Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 105.[1] Alkylidyne Tungsten and Molybdenum Complexes with Pyrazolylmethane Ligands

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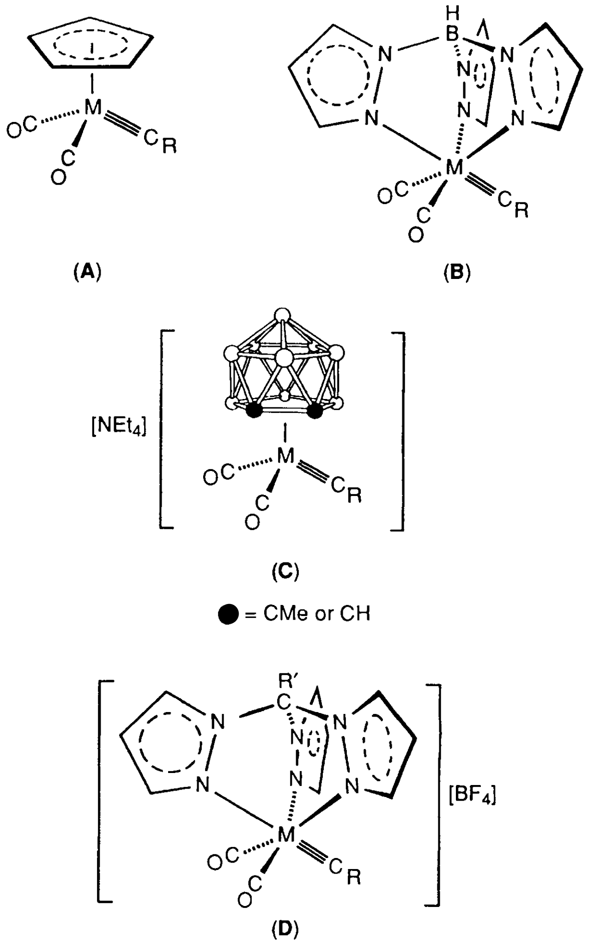
The alkylidynemetal complexes $[M(\equiv CR)(CO)_2\{HC(pz)_3\}][BF_4]$ $[HC(pz)_3$ = tris(pyrazol-1-yl)methane; M = W, R = Me, C_6H_4Me-4, or $C_6H_3Me_2$-2,6; M = Mo, R = Me or C_6H_4Me-4], $[W(\equiv CMe)(CO)_2\{MeC(pz)_3\}][BF_4]$ $[MeC(pz)_3$ = 1,1,1-tris(pyrazol-1-yl)ethane], and $[W(\equiv CMe)(CO)_3\{H_2C(pz)_2\}][BF_4]$ $[H_2C(pz)_2$ = bis(pyrazol-1-yl)methane] have been prepared by treating the complexes $[MBr(\equiv CR)(CO)_4]$ in thf (tetrahydrofuran) with $TlBF_4$ and $HC(pz)_3$, $MeC(pz)_3$, and $H_2C(pz)_2$, respectively. Reactions of the salts $[W(\equiv CR)(CO)_2\{HC(pz)_3\}][BF_4]$ (R = Me or C_6H_4Me-4) with the compounds $[Co_2(CO)_8]$, $[Pt(nb)_3]$ (nb = norbornene = bicyclo[2.2.1]heptene), and $[Pt(nb)(PMe_2Ph)_2]$ afford the mixed-metal complexes $[WCo_2(\mu_3\text{-}CR)(CO)_8\{HC(pz)_3\}][BF_4]$, $[W_2Pt(\mu\text{-}CR)_2(CO)_4\{HC(pz)_3\}_2][BF_4]_2$, and $[WPt(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$, respectively. A trimetal complex $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$ has been prepared by addition of $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) to $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$ in thf. The n.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$) for the new compounds are reported and discussed in relation to the structures proposed.

In previous papers in this series we have described results showing that the alkylidynemetal compounds $[M(\equiv CR)(CO)_2L]$ {M = Mo or W, R = alkyl, alkynyl, or aryl, L = η-C_5H_5 or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]} [Scheme, (A) and (B)] readily add metal–ligand fragments to afford numerous di-, tri-, or poly-nuclear metal complexes containing μ-CR or μ_3-CR groups.[2] The reactivity of these reagents is associated with the ligating properties of their C≡M bonds.[3] A new dimension was added to this area with the discovery that salts of the anionic complexes $[M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9\text{-}R'_2)]^-$ (M = Mo or W, R = alkyl, alkynyl, or aryl, R′ = H or Me) are also useful reagents for preparing compounds with metal–metal bonds.[1,4] Salts such as (C) (Scheme) are particularly versatile synthons. The anions contain both an alkylidyne group and a carbaborane cage, and in many reactions the latter plays a non-spectator role. Following co-ordination of metal–ligand fragments at the C≡M bonds further processes often occur, leading to di- or tri-metal compounds displaying unusual structural features.[5]

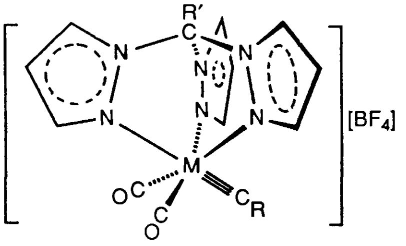
In (C) the alkylidyne ligand forms part of an anionic group, whereas in the reagents (A) or (B) it is present in a neutral species. Complexes in which the alkylidyne moiety is part of a cationic group, *e.g.* $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]^+$ (M = Mn or Re, R = aryl),[6,7] have been employed only to a limited extent in the syntheses of compounds containing metal–metal bonds. We were prompted, therefore, to prepare and study the reactions of a new series of cationic alkylidyne-tungsten and -molybdenum complexes containing the ligand $HC(pz)_3$ [tris(pyrazol-1-yl)-methane]. The latter, like $[HB(pz)_3]^-$, is formally a six-electron donor,[8] and the relationship (Scheme) between neutral complexes of type (B) and the salts (D), with the alkylidyne group in the cation, is thus apparent.



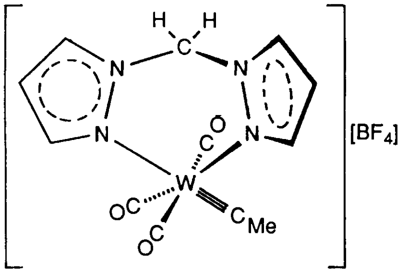
Scheme. M = Mo or W, R = alkyl or aryl, R′ = H or Me

Results and Discussion

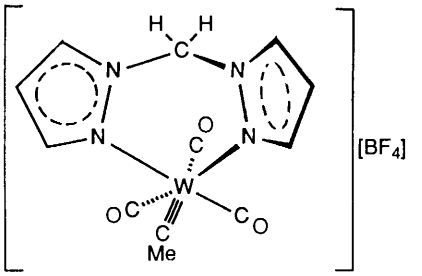
Treatment of a thf (tetrahydrofuran) solution of $[WBr(\equiv CMe)(CO)_4]$ at −30 °C with $HC(pz)_3$, in the presence of $TlBF_4$,



	M	R	R′
(**1a**)	W	Me	H
(**1b**)	W	C_6H_4Me-4	H
(**1c**)	W	$C_6H_3Me_2$-2,6	H
(**1d**)	Mo	Me	H
(**1e**)	Mo	C_6H_4Me-4	H
(**1f**)	W	Me	Me



(**2a**)



(**2b**)

afforded the complex [W(≡CMe)$(CO)_2${HC$(pz)_3$}][BF_4] (**1a**). The salts [M(≡CR)$(CO)_2${HC$(pz)_3$}][BF_4] (**1b**; M = W, R = C_6H_4Me-4), (**1c**; M = W, R = $C_6H_3Me_2$-2,6), (**1d**; M = Mo, R = Me), and (**1e**; M = Mo, R = C_6H_4Me-4) were similarly prepared from the appropriate reagents [MBr(≡CR)$(CO)_4$], HC$(pz)_3$, and $TlBF_4$. Likewise, [W(≡CMe)$(CO)_2${MeC$(pz)_3$}]-[BF_4] [**1f**; MeC$(pz)_3$ = 1,1,1-tris(pyrazol-1-yl)ethane] was obtained from [WBr(≡CMe)$(CO)_4$], MeC$(pz)_3$, and $TlBF_4$.

The new compounds were characterised by microanalysis, and by i.r. and n.m.r. spectroscopy (Tables 1 and 2). As expected, each species displays two CO stretching bands in its i.r. spectrum. For (**1a**) these absorptions appear at 1 994 and 1 907 cm^{-1}, which may be compared with those in the spectrum of [W(≡CMe)$(CO)_2${HB$(pz)_3$}][9a] at 1 983 and 1 899 cm^{-1}. In the ^{13}C-{^1H} n.m.r. spectra of (**1a**)—(**1c**) diagnostic resonances for the ligated carbon atoms of the alkylidyne groups occur at δ 304.0, 292.6, and 296.0 p.p.m., respectively. The corresponding peaks in the spectra of the molybdenum compounds (**1d**) (318.7 p.p.m.) and (**1e**) (303.7 p.p.m.) are somewhat more deshielded than those of their tungsten analogues. This is a general phenomenon.[10] Thus in the spectrum of [W(≡CC_6H_4Me-4)-$(CO)_2${HB$(pz)_3$}] the *C*C_6H_4Me-4 signal occurs at δ 284.8 p.p.m., whereas in the spectrum of [Mo(≡CC_6H_4Me-4)-$(CO)_2${HB$(pz)_3$}] the corresponding peak is at 293.1 p.p.m.[9]

The data for compound (**1f**) are also in agreement with the structure proposed. The i.r. spectrum reveals two CO stretching bands (1 993 and 1 905 cm^{-1}), and in the ^{13}C-{^1H} n.m.r. spectrum the resonance of the C≡W group occurs at δ 305.6 p.p.m. In the ^{13}C-{^1H} n.m.r. spectra of all the complexes (**1a**)—(**1f**) there is one CO resonance (Table 2), in accord with a symmetrical structure in which the metal atom, the ≡CR and CR′ groups, and one pyrazole ring lie in a plane of symmetry, with the carbonyl ligands on either side of this plane.

The complex [W(≡CMe)$(CO)_3${$H_2C(pz)_2$}][BF_4] [**2**; $H_2C(pz)_2$ = bis(pyrazol-1-yl)methane] was prepared by treating [WBr(≡CMe)$(CO)_4$] in thf with $H_2C(pz)_2$, in the presence of $TlBF_4$. Data for compound (**2**) are given in Tables 1 and 2. This product is related to the previously reported species [W(≡CMe)$(CO)_3${$H_2B(pz)_2$}] [$H_2B(pz)_2$ = dihydrobis(pyrazol-1-yl)borate)].[11] Interestingly, unlike the latter, complex (**2**) exists in solution as a mixture of two isomers, as revealed by ^1H and ^{13}C-{^1H} n.m.r. studies. In one isomer (**2a**) the alkylidyne group would be *trans* to a pyrazolyl ring, and in the other (**2b**) *trans* to a CO ligand. In the ^{13}C-{^1H} n.m.r. spectrum measured at 50 °C only one CO peak and the two signals for one ≡CMe group are observed, due to rapid interconversion between the two isomers on the n.m.r. time-scale. The ^1H n.m.r. spectrum likewise shows peaks corresponding to one species, but when measured at −40 °C (Table 2) resonances for both isomers are clearly seen. From the relative peak intensities the two isomers are present in a ratio of *ca.* 2:1. The limiting low-temperature ^{13}C-{^1H} n.m.r. spectrum for (**2**) was especially informative, displaying two C≡W signals (δ 299.3 and 293.3) and four CO peaks (δ 226.6, 219.0, 218.5, and 209.2 p.p.m.) in the expected intensity ratio of *ca.* 1:2:2:1 for (**2a**) and (**2b**). Moreover, two resonances were observed for the C^b (δ 64.0 and 63.6) and C*Me* nuclei (δ 37.6 and 37.2 p.p.m.), as well as multiple peaks for the pyrazolyl rings.

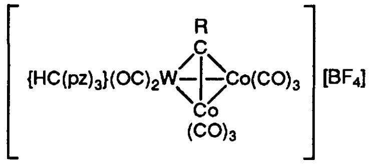
Reactions between [$Co_2(CO)_8$] and the compounds (**1a**) and (**1b**) were next investigated, since we have previously shown that species of type (**A**)—(**C**) (Scheme) readily react with dicobalt octacarbonyl to form in high yield trimetal complexes of formulation [$MCo_2(\mu_3$-CR)$(CO)_8$L] [L = η-C_5H_5 or HB$(pz)_3$][9,12] and [NEt_4][$WCo_2(\mu_3$-CR)$(CO)_8(\eta^5$-$C_2B_9H_9$-Me_2)],[13] respectively. In thf solutions, [$Co_2(CO)_8$] reacts at room temperature with (**1a**) and (**1b**) to afford the complexes [$WCo_2(\mu_3$-CR)$(CO)_8${HC$(pz)_3$}][BF_4] (**3a**; R = Me) and (**3b**; R = C_6H_4Me-4) in moderate yields. Data for these compounds are given in Tables 1 and 2. In their i.r. spectra both (**3a**) and (**3b**) show several CO stretching bands suggesting the presence of rotational isomers, a phenomenon discussed elsewhere.[9,12] In the ^{13}C-{^1H} n.m.r. spectra there are diagnostic signals for the μ_3-C groups: for (**3a**) at 294.3 p.p.m. and for (**3b**) at 286.2 p.p.m. These data may be compared with the corresponding resonances in the spectra of the compounds [$WCo_2(\mu_3$-CR)$(CO)_8${HB$(pz)_3$}] (R = Me, δ 263.4; R = C_6H_4Me-4, δ 265.7 p.p.m.).[9a] Evidently, these alkylidyne-carbon signals are more deshielded in the cationic tris(pyrazol-1-yl)methane complexes (**3**) than in their neutral hydrotris(pyrazol-1-yl)-borate analogues. The appearance in the spectra of the compounds (**3**) of only one WCO and one CoCO resonance indicates that the carbonyl groups undergo site-exchange at their respective metal centres. Similar dynamic behaviour is displayed by the complexes [$WCo_2(\mu_3$-CR)$(CO)_8${HB$(pz)_3$}].[9a]

A characteristic reaction occurs between the species (**A**) or (**B**) (Scheme) and the platinum complexes [Pt$(alkene)_n$] (*n* = 3 or 4), yielding trimetal species [$M_2Pt(\mu$-CR$)_2(CO)_4L_2$] [M = Mo or W, L = η-C_5H_5 or HB$(pz)_3$].[14] It was of interest to establish whether related compounds would be formed by employing the reagents (**1a**) and (**1b**). Treatment of these two salts in thf with [Pt$(nb)_3$] (nb = norbornene = bicyclo[2.2.1]heptene) afforded the trimetal complexes [$W_2Pt(\mu$-CR$)_2(CO)_4${HC$(pz)_3$}$_2$]-

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

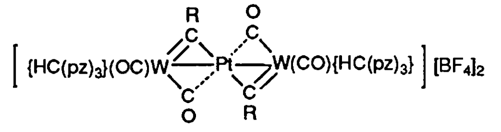
	Compound	Colour	Yield (%)	$\nu_{max.}(CO)^b/cm^{-1}$	Analysis (%) C	H	N
(**1a**)	$[W(\equiv CMe)(CO)_2\{HC(pz)_3\}][BF_4]$	Yellow	68	1 994s, 1 907s	29.5 (29.6)	2.4 (2.3)	14.7 (14.8)
(**1b**)	$[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HC(pz)_3\}]\text{-}[BF_4]$	Orange	83	1 995s, 1 912s	37.1 (37.3)	2.8 (2.7)	13.1 (13.0)
(**1c**)	$[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2\{HC(pz)_3\}]\text{-}[BF_4]$	Orange	77	1 990s, 1 911s	37.6 (38.3)	3.3 (2.9)	12.2 (12.8)
(**1d**)	$[Mo(\equiv CMe)(CO)_2\{HC(pz)_3\}][BF_4]^c$	Green	56	2 011s, 1 928s			
(**1e**)	$[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HC(pz)_3\}]\text{-}[BF_4]$	Orange	62	2 007s, 1 930s	42.6 (43.2)	3.7 (3.1)	14.8 (15.1)
(**1f**)	$[W(\equiv CMe)(CO)_2\{MeC(pz)_3\}][BF_4]$	Yellow	79	1 993s, 1 905s	31.0 (31.0)	2.6 (2.6)	14.3 (14.4)
(**2**)	$[W(\equiv CMe)(CO)_3\{H_2C(pz)_2\}][BF_4]$	Yellow	62	1 994s, 1 902s	26.3 (27.2)	2.7 (2.1)	10.9 (10.6)
(**3a**)	$[WCo_2(\mu_3\text{-}CMe)(CO)_8\{HC(pz)_3\}]\text{-}[BF_4]$	Green	43	2 090s, 2 050s, 2 036s, 2 018m(sh), 2 005m(sh), 1 981w, 1 966w, 1 902w(br), 1 841w(br)	[d]26.1 (26.8)	1.8 (1.6)	9.2 (9.0)
(**3b**)	$[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\text{-}\{HC(pz)_3\}][BF_4]$	Green	37	2 090s, 2 052s, 2 043s, 2 019w, 2 004m, 1 901m, 1 837m(br)	32.5 (33.5)	2.2 (1.8)	9.0 (9.0)
(**4a**)	$[W_2Pt(\mu\text{-}CMe)_2(CO)_4\{HC(pz)_3\}_2]\text{-}[BF_4]_2$	Red	77	1 973s(sh), 1 954s, 1 812m(br)	24.9 (25.3)	2.2 (2.0)	11.8 (12.6)
(**4b**)	$[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\text{-}\{HC(pz)_3\}_2][BF_4]_2$	Red	72	1 984s(sh), 1 962s, 1 817m(br)	32.0 (32.4)	2.5 (2.3)	11.0 (11.3)
(**5a**)	$[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\text{-}\{HC(pz)_3\}][BF_4]$	Red	49	1 895s, 1 773m(br)	34.3 (34.7)	3.6 (3.4)	7.9 (8.1)
(**5b**)	$[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\text{-}(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$	Red	36	1 912s, 1 749m(br)	38.4 (38.8)	3.8 (3.5)	7.2 (7.5)
(**6**)	$[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2\text{-}(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$	Green	87	1 924s, 1 776m	30.6 (30.8)	2.6 (2.5)	6.0 (6.0)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2. [c] Compound unstable (see text). [d] Crystallises with one molecule of CH_2Cl_2.



R

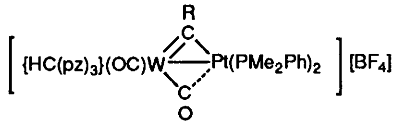
(**3a**) Me
(**3b**) $C_6H_4Me\text{-}4$



R

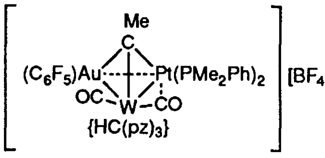
(**4a**) Me
(**4b**) $C_6H_4Me\text{-}4$

$[BF_4]_2$ (**4a**; R = Me) and (**4b**; R = C_6H_4Me-4). The i.r. spectra of these products show three CO stretching bands, including one at relatively low frequency (*ca.* 1 815 cm^{-1}). A similar band pattern is shown by the paradigmatic molecule $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$, with absorptions at 1 965, 1 942, and 1 828 cm^{-1}. An *X*-ray diffraction study[15] on the latter revealed that the metal–metal bonds were spanned by the alkylidyne ligands and that one CO group on each tungsten atom interacts with the platinum, thus accounting for the i.r. band at 1 828 cm^{-1}. Presumably similar weak CO bridge bonding occurs in the complexes (**4**).



R

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

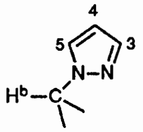


(**6**)

The presence of the μ-C groups in the cations of the salts (**4**) was revealed by signals in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra at δ 317.1 for (**4a**) and at 303.9 p.p.m. for (**4b**). In the compounds $[W_2Pt(\mu\text{-}CR)_2(CO)_4\{HB(pz)_3\}_2]$ the alkylidyne-carbon resonances are seen in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra at δ 310.3 (*C*Me) and 313.6 p.p.m. (*C*C_6H_4Me-4).[16]

Reactions between the reagents (**1a**) or (**1b**) and the platinum compound $[Pt(nb)(PMe_2Ph)_2]$, generated *in situ* from $[Pt(nb)_3]$ and PMe_2Ph, were next investigated, and found to give the dimetal compounds $[WPt(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$ (**5a**; R = Me) and (**5b**; R = C_6H_4Me-4). Data characterising these complexes are listed in Tables 1—3. In the i.r. spectra of both products there are two CO bands, as expected, but one absorption, at 1 773 cm^{-1} for (**5a**) and at 1 749 cm^{-1} for (**5b**), is at a frequency suggesting the presence of a

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



Compound	^{1}H (δ)	^{13}C (δ)[b]
(1a)	2.46 (s, 3 H, Me), 6.47 (m, 1 H, H^4), 6.55 (m, 2 H, H^4), 7.84 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.13 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.48 [d, 1 H, H^5, J(H^{4}H^5) 3], 8.53 [d, 2 H, H^5, J(H^{4}H^5) 3], 9.64 (s, 1 H, H^b)	304.0 (C≡W), 220.1 (CO), 147.5, 146.5, 134.7, 108.8 ($C_3H_3N_2$), 76.3 (C^b), 38.6 (Me)
(1b)	2.32 (s, 3 H, Me-4), 6.50 (m, 1 H, H^4), 6.55 (m, 2 H, H^4), 7.14, 7.32 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 7.90 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.19 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.44 [d, 1 H, H^5, J(H^{4}H^5) 3], 8.46 [d, 2 H, H^5, J(H^{4}H^5) 3], 9.56 (s, 1 H, H^b)	292.6 (C≡W), 221.2 (CO), 148.0, 147.0, 140.8, 135.3, 129.8, 129.2, 109.3 (C_6H_4 and $C_3H_3N_2$), 76.8 (C^b), 22.0 (Me-4)
(1c)	2.44 (s, 6 H, Me$_2$-2,6), 6.50 (m, 1 H, H^4), 6.56 (m, 2 H, H^4), 6.94—7.14 (m, 3 H, C_6H_3), 7.89 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.23 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.45 [d, 1 H, H^5, J(H^{4}H^5) 3], 8.51 [d, 2 H, H^5, J(H^{4}H^5) 3], 9.62 (s, 1 H, H^b)	296.0 (C≡W), 222.8 (CO), 148.3, 146.8, 141.4, 135.4, 135.2, 129.5, 127.8, 109.3 (C_6H_3 and $C_3H_3N_2$), 76.8 (C^b), 20.8 (Me-2,6)
(1d)	2.54 (s, 3 H, Me), 6.41 (m, 1 H, H^4), 6.50 (m, 2 H, H^4), 7.76 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.03 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.36 [d, 1 H, H^5, J(H^{4}H^5) 2], 8.41 [d, 2 H, H^5, J (H^{4}H^5) 2], 9.44 (s, 1 H, H^b)	318.7 (C≡Mo), 222.6 (CO), 146.9, 145.8, 134.9, 134.7, 108.3 ($C_3H_3N_2$), 76.1 (C^b), 38.1 (Me)
(1e)	2.35 (s, 3 H, Me-4), 6.46 (m, 1 H, H^4), 6.51 (m, 2 H, H^4), 7.15, 7.42 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 7.82 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.08 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.40 [d, 1 H, H^5, J(H^{4}H^5) 2], 8.44 [d, 2 H, H^5, J(H^{4}H^5) 3], 9.48 (s, 1 H, H^b)	303.7 (C≡Mo), 223.3 (CO), 141.7, 141.4, 134.4, 134.3, 130.4, 129.5, 129.0, 108.3, 107.1 (C_6H_4 and $C_3H_3N_2$), 75.8 (C^b), 21.7 (Me-4)
(1f)	2.36 (s, 3 H, W≡CMe), 3.39 (s, 3 H, Me), 6.44 (m, 1 H, H^4), 6.52 (m, 2 H, H^4), 7.80 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.11 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.24 [d, 1 H, H^5, J(H^{4}H^5) 3], 8.29 [d, 2 H, H^5, J(H^{4}H^5) 3]	305.6 (C≡W), 220.8 (CO), 148.2, 147.0, 132.9, 108.9 ($C_3H_3N_2$), 85.5 (C^b), 39.2 (W≡C*Me*), 22.5 (Me)
(2)[c]	Isomer I: 2.31 (s, 3 H, Me), 6.66 (m, 2 H, H^4), 7.06 [d of d, 2 H, CH$_2$, J(HH) 14], 8.17 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.37 [d, 2 H, H^5, J(H^{4}H^5) 2]. Isomer II: 2.41 (s, 3 H, Me), 6.57 (m, 2 H, H^4), 7.18 [d of d, 2 H, CH$_2$, J(HH) 14], 8.21 [d, 2 H, H^3, J(H^{3}H^4) 2], 8.41 [d, 2 H, H^5, J(H^{4}H^5) 2]	299.3, 293.3 (C≡W), 226.6, 219.0, 218.5, 209.2 (CO), 146.6, 146.5, 135.0, 134.9, 108.2 ($C_3H_3N_2$), 64.0, 63.6 (C^b), 37.6, 37.2 (Me)
(3a)	3.77 (s, 3 H, Me), 6.61 (s, 2 H, H^4), 6.73 (s, 1 H, H^4), 7.94—8.71 (m, 6 H, H^3 and H^5), 9.86 (s, 1 H, H^b)	294.3 (μ$_3$-C), 226.5 (WCO), 199.5 (CoCO), 148.8, 147.8, 136.6, 110.2, 109.5 ($C_3H_3N_2$), 76.2 (C^b), 43.5 (Me)
(3b)	2.24 (s, 3 H, Me-4), 6.47 (s, 2 H, H^4), 6.62 (s, 1 H, H^4), 6.91, 7.06 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 8.08—9.51 (m, 6 H, H^3 and H^5), 9.57 (s, 1 H, H^b)	286.2 (μ$_3$-C), 226.1 (WCO), 198.5 (CoCO), 156.6 [C^1(C_6H_4)], 148.5, 147.0, 137.4, 136.1, 128.1, 127.8, 109.7, 109.1 (C_6H_4 and $C_3H_3N_2$), 75.7 (C^b), 20.6 (Me-4)
(4a)	3.18 (s, 3 H, Me), 6.79 (m, 1 H, H^4), 6.86 (m, 2 H, H^4), 8.33 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.56 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.60 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.66 [d, 1 H, H^5, J(H^{4}H^5) 2], 8.71 [d, 1 H, H^5, J(H^{4}H^5) 3], 8.72 [d, 1 H, H^5, J(H^{4}H^5) 3], 9.87 (s, 1 H, H^b)	317.1 (μ-C), 225.9, 221.1 (CO), 148.4, 147.8, 145.9, 136.5, 136.1, 135.9, 109.6, 109.1 ($C_3H_3N_2$), 76.8 (C^b), 40.5 (Me)
(4b)	2.32 (s, 3 H, Me-4), 6.24 (m, 1 H, H^4), 6.48 (m, 1 H, H^4), 6.63 (m, 1 H, H^4), 6.86, 7.10 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 6.96 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.06 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.18 [d, 1 H, H^3, J(H^{3}H^4) 2], 8.44 [d, 1 H, H^5, J(H^{4}H^5) 3], 8.49 [d, 1 H, H^5, J(H^{4}H^5) 2], 8.54 [d, 1 H, H^5, J(H^{4}H^5) 3], 9.67 (s, 1 H, H^b)	303.9 (μ-C), 224.1, 221.5 (CO), 150.6 [C^1(C_6H_4)], 146.9, 146.7, 146.5 ($C_3H_3N_2$), 139.0, 135.2, 134.7, 134.6, 129.3, 125.2 (C_6H_4 and $C_3H_3N_2$), 109.5, 109.0, 108.4 ($C_3H_3N_2$), 76.1 (C^b), 21.3 (Me-4)
(5a)	1.43 [d, 6 H, MeP, J(PH) 9, J(PtH) 18], 1.87 [d, 6 H, MeP, J(PH) 8, J(PtH) 11], 2.66 (m, 3 H, Me), 6.34 (m, 2 H, H^4), 6.46 (m, 1 H, H^4), 7.23—8.41 (m, 16 H, Ph, H^3 and H^5), 9.50 (s, 1 H, H^b)	355.2 [d, μ-C, J(PC) 57], 228.8 (CO), 147.2—108.8 (Ph and $C_3H_3N_2$), 76.7 (C^b), 42.3 (Me), 18.2 [d, MeP, J(PC) 26], 15.9 [d, MeP, J(PC) 24]
(5b)	1.08 [d, 6 H, MeP, J(PH) 9, J(PtH) 17], 1.76 [d, 6 H, MeP, J(PH) 8, J(PtH) 12], 2.22 (s, 3 H, Me-4), 6.18, 6.77 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 6.24 (m, 2 H, H^4), 6.50 (m, 1 H, H^4), 7.12—8.47 (m, 16 H, Ph, H^3 and H^5), 9.53 (s, 1 H, H^b)	339.7 [d, μ-C, J(PC) 55], 231.6 (CO), 159.4 [C^1(C_6H_4)], 147.6—107.8 (Ph, C_6H_4, and $C_3H_3N_2$), 76.3 (C^b), 20.8 (Me-4), 15.8 [d, MeP, J(PC) 27], 15.1 [d, MeP, J(PC) 24]

Table 2 (*continued*)

(**6**)	1.41 [d, MeP, 3 H, J(PH) 10, J(PtH) 18], 1.67 [d, MeP, 3 H, J(PH) 9, J(PtH) 20], 1.90 [d, MeP, 3 H, J(PH) 8, J(PtH) 16], 1.99 [d, MeP, 3 H, J(PH) 9, J(PtH) 12], 2.60 (m, 3 H, Me), 6.21 (m, 1 H, H^4), 6.57 (m, 1 H, H^4), 6.63 (m, 1 H, H^4), 6.87 [d, 1 H, H^3, $J(H^3H^4)$ 2], 7.31—7.75 (m, 10 H, Ph), 8.33 [d, 1 H, H^5, $J(H^4H^5)$ 3], 8.47 [d, 1 H, H^3, $J(H^3H^4)$ 2], 8.49 [d, 1 H, H^5, $J(H^4H^5)$ 3], 8.52 [d, 1 H, H^5, $J(H^4H^5)$ 3], 8.86 [d, 1 H, H^3, $J(H^3H^4)$ 2], 9.65 (s, 1 H, H^b)	313.3 [d, μ_3-C, J(PC) 58], 235.3 [d, CO, J(PC) 9], 221.4 (CO), 149.2, 147.6, 147.0 ($C_3H_3N_2$), 132.0—128.5 (Ph and $C_3H_3N_2$), 109.7, 109.1, 108.5 ($C_3H_3N_2$), 76.0 (C^b), 41.5 (Me), 18.8—11.1 (m, MeP)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measured in CD_2Cl_2 at ambient temperatures unless otherwise stated. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (0.0 p.p.m.). [c] Measured in $(CD_3)_2CO$ at −40 °C.

Table 3. Phosphorus-31 and fluorine-19 n.m.r. data[a]

Compound	$^{31}P(\delta)^b$
(**5a**)	5.2 [d, J(PP) 17, J(PtP) 2 094], −7.0 [d, J(PP) 17, J(PtP) 1 363]
(**5b**)	−0.2 [d, J(PP) 5, J(PtP) 1 965], −6.8 [d, J(PP) 5, J(PtP) 1 482]
(**6**)	1.2 [s, J(PtP) 2 041], −13.2 [s, J(PtP) 1 458]
	$^{19}F(\delta)^c$
(**6**)	−114.5 [d, 2 F, J(FF) 24], −159.8 (m, 1 F), −162.5 (m, 2 F)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements in CD_2Cl_2 at ambient temperatures. [b] Hydrogen-1 decoupled, chemical shifts to high frequency of 85% H_3PO_4 (external) taken as positive. [c] Hydrogen-1 decoupled, chemical shifts to high frequency of CCl_3F (0.0 p.p.m.).

bridging or strongly semi-bridging carbonyl ligand. The i.r. spectrum of the related compound [$WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2\{HB(pz)_3\}$][9a] also displays two CO peaks (1 914 and 1 764 cm^{-1}), corresponding to a terminal and a bridging or a semi-bridging carbonyl ligand. In contrast, in the i.r. spectrum of the cyclopentadienyl species [$WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)$][17] the carbonyl stretching bands are at 1 898 and 1 818 cm^{-1}, the lower-frequency absorption being at an appreciably higher wavenumber than those of the corresponding bands in the aforementioned $HB(pz)_3$ and $HC(pz)_3$ complexes.

Although the i.r. spectra of the complexes (**5**) display two CO bands, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra only one CO resonance is seen (Table 2). Evidently site exchange of the two CO ligands occurs in solution on the n.m.r. time-scale. Diagnostic resonances for the μ-C nuclei are seen at δ 355.2 for (**5a**) and 339.7 p.p.m. for (**5b**). Each signal is a doublet due to $^{31}P\text{-}^{13}C$ coupling (*ca.* 55 Hz), with the transoid PMe_2Ph group. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of compounds (**5a**) and (**5b**) (Table 3) show characteristic resonances for the presence of *cis*-$Pt(PMe_2Ph)_2$ groups. In each spectrum there are two doublet signals due to the non-equivalent PMe_2Ph groups, the doublets arising from $^{31}P\text{-}^{31}P$ coupling. The resonances also display $^{195}Pt\text{-}^{31}P$ satellite peaks, as expected, and the signal in each spectrum associated with the larger coupling can be ascribed to the PMe_2Ph ligand transoid to the Pt–W bond.[18]

Treatment of compound (**5a**) in thf with [$Au(C_6F_5)(tht)$] (tht = tetrahydrothiophene) afforded the trimetal complex [$WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}$][$BF_4$] (**6**), characterised by microanalysis and by its spectroscopic properties (Tables 1—3). The i.r. spectrum displays two CO bands at 1 924 and 1 776 cm^{-1}, indicating the presence of a terminal and a semi-bridging or bridging ligand. Correspondingly, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum there are two CO resonances (δ 235.3 and 221.4 p.p.m.). The more deshielded signal may be attributed to the bridging carbonyl group. Moreover, it is a doublet due to $^{31}P\text{-}^{13}C$ coupling (9 Hz), implying that the CO molecule bridges the W–Pt rather than the W–Au bond. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum also shows as expected a μ_3-C resonance at δ 313.3 p.p.m. [J(PC) 58 Hz].

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (Table 3) displays two resonances corresponding to the non-equivalent PMe_2Ph groups. Both peaks are singlets with ^{195}Pt satellite peaks. The absence of $^{31}P\text{-}^{31}P$ coupling is not unusual for a *cis*-$Pt(PMe_2Ph)_2$ fragment. The $^{19}F\text{-}\{^1H\}$ n.m.r. spectrum shows three groups of peaks with relative intensity 2:1:2, as expected for a C_6F_5 group.

The cation of compound (**6**) has a μ_3-CWPtAu core, similar to those in the neutral species [$WPtAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(L_2)L'(\eta^5\text{-}C_2B_9H_9Me_2)$] (L = L′ = PMe_2Ph; L_2 = cod = cyclo-octa-1,5-diene, L′ = PPh_3).[19] These cluster compounds have 44 valence electrons and it is likely that the core has a 'butterfly' configuration with the C–W group forming the body and the Pt and Au atoms occupying the wing-tip sites. Indeed, this structure has been established by *X*-ray diffraction for the cation in the salt [$WPtAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)$][$PF_6$],[20] a 44 cluster-valence-electron species which is clearly related to (**6**).

The results described in this paper establish that cationic alkylidynemetal complexes containing the ligands $RC(pz)_3$ (R = H or Me) and $H_2C(pz)_2$ can be prepared. It has also been shown that the salts (**1a**) and (**1b**) react with [$Co_2(CO)_8$], and with zero-valent platinum complexes, to afford di- or tri-metal compounds akin to those previously obtained employing as reagents the species [$M(\equiv CR)(CO)_2L$] or [NEt_4][$M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$] of the Scheme. The generality of the method of obtaining compounds with heteronuclear metal–metal bonds by addition of metal–ligand fragments to species containing C≡M linkages has thus been further extended. In succeeding papers we shall describe further reactions of the reagents (**1**) leading to new compounds containing heteronuclear metal–metal bonds.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. Light petroleum refers to that fraction of b.p. 40—60 °C. The instrumentation employed for spectroscopic measurements has been described previously.[4a] The compounds $RC(pz)_3$ (R = H or Me), $H_2C(pz)_2$,[21] [$WBr(\equiv CR)(CO)_4$] (R = alkyl or aryl),[22] [$Pt(nb)(PMe_2Ph)_2$],[19] [$Pt(nb)_3$],[23] and [$Au(C_6F_5)(tht)$][24] were prepared by methods previously reported. Analytical and physical data for the new compounds are given in Table 1.

Preparation of the Alkylidyne Complexes $[M(\equiv CR)(CO)_2\{R'C(pz)_3\}][BF_4]$ (M = Mo *or* W, R = alkyl *or* aryl, R′ = H or Me) *and* $[W(\equiv CMe)(CO)_3\{H_2C(pz)_2\}][BF_4]$.—A thf (100 cm^3) solution of $[WBr(\equiv CMe)(CO)_4]$ (3.88 g, 9.55 mmol) at −30 °C was treated with $HC(pz)_3$ (2.25 g, 10.51 mmol) and $TlBF_4$ (2.78 g, 9.55 mmol). The mixture was stirred at −15 °C for *ca.* 12 h, followed by removal of solvent *in vacuo*. The residue was extracted with CH_2Cl_2 (5 × 50 cm^3), and the extracts filtered through a Celite pad (*ca.* 2 cm). Removal of solvent *in vacuo* afforded a yellow powder. The latter was purified by dissolution in a minimum quantity of CH_2Cl_2 (*ca.* 50 cm^3), filtration through Celite (*ca.* 2 cm), addition of hexane (50 cm^3), and slow removal of solvent *in vacuo* at 0 °C. The solid formed was allowed to settle, and the supernatant liquid removed with a syringe. The solid was washed with Et_2O (10 × 5 cm^3) and dried *in vacuo* to yield yellow *microcrystals* of $[W(\equiv CMe)(CO)_2\{HC(pz)_3\}][BF_4]$ (**1a**) (3.6 g).

A similar procedure was used to prepare the other mononuclear metal alkylidyne salts using the following quantities of reagents.

(*i*) For $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HC(pz)_3\}][BF_4]$ (**1b**) (3.23 g) the reactants were $[WBr(\equiv CC_6H_4Me\text{-}4)(CO)_4]$ (2.90 g, 6.05 mmol), $TlBF_4$ (1.76 g, 6.05 mmol), and $HC(pz)_3$ (1.35 g, 6.31 mmol).

(*ii*) For $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2\{HC(pz)_3\}][BF_4]$ (**1c**) (7.95 g) the compounds $[WBr(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_4]$ (7.80 g, 15.87 mmol), $TlBF_4$ (4.65 g, 15.98 mmol), and $HC(pz)_3$ (3.45 g, 16.12 mmol) were used.

(*iii*) For $[Mo(\equiv CMe)(CO)_2\{HC(pz)_3\}][BF_4]$ (**1d**) (3.22 g) the synthesis was carried out at −40 °C for 8 h using $[MoBr(\equiv CMe)(CO)_4]$ (3.78 g, 12.00 mmol), $TlBF_4$ (3.72 g, 12.78 mmol), and $HC(pz)_3$ (2.82 g, 13.18 mmol).

(*iv*) For $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HC(pz)_3\}][BF_4]$ (**1e**) (4.25 g) the reagents $[MoBr(\equiv CC_6H_4Me\text{-}4)(CO)_4]$ (4.83 g, 12.34 mmol), $TlBF_4$ (3.96 g, 13.61 mmol), and $HC(pz)_3$ (4.07 g, 12.96 mmol) were used at −40 °C, with a reaction time of *ca.* 8 h.

(*v*) For $[W(\equiv CMe)(CO)_2\{MeC(pz)_3\}][BF_4]$ (**1f**) (2.88 g) the compounds $[WBr(\equiv CMe)(CO)_4]$ (2.53 g, 6.26 mmol), $TlBF_4$ (1.83 g, 6.29 mmol), and $MeC(pz)_3$ (1.43 g, 6.27 mmol) were employed.

(*vi*) Complex $[W(\equiv CMe)(CO)_3\{H_2C(pz)_2\}][BF_4]$ (**2**) (1.89 g) was obtained from $[WBr(\equiv CMe)(CO)_4]$ (2.15 g, 5.73 mmol), $TlBF_4$ (1.67 g, 5.74 mmol), and $H_2C(pz)_2$ (0.93 g, 6.38 mmol).

Synthesis of the Tungstendicobalt Complexes.—(*i*) A thf (15 cm^3) solution of compound (**1a**) (0.20 g, 0.35 mmol) was treated with $[Co_2(CO)_8]$ (0.21 g, 0.61 mmol), and the mixture was stirred for 16 h at *ca.* 30 °C. Solvent was removed *in vacuo*, and the residue was washed with Et_2O (10 × 10 cm^3) and then taken up in CH_2Cl_2 (*ca.* 10 cm^3). After passage through a Celite pad (*ca.* 2 cm), hexane (30 cm^3) was added, and solvent slowly removed *in vacuo* until microcrystals appeared. Removal of the supernatant liquid with a syringe gave green *microcrystals* of $[WCo_2(\mu_3\text{-}CMe)(CO)_8\{HC(pz)_3\}][BF_4]$ (**3a**) (0.13 g).

(*ii*) The trimetal complex $[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8\{HC(pz)_3\}][BF_4]$ (**3b**) (0.18 g) was similarly obtained from (**1b**) (0.35 g, 0.54 mmol) and $[Co_2(CO)_8]$ (0.30 g, 0.87 mmol) in thf (15 cm^3).

Synthesis of the Tungstenplatinum Complexes.—(*i*) The salt (**1a**) (0.25 g, 0.44 mmol) in thf (5 cm^3) was treated portionwise with $[Pt(nb)_3]$ (0.10 g, 0.22 mmol), and the mixture was stirred for 4 h. A red crystalline solid was deposited. The supernatant liquid was removed with a syringe, the solid was washed with thf (2 × 3 cm^3 at 0 °C), and dried *in vacuo* to give $[W_2Pt(\mu\text{-}CMe)_2(CO)_4\{HC(pz)_3\}_2][BF_4]_2$ (**4a**) (0.22 g) as red *microcrystals*.

The complex $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{HC(pz)_3\}_2][BF_4]_2$ (**4b**) (0.28 g) was similarly prepared from (**1b**) (0.35 g, 0.54 mmol) and $[Pt(nb)_3]$ (0.13 g, 0.27 mmol) in thf (10 cm^3), except that the reaction mixture was cooled to −78 °C to facilitate precipitation of the product.

(*ii*) A thf (10 cm^3) solution of $[Pt(nb)(PMe_2Ph)_2]$ (0.38 mmol), prepared *in situ* from $[Pt(nb)_3]$ and PMe_2Ph, was added to a thf (20 cm^3) solution of compound (**1a**) (0.20 g, 0.35 mmol). The mixture was stirred at room temperature for 4 h, during which period the mixture changed from yellow to red. Solvent was removed *in vacuo*, and the residue was taken up in CH_2Cl_2 (10 cm^3). After passage through a Celite pad (*ca.* 2 cm), hexane was added, and the solvent partially removed *in vacuo* at 0 °C, thereby affording red *microcrystals* of $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$ (**5a**) (0.18 g), dried *in vacuo* after removal of solvent with a syringe.

The complex $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$ (**5b**) (0.19 g) was similarly obtained from (**1b**) (0.30 g, 0.47 mmol) and $[Pt(nb)(PMe_2Ph)_2]$ (0.51 mmol).

Preparation of $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$.—A thf (10 cm^3) solution of compound (**5a**) (0.20 g, 0.19 mmol) was treated with $[Au(C_6F_5)(tht)]$ (0.10 g, 0.22 mmol). There was an immediate colour change from red to green, and completion of reaction was confirmed by i.r. spectroscopy. Solvent was removed *in vacuo*, the residue was washed with Et_2O (3 × 10 cm^3) and then taken up in CH_2Cl_2 (10 cm^3). After passage through a Celite pad (*ca.* 2 cm), hexane (30 cm^3) was added. Slow removal of solvent *in vacuo* afforded green *microcrystals* of $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{HC(pz)_3\}][BF_4]$ (**6**) (0.23 g).

Acknowledgements

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