Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 106.[1] Synthesis and Reactions of the Alkylidyne Complexes $[M(\equiv CR)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (M = W or Mo, R = alkyl or aryl, pz = pyrazol-1-yl); Crystal Structure of $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ *

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Treatment of the salts $[M(\equiv CR)(CO)_2\{HC(pz)_3\}][BF_4]$ [M = W or Mo, R = alkyl or aryl, $HC(pz)_3$ = tris(pyrazol-1-yl)methane] in thf (tetrahydrofuran) with NaOEt, followed by $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene), affords the neutral alkylidynemetal compounds $[M(\equiv CR)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (M = W or Mo, R = C_6H_4Me-4; M = W, R = Me or $C_6H_3Me_2$-2,6). The complexes (M = W, R = Me or C_6H_4Me-4) have been used to prepare several compounds containing heteronuclear metal–metal bonds, including $[WAuX(\mu\text{-}CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (X = Cl or C_6F_5), $[WCo_2(\mu_3\text{-}CR)(CO)_8\{(C_6F_5)AuC(pz)_3\}]$, $[WPt(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$, and $[W_2Pt(\mu\text{-}CR)_2(CO)_4\{(C_6F_5)AuC(pz)_3\}_2]$. The cluster compound $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ has been synthesised by different routes, and its structure established by *X*-ray diffraction. The core of the molecule consists of a WPtAu triangle [W–Pt 2.798(2), W–Au 2.841(2), and Pt–Au 2.932(2) Å] asymmetrically capped by an ethylidyne group [μ-C–W 2.06(3), μ-C–Pt 2.05(3), and μ-C–Au 2.31(3) Å]. The latter lies appreciably further from the Au atom than from the W or Pt atoms. The two carbonyl ligands semi-bridge the W–Pt [W–C–O 160(2)°] and W–Au [W–C–O 165(3)°] bonds. The Pt atom carries the PMe_2Ph groups [P–Pt 2.26(1) and 2.32(1) Å], and the Au atom is co-ordinated by the C_6F_5 group [C–Au 2.04(3) Å]. The W atom is ligated by the three nitrogens of the $(C_6F_5)AuC(pz)_3$ moiety (N–W average 2.21 Å). The n.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$, and $^{19}F\text{-}\{^1H\}$) for the new compounds are reported and discussed where appropriate.

In the previous paper[1] we reported the synthesis of the alkylidyne-tungsten and -molybdenum compounds $[M(\equiv CR)(CO)_2\{R'C(pz)_3\}][BF_4]$ (**1**; M = Mo or W; R = Me, C_6H_4-Me-4, or $C_6H_3Me_2$-2,6; R′ = H or Me; pz = pyrazol-1-yl), and described reactions of some of these salts with $[Co_2(CO)_8]$ and the zerovalent platinum complexes $[Pt(nb)_3]$ (nb = norbornene = bicyclo[2.2.1]heptene) and $[Pt(nb)(PMe_2Ph)_2]$. The products isolated showed that the dicobalt or platinum species readily add to the C≡M bonds in the reagents (**1**) to form di- or tri-metal compounds, as has been observed previously with the related neutral complexes $[M(\equiv CR)(CO)_2\{HB(pz)_3\}]$ [M = Mo or W; $HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate].[2]

In this paper we further develop the derivative chemistry of the salts (**1**). It was anticipated that treatment of the latter with nucleophiles (Nu^- = H^-, Me^-, or OEt^-) would afford neutral alkylidene metal complexes of formulation $[M\{=C(R)Nu\}(CO)_2\{R'C(pz)_3\}]$. In practice the reactions followed a different course, with the compounds (**1a**)—(**1d**) undergoing deprotonation at the bridgehead carbon, while treatment of (**1e**) with the nucleophiles led only to decomposition.

Results and Discussion

Preliminary studies revealed that treatment of compound (**1a**) or (**1b**) in thf (tetrahydrofuran) at −78 °C with NaOEt, LiMe, LiBu, NaH, or $K[BH(CHMeEt)_3]$ resulted in formation of the same neutral but unstable product, which displayed $\nu_{max.}(CO)$ at 1 978 and 1 888 cm^{-1}. These frequencies are lower than those for (**1a**) (1 994 and 1 907 cm^{-1}),[1] as expected for formation of a neutral species. The latter reverted to (**1a**) on warming to room temperature, evidently scavenging a proton from the reaction mixture. Interestingly, addition of MeI at −78 °C afforded the salt (**1e**). The latter has been prepared previously by treating $[WBr(\equiv CMe)(CO)_4]$ with $MeC(pz)_3$ [1,1,1-tris(pyrazol-1-yl)ethane] in the presence of $TlBF_4$.[1] It was evident from these results that nucleophiles were deprotonating the salt (**1a**) and forming in solution a zwitterionic species $[\,\ddot{:}C(pz)_3W(\equiv CMe)(CO)_2]$. However, the presence of the pyrazol-1-yl rings in the latter allows for delocalisation of the charge from the bridgehead carbon into the rings and subsequently on to the metal centre. Consequently, several canonical forms can be written for the $C(pz)_3W$ fragment in such an intermediate.

The species formed on deprotonation of (**1a**)—(**1d**) can be captured by treating these salts in thf at −78 °C with a slight excess (1.2 equivalents) of NaOEt, followed by $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene). Since the latter reagent functions as a source of the Lewis-acid fragment $Au(C_6F_5)$, isolobal with a proton, the products formed are the neutral alkylidyne metal complexes $[M(\equiv CR)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ [M = W, R = Me (**2a**), C_6H_4Me-4 (**2b**), and $C_6H_3Me_2$-2,6 (**2c**); M = Mo, R = C_6H_4Me-4, (**2d**)] in which the bridgehead carbon atom ligates a pentafluorophenylgold moiety. The new compounds were characterised by the data given in Tables 1 and 2.

As expected the complexes (**2a**)—(**2d**) display two strong CO stretching bands in their i.r. spectra, and it is interesting to compare the bands for (**2a**) (1 985 and 1 894 cm^{-1}) with those observed in the spectrum of the related compound

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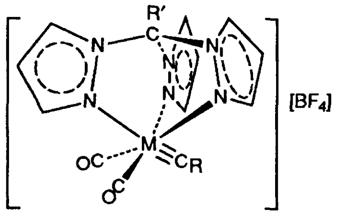
* Dicarbonyl-1κ^2C-bis(dimethylphenylphosphine)-2κ^2P-μ_3-ethylidyne-pentafluorophenyl-3κC[pentafluorophenylauriotris(pyrazol-1-yl)methane-1$\kappa^3N^2,N^{2'},N^{2''}$]-*triangulo*-3-gold-2-platinum-1-tungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

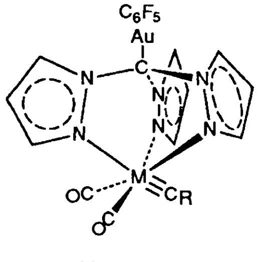
Table 1. Analytical[a] and physical data for the complexes

	Compound	Colour	Yield (%)	$\nu_{max.}$(CO)[b]/cm^{-1}	Analysis (%) C	Analysis (%) H	Analysis (%) N
(2a)	$[W(\equiv CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$	Yellow	56	1 985s, 1 894s	28.4 (28.4)	1.8 (1.4)	9.4 (9.9)
(2b)	$[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$	Orange	73	1 985s, 1 899s	34.0 (33.9)	2.1 (1.8)	8.7 (9.1)
(2c)	$[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$	Orange	68	1 986s, 1 900s	34.8 (34.7)	2.0 (1.9)	8.8 (9.0)
(2d)	$[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$	Orange	78	1 999s, 1 919s	38.2 (37.5)	2.7 (2.0)	9.5 (10.1)
(3a)	$[WAu(C_6F_5)(\mu\text{-}CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$	Yellow	88	2 017s, 1 938s	25.7 (25.8)	1.0 (1.0)	6.5 (6.9)
(3b)	$[WAuCl(\mu\text{-}CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$	Yellow	100[c]	2 020s, 1 941s	21.8 (22.3)	1.1 (1.1)	7.9 (7.8)
(4)	$[WMnAu(\mu\text{-}CMe)(CO)_7\{(C_6F_5)AuC(pz)_3\}]$	Yellow	8	2 063w, 2 006m, 1 958s, 1 931m	24.0 (24.3)	1.1 (1.0)	6.4 (6.8)
(5a)	$[WCo_2(\mu_3\text{-}CMe)(CO)_8\{(C_6F_5)AuC(pz)_3\}]$	Green	39	2 084s, 2 045s, 2 038s, 2 014m (sh), 1 995m (sh), 1 986m, 1 899s, 1 838w (br)	27.3 (27.6)	1.1 (1.1)	7.3 (7.4)
(5b)	$[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\text{-}\{(C_6F_5)AuC(pz)_3\}]$	Green	32	2 086s, 2 047s, 2 039s, 2 016m, 1 993m, 1 987m, 1 899m, 1 834w (br)	30.9 (31.9)	1.1 (1.3)	6.4 (7.0)
(6a)	$[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\text{-}\{(C_6F_5)AuC(pz)_3\}]$	Red	36	1 886s, 1 785m(br)	31.9 (32.9)	3.1 (2.6)	5.8 (6.4)
(6b)	$[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2\text{-}\{(C_6F_5)AuC(pz)_3\}]$	Red	76	1 904s, 1 743m (br)	36.4 (36.3)	3.3 (2.8)	5.8 (6.0)
(7a)	$[W_2Pt(\mu\text{-}CMe)_2(CO)_4\{(C_6F_5)AuC(pz)_3\}_2]$	Orange	72	1 964m (sh), 1 945s, 1 800m (br)	26.1 (25.5)	1.5 (1.3)	8.6 (8.9)
(7b)	$[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\text{-}\{(C_6F_5)AuC(pz)_3\}_2]$	Red	78	1 976s; 1 953s, 1 809m (br)	30.4 (30.7)	1.6 (1.6)	7.5 (8.2)
(8)	$[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\text{-}\{(C_6F_5)AuC(pz)_3\}]$	Green	30	1 919s, 1 761m (br)	29.4 (30.0)	2.3 (2.0)	4.9 (5.0)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2. [c] Complex formed essentially quantitatively.



	M	R	R'
(1a)	W	Me	H
(1b)	W	$C_6H_4Me\text{-}4$	H
(1c)	W	$C_6H_3Me_2\text{-}2,6$	H
(1d)	Mo	$C_6H_4Me\text{-}4$	H
(1e)	W	Me	Me



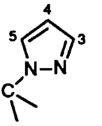
	M	R
(2a)	W	Me
(2b)	W	$C_6H_4Me\text{-}4$
(2c)	W	$C_6H_3Me_2\text{-}2,6$
(2d)	Mo	$C_6H_4Me\text{-}4$

$[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$[2a] at 1 983 and 1 899 cm^{-1}. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the compounds (**2**) diagnostic resonances for the ligated carbon atoms of the alkylidyne groups occur at δ 301.6 (**2a**), 290.0 (**2b**), 293.9 (**2c**), and 300.7 p.p.m. (**2d**). Again these data are similar to those for the species $[M(\equiv CR)(CO)_2\{HB(pz)_3\}]$. Thus the $CC_6H_4Me\text{-}4$ resonance in the spectrum of $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$[2d] occurs at 293.1 p.p.m., compared with that at 300.7 p.p.m. for (**2d**).

Treatment of complex (**2a**), prepared *in situ* from (**1a**), NaOEt, and $[Au(C_6F_5)(tht)]$, with the compounds $[AuX(tht)]$ ($X = C_6F_5$ or Cl) in CH_2Cl_2, affords the species $[WAuX(\mu\text{-}CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (**3a**; $X = C_6F_5$) and (**3b**; X = Cl), respectively. Data for these products are given in Tables 1 and 2, although (**3b**) was too insoluble to obtain meaningful $^{13}C\text{-}\{^1H\}$ n.m.r. measurements. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**3a**) the μ-*C*Me resonance (288.3 p.p.m.) is appreciably less deshielded than expected if the ethylidyne ligand were fully bridging the metal–metal bond. In the latter situation μ-*C*R (R = alkyl or aryl) resonances generally occur in the range δ 300—400 p.p.m.[3] It is likely that in both compounds (**3**) the ethylidyne group remains much closer to the tungsten, so that the C≡W group is relatively unperturbed by ligation of the AuX groups. *X*-Ray diffraction studies have shown that this is the situation for the $\mu\text{-}CC_6H_4Me\text{-}4$ groups in the complexes $[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$,[4a] $[MoWCoAu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$,[4b] and $[WRhAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PPh_3)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_{11})]$.[4c] Moreover, as discussed below, there is evidence that in reactions of the species (**3**) the AuX groups readily dissociate.

Attempts were made to use the complex (**3b**) as a precursor to

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes



Compound	^{1}H (δ)	^{13}C (δ)[b]
(2a)	2.41 (s, 3 H, Me), 6.29 (m, 1 H, H^4), 6.37 (m, 2 H, H^4), 7.76 [d, 1 H, H^3, J(H^{3}H^4) 3], 8.05 [d, 2 H, H^3, J(H^{3}H^4) 3], 8.90 [d, 1 H, H^5, J (H^{4}H^5) 3], 8.97 [d, 2 H, H^5, J(H^{4}H^5) 3]	301.6 (C≡W), 221.8 (CO), 150.9 [d, C_6F_5, J(FC) 24], 147.6 [d, C_6F_5, J(FC) 22], 146.1, 145.1 ($C_3H_3N_2$), 140.5 (C_6F_5), 138.8 [d, C_6F_5, J(FC) 29], 138.0 ($C_3H_3N_2$), 135.3 [d, C_6F_5, J(FC) 27], 106.0 ($C_3H_3N_2$), 38.4 (Me)
(2b)	2.30 (s, 3 H, Me-4), 6.32 (m, 1 H, H^4), 6.37 (m, 2 H, H^4), 7.12, 7.32 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 7.81 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.11 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.92 [d, 1 H, H^5, J(H^{4}H^5) 2], 8.97 [d, 2 H, H^5, J(H^{4}H^5) 3]	290.0 (C≡W), 222.6 (CO), 147.3 [C^1(C_6H_4)], 146.3—106.2 (C_6H_4, C_6F_5, and $C_3H_3N_2$), 21.6 (Me-4)
(2c)	2.43 (s, 6 H, Me$_2$-2,6), 6.32 (m, 1 H, H^4), 6.38 (m, 2 H, H^4), 6.92—7.11 (m, 3 H, C_6H_3), 7.80 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.15 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.92 [d, 1 H, H^5, J(H^{4}H^5) 2], 9.01 [d, 2 H, H^5, J(H^{4}H^5) 3]	293.9 (C≡W), 224.5 (CO), 146.6 [C^1(C_6H_3)], 145.1—106.1 (C_6H_3, C_6F_5, and $C_3H_3N_2$), 20.5 (Me$_2$-2,6)
(2d)	2.27 (s, 3 H, Me-4), 6.23 (m, 1 H, H^4), 6.28 (m, 2 H, H^4), 7.07, 7.35 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 7.66 [d, 1 H, H^3, J(H^{3}H^4) 2], 7.94 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.86 [d, 1 H, H^5, J(H^{4}H^5) 3], 8.92 [d, 2 H, H^5, J(H^{4}H^5) 3]	300.7 (C≡Mo), 224.6 (CO), 145.5—105.5 (C_6H_4, C_6F_5, and $C_3H_3N_2$), 21.6 (Me-4)
(3a)	3.04 (s, 3 H, Me), 6.43 (m, 2 H, H^4), 6.49 (m, 1 H, H^4), 8.09 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.23 [d, 2 H, H^3, J(H^{3}H^4) 2], 9.01 [d, 2 H, H^5, J(H^{4}H^5) 3], 9.03 [d, 1 H, H^5, J(H^{4}H^5) 3]	288.3 (μ-C), 215.4 (CO), 147.4—106.9 (C_6F_5 and $C_3H_3N_2$), 41.6 (Me)
(3b)[c]	3.04 (s, 3 H, Me), 6.46 (m, 3 H, H^4), 8.08 [d, 1 H, H^3, J(H^{3}H^4) 3], 8.18 [d, 2 H, H^3, J(H^{3}H^4) 2], 9.00 [d, 2 H, H^5, J(H^{4}H^5) 3], 9.02 [d, 1 H, H^5, J(H^{4}H^5) 3]	
(4)	2.82 (s, 3 H, Me), 6.44 (m, 3 H, H^4), 8.00 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.15 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.96 [d, 2 H, H^5, J(H^{4}H^5) 3], 9.02 [d, 1 H, H^5, J(H^{4}H^5) 3]	283.2 (μ-C), 220.0 (MnCO), 215.7 (WCO), 147.0—106.8 (C_6F_5 and $C_3H_3N_2$), 39.1 (Me)
(5a)	3.84 (s, 3 H, Me), 6.49 (s, 2 H, H^4), 6.51 (s, 1 H, H^4), 7.83 (s, 2 H, H^3 or H^5), 8.14 (s, 1 H, H^3 or H^5), 9.05 (s, 3 H, H^3 or H^5)	[d]225.3 (WCO), 198.8 (CoCO), 146.1—100.3 (C_6F_5 and $C_3H_3N_2$), 43.9 (Me)
(5b)	2.29 (s, 3 H, Me-4), 6.32 (s, 2 H, H^4), 6.45 (s, 1 H, H^4), 6.98—7.14 (m, 4 H, C_6H_4), 8.03 (s, 2 H, H^3 or H^5), 8.11 (s, 1 H, H^3 or H^5), 8.97 (s, 1 H, H^3 or H^5), 9.02 (s, 2 H, H^3 or H^5)	290.0 (μ_3-C), 226.9 (WCO), 199.3 (CoCO), 157.5 [C^1(C_6H_4)], 147.5—106.1 (C_6H_4, C_6F_5, and $C_3H_3N_2$), 20.7 (Me-4)
(6a)	1.50 [d, 6 H, MeP, J(PH) 9, J(PtH) 18], 1.96 [d, 6 H, MeP, J(PH) 8, J(PtH) 8], 2.70 (m, 3 H, CMe), 6.24 (m, 2 H, H^4), 6.38 (m, 1 H, H^4), 7.30—7.72 (m, 12 H, H^3 or H^5 and Ph), 8.15 (s, 1 H, H^3 or H^5), 8.96 (m, 3 H, H^3 or H^5)	352.5 [d, μ-C, J(PC) 53], 229.3 (CO), 145.9—105.7 (Ph, C_6F_5, and $C_3H_3N_2$), 41.6 (C*Me*), 17.8 [d, MeP, J(PC) 27], 15.5 [d, MeP, J(PC) 22]
(6b)	1.06 [d, 6 H, MeP, J(PH) 9, J(PtH) 17], 1.76 [d, 6 H, MeP, J(PH) 8, J(PtH) 12], 2.21 (s, 3 H, Me-4), 6.10 (m, 2 H, H^4), 6.21, 6.74 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 6.38 (m, 1 H, H^4), 7.16—7.56 (m, 12 H, H^3 and Ph), 8.07 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.88 [d, 2 H, H^5, J(H^{4}H^5) 3], 8.93 [d, 1 H, H^5, J(H^{4}H^5) 2]	337.1 [d, μ-C, J(PC) 55], 233.2 (CO), 146.1—105.2 (C_6H_4, Ph, C_6F_5, and $C_3H_3N_2$), 20.8 (Me-4), 15.9 [d, MeP, J(PC) 27], 15.2 [d, MeP, J(PC) 26]
(7a)	3.01 (s, 6 H, Me), 6.34 (m, 2 H, H^4), 6.43 (m, 2 H, H^4), 6.48 (m, 2 H, H^4), 7.98 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.06 [d, 2 H, H^5, J(H^{4}H^5) 3], 8.16 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.96—8.99 (m, 4 H, H^3 and H^5), 9.05 [d, 2 H, H^5, J(H^{4}H^5) 3]	314.6 (μ-C), 229.0, 221.7 (CO), 146.2—106.3 (C_6F_5 and $C_3H_3N_2$), 40.2 (Me)
(7b)	2.31 (s, 6 H, Me-4), 6.08 (m, 2 H, H^4), 6.31 (m, 2 H, H^4), 6.45 (m, 2 H, H^4), 6.88, 7.07 [(AB)$_2$, 8 H, C_6H_4, J(AB) 8], 6.98 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.00 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.10 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.92 [d, 2 H, H^5, J(H^{4}H^5) 3], 8.98 [d, 4 H, H^5, J(H^{4}H^5) 3]	303.1 (μ-C), 226.2, 224.0 (CO), 151.3 [C^1(C_6H_4)], 145.7—105.8 (C_6H_4, C_6F_5, and $C_3H_3N_2$), 21.4 (Me-4)
(8)	1.41 [d, 3 H, MeP, J(PH) 10, J(PtH) 18], 1.65 [d, 3 H, MeP, J(PH) 9, J(PtH) 19], 1.88 [d, 3 H, MeP, J(PH) 8, J(PtH) 17], 1.99 [d, 3 H, MeP, J(PH) 9, J(PtH) 17], 2.60 (m, 3 H, C*Me*), 6.03, 6.40, 6.47 (m × 3, 3 H, H^4), 6.81 [d, 1 H, H^3, J(H^{3}H^4) 2], 7.28—7.74 (m, 10 H, Ph), 8.37 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.79 [d, 1 H, H^5, J(H^{4}H^5) 3], 8.85 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.96 [d, 1 H, H^5, J(H^{4}H^5) 3], 9.01 [d, 1 H, H^5, J(H^{4}H^5) 3]	309.6 [d, μ_3-C, J(PC) 58, J(PtC) 244], 236.3 [d, μ-CO, J(PC) 9, J(PtC) 40], 222.5 (CO), 147.0—104.8 (Ph, C_6F_5, and $C_3H_3N_2$), 40.1 (C*Me*), 17.9 [d, MeP, J(PC) 29], 17.6 [d, MeP, J(PC) 33], 14.8 [d, MeP, J(PC) 29], 10.2 [d, MeP, J(PC) 26]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures in CD_2Cl_2. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (0.0 p.p.m.). [c] Carbon-13 spectrum not recorded due to insolubility of complex. [d] μ_3-*C*Me signal not observed due to low solubility of complex.

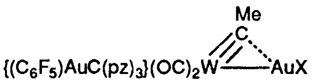
other species with metal–metal bonds by treatment with metal carbonyl anions. However, only Na[Mn(CO)$_5$] afforded a stable complex [WMnAu(μ-CMe)(CO)$_7${(C_6F_5)AuC(pz)$_3$}] **(4)**, and the latter was formed only in low yield (Table 1). It was established that failure to replace Cl in **(3b)** by metal carbonyl fragments was due to loss of AuCl, with formation of **(2a)** as a by-product.

Both **(2a)** and **(2b)** reacted slowly with [$Co_2(CO)_8$] in thf at *ca.* 35 °C to afford the complexes [WCo_2(μ_3-CR)(CO)$_8$-{(C_6F_5)AuC(pz)$_3$}] (**5a**; R = Me) and (**5b**; R = C_6H_4Me-4), data for which are given in Tables 1 and 2. These species are closely related to the salts [WCo_2(μ_3-CR)(CO)$_8${HC(pz)$_3$}]-[BF_4] (R = Me or C_6H_4Me-4) described in a previous paper.[1] They belong to a large family of compounds of formulation [WCo_2(μ_3-CR)(CO)$_8$L] [R = alkyl, alkynyl, or aryl; L = η-C_5H_5, η-C_5Me_5, HB(pz)$_3$, *etc.*] having similar core structures, consisting of a WCo_2 triangle capped by an alkylidyne group.[2d,3a,5] These species exist in solution as mixtures of diastereoisomers, apparently resulting from different orientations of the W(CO)$_2$L groups with respect to the μ_3-CCo_2 fragment. As a result the compounds display more than the expected number of CO bands for a single species in

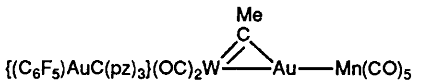
Table 3. Selected internuclear distances (Å) and angles (°) for the complex $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ (**8**)

Au(1)–Pt	2.932(2)	Au(1)–W	2.841(2)	Pt–W	2.798(2)	Pt–P(1)	2.32(1)
Pt–P(2)	2.26(1)	Au(1)–C(1)	2.31(3)	Pt–C(1)	2.05(3)	W–C(1)	2.06(3)
Au(1) • • • C(3)	2.62(4)	W–C(3)	2.10(4)	Pt • • • C(4)	2.44(3)	W–C(4)	1.95(3)
W–N(1)	2.17(3)	W–N(3)	2.20(3)	W–N(5)	2.25(2)	Au(2)–C(14)	2.09(3)
Au(1)–C(37)	2.04(3)	Au(2)–C(31)	2.05(4)	P(1)–C(15)	1.84(3)	P(1)–C(16)	1.81(4)
P(1)–C(17)	1.86(3)	P(2)–C(23)	1.82(4)	P(2)–C(24)	1.83(3)	P(2)–C(25)	1.76(4)
C(1)–C(2)	1.33(4)	C(3)–O(3)	1.11(5)	C(4)–O(4)	1.18(4)	N(1)–N(2)	1.37(3)
N(3)–N(4)	1.35(4)	N(5)–N(6)	1.32(4)	N(2)–C(14)	1.46(4)	N(4)–C(14)	1.50(4)
N(6)–C(14)	1.43(4)						

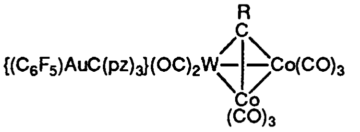
Pt–Au(1)–W	58.0(1)	Au(1)–Pt–W	59.4(1)	Au(1)–W–Pt	62.6(1)	Au(1)–Pt–P(1)	115.6(2)
Au(1)–Pt–P(2)	105.0(2)	W–Pt–P(1)	118.0(2)	W–Pt–P(2)	141.9(2)	Pt–Au(1)–C(1)	44.2(7)
W–Au(1)–C(1)	45.6(8)	W–Pt–C(1)	47.1(9)	Au(1)–C(1)–Pt	84(1)	Au(1)–C(1)–W	81(1)
Au(1)–W–N(1)	132(1)	Au(1)–W–N(3)	146(1)	Au(1)–W–N(5)	89(1)	Pt–W–N(1)	98(1)
Pt–W–N(3)	143(1)	Pt–W–N(5)	139(1)	P(1)–Pt–P(2)	100.0(3)	P(1)–Pt–C(1)	163(1)
P(2)–Pt–C(1)	95(1)	Au(1)–C(1)–C(2)	105(2)	Pt–C(1)–C(2)	142(2)	W–C(1)–C(2)	132(1)
N(1)–W–C(1)	80(1)	N(3)–W–C(1)	155(1)	N(5)–W–C(1)	93(1)	W–C(3)–O(3)	165(3)
W–C(4)–O(4)	160(2)	N(1)–W–C(3)	167(1)	N(3)–W–C(3)	91(1)	N(5)–W–C(3)	102(1)
N(1)–W–C(4)	90(1)	N(3)–W–C(4)	85(1)	N(5)–W–C(4)	159(1)	N(1)–W–N(3)	76(1)
N(1)–W–N(5)	78(1)	N(3)–W–N(5)	76(1)	Au(2)–C(14)–N(2)	112(2)	Au(2)–C(14)–N(4)	112(2)
Au(2)–C(14)–N(6)	114(2)	C(14)–Au(2)–C(31)	177(2)				



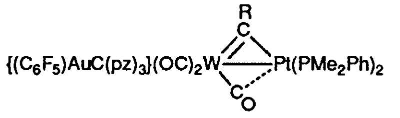
X
(3a) C_6F_5
(3b) Cl



(4)



R
(5a) Me
(5b) $C_6H_4Me\text{-}4$



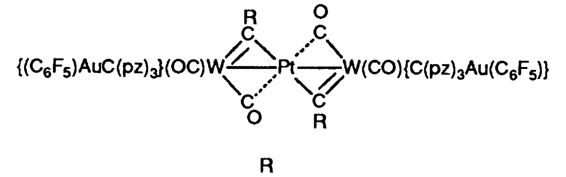
R
(6a) Me
(6b) $C_6H_4Me\text{-}4$

their i.r. spectra. However, the rotational isomers interconvert rapidly on the n.m.r. time-scale even at very low temperatures, and so only averaged signals are seen in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra. The compounds (**5**) are no exception to this pattern of behaviour, displaying eight CO bands in their i.r. spectra (Table 1), but only two CO resonances in their $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (Table 2). Indeed, this latter property also reveals that the carbonyl ligands are undergoing site exchange at their respective metal centres. Due to low solubility, it was not possible to observe a good quality $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**5a**), and so only the peak for the Me group (δ 43.9 p.p.m.) of the μ_3-CMe ligand was seen. However, for (**5b**) the μ_3-C signal was observed at 290.0 p.p.m. This chemical shift is somewhat more deshielded than the μ_3-C resonance (265.7 p.p.m.) in the spectrum of $[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\{HB(pz)_3\}]$,[2a] but is comparable with that observed (302.4 p.p.m.) for the μ_3-C group in $[NEt_4][WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$.[6]

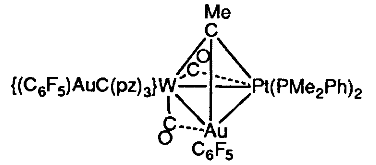
A characteristic property of compounds of the type $[W(\equiv CR)(CO)_2L]$ [R = alkyl or aryl; L = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, or $HB(pz)_3$] is the addition of low-valent platinum species to the W≡C bonds, thereby affording products containing W(μ-CR)Pt ring systems.[2a,c,d,h,7] To test whether this also occurs with the complexes (**2a**) and (**2b**), reactions with $[Pt(nb)(PMe_2Ph)_2]$ (nb = norbornene = bicyclo[2.2.1]heptene) and with $[Pt(nb)_3]$ were investigated.

Treatment of compound (**2a**) in thf with $[Pt(nb)(PMe_2Ph)_2]$ afforded a chromatographically separable mixture of the expected product $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ (**6a**) and, surprisingly, the complex $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ (**8**). After the latter had been fully characterised (see below) it was prepared in a more logical manner by treating (**6a**) with the reagent $[Au(C_6F_5)(tht)]$. The formation of (**8**) in the synthesis of (**6a**) apparently results from loss of a AuC_6F_5 fragment either from (**2a**), which subsequently adds to (**6a**), or from the latter. Interestingly, compound (**8**) is also formed in the reaction between (**3a**) and $[Pt(nb)(PMe_2Ph)_2]$, but monitoring this reaction by i.r. spectroscopy revealed formation of (**2a**) initially, which was subsequently consumed by the species $Pt(PMe_2Ph)_2$ and AuC_6F_5, present in solution, thereby affording the metal cluster (**8**). It is evident from these observations that both (**2a**) and (**3**) can function as sources of the AuC_6F_5 fragment in certain reactions.

The reaction between (**2b**) and $[Pt(nb)(PMe_2Ph)_2]$ gave $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ (**6b**) as the only product. As might be expected from this observation, compound (**6b**) fails to react with $[Au(C_6F_5)(tht)]$. Data characterising compounds (**6a**) and (**6b**) are listed in Tables 1 and 2. Both complexes show two CO stretching bands, but one absorption in each spectrum [1 785 (**6a**) and 1 743 cm^{-1} (**6b**)] is at low frequency suggesting that one ligand semi-bridges the W–Pt bond.[7] In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of both complexes there is only one CO resonance indicating site exchange between the carbonyl ligands on the n.m.r. time-scale.



R
(7a) Me
(7b) C_6H_4Me-4



(8)

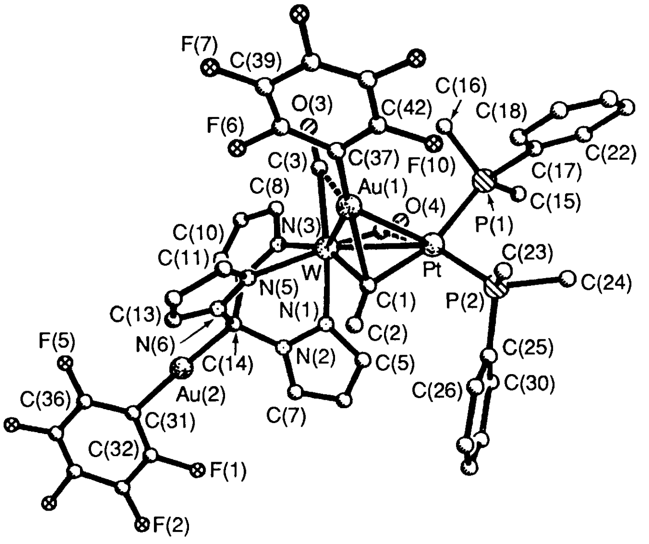


Figure. Molecular structure of $[WPtAu(C_6F_5)(\mu_3\text{-CMe})(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ (**8**), showing the crystallographic numbering scheme

Diagnostic signals for the μ-C groups appear as doublets [*J*(PC) *ca.* 54 Hz] at δ 352.5 (**6a**), and 337.1 p.p.m. (**6b**). In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of $[WPt(\mu\text{-CC}_6H_4Me\text{-}4)(CO)_2(PMe_3)_2\{HB(pz)_3\}]$ the μ-C resonance is a doublet [*J*(PC) 54 Hz] at δ 332.0 p.p.m.[2a] The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the compounds (**6**) (see Experimental section) show a characteristic pattern for *cis*-$(PMe_2Ph)_2$ groups, consisting of two doublet signals [*J*(PP) *ca.* 15 Hz] for the non-equivalent PMe_2Ph ligands, each signal displaying ^{195}Pt satellite peaks [*J*(PtP) *ca.* 2 000 and 1 400 Hz]. In each spectrum the resonance associated with the larger $^{195}Pt\text{-}^{31}P$ coupling can be attributed to the transoid $W\text{-}Pt\text{-}PMe_2Ph$ group.[7]

Treatment of complexes (**2a**) or (**2b**) with $[Pt(nb)_3]$ in thf afforded the compounds $[W_2Pt(\mu\text{-CR})_2(CO)_4\{(C_6F_5)AuC(pz)_3\}_2]$ (**7a**; R = Me) and (**7b**; R = C_6H_4Me-4). In these products platinum is ligated by the two $RC\equiv W(CO)_2\{(C_6F_5)AuC(pz)_3\}$ groups. Hence structurally these species are related to numerous other compounds in which a Pt atom is co-ordinated by two C≡M (M = Mo or W) bonds.[2h,8] The spectroscopic properties of the complexes (**7**) are in agreement with the formulations shown. Diagnostic resonances for the μ-C nuclei appear in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra at δ 314.6 (**7a**) and 303.1 p.p.m. (**7b**), and the remaining signals in these spectra, and in the ^1H n.m.r. spectra, are readily assigned (Table 2).

The various synthetic routes to the compound (**8**) were referred to earlier. The structure of this species was established by a single-crystal *X*-ray diffraction study. The significant bond distances and angles are given in Table 3, and the molecule is shown in the Figure. The core of the molecule consists of a WPtAu triangle [W–Au 2.841(2), W–Pt 2.798(2), and Pt–Au 2.932(2) Å] capped by an ethylidyne group [C(1)–W 2.06(3), C(1)–Pt 2.05(3), and C(1)–Au 2.31(3) Å]. However, the μ_3-C–Au separation is appreciably longer than the μ_3-C–W or μ_3-C–Pt distances. A similar structural feature is found in $[WPtAu(\mu_3\text{-CC}_6H_4Me\text{-}4)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$ [μ_3-C–W 2.01(4), μ_3-C–Pt 1.97(4), and μ_3-C–Au 2.21(4) Å], which also contains a μ_3-CWPtAu core.[9] The metal–metal distances in the latter [W–Au 2.801(2), W–Pt 2.770(2), and Pt–Au 2.956(2) Å] are close to those in compound (**8**). Moreover, the two structures are also similar in that the CO ligands are not terminally co-ordinated to the W atom, but asymmetrically bridge metal–metal bonds. Thus in complex (**8**), W–C(3)–O(3) 165(3)° with Au···C(3) 2.62(4) Å, and W–C(4)–O(4) 160(2)° with Pt···C(4) 2.44(3) Å. The W–C–O angles in $[WPtAu(\mu_3\text{-CC}_6H_4Me\text{-}4)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$ are 145(5) and 162(3)°. However, in this compound both CO ligands semi-bridge the W–Pt bond [Pt–CO 2.46(4) and 2.66(8) Å], whereas in (**8**) these ligands semi-bridge the W–Au and W–Pt bonds, respectively.

The trimetallatetrahedrane cores of compound (**8**) and the salt $[WPtAu(\mu_3\text{-CC}_6H_4Me\text{-}4)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$ are also present in the recently reported complexes $[WPtAu(\mu_3\text{-CR})(CO)_2L_2(L')(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-4, L = L′ = PMe_2Ph; R = C_6H_4Me-4 or Ph, L_2 = cod = cycloocta-1,5-diene, L′ = PPh_3; R = C≡CBu^t, L = PMe_2Ph, L′ = PPh_3).[10] All these species are related by the isolobal interchange of $\eta\text{-}C_5H_5$, $\eta^5\text{-}C_2B_9H_9Me_2$, or $(C_6F_5)AuC(pz)_3$ groups, with appropriate substitution of $AuPR_3$ (R = alkyl or aryl) by AuC_6F_5 fragments. The number of cluster valence electrons in these compounds is 44, and so all the metal centres in the core cannot attain 18-electron filled-shell configurations. This is usual for trimetal clusters containing platinum or gold, and electron counts at the individual metal centres for these unsaturated clusters are not meaningful.

The spectroscopic properties of complex (**8**) are interesting. In the i.r. spectrum there are two CO bands at 1 919 and 1 761 cm^{-1}. The latter may be assigned to a bridging or semi-bridging carbonyl group as found in the *X*-ray diffraction study, but the former is in the region for a terminally co-ordinated ligand. Evidently in solution the molecule adopts a somewhat different structure to that found in the solid state, where two asymmetrically bridging CO ligands were found. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum displays two CO resonances at δ 236.3 and 222.5 p.p.m. The former may be assigned to the $\overline{W(\mu\text{-CO})Pt}$ group since the signal shows both $^{31}P\text{-}^{13}C$ (9 Hz) and $^{195}Pt\text{-}^{13}C$ (40 Hz) coupling. The diagnostic resonance for the μ_3-*C*Me nucleus is at δ 309.6 p.p.m., and is a doublet [*J*(PC) 58 Hz] with ^{195}Pt satellite peaks [*J*(PtC) 244 Hz]. As expected, the diastereotopic Me groups of the PMe_2Ph ligands give rise to four resonances for these groups in both the $^{13}C\text{-}\{^1H\}$ and the ^1H n.m.r. spectra (Table 2). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (see Experimental section) consists of two singlet peaks at δ 0.6 and −13.3 p.p.m., with $^{195}Pt\text{-}^{31}P$ couplings of 2 014 and 1 468 Hz, respectively. The failure to observe $^{31}P\text{-}^{31}P$ coupling between the non-equivalent PMe_2Ph groups is not unusual for a *cis*-$Pt(PMe_2Ph)_2$ fragment.

All the new compounds reported in this paper contain an

AuC_6F_5 group. The ^{19}F n.m.r. spectra of all the complexes were measured. For those species containing a single AuC_6F_5 moiety three peaks are observed at δ −116.9, −160.0, and −163.2 (±0.2) p.p.m. and these resonances are of relative intensity 2:1:2, as expected. The peaks near −117 p.p.m. are doublets [J(FF) *ca.* 18—24 Hz], and may be assigned to the *ortho*-fluorine nuclei of the AuC_6F_5 group. The peak near −160 p.p.m., due to one fluorine nucleus, is a triplet [J(FF) *ca.* 18—24 Hz] and is clearly due to the *para*-fluorine. The multiplet close to δ −163 p.p.m. is thus assigned to the *meta*-fluorines. Complexes (**3a**), (**7a**), and (**7b**) also show three signals in their ^{19}F n.m.r. spectra and these again are in relative intensity 2:1:2. However, it was not possible to resolve the ^{19}F–^{19}F coupling in some spectra, the peaks being multiplets. The ^{19}F n.m.r. spectrum of (**8**) displayed resonances at δ −114.4 [d, J(FF) 24], −117.0 [d, J(FF) 24], −160.3, and −163.4 p.p.m. of relative intensity 2:2:4:4, the last two signals being multiplets.

The results described in this paper show that compounds of type (**2**) can be used in the synthesis of complexes containing heteronuclear metal–metal bonds. Moreover, it is interesting to note the close relationship between the neutral complexes described in this paper with the cationic complexes reported in a previous paper.[1] We have alluded earlier to the mapping of the species (**5**) with the salts $[WCo_2(\mu_3\text{-}CR)(CO)_8\{HC(pz)_3\}][BF_4]$, and several similar correlations exist, *e.g.* complexes (**7**) with $[W_2Pt(\mu\text{-}CR)_2(CO)_4\{HC(pz)_3\}_2][BF_4]_2$, and compound (**8**) with $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$.[1] These relationships exist because formally the $HC(pz)_3$ ligand is a six-electron donor whereas the $(C_6F_5)AuC(pz)_3$ ligand is a five-electron donor. Further studies are continuing with the reagents (**1**) and (**2**).

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. Light petroleum refers to that fraction of b.p. 40—60 °C. All solvents were rigorously dried before use. Alumina used in chromatography columns (*ca.* 20 cm in length and 1.5 cm in diameter) was BDH aluminium oxide (Brockman Activity II). The instrumentation employed for the spectroscopic measurements has been listed in previous Parts of this series. Phosphorus-31 n.m.r. chemical shifts are positive to high frequency of 85% H_3PO_4 (external), and fluorine-19 n.m.r. chemical shifts are positive to high frequency of CCl_3F (external), all spectra being measured in CD_2Cl_2. The compounds (**1a**)—(**1d**),[1] [AuCl(tht)], $[Au(C_6F_5)(tht)]$,[11] $[Pt(nb)_3]$,[12] and $[Pt(nb)(PMe_2Ph)_2]$[1] were prepared as described earlier. Analytical data for the new complexes are given in Table 1.

Preparation of the Complexes $[M(\equiv CR)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (M = W *or* Mo, R = Me, C_6H_4Me-4, *or* $C_6H_3Me_2$-2,6).—To a thf (25 cm^3) solution of compound (**1a**) (0.15 g, 0.26 mmol), cooled to −78 °C, was added NaOEt (0.35 mmol, from a standard solution prepared by dissolving NaH in EtOH), followed immediately by $[Au(C_6F_5)(tht)]$ (0.11 g, 0.26 mmol). The mixture was stirred while slowly warming to room temperature. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (2 cm^3) and chromatographed. Elution with CH_2Cl_2–hexane (7:3) removed a yellow fraction from which slow removal of solvent *in vacuo* afforded yellow *microcrystals* of $[W(\equiv CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (**2a**) (0.12 g).

A similar procedure was employed to prepare compounds (**2b**)—(**2d**) using the following quantities of reagents: (*i*) $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (**2b**) (0.21 g) was obtained from (**1b**) (0.20 g, 0.31 mmol), NaOEt (0.37 mmol), and $[Au(C_6F_5)(tht)]$ (0.14 g, 0.31 mmol); (*ii*) (**1c**) (0.25 g, 0.38 mmol), NaOEt (0.46 mmol), and $[Au(C_6F_5)(tht)]$ (0.17 g, 0.38 mmol) gave $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (**2c**) (0.24 g); (*iii*) (**1d**) (0.25 g, 0.45 mmol), NaOEt (0.54 mmol), and $[Au(C_6F_5)(tht)]$ (0.21 g, 0.45 mmol) afforded $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (**2d**) (0.29 g).

Reactions of the Complexes $[W(\equiv CR)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (R = Me *or* C_6H_4Me-4).—(*i*) A CH_2Cl_2 (10 cm^3) solution of compound (**2a**) (0.20 g, 0.24 mmol) was treated with $[Au(C_6F_5)(tht)]$ (0.12 g, 0.27 mmol), and the mixture was stirred. Reaction occurred immediately, and the solution was chromatographed at 0 °C, eluting with CH_2Cl_2–hexane (4:1). A single yellow fraction was collected. Solvent was removed *in vacuo* at 0 °C giving yellow *microcrystals* of $[WAu(C_6F_5)(\mu\text{-}CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (**3a**) (0.25 g).

The complex $[WAuCl(\mu\text{-}CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ (**3b**) (0.19 g) was prepared in a similar manner from (**2a**) (0.20 g, 0.24 mmol) and [AuCl(tht)] (0.08 g, 0.26 mmol), except that the reaction mixture was filtered through a Celite pad (3 × 2 cm), following which hexane (20 cm^3) was added, and solvent removed *in vacuo*.

(*ii*) To a freshly prepared thf (10 cm^3) solution of compound (**3b**) (0.33 g, 0.31 mmol), cooled to −25 °C, was added an excess of $Na[Mn(CO)_5]$ (*ca.* 1.50 mmol) in thf (15 cm^3). The mixture was warmed slowly to room temperature and solvent was partially removed *in vacuo*. Alumina (*ca.* 2 g) was added to adsorb the residue, which was transferred to the top of a chromatography column. Elution with CH_2Cl_2–hexane (1:3) removed compound (**2a**) (0.16 g). Further elution with CH_2Cl_2–hexane (3:2) gave a second fraction, which after slow removal of solvent *in vacuo* afforded yellow *microcrystals* of $[WMnAu(\mu\text{-}CMe)(CO)_7\{(C_6F_5)AuC(pz)_3\}]$ (**4**) (0.03 g).

(*iii*) A thf (15 cm^3) solution of compound (**2a**) (0.15 g, 0.18 mmol) was treated with $[Co_2(CO)_8]$ (0.075 g, 0.22 mmol), and the mixture was warmed to *ca.* 35 °C and stirred for 10 h. Solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 (2 cm^3) and chromatographed, eluting with CH_2Cl_2–hexane (3:2). A single green fraction was collected, which after slow removal of solvent *in vacuo* gave green *microcrystals* of $[WCo_2(\mu_3\text{-}CMe)(CO)_8\{(C_6F_5)AuC(pz)_3\}]$ (**5a**) (0.08 g).

The complex $[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\{(C_6F_5)AuC(pz)_3\}]$ (**5b**) (0.10 g) was similarly obtained from (**2b**) (0.25 g, 0.27 mmol) and $[Co_2(CO)_8]$ (0.12 g, 0.33 mmol) in thf (15 cm^3).

(*iv*) Compound (**2a**) (0.15 g, 0.18 mmol) in thf (15 cm^3) was treated with a thf (10 cm^3) solution of $[Pt(nb)(PMe_2Ph)_2]$ (0.19 mmol), prepared *in situ* from $[Pt(nb)_3]$ (0.09 g, 0.19 mmol) and PMe_2Ph (0.38 mmol). Although there was an immediate colour change from yellow to red upon addition of the platinum compound, i.r. spectroscopy showed that a reaction time of *ca.* 4 h was required for consumption of all the reactants. Volatile material was partially removed *in vacuo*, and the residue was adsorbed on alumina (*ca.* 2 g). The latter was transferred to the top of a chromatography column, which was maintained at −10 °C and eluted with CH_2Cl_2–hexane (2:3). A green eluate from the column was followed by a red eluate. Removal of solvent *in vacuo* from the latter afforded red *microcrystals* of $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ (**6a**) (0.08 g) {^{31}P-{^1H} n.m.r.: δ 5.1 [d, J(PP) 15, J(PtP) 2 100] and −7.0 p.p.m. [d, J(PP) 15, J(PtP) 1 360 Hz]}. The green eluate yielded *microcrystals* of $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ (**8**) (0.09 g) {^{31}P-{^1H} n.m.r.: δ 0.6 [s, J(PtP) 2 014] and −13.3 p.p.m. [s, J(PtP) 1 468 Hz]}. The latter complex was also prepared by treating (**6a**) with $[Au(C_6F_5)(tht)]$ in 1:1 mol ratio in thf.

The compound $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ (**6b**) (0.17 g) {^{31}P-{^1H} n.m.r.: δ −0.8 [d, J(PP) 14, J(PtP) 1 953] and −7.2 p.p.m. [d, J(PP) 14, J(PtP) 1 484 Hz]} was obtained using a similar procedure to that for (**6a**), employing (**2b**) (0.15 g, 0.16 mmol) and $[Pt(nb)(PMe_2$-

Table 4. Fractional atomic co-ordinates (× 10^4) for complex (**8**) with estimated standard deviations in parentheses

Atom	x	y	z
Au(1)	9 446(1)	2 261(1)	2 332(1)
Au(2)	8 733(1)	964(1)	−1 142(1)
Pt	9 686(1)	4 300(1)	1 861(1)
W	8 895(1)	2 853(1)	1 116(1)
P(1)	9 020(6)	5 586(6)	2 272(4)
P(2)	10 850(6)	4 721(6)	2 261(5)
F(1)	9 629(12)	1 505(16)	−2 269(11)
F(2)	9 629(13)	765(19)	−3 379(12)
F(3)	8 786(15)	−901(18)	−3 714(11)
F(4)	7 914(13)	−1 711(15)	−2 938(12)
F(5)	7 848(12)	−948(14)	−1 830(11)
F(6)	8 685(10)	179(14)	2 605(9)
F(7)	8 502(13)	−805(15)	3 617(10)
F(8)	9 030(17)	−30(18)	4 746(10)
F(9)	9 812(18)	1 750(17)	4 809(12)
F(10)	10 016(15)	2 725(15)	3 789(10)
O(3)	7 628(15)	2 569(20)	1 996(14)
O(4)	8 289(13)	5 030(15)	932(10)
N(1)	9 448(15)	3 067(17)	296(11)
N(2)	9 343(14)	2 467(16)	−216(10)
N(3)	8 011(15)	2 670(17)	349(12)
N(4)	8 081(15)	2 141(17)	−168(13)
N(5)	9 028(17)	1 250(16)	802(15)
N(6)	8 972(14)	948(17)	221(11)
C(1)	9 978(18)	2 932(20)	1 511(14)
C(2)	10 564(17)	2 351(19)	1 458(14)
C(3)	8 133(22)	2 676(23)	1 763(17)
C(4)	8 609(19)	4 279(22)	1 085(15)
C(5)	10 038(21)	3 675(23)	184(17)
C(6)	10 204(22)	3 530(24)	−393(18)
C(7)	9 780(20)	2 781(23)	−639(17)
C(8)	7 299(20)	3 006(21)	305(16)
C(9)	6 916(22)	2 683(23)	−242(17)
C(10)	7 367(20)	2 164(22)	−518(17)
C(11)	9 232(19)	418(22)	1 191(17)
C(12)	9 237(22)	−390(28)	737(19)
C(13)	9 069(19)	−48(22)	183(16)
C(14)	8 802(19)	1 643(21)	−274(15)
C(15)	8 866(20)	6 814(21)	1 878(16)
C(16)	8 083(22)	5 173(28)	2 354(19)
C(17)	9 354(19)	5 894(21)	3 085(15)
C(18)	9 571(22)	5 076(27)	3 464(18)
C(19)	9 856(24)	5 270(30)	4 108(20)
C(20)	9 868(28)	6 220(33)	4 278(25)
C(21)	9 655(25)	7 047(32)	3 966(21)
C(22)	9 377(22)	6 849(25)	3 316(18)
C(23)	11 263(22)	4 065(23)	2 951(17)
C(24)	11 044(22)	6 020(22)	2 518(18)
C(25)	11 514(20)	4 547(22)	1 740(16)
C(26)	12 083(24)	3 807(26)	1 862(21)
C(27)	12 537(27)	3 703(30)	1 342(22)
C(28)	12 471(27)	4 252(29)	797(22)
C(29)	11 959(26)	4 934(30)	667(22)
C(30)	11 464(25)	5 059(28)	1 184(19)
C(31)	8 722(22)	291(24)	−1 986(17)
C(32)	9 173(23)	683(26)	−2 396(19)
C(33)	9 204(26)	299(29)	−3 006(22)
C(34)	8 722(24)	−535(27)	−3 122(20)
C(35)	8 305(21)	−929(24)	−2 762(17)
C(36)	8 263(22)	−516(24)	−2 190(18)
C(37)	9 370(19)	1 519(21)	3 142(16)
C(38)	8 966(19)	590(20)	3 161(15)
C(39)	8 840(22)	68(27)	3 635(18)
C(40)	9 131(23)	470(26)	4 207(19)
C(41)	9 490(22)	1 347(26)	4 261(19)
C(42)	9 623(22)	1 835(26)	3 733(18)

Ph)$_2$] (0.16 mmol). The reaction mixture was chromatographed at room temperature, eluting with CH_2Cl_2–hexane (4:1).

(*v*) The complex (**2a**) (0.10 g, 0.12 mmol) in thf (20 cm^3) was treated portionwise with [Pt(nb)$_3$] (0.03 g, 0.06 mmol), and the mixture was stirred for *ca.* 15 h. Solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 (2 cm^3), and then chromatographed. Elution with CH_2Cl_2–hexane (4:1) removed a single red band which was collected. Slow removal of solvent *in vacuo* afforded orange *microcrystals* of [$W_2Pt(\mu\text{-CMe})_2(CO)_4\{(C_6F_5)AuC(pz)_3\}_2$] (**7a**) (0.08 g).

The compound [$W_2Pt(\mu\text{-CC}_6H_4Me\text{-}4)_2(CO)_4\{(C_6F_5)AuC(pz)_3\}_2$] (**7b**) (0.17 g) was similarly obtained from (**2b**) (0.20 g, 0.22 mmol) and [Pt(nb)$_3$] (0.05 g, 0.11 mmol).

Crystal-structure Determination of Compound (**8**).—Crystals were grown as deep green plates by allowing light petroleum to diffuse slowly into a CH_2Cl_2 solution of the complex. A crystal of suitable dimensions (*ca.* 0.51 × 0.33 × 0.12 mm) was sealed under nitrogen in a Lindemann tube. Diffracted intensities were measured (θ—2θ scans) at 298 K, in the range $4 \leqslant 2\theta \leqslant 50°$ on a Siemens R3m/V four-circle diffractometer. Of 9 185 unique data, 4 721 had $F \geqslant 4\sigma(F)$, and only these were used in the solution and refinement of the structure. The data were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter based on a semiempirical method based on azimuthal scan data.[13]

Crystal data. $C_{42}H_{34}Au_2F_{10}N_6O_2P_2PtW$, M = 1 679.4, monoclinic, space group $P2_1/n$ (no. 14), a = 18.132(4), b = 13.203(2), c = 21.870(4) Å, β = 96.53(2)°, U = 5 201(2) Å^3, Z = 4, D_c = 2.15 g cm^{-3}, $F(000)$ 3 096, Mo-K_α, *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 107.1 cm^{-1}.

The structure was solved by use of direct methods to locate the metal atoms, the lighter atoms being subsequently located from successive Fourier difference syntheses. Refinement by full-matrix least squares, with anisotropic thermal parameters for all non-carbon atoms and refined isotropic thermal parameters for the carbon atoms, led to R = 0.0789 (R' = 0.0672). Hydrogen atoms were included at calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (*ca.* $1.2U_{\text{equiv.}}$ of the parent carbon atom). A weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.0005|F_o|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks $\geqslant 2.24$ or $\leqslant -3.25$ e Å^{-3}. Refinement was performed on a Digital μ-Vax computer using the SHELXTL PLUS system of programs.[13] Scattering factors with corrections for anomalous dispersion were taken from ref. 14. Atomic co-ordinates are listed in Table 4.

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

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