 CO, *J*(WC) 188 Hz], 162.9 [C^1 (C_6H_4)], 135.4 [C^4 (C_6H_4)], 128.4, 120.9 [C^2 and C^3 (C_6H_4)], 93.7 (C_5H_5), and 21.3 p.p.m. (Me-4).

A mixture of $[W(CO)_3(NCMe)_3]$ (0.50 g, 1.29 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.50 g, 1.23 mmol) in hexane (20 cm^3) was refluxed for 3.5 h. Hot solvent was de-

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* There is no very simple way of comparing the distortions in the geometry of molecules of type (*a*) $[MW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with those in molecules of type (*b*) $[MW_2(\mu\text{-}CR)_2(CO)_6(\eta\text{-}C_5H_5)_2]$ which contain an extra pair of *cis* terminal carbonyl ligands on the central atom M. In both types of molecule, two three-membered ring systems have a common apex in metal atom M, but constraints are already imposed by the tungsten–carbyne geometry which prevents these triangles from being isosceles. The tetrahedral distortion is thus extreme, and although a kind of pseudo-D_{2d} geometry might be visualised for type (*a*), in fact the bisectors of the two C–M–W angles are unlikely to be precisely collinear. For molecules of type (*b*) these two bisectors are bound to be forced away from the *cis* carbonyl ligands on the central atom, for steric reasons. The dihedral angle between the planes of the three-membered rings, or the angle W–M–W, are not by themselves very informative, because there are too many variables. If, for example, the case where one M–C–W ring occupies a horizontal plane and the other ring a vertical plane is considered, there are an infinite number of possible values for the W–M–W angle within this constraint.

Table 3. Atomic co-ordinates for $[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (1)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	0.925 55(6)	−0.110 66(4)	0.798 63(3)	C(141)	1 206(2)	−0.116 9(12)	0.761 2(11)
W(2)	0.676 51(6)	0.248 93(4)	0.904 36(3)	C(151)	1.182(2)	−0.155 7(13)	0.827 0(11)
Mo	0.789 96(12)	0.055 80(7)	0.794 80(7)	C(161)	1.036(2)	−0.251 8(13)	0.782 6(12)
C(1)	0.588(2)	0.003 2(9)	0.685 8(9)	C(171)	0.977(2)	−0.274 0(11)	0.686 5(10)
O(1)	0.472 1(12)	−0.024 9(7)	0.622 1(7)	C(181)	1.082(3)	−0.193 5(12)	0.672 0(10)
C(2)	0.959(2)	0.061 6(9)	0.704 3(9)	C(52)	0.826 4(15)	0.213 0(9)	0.803 8(8)
O(2)	1.051 4(12)	0.063 8(8)	0.650 9(7)	C(62)	0.901(2)	0.266 6(10)	0.749 3(9)
C(3)	0.625 4(15)	0.124 0(9)	0.921 1(8)	C(72)	1.042(2)	0.365 7(10)	0.797 3(9)
O(3)	0.600 8(11)	0.038 5(7)	0.917 2(6)	C(82)	1.098(2)	0.424 1(11)	0.747 3(11)
C(4)	0.995 7(2)	0.041 3(10)	0.897 6(8)	C(92)	1.021(2)	0.384 5(11)	0.649 5(9)
O(4)	1.025 3(12)	0.137 4(7)	0.948 9(6)	C(102)	0.887(2)	0.285 3(11)	0.602 8(9)
C(51)	0.741 6(15)	−0.120 8(9)	0.704 5(8)	C(112)	0.824(2)	0.224 4(10)	0.649 4(9)
C(61)	0.643 7(14)	−0.206 3(8)	0.604 8(8)	C(122)	1.081(3)	0.448 3(13)	0.597 4(12)
C(71)	0.509(2)	−0.301 2(9)	0.590 1(9)	C(132)	0.896(2)	0.323 5(10)	1.009 5(9)
C(81)	0.430(2)	−0.388 3(10)	0.497 3(9)	O(132)	1.029 0(14)	0.372 0(8)	1.067 0(7)
C(91)	0.477(2)	−0.385 3(10)	0.413 4(8)	C(142)	0.386(3)	0.246 9(13)	0.866 8(14)
C(101)	0.611(2)	−0.291 7(10)	0.427 7(9)	C(152)	0.489(3)	0.288(2)	0.816 9(14)
C(111)	0.687(2)	−0.205 4(10)	0.519 6(9)	C(162)	0.613(3)	0.385(2)	0.885(2)
C(121)	0.390(2)	−0.482 7(11)	0.311 9(9)	C(172)	0.571(3)	0.400 2(13)	0.975 0(15)
C(131)	0.735(2)	−0.147 9(11)	0.868 7(9)	C(182)	0.435(2)	0.314 3(14)	0.962 6(13)
O(131)	0.623(2)	−0.177 5(10)	0.901 7(9)				

Table 4. Atomic co-ordinates (× 10^4) for $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ (3)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	2 415(1)	2 500	7 500	C(13)	1 510(21)	668(9)	8 335(14)
W	2 004(1)	1 678(1)	8 949(1)	C(14)	1 768(21)	652(9)	9 293(14)
P	7 500	5 000	7 184(5)	C(15)	3 091(23)	831(10)	9 479(16)
F(1)	6 392(13)	5 023(8)	6 361(9)	C	2 865(18)	2 404(7)	8 981(12)
F(2)	7 494(21)	4 297(6)	7 177(11)	C(01)	3 731(17)	2 923(8)	9 328(13)
F(3)	8 619(16)	4 986(9)	7 967(9)	C(02)	3 605(20)	3 129(8)	10 279(15)
C(1)	1 484(21)	1 863(9)	10 303(14)	C(03)	4 392(22)	3 600(9)	10 633(15)
O(1)	1 226(14)	1 960(6)	11 098(10)	C(04)	5 317(20)	3 895(9)	10 036(16)
C(2)	181(17)	1 877(9)	8 498(14)	C(05)	5 442(18)	3 671(9)	9 097(15)
O(2)	−901(15)	1 981(7)	8 220(12)	C(06)	4 670(19)	3 213(9)	8 756(15)
C(11)	3 677(22)	986(10)	8 606(13)	C(41)	6 139(23)	4 407(10)	10 392(16)
C(12)	2 678(21)	888(9)	7 892(15)				

canted and the dark residue washed with light petroleum (5 × 20 cm^3). The residue was extracted with diethyl ether (10 × 20 cm^3) and the extracts filtered through an alumina pad (*ca.* 2.5 × 4 cm). Removal of solvent *in vacuo* gave deep red-violet *crystals* of $[W_3(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (2) (0.20 g, 15%), recrystallised from diethyl ether–light petroleum (1 : 4) (Found: C, 36.4; H, 2.5. $C_{32}H_{24}O_6W_3$ requires C, 36.4; H, 2.3%); $\nu_{max.}(CO)$ at 2 002w, 1 969s, 1 937m br, and 1 852w br cm^{-1} (CH_2Cl_2); 2 002m, 1 979s, 1 967s, 1 919s, 1 844s, and 1 728w cm^{-1} (Nujol). N.m.r.: ^1H, δ 6.88 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8 Hz], 5.47 (s, 5 H, C_5H_5), and 2.39 (s, 3 H, Me-4); $^{13}C\text{-}\{^1H\}$, δ 376.2 (μ-C), 228.1 [2 CO, *J*(WC) 171], 226.0 [2 CO, *J*(WC) 173], 214.9 [2 CO, *J*(WC) 189 Hz], 164.9 [C^1 (C_6H_4)], 135.2 [C^4 (C_6H_4)], 128.0, 120.4 [C^2 and C^3 (C_6H_4)], 93.7 (C_5H_5), and 21.2 p.p.m. (Me-4).

Synthesis of $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$.—The compound [AuCl(tht)] (0.16 g, 0.50 mmol) was added to a vigorously stirred thf (20 cm^3) solution of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.50 g, 1.22 mmol) and $TlPF_6$ (0.52 g, 1.5 mmol). After 20 min the mixture was filtered through a Celite plug (*ca.* 2 × 2 cm) and the solution reduced in volume *in vacuo* to *ca.* 10 cm^3. Slow addition of diethyl ether (*ca.* 80 cm^3) produced an orange-red precipitate which was washed with diethyl ether (5 × 20 cm^3) and dried *in vacuo* to afford yellow-orange *microcrystals* of $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ (3) (0.50 g, 86%) (Found: C, 31.0; H, 2.2. $C_{30}H_{24}AuF_6O_4PW_2$ requires C, 31.1; H, 2.1%); $\nu_{max.}(CO)$ at 2 024s and 1 969s cm^{-1} (CH_2Cl_2). N.m.r.: ^1H, δ 7.23 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8 Hz], 5.80 (s, 5 H, C_5H_5), and 2.34 (s, 3 H, Me-4); $^{13}C\text{-}\{^1H\}$, δ 295.8 [μ-C, *J*(WC) 153], 211.8 [CO, *J*(WC) 180], 148.2 [C^1 (C_6H_4), *J*(WC) 31 Hz], 143.5 [C^4 (C_6H_4)], 130.6, 129.9 [C^2 and C^3 (C_6H_4)], 93.3 (C_5H_5), and 22.1 p.p.m. (Me-4).

Treatment of (3) (0.16 g, 0.14 mmol) in CH_2Cl_2 (20 cm^3) with PPh_3 (0.07 g, 0.27 mmol) led to immediate reaction (i.r. spectrum). Concentration of the solution to *ca.* 3 cm^3 *in vacuo*, followed by addition of diethyl ether (*ca.* 40 cm^3) gave white *microcrystals* of $[Au(PPh_3)_2][PF_6]$ (0.10 g, 74%) (Found: C, 49.8; H, 3.5. Calc. for $C_{36}H_{30}AuF_6P_3$: C, 49.9; H, 3.5%); $^{31}P\text{-}\{^1H\}$ n.m.r. (CH_2Cl_2), δ 45.0 (s, PPh_3) and −144.2 p.p.m. [heptet, PF_6, *J*(PF) 710 Hz].

Synthesis of $[AgW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$.—A sample of $AgBF_4$ (0.11 g, 0.57 mmol) in MeCN (*ca.* 4 cm^3) was reduced in volume to *ca.* 1 cm^3 and the solution treated with diethyl ether (40 cm^3), producing colourless crystals presumed to be $[Ag(NCMe)_4][BF_4]$. The solvent was decanted and the crystals dissolved in CH_2Cl_2 (10 cm^3). To this solution was added $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.46 g, 1.13 mmol), and the mixture stirred (15 min), concentrated *in vacuo* to *ca.* 5 cm^3, and treated with diethyl ether in the minimum amount required to produce orange crystals.

Solvent was decanted, and the crystals, after washing with diethyl ether (5 × 10 cm^3), were dissolved in CH_2Cl_2 (15 cm^3). The mixture was filtered through a Celite pad (2 × 2 cm) and the filtrate concentrated to *ca.* 4 cm^3. Slow addition of diethyl ether (60 cm^3) produced orange crystals which after washing with diethyl ether (5 × 20 cm^3) and drying *in vacuo* afforded yellow *microcrystals* of $[AgW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$ (4) (0.20 g, 35%) (Found: C, 35.2; H, 2.3. $C_{30}H_{24}AgBF_4O_4W_2$ requires C, 35.7; H, 2.4%); $\nu_{max.}$(CO) at 2 020vs and 1 956s cm^{-1} (CH_2Cl_2). N.m.r.: ^1H, δ 7.26 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8 Hz], 5.79 (s, 5 H, C_5H_5), and 2.29 (s, 3 H, Me-4); $^{13}C\text{-}\{^1H\}$ (−90 °C), δ 294.2 [d, μ-C, *J*(AgC) 37, *J*(WC) 174], 213.6 [CO, *J*(WC) 40], 148.5 [C^1 (C_6H_4), *J*(WC) 40 Hz], 142.9 [C^4 (C_6H_4)], 129.6 [C^2 and C^3 (C_6H_4)], 92.7 (C_5H_5), and 22.4 p.p.m. (Me-4).

Crystal Structure Determinations.—$[MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (1). Crystals of (1) grow as red-violet columns from light petroleum. Diffracted intensities were measured (θ–2θ scan) at 210 K from a crystal of dimensions 0.35 × 0.15 × 0.10 mm on a Nicolet *P*3*m* four-circle diffractometer. Of the total 4 321 reflections measured for $2.9 \leqslant 2\theta \leqslant 55°$, 3 711 which satisfied the criterion $I \geqslant 2.5\sigma(I)$ after correction for Lorentz, polarisation, and *X*-ray absorption effects were used in the solution and refinement of the structure.

Crystal data for (1). $C_{32}H_{24}MoO_6W_2$, $M = 968$, triclinic, $a = 7.829(1)$, $b = 14.709(2)$, $c = 15.579(2)$ Å, $\alpha = 118.27(1)$, $\beta = 92.21(1)$, $\gamma = 105.32(1)°$, $U = 1\,495(1)$ Å^3, D_m not measured, $Z = 2$, $D_c = 2.15$ g cm^{-3}, $F(000) = 908$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation, graphite monochromator, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 82.9 cm^{-1}.

The structure was solved by heavy-atom methods and the hydrogen atoms, which were not located with any certainty on the electron-density maps, were incorporated to ride on the attached carbon atom with C–H = 0.96 Å and $U_H = 1.2U_C$ (equivalent). All other atoms were ascribed anisotropic thermal motion. Refinement was carried out by blocked-matrix cascade least squares, with weights $w = [\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$, where $\sigma(F_o)$ is the estimated error in $|F_o|$ based on counting statistics only. Convergence was reached at $R = 0.038$ ($R' = 0.038$). Atomic scattering factors, with corrections for anomalous dispersion, were taken from ref. 26, and all computations were carried out within the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[27] Atomic co-ordinates for (1) are in Table 3.

$[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ (3). Crystals of (3) grow as wafer-thin yellow plates from thf–diethyl ether. The crystal used was of dimensions 0.17 × 0.03 × 0.10 mm (faces {1 0 0}, {0 1 0}, {0 0 1}). Of the total 1 748 reflections measured at 200 K to 2θ = 50°, 1 654 with $I \geqslant 2\sigma(I)$ were used. Corrections were as for (1).

Crystal data for (3). $C_{30}H_{24}AuF_6O_4PW_2$, $M = 1\,158$, orthorhombic, $a = 10.024(11)$, $b = 22.247(12)$, $c = 13.905(5)$ Å, $U = 3\,101(4)$ Å^3, D_m not measured, $Z = 4$, $D_c = 2.42$ g cm^{-3}, $F(000) = 2\,128$, space group *Pnna* (no. 52), μ(Mo-K_α) = 123.9 cm^{-1}.

The structure was solved by a combination of heavy-atom and direct methods. Hydrogen atoms, though many were found on electron-density maps, were constrained to ride on their attached C atoms but were allowed to refine isotropically. The carbon atoms of the cyclopentadienyl ligand [C(11)—C(15)] and C(1) were restrained to isotropic thermal motion, but all other atoms were allowed anisotropic thermal motion. Weights $w = [\sigma^2(F_o) + 0.000\,52|F_o|^2]^{-1}$ gave convergence in refinement at $R = 0.050$ ($R' = 0.046$). Atomic co-ordinates for (3) are in Table 4.

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