Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 31.[1] Synthesis and Crystal Structures of the Compounds $[AuW(\mu\text{-}CHR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$ and $[AuPtW(\mu_3\text{-}CR)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$ ($R = C_6H_4Me\text{-}4$) *

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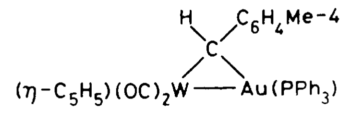
Treatment of a mixture of the salts $[N(PPh_3)_2][W_2\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_7(\eta\text{-}C_5H_5)]$ and $TlPF_6$ in tetrahydrofuran (thf) with $[AuCl(PPh_3)]$ affords the bridged *p*-tolylmethylidene complex $[AuW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$, the structure of which has been established by a single-crystal *X*-ray diffraction study. As expected, the Au–W bond [2.729(1) Å] is spanned by the $CH(C_6H_4Me\text{-}4)$ group. The μ-C–W separation is relatively short [2.058(14) Å] whereas the μ-C–Au distance is relatively long [2.268(14) Å]. To account for these features a three-centre two-electron μ-C–Au–W interaction is postulated. Addition of $[Au(PR'_3)]^+$ [$PR'_3 = PPh_3$ or $P(cyclo\text{-}C_6H_{11})_3$] fragments, generated *in situ* from $[AuCl(PR'_3)]$ and $TlPF_6$ in dichloromethane, to the alkylidynetungsten compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$ or Me) affords the salts $[AuW(\mu\text{-}CR)(CO)_2(PR'_3)(\eta\text{-}C_5H_5)][PF_6]$ [$R = C_6H_4Me\text{-}4$, $PR'_3 = PPh_3$ or $P(C_6H_{11})_3$; R = Me, $PR'_3 = PPh_3$]. N.m.r. studies (^1H, $^{31}P\text{-}\{^1H\}$, and $^{13}C\text{-}\{^1H\}$) on solutions of these salts, however, reveal that the cations dissociate, affording equilibrium mixtures containing the species $[Au\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ and $[Au(PR'_3)_2]^+$. The trimetal compound $[AuPtW(\mu_3\text{-}CR)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$ ($R = C_6H_4Me\text{-}4$) has been prepared by two routes: from the reaction between $[Au\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$ and $[Pt(C_2H_4)(PMe_3)_2]$, and by addition of $[Au(thf)(PMe_3)][PF_6]$ to $[PtW(\mu\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$. The structure of $[AuPtW(\mu_3\text{-}CR)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$ has been established by *X*-ray crystallography. A triangular array of metal atoms [Au–W 2.801(2), Au–Pt 2.956(2), and Pt–W 2.770(2) Å] is asymmetrically bridged by the CR ligand [μ_3-C–Au 2.21(4), μ_3-C–Pt 1.97(4), and μ_3-C–W 2.01(4) Å]. The Au–Pt separation suggests that there is little or no direct metal–metal bonding between these two metal atoms. The tungsten atom carries the cyclopentadienyl ligand and two CO groups, but the latter are appreciably non-linear. The gold and platinum atoms are ligated by one and two PMe_3 groups, respectively.

We have previously shown that the compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) combines with a variety of low-valent metal–ligand fragments to afford complexes with bonds between tungsten and other transition elements (Ti, Zr, V, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt).[1-3] In the various products the heteronuclear metal–metal bonds are bridged by the *p*-tolylmethylidyne group. Recently we have extended our studies to species in which tungsten is bonded to Cu,[4] Ag, or Au.[5,6] Herein we report further syntheses of gold–tungsten complexes. A preliminary description of one of the compounds has been given.[7]

Results and Discussion

The neutral compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$[8] ($R = C_6H_4Me\text{-}4$) combines with $[N(PPh_3)_2][WH(CO)_5]$[9] to form the ditungsten salt $[N(PPh_3)_2][W_2(\mu\text{-}CHR)(CO)_7(\eta\text{-}C_5H_5)]$.[7] Treatment of the latter with $HBF_4\cdot Et_2O$ does not afford an isolable neutral ditungsten complex. Decomposition occurs to give $W(CO)_6$ and unidentified products. In view of this result, the reaction between $[N(PPh_3)_2][W_2(\mu\text{-}CHR)(CO)_7(\eta\text{-}C_5H_5)]$ and $[AuCl(PPh_3)]$ was next investigated. The groups H^+ and $[Au(PPh_3)]^+$ are isolobal, and it was thought that the latter might afford a stable complex where protonation had not. The reaction was carried out in the presence of $TlPF_6$ in order to remove chloride as TlCl, and generate $[Au(PPh_3)]^+$ *in situ*. A purple crystalline compound, $[AuW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (1), was isolated after chromatography of the mixture on alumina.



(1)

The n.m.r. data for (1) were informative, but did not unambiguously define the structure. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table 1) showed two signals for CO ligands, in agreement with the observation of two bands in the i.r. spectrum at 1 888 and 1 793 cm^{-1} (in CH_2Cl_2). In addition, a doublet resonance at δ 228.9 p.p.m. with ^{183}W satellite peaks [*J*(PC) 15 and *J*(WC) 103 Hz] was in accord with the presence of an alkylidene carbon nucleus *C*HR in (1). However, this signal is somewhat more deshielded than those customarily found (210—100 p.p.m.) for μ-*C*HR groups spanning a metal–metal bond.[10] The ^1H n.m.r. spectrum showed resonances due to the C_5H_5, C_6H_4, C_6H_5, and Me-4 moieties. However, a further signal at δ 13.2 was assigned to a μ-C*H*R group, even though it was outside the normal range (δ 9—11) for protons of this kind.

In order to establish the structure of (1), particularly with

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* 2,2-Dicarbonyl-2-η^5-cyclopentadienyl-μ-*p*-tolylmethylidene-1-(triphenylphosphine)goldtungsten–dichloromethane (1/1) and 3,3-dicarbonyl-3-η^5-cyclopentadienyl-μ_3-*p*-tolylmethylidyne-1,2,2-tris(trimethylphosphine)goldplatinumtungsten(*W–Au*)(*W–Pt*) hexafluorophosphate respectively.

Supplementary data available (No. SUP 56032, 10 pp.): H-atom co-ordinates, complete listings of bond distances and angles, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. data [a] for the gold–tungsten complexes

Compound	^{1}H (δ) [b]	^{13}C-{^{1}H} [c]	^{31}P-{^{1}H} [d]
(1) [AuW{μ-CH(C$_6$H$_4$Me-4)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]	2.15 (s, 3 H, Me-4), 5.80 (s, 5 H, C$_5$H$_5$), 7.6—7.8 (m, 19 H, C$_6$H$_5$ and C$_6$H$_4$), 13.20 (s, 1 H, μ-CH)	246.3 [CO, J(WC) 161], 238.9 [CO, J(WC) 183], 228.9 [d, μ-C, J(PC) 15, J(WC) 103], 154.5 [C^1(C$_6$H$_4$)], 137.0—128.0 (C$_6$H$_4$ and C$_6$H$_5$), 93.4 (C$_5$H$_5$), 21.6 (Me-4)	63.4 (PPh$_3$)
(2a) [AuW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)][PF$_6$] [c]	2.33 (br, 3 H, Me-4), 5.94 (s, 5 H, C$_5$H$_5$), 7.1—7.3 (m, 4 H, C$_6$H$_4$), 7.4—7.6 (m, 15 H, C$_6$H$_5$)	292.6 [d, μ-C, J(PC) 24], 210.8 [CO, J(WC) 178], 148.4 [C^1(C$_6$H$_4$), J(WC) 32], 143.0—126.0 (C$_6$H$_4$ and C$_6$H$_5$), 92.9 (C$_5$H$_5$), 21.8 (Me-4)	57.2 (PPh$_3$), −144.1 [heptet, PF$_6^-$, J(PF) 711]
(2b) [AuW(μ-CMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)][PF$_6$] [e]	2.49 (s, 3 H, Me), 5.83 (s, 5 H, C$_5$H$_5$), 7.2—7.7 (m, 15 H, C$_6$H$_5$)	[f] 304.7 (μ-C), 210.2 [CO, J(WC) 178], 134.0—126.8 (C$_6$H$_5$), 92.7 (C$_5$H$_5$), 42.9 [Me, J(WC) 34]	56.6 (PPh$_3$), −144.2 [heptet, PF$_6^-$, J(PF) 713]
(2c) [AuW(μ-CC$_6$H$_4$Me-4)(CO)$_2${P(C$_6$H$_{11}$)$_3$}(η-C$_5$H$_5$)][PF$_6$] [e]	0.7—2.9 (m, 36 H, C$_6$H$_{11}$ and Me-4), 5.92 (s, 5 H, C$_5$H$_5$), 6.9—7.6 (m, 4 H, C$_6$H$_4$)	292.3 [d, μ-C, J(PC) 24, J(WC) 177], 211.5 [CO, J(WC) 181], 148.5 [C^1(C$_6$H$_4$)], 142.5—129.4 (C$_6$H$_4$), 93.0 (C$_5$H$_5$), 34—25 (m, C$_6$H$_{11}$), 21.9 (Me-4)	76.3 [P(C$_6$H$_{11}$)], −144.2 [heptet, PF$_6^-$, J(PF) 713]
(5) [AuPtW(μ$_3$-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_3$(η-C$_5$H$_5$)][PF$_6$]	[g] 1.29 [d, 9 H, Me$_3$PPt, J(PH) 9, J(PtH) 38], 1.58 [d, 9 H, Me$_3$PAu, J(PH) 9], 1.71 [d, 9 H, Me$_3$PPt, J(PH) 9, J(PtH) 40], 2.38 (s, 3 H, Me-4), 5.50 (s, 5 H, C$_5$H$_5$), 6.47 [AB, 2 H, C$_6$H$_4$, J(AB) 7], 7.06 [AB, 2H, C$_6$H$_4$, J(AB) 7]	[g] 303.3 (m, μ-C), 222.7 (CO), 214.4 (CO), 158.3 [C^1(C$_6$H$_4$)], 135.0—118.8 (C$_6$H$_4$), 93.6 (C$_5$H$_5$), 21.2 (Me-4), 18.7 [d, MeP, J(PC) 32], 17.5 [d, MeP, J(PC) 29], 16.2 [d, MeP, J(PC) 34]	21.3 [d of d, PAu, J(PP) 6 and 3], −15.3 [d of d, PPt, J(PP) 6 and 3, J(PPt) 3 982], −26.5 [d of d, PPt, J(PP) 6 and 3, J(PPt) 2 810], −144.3 [heptet, PF$_6^-$, J(PF) 710]

[a] Chemical shifts in p.p.m., coupling constants in Hz. [b] Measured in CD$_2$Cl$_2$ unless otherwise stated. [c] Measured in CD$_2$Cl$_2$–CH$_2$Cl$_2$, unless otherwise stated, positive values representing shifts to high frequency of SiMe$_4$. [d] Measured in CD$_2$Cl$_2$–CH$_2$Cl$_2$ unless otherwise stated, positive values representing shifts to high frequency of 85% H$_3$PO$_4$ (external). [e] Spectra measured in CDCl$_3$. [f] Multiplet, see text. [g] Spectra measured at −40 °C.

Table 2. Selected internuclear distances (Å) and angles (°) with estimated standard deviations in parentheses for [AuW{μ-CH(C$_6$H$_4$Me-4)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]·CH$_2$Cl$_2$ (1)

Au–W	2.729(1)	Au–P	2.262(4)
Au–C(1A)	2.268(14)	W–C(1A)	2.058(14)
W–C(1)	1.97(2)	W–C(2)	1.94(2)
C(1)–O(1)	1.16(2)	C(2)–O(2)	1.15(2)
C(1A)–C(1B)	1.47(2)	C(1A)–H(1A)	0.98(10)
P–C(11)	1.805(9)	P–C(21)	1.810(10)
P–C(31)	1.805(9)	mean W–C(cp) [a]	2.36(2)
		mean C–Cl [b]	1.72(2)
W–Au–P	159.2(1)	W–Au–C(1A)	47.5(3)
P–Au–C(1A)	151.8(4)	Au–W–C(1A)	54.4(4)
C(1)–W–C(2)	74.1(7)	C(1)–W–C(1A)	87.0(6)
Au–W–C(1)	116.3(4)	Au–W–C(2)	73.0(4)
C(2)–W–C(1A)	107.2(6)	Au–C(1A)–W	78.1(5)
Au–C(1A)–C(1B)	100.7(8)	W–C(1A)–C(1B)	137.6(10)
Au–C(1A)–H(1A)	108(6)	W–C(1A)–H(1A)	101(6)
C(1B)–C(1A)–H(1A)	119(6)	Au–P–C(11)	110.8(3)
Au–P–C(21)	116.1(3)	Au–P–C(31)	113.1(3)
W–C(1)–O(1)	177(1)	W–C(2)–O(2)	177(1)

[a] cp = η-C$_5$H$_5$. [b] CH$_2$Cl$_2$.

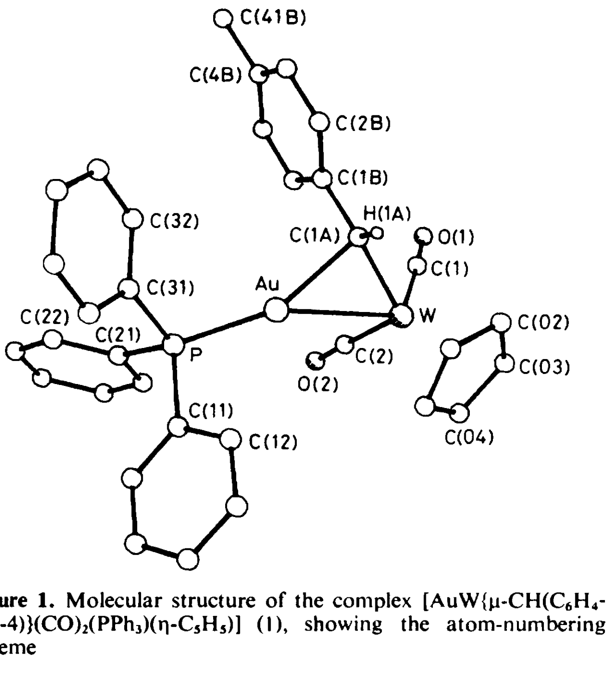


Figure 1. Molecular structure of the complex [AuW{μ-CH(C$_6$H$_4$-Me-4)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] (1), showing the atom-numbering scheme

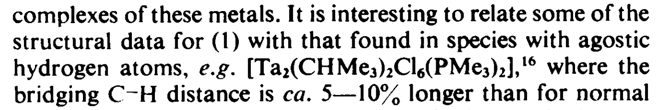
respect to resolving the bridging or non-bridging nature of the CHR group, an *X*-ray diffraction study was carried out. The results of this study are summarised in Table 2, and the molecule is shown in Figure 1, together with the atom-numbering scheme.

The molecule has an Au–W bond bridged by the CHR group. The Au–W separation [2.729(1) Å] may be compared with those found in [AuW(CO)$_3$(PPh$_3$)(η-C$_5$H$_5$)] [2.698(3) Å] [11] and [Au{W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)}$_2$][PF$_6$] [2.752(1) Å].[6] The W–C(1A) distance [2.058(14) Å] is relatively short, suggesting a degree of double bond character. Thus in [W(=CPh$_2$)(CO)$_5$], with a carbon–tungsten double bond, the carbon–tungsten separation is 2.14(2) Å,[12] and in the μ-methoxy(aryl)methylidene compounds [WPt{μ-C(OMe)Ph}(CO)$_5$(PMe$_3$)$_2$] and [WPt{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_4$-

$(PMe_3)_3]$ the W–C distances are 2.48(1) and 2.37(1) Å, respectively.[13] The short W–C(1A) bond in (1) is accompanied by a relatively long Au–C(1A) separation [2.268(14) Å]. Thus the Au–C σ-bond distances in $[AuMe(PPh_3)]$ [2.124(28) Å][14] and $[Au\{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ [2.119(7) Å][6] are appreciably shorter.

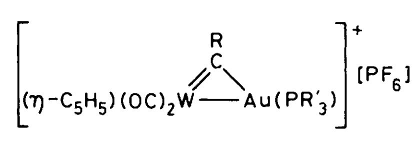
The tungsten atom carries the η-C_5H_5 group and two CO ligands. The W–C–O angles deviate little from linearity, yet the CO ligands in the i.r. spectrum give rise to bands at relatively low frequencies [1 881 and 1 786 cm^{-1} (in Nujol)], as might be expected for the presence of semi-bridging or bridging groups. The explanation for this must lie in extensive back bonding to the CO groups, the tungsten centre being relatively electron rich, a feature which is discussed further below. The plane defined by the $W(CO)_2$ fragment is at 98° to the plane $\overline{\text{Au}\{\mu\text{-C(1A)}\}\text{W}}$, and the angle between the latter and the CC_6H_4Me-4 system is 78°.

The above mentioned differences in the C–W and C–Au distances in the $\overline{\text{Au}(\mu\text{-CHR})\text{W}}$ dimetallacyclopropane ring of (1) correlate with the ^1H and ^{13}C n.m.r. shifts, mentioned earlier. The n.m.r. data correspond more closely with those expected for a terminally bound CHR group rather than for this ligand bridging a metal–metal bond. In this context, the bonding in the $\overline{\text{Au}(\mu\text{-CHR})\text{W}}$ ring system is of considerable interest. The formulation shown for (1) implies 17 and 15 electron counts at the tungsten and gold centres, respectively. To account for the diamagnetism of the compound, electron pairing *via* a Au=W bond could be invoked, but the observed Au–W distance is not in accord with this feature. There is the possibility of a three-centre two-electron interaction formed by a combination of the hybrid atomic orbitals of Au (*sp*), C (*sp*^{3}), and W (*d*^{2}*sp*^{3}), so that the ring system could be represented by (1a). The 'half-arrow' convention of Green and co-workers[15] used for agostic hydrogen atoms is extended to the isolobal $Au(PPh_3)$ fragment in this representation. The formal valence-electron counts at tungsten and gold would be 18 and 14, respectively, as is generally found in organo-complexes of these metals. It is interesting to relate some of the structural data for (1) with that found in species with agostic hydrogen atoms, *e.g.* $[Ta_2(CHMe_3)_2Cl_6(PMe_3)_2]$,[16] where the bridging C–H distance is *ca.* 5—10% longer than for normal C–H bonds. The relatively long Au–μ-C distance in (1) was mentioned above. An equally valid representation for (1) is (1b), *i.e.* the molecule contains a 'semi-bridging carbene' akin to a semi-bridging carbonyl. This would account for the short W–C(1A) bond, the slightly longer Au–C(1A) distance, and the n.m.r. data with relatively high frequency ^1H and ^{13}C resonances for the μ-CHR group.

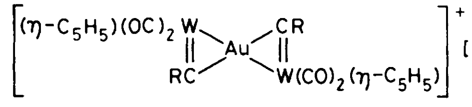

(a) (b)

(1)

Treatment of (1) with $[CPh_3][BF_4]$ afforded an orange solid. This solid was more satisfactorily prepared from the reaction between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[AuCl(PPh_3)]$ carried out in the presence of $TlPF_6$. Although the product gave microanalytical data consistent with it being (2a), a 1 : 1 adduct of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Au(PPh_3)][PF_6]$, examination of the n.m.r. spectra (^1H, ^{31}P-$\{^1H\}$, and ^{13}C-$\{^1H\}$) revealed that in solution a mixture of complexes was present.



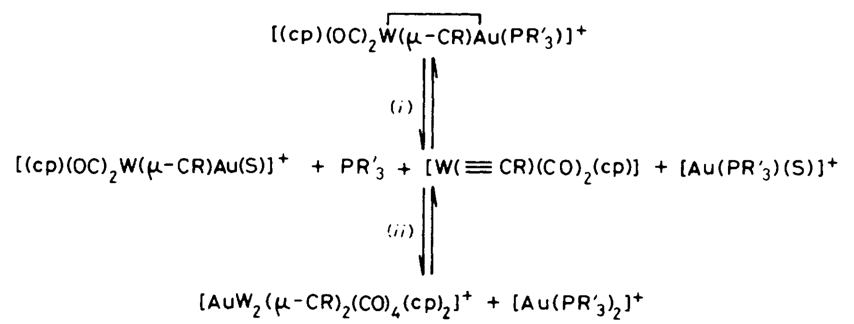
	R	PR'$_3$
(2a)	C_6H_4Me-4	PPh_3
(2b)	Me	PPh_3
(2c)	C_6H_4Me-4	$P(C_6H_{11})_3$



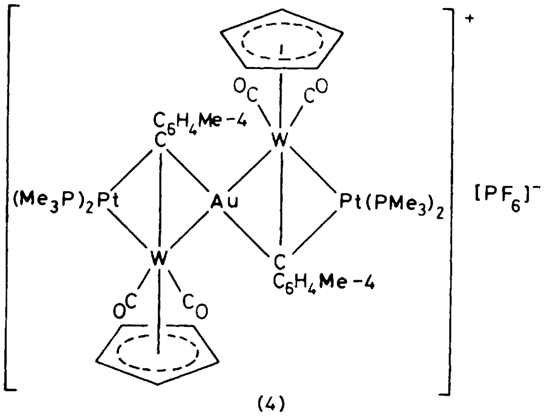
	R
(3a)	C_6H_4Me-4
(3b)	Me

The ^{31}P-$\{^1H\}$ n.m.r. spectrum was especially informative with three resonances at δ 45.2, 57.2, and −144.1 p.p.m. The latter was a heptet signal [*J*(PF) 711 Hz], and this can be ascribed to the $[PF_6]^-$ anion. The peak at δ 45.2 was shown to be due to the cation $[Au(PPh_3)_2]^+$, by independently preparing $[Au(PPh_3)_2][PF_6]$ and measuring its ^{31}P-$\{^1H\}$ n.m.r. spectrum. The resonance at 57.2 p.p.m. is thus assigned to (2a). Examination of the ^{13}C-$\{^1H\}$ n.m.r. spectrum of the orange product showed that as well as (2a) and $[Au(PPh_3)_2]^+$, the previously prepared[6] compound $[Au\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5\}_2][PF_6]$ (3a) was present, having characteristic resonances at δ 294.7 (μ-*C*R) and 211.3 (CO).[6] For (2a) the corresponding signals are seen (Table 1) at δ 292.6 (μ-*C*R) and 210.8 (CO). Other ^{13}C-$\{^1H\}$ n.m.r. resonances for (2a) were assigned after identifying all the peaks in the spectrum of the mixture due to the two species $[Au(PPh_3)_2]^+$ and (3a). The presence of (2a) and (3a) in the equilibrium mixture formed by dissolving the orange solid in dichloromethane was further confirmed from the ^1H n.m.r. spectrum. This mixture showed two C_5H_5 signals at δ 5.94 and 5.86 p.p.m. The latter is due to (3a) and hence the former is due to (2a). Although only one resonance for an Me-4 substituent was observed, the peak was broad, and integration relative to the C_5H_5 signals showed that it was due to two methyl groups. From the relative intensity of the peaks in the ^1H n.m.r. spectrum, it was estimated that *ca.* 27% of the mixture consisted of the species $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$. The i.r. spectrum of the mixture showed two strong but broad peaks at 2 025 and 1 970 cm^{-1} in CH_2Cl_2. The spectrum could not be measured in hexane since the orange solid was too insoluble. Measurement of the spectrum in tetrahydrofuran (thf) led to the discovery that in this solvent (2a) decomposed into $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Au(PPh_3)(thf)][PF_6]$. Removal of solvent, and addition of dichloromethane afforded the equilibrium mixture again (Scheme). Addition of PPh_3 resulted in the formation of $[Au(PPh_3)_2][PF_6]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$.

Reactions were also investigated between $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and $[AuCl(PPh_3)]$, and between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[AuCl\{P(cyclo\text{-}C_6H_{11})_3\}]$, in the presence of $TlPF_6$, with dichloromethane as solvent. Solid products were obtained, corresponding to the salts (2b) and (2c) by microanalysis, but n.m.r. studies on the solutions revealed dissociation of these complexes, as described above for (2a) (Scheme). The peak assignments in the n.m.r. spectra (Table 1) were made from a knowledge of the data for $[Au\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$ (3) (R = C_6H_4Me-4 or



Scheme. cp = η-C_5H_5; R = C_6H_4Me-4, PR'$_3$ = PPh_3; R = Me, PR'$_3$ = PPh_3; R = C_6H_4Me-4, PR'$_3$ = P(cyclo-C_6H_{11})$_3$: (*i*) +S (CH_2Cl_2 or thf), (*ii*) $-CH_2Cl_2$



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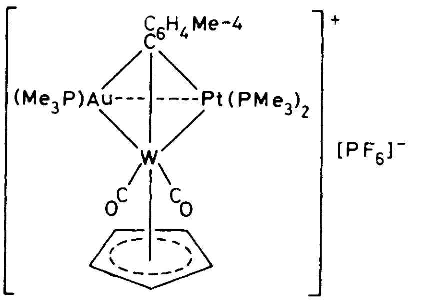

(5)

Me) and [Au(PR'$_3$)$_2$][PF$_6$] [PR'$_3$ = PPh_3 or P(cyclo-C_6H_{11})$_3$] which allowed the peaks for (2b) and (2c) to be identified in the mixtures. From the relative intensities of the peaks in the ^{1}H spectra, it was estimated that at equilibrium *ca.* 33% of (2b) and 80% of (2c) were present in solution. In the ^{13}C-{^{1}H} n.m.r. spectrum of (2c) the resonance for the μ-*C*(C_6H_4Me-4) nucleus at δ 292.3 p.p.m. was a doublet [*J*(PC) 24 Hz] and it also showed ^{183}W satellite peaks [*J*(WC) 177 Hz]. The μ-*C*Me signal in the spectrum of (2b) (δ 304.7) was a multiplet, overlapping the μ-*C*Me resonance for the cation of (3b).

We have recently prepared the gold–tungsten–platinum complex (4), by treating [PtW(μ-CR)(CO)$_2$(PMe$_3$)$_2$(η-C_5H_5)] with [AuCl{$\overline{S(CH_2)_3CH_2}$}] and $TlPF_6$ in tetrahydrofuran.[5] It seemed logical that (4) might also be prepared by adding two equivalents of [Pt(C_2H_4)(PMe$_3$)$_2$] to (3a). However, examination of the spectroscopic (i.r. and n.m.r.) properties and microanalysis of the product (5) of this reaction showed that an unexpected pathway had been followed. Compound [AuPtW(μ$_3$-CR)(CO)$_2$(PMe$_3$)$_3$(η-C_5H_5)][PF$_6$] (5) had CO stretching bands at 1 936 and 1 831 cm^{-1} (in CH_2Cl_2), the latter absorption suggesting the presence of a semi-bridging carbonyl group. The ^{31}P-{^{1}H} n.m.r. spectrum (Table 1) was informative showing four resonances. Of these signals, that observed at δ −144.3 [heptet, *J*(PF) 710 Hz] was assigned to a [PF$_6$]$^-$ anion. Two of the remaining three signals, at δ −15.3 [*J*(PtP) 3 982 Hz] and at −26.5 [*J*(PtP) 2 810 Hz], were obviously due to PMe$_3$ ligands in different environments and attached to platinum. No ^{195}Pt satellite peaks were seen on the fourth resonance at 21.3 p.p.m., and this observation together with the chemical shift suggested that it was due to a Au(PMe$_3$) group. The ^{13}C-{^{1}H} n.m.r. spectrum showed a resonance at δ 303.3 p.p.m., ascribable to a μ-*C*R group, but with a different chemical shift from those observed for this group in the spectra of either (3a) or (4).[5,6]

Table 3. Selected internuclear distances (Å) and angles (°) with estimated standard deviations in parentheses for [AuPtW(μ$_3$-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_3$(η-C_5H_5)][PF$_6$] (5)

Au–W	2.801(2)	Au–Pt	2.956(2)
Pt–W	2.770(2)	C–Au	2.21(4)
C–Pt	1.97(4)	C–W	2.01(4)
C–C(1)	1.52(6)	P(3)–Au	2.27(1)
P(1)–Pt	2.26(1)	P(2)–Pt	2.32(2)
W–C(01)	1.90(4)	W–C(02)	1.89(10)
C(01)–O(01)	1.26(5)	C(02)–O(02)	1.40(11)
W–C(cp)	2.36(4) *	C(4)–C(04)	1.43(7)
P(1)–C(Me)	1.88(6) *	P(2)–C(Me)	1.83(5) *
P(3)–C(Me)	1.84(6) *	P–F	1.55(6) *
Pt · · · C(01)	2.46(4)	Pt · · · C(02)	2.66(8)

Pt–Au–W	57.4(1)	Pt–C–Au	90(2)
Au–Pt–W	58.5(1)	Au–C–W	83(3)
Pt–W–Au	64.1(1)	W–C–Pt	88(2)
W–C(01)–O(01)	162(3)	W–C–C(1)	134(3)
W–C(02)–O(02)	145(5)	Au–C–C(1)	114(2)
P(1)–Pt–P(2)	97.5(5)	Pt–C–C(1)	132(2)
P(1)–Pt–Au	97.3(3)	P(3)–Au–Pt	133.8(4)
P(2)–Pt–Au	122.1(3)	P(3)–Au–W	157.4(4)
P(1)–Pt–W	145.1(4)	P(3)–Au–C	157(1)
P(2)–Pt–W	116.4(3)	P(1)–Pt–C	99(1)
		P(2)–Pt–C	162(1)
		W–Pt–C	46(1)

* Mean value.

In order to establish the structure of (5) a single-crystal *X*-ray diffraction study was carried out. Unfortunately only a very small crystal could be obtained, and some decay occurred during exposure to the *X*-ray beam (Experimental section), consequently the data obtained were limited but nevertheless the nature of (5) was unambiguously defined. The results are summarised in Table 3. The structure of the cation is shown in Figure 2, together with the atom-numbering scheme.

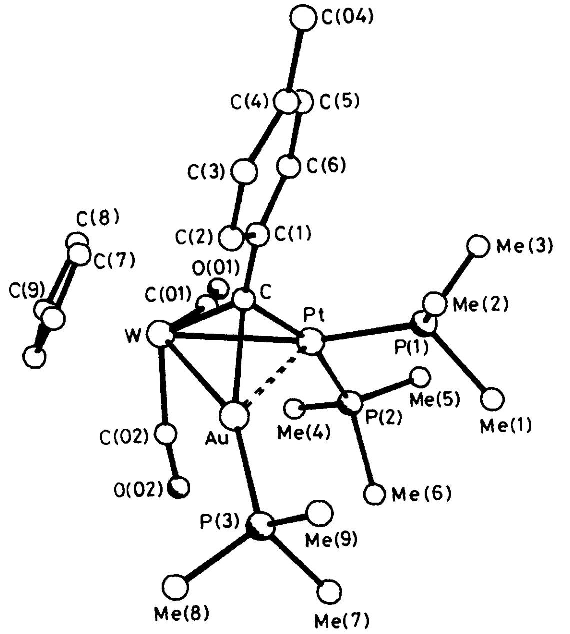

Figure 2. Molecular structure of the cation $[AuPtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)]^+$ of (5), showing the atom-numbering scheme

A triangle of metal atoms is capped by the *p*-tolylmethylidyne group. The Pt–W separation [2.770(2) Å] is similar to those found in the cluster compounds $[Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]$ (cod = cyclo-octa-1,5-diene) [2.750(1) Å][5] and $[FePtW(\mu_3\text{-}CR)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ [2.775(1) Å][17] which also contain triangular arrays of metal atoms spanned by μ_3-CR groups. The Au–W distance [2.801(2) Å] may be compared with that found [2.752(1) Å] in (3a).[6] The Au–Pt separation [2.956(2) Å] is appreciably longer, and may indicate little direct metal–metal bonding. The Au–Pt distance would then be defined by the geometrical requirements of the bridging $RC{\equiv}W(CO)_2(\eta\text{-}C_5H_5)$ group which would use its two orthogonal π orbitals to form bonds with the $Au(PMe_3)$ and $Pt(PMe_3)_2$ fragments. The cation has 44 cluster valence electrons, two less than in $[Pt_2W(\mu_3\text{-}CR)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ where the Pt–Pt distance [2.989(3) Å] has also been taken to imply little or no metal–metal bonding.[18] The presence of platinum or gold atoms in clusters commonly leads to stable species with fewer valence electrons than the number associated with clusters containing d^6—d^9 elements. The latter generally form tri- or tetra-nuclear low-valent compounds with 48 or 60 cluster valence electrons, respectively, each metal centre having an 18-electron environment.

The alkylidyne carbon atom in (5) asymmetrically bridges the metal triangle [C–Au 2.21(4), C–Pt 1.97(4), and C–W 2.01(4) Å]. The tungsten atom carries the cyclopentadienyl ligand and two carbonyl groups. The latter are distorted towards the platinum atom, but the low resolution of the W–C–O angles (Table 3) makes critical discussion unwarranted. The C_5H_5 ring is inclined at 72° to the metal triangle, while the μ_3-CC_6H_4Me-4 group on the other side is nearly perpendicular (84°) to it. If direct Au–Pt bonding is neglected, the platinum atom is in a distorted square-planar environment, defined by C, P(1), P(2), and W, with the atoms C and W lying 0.24 and 0.37 Å, respectively, from the P_2Pt plane. The P(2)–Pt distance [2.32(2) Å] is significantly longer than P(1)–Pt [2.26(1) Å], in accord with P(2) being transoid to μ_3-C [P(2)–Pt–C 162(1) and P(1)–Pt–C 99(1)°].[19] A similar effect is seen in the trimetal cluster $[FePtW(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ [P–Pt, 2.331(4) and 2.289(3) Å].[17] The Au–P distance [2.27(1) Å] is as expected,[20] being similar to that found in (1).

Having established the structure of (5) by *X*-ray crystallography, it was possible to devise a rational synthesis involving treatment of $[PtW(\mu\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$[21] with $[Au(PMe_3)]^+$, the latter being generated *in situ* from $[AuCl(PMe_3)]$ and $AgPF_6$ in thf–MeOH. Since the groups $[Au(PMe_3)]^+$ and H^+ are isolobal, it is interesting to compare this synthesis of (5) with the protonation of $[PtW(\mu\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ which gives[22] the cation $[PtW(\mu\text{-}CHR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$.

The unexpected formation of (5) from the reaction between (3a) and $[Pt(C_2H_4)(PMe_3)_2]$ in thf suggests that some free PMe_3 is present, which is captured by a weakly ligated gold atom so as to produce the $Au(PMe_3)$ fragment in the product. We have previously mentioned[6] the tendency of (3a) in solution to dissociate $[W({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$, and this property (Scheme) could lead to a species $[(\eta\text{-}C_5H_5)(OC)_2\overline{W(\mu\text{-}CR)Au}(thf)]^+$. Combination of the latter with PMe_3 and $Pt(PMe_3)_2$ would yield (5), as the most thermodynamically stable product among the various species present in the equilibrium mixture.

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. The n.m.r. measurements were made with JNM-FX 90Q and FX 200 instruments, and i.r. spectra with a Nicolet 10-MX FT spectrophotometer. The compounds $[W({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me),[8] $[Pt(cod)_2]$,[23] $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$,[6] $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$,[21] and $[N(PPh_3)_2][W_2\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_7(\eta\text{-}C_5H_5)]$[7] were prepared as previously described.

Synthesis of $[AuW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (1).—A mixture of $[N(PPh_3)_2][W_2\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_7(\eta\text{-}C_5H_5)]$ (1.11 g, 0.87 mmol) and $TlPF_6$ (0.50 g, 1.43 mmol) in thf (10 cm^3) was treated with $[AuCl(PPh_3)]$ (0.43 g, 0.87 mmol). After stirring for 1 h, during which time the mixture turned black, solvent was removed *in vacuo*. The residue was dissolved in light petroleum–dichloromethane (3 : 2) and chromatographed on a Florisil column (*ca.* 2.5 × 15 cm), at −20 °C, eluting with light petroleum–dichloromethane (3 : 2). Removal of solvent *in vacuo* from the purple eluate afforded purple *microcrystals* of $[AuW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$ (1) (0.32 g, 42%) (Found: C, 43.9; H, 3.2. $C_{33}H_{28}AuO_2PW\cdot CH_2Cl_2$ requires C, 43.5; H, 3.1%); $\nu_{max.}$(CO) at 1 888s and 1 793m cm^{-1} (CH_2Cl_2), and at 1 881s and 1 786s cm^{-1} (Nujol).

Reactions between $[W({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 *or* Me) *and* $[AuCl(PR_3)]$ [PR_3 = PPh_3 *or* $P(cyclo\text{-}C_6H_{11})_3$].—Similar procedures were used to prepare the compounds (2) (Table 1). Thus $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.13 g, 0.31 mmol) in dichloromethane (10 cm^3) was treated with $[AuCl(PPh_3)]$ (0.15 g, 0.31 mmol), and $TlPF_6$ (0.18 g, 0.50 mmol) was then added. After stirring the mixture for 1 h, i.r. analysis showed that all the $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ had been consumed. The mixture was filtered through a Celite plug (*ca.* 1 × 3 cm), and the solvent was removed *in vacuo*. Washing the residue obtained with light petroleum (2 × 15 cm^3) gave an orange powder (0.29 g), the n.m.r. data for which showed the salt $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$-

Table 4. Atomic positional parameters (fractional co-ordinates × 10^4) for complex (1), with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Au	1 844(1)	1 987(1)	2 487(1)
W	−498(1)	1 177(1)	1 355(1)
P	3 084(4)	3 072(3)	3 543(2)
C(01) [a]	−795(18)	3 203(20)	668(13)
C(02)	−1 576	2 178	191
C(03)	−2 782	1 794	491
C(04)	−2 746	2 581	1 153
C(05)	−1 517	3 452	1 263
C(01A) [a]	−838(29)	2 884(33)	345(16)
C(02A)	−766	3 590	1 036
C(03A)	−1 998	3 207	1 316
C(04A)	−2 830	2 264	798
C(05A)	−2 113	2 064	198
C(12) [a]	1 596(9)	5 483(8)	3 026(4)
C(13)	860	6 739	3 087
C(14)	666	7 192	3 785
C(15)	1 208	6 389	4 422
C(16)	1 943	5 134	4 361
C(11)	2 137	4 681	3 663
C(22) [a]	4 633(9)	2 211(9)	4 989(5)
C(23)	4 730	1 577	5 674
C(24)	3 503	902	5 789
C(25)	2 179	860	5 218
C(26)	2 083	1 493	4 532
C(21)	3 310	2 169	4 418
C(32) [a]	5 853(9)	2 526(7)	3 244(5)
C(33)	7 301	2 828	3 203
C(34)	7 857	4 104	3 434
C(35)	6 965	5 077	3 707
C(36)	5 517	4 776	3 748
C(31)	4 961	3 500	3 516
C(1A)	1 741(14)	1 000(13)	1 347(8)
C(1B)	2 987(13)	−23(12)	1 547(7)
C(2B)	4 219(15)	78(14)	1 226(8)
C(3B)	5 413(16)	−901(14)	1 398(8)
C(4B)	5 431(14)	−1 969(12)	1 872(7)
C(5B)	4 238(15)	−2 031(14)	2 178(8)
C(6B)	3 029(14)	−1 084(13)	2 018(7)
C(41B)	6 742(17)	−2 940(15)	2 042(9)
C(1)	−575(16)	−792(22)	1 138(9)
O(1)	−622(12)	−1 955(13)	1 039(7)
C(2)	−696(16)	329(16)	2 273(10)
O(2)	−888(11)	−152(10)	2 805(7)
Cl(1) [b]	3 868(5)	4 288(4)	1 626(2)
Cl(2) [b]	3 113(5)	3 789(5)	29(3)
C [b]	3 794(19)	4 928(17)	755(9)
Ha [b]	3 147	5 735	683
Hb [b]	4 791	5 155	737

[a] The rings are defined with regular geometry and common e.s.d.s.
[b] CH_2Cl_2 of crystallisation.

Table 5. Atomic positional parameters (fractional co-ordinates) (× 10^4) for complex (5), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	5 832(2)	3 348(1)	2 998(1)
Au	3 871(2)	1 403(2)	1 991(2)
W	3 325(2)	3 809(2)	1 593(1)
P(1)	6 962(12)	2 378(10)	4 392(10)
P(2)	7 640(12)	3 819(11)	2 609(11)
P(3)	4 052(16)	−541(11)	1 670(11)
P	9 706(14)	8 871(13)	2 049(10)
F(1)	11 028(50)	9 007(43)	2 991(34)
F(2)	8 412(72)	8 732(64)	1 134(52)
F(3)	9 154(54)	7 801(47)	2 375(37)
F(4)	10 252(53)	10 043(47)	1 724(37)
F(5)	10 502(56)	8 044(49)	1 605(39)
F(6)	8 882(61)	9 616(53)	2 459(42)
Me(1)	8 333(51)	1 413(46)	4 367(37)
Me(2)	6 042(58)	1 255(52)	4 859(41)
Me(3)	7 719(60)	3 324(54)	5 505(42)
Me(4)	7 414(53)	4 925(48)	1 758(38)
Me(5)	9 246(51)	4 376(45)	3 620(36)
Me(6)	8 170(47)	2 515(41)	2 105(33)
Me(7)	5 628(56)	−867(49)	1 500(39)
Me(8)	2 674(66)	−1 149(60)	569(46)
Me(9)	3 978(53)	−1 561(47)	2 555(38)
C(7) *	1 248(41)	4 044(34)	1 659(23)
C(8)	1 665	5 146	1 392
C(9)	1 694	4 990	461
C(10)	1 295	3 790	153
C(11)	1 020	3 206	894
C(01)	4 663(41)	5 046(36)	2 038(29)
O(01)	5 262(33)	6 040(30)	2 123(24)
C(02)	4 553(83)	3 350(75)	1 071(60)
O(02)	4 720(46)	3 080(41)	216(33)
C	3 995(38)	3 006(34)	2 886(27)
C(1) *	3 431(27)	2 819(25)	3 655(17)
C(2)	2 524	1 886	3 590
C(3)	2 039	1 749	4 315
C(4)	2 461	2 545	5 105
C(5)	3 367	3 478	5 170
C(6)	3 852	3 615	4 444
C(04)	2 007(52)	2 322(45)	5 863(36)

* The rings are defined with regular geometry and common e.s.d.s.

[PF$_6$] (2a) to be present (Table 1), together with [Au{W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)}$_2$][PF$_6$] (3a) and [Au(PPh$_3$)$_2$][PF$_6$] (see Results and Discussion section).

Synthesis of [AuPtW(μ$_3$-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_3$(η-C$_5$H$_5$)][PF$_6$] (5).—The compound [Pt(cod)$_2$] (0.2 g, 0.5 mmol) in ethylene-saturated light petroleum (5 cm^3) at 0 °C was treated with a solution of PMe$_3$ (1.1 mmol) in 2.1 cm^3 of the same solvent to generate [Pt(C$_2$H$_4$)(PMe$_3$)$_2$] *in situ*. This reagent was then treated with [Au{W(≡CR)(CO)$_2$(η-C$_5$H$_5$)}$_2$][PF$_6$] (3a) (0.2 g, 0.17 mmol) in thf (15 cm^3), and the mixture stirred (0.5 h) under an ethylene atmosphere. The solution was concentrated *in vacuo* to *ca.* 5 cm^3, after which diethyl ether (60 cm^3) was added, affording a precipitate. Solvent was removed (syringe), and the precipitate was washed with diethyl ether (5 × 15 cm^3), dissolved in thf (30 cm^3), and passed through a Celite pad (*ca.* 2.5 × 5 cm). Concentration to *ca.* 10 cm^3 and slow addition of diethyl ether gave brown *crystals* of [AuPtW(μ$_3$-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_3$(η-C$_5$H$_5$)][PF$_6$] (5) (0.15 g, 75%) (Found: C, 24.6; H, 3.3. $C_{24}H_{39}AuF_6O_2P_4PtW$ requires C, 24.6; H, 3.3%); $\nu_{max.}$(CO) at 1 936s and 1 831m br cm^{-1} (in CH$_2$Cl$_2$), and 1 932s and 1 840s br cm^{-1} (in Nujol).

Compound (5) can also be prepared by the following route. A suspension of [AuCl(PMe$_3$)] (0.033 g, 0.107 mmol) in thf (10 cm^3) was treated with AgPF$_6$ (0.025 g, 0.099 mmol) in methanol (1 cm^3). After filtration to remove AgCl, the filtrate was added to [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (0.089 g, 0.118 mmol) in thf (5 cm^3), and the solution stirred (5 min). Concentration *in vacuo* to *ca.* 5 cm^3 and addition of diethyl ether (*ca.* 60 cm^3) gave, after removal of solvent, brown *crystals* of (5) (0.65 g, 56%).

Crystal Structure Determinations.—Crystals of (1) grew as purple rhombs from dichloromethane–light petroleum; those of (5) were very small, almost black, prisms obtained from diethyl ether. Crystals were sealed under nitrogen in glass capillary tubes, and diffracted intensities were collected (ω scans) on a Nicolet *P*3*m* four-circle diffractometer at 200 K for (1) and at 298 K for (5). For (1) the crystal dimension was *ca.* 0.20 × 0.22 × 0.32 mm, and for both species data were recorded in the range $2.9 \leqslant 2\theta \leqslant 50°$. For (1), of 5 831 intensities, 4 983 had $I \geqslant 1\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, and these were used in the solution and final refinement of the structure, after the data had been corrected for Lorentz and polarisation effects, decay factors, and a numerical correction applied for *X*-ray absorption.[24] The corresponding data from the very small crystal of (5) [3 147, having 2 168 with $I \geqslant 5\sigma(I)$] were extremely limited and of low resolution, reflected in the higher cut off [$I \geqslant 5\sigma(I)$]. This coupled with the reduction in diffracting power on exposure to *X*-rays (>10% in 72 h) led to an overall low precision in the molecular parameters.

Crystal data for (1). $C_{33}H_{28}AuO_2PW{\cdot}CH_2Cl_2$, $M = 953.4$, triclinic, $a = 9.219(5)$, $b = 9.845(6)$, $c = 18.393(14)$ Å, $\alpha = 90.35(6)$, $\beta = 104.77(5)$, $\gamma = 87.27(4)°$, $U = 1\,612(2)$ Å^3, $Z = 2$, $D_c = 1.98$ g cm^{-3}, $F(000) = 904$, space group $P\bar{1}$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 83.4 cm^{-1}.

Crystal data for (5). $C_{24}H_{39}AuF_6O_2P_4PtW$, $M = 1\,173.3$, triclinic, $a = 10.920(8)$, $b = 11.237(7)$, $c = 15.002(17)$ Å, $\alpha = 90.18(7)$, $\beta = 113.63(9)$, $\gamma = 91.79(6)°$, $U = 1\,685(3)$ Å^3, $Z = 2$, $D_c = 2.32$ g cm^{-3}, $F(000) = 1\,088$, space group $P\bar{1}$, Mo-K_α (*X*-radiation), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 122.4 cm^{-1}.

Structure solution and refinement. The structures were solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods, with refinements by blocked-cascade least squares. In (1) the cyclopentadienyl carbon atoms showed a positional disorder with the two possible orientations of the ring in a ratio of 3 : 2. All other atoms of (1) were refined with anisotropic thermal parameters, and hydrogen atoms of the C_6 and C_5 rings were incorporated at calculated 'riding' positions (C–H = 0.96 Å), with common group isotropic thermal parameters. The hydrogen atoms of the Me-4 group were constrained to tetrahedral geometry. However, the hydrogen atom [H(1A)] bound to the alkylidene-bridged carbon atom was located from the difference-density maps, and was satisfactorily refined. One molecule of CH_2Cl_2 co-crystallises in the lattice and was refined satisfactorily with anisotropic thermal parameters for Cl and isotropic parameters for the CH_2 group. For (5), only the metal triangle and the attached phosphorus atoms were refined with anisotropic thermal parameters. All other atoms were refined isotropically, and no hydrogens were included in the structure factor calculation. The $[PF_6]^-$ anion exhibited considerable thermal activity, but no positional disorder was detectable. The closest contacts occur between the Me carbon atoms of the PMe_3 groups and the F atoms of the anion (>3.3 Å), otherwise there are no particularly short inter- or intra-molecular contacts.

Weighting schemes were applied of the form $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$, where $g = 0.0063$ for (1) and 0.0025 for (5). The analyses of these were reasonable. The final electron-density difference synthesis for (1) showed no peaks >*ca.* 2 e Å^{-3}; the largest peaks were close to the W atoms. For (5) there was considerable ripple and residual peaks *ca.* 3.5 e Å^{-3} close to the heavy-metal atom triangle. Scattering factors and corrections for anomalous dispersions were from ref. 25. Refinements converged for (1) at *R* 0.044 (*R′* 0.045) and for (5) at *R* 0.088 (*R′* 0.094). All calculations were performed on an 'Eclipse' Data General computer with the SHELXTL system of programs.[24] Atom coordinates for compounds (1) and (5) are listed in Tables 4 and 5, respectively.

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