Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 108.[1] Synthesis and Reactions of the Alkylidynetungsten Complexes $[W(\equiv CR)(CO)_2\{(F_3B)C(pz)_3\}]$ (R = Me or C_6H_4Me-4, pz = pyrazol-1-yl) and Their Use as Reagents for preparing Di- and Tri-metal Compounds

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Treatment of thf (tetrahydrofuran) solutions of the salts $[W(\equiv CR)(CO)_2\{HC(pz)_3\}][BF_4]$ [R = Me or C_6H_4Me-4, $HC(pz)_3$ = tris(pyrazol-1-yl)methane] with LiBu, followed by $BF_3 \cdot Et_2O$, affords the neutral alkylidynetungsten complexes $[W(\equiv CR)(CO)_2\{(F_3B)C(pz)_3\}]$. The species with R = Me was also prepared from the reaction between $[W(\equiv CMe)Br(CO)_4]$ and $Li[(F_3B)C(pz)_3]$ in thf. The compounds $[W(\equiv CMe)(CO)_2\{(F_3B)C(pz)_3\}]$ and $[Pt(nb)(PMe_2Ph)_2]$ (nb = norbornene = bicyclo[2.2.1]heptene) react in thf to yield the dimetal complex $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$, and the latter with $[AuR(tht)]$ (R = Cl or C_6F_5, tht = tetrahydrothiophene) or CuCl in CH_2Cl_2, yields the trimetal species $[WPtMR(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ (M = Au, R = Cl or C_6F_5; M = Cu, R = Cl), respectively. Addition of $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene) to a thf solution of $[W(\equiv CMe)(CO)_2\{(F_3B)C(pz)_3\}]$ gives a chromatographically separable mixture of the compounds $[WPt(\mu\text{-}CMe)(CO)_2(cod)\{(F_3B)C(pz)_3\}]$, $[W_2Pt(\mu\text{-}CMe)_2(CO)_4\{(F_3B)C(pz)_3\}_2]$ and $[WPt_2(\mu_3\text{-}CMe)(CO)_2(cod)_2\{(F_3B)C(pz)_3\}]$. The complexes $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)\{(F_3B)C(pz)_3\}]$ and $[WPt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)_2\{(F_3B)C(pz)_3\}]$ have been similarly obtained from $[Pt(cod)_2]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{(F_3B)C(pz)_3\}]$. Treatment of the latter with $[Pt(nb)_3]$ in thf affords the trimetal compound $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{(F_3B)C(pz)_3\}_2]$. The NMR data ($^1H$, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$) for the new compounds are reported and discussed.

The addition of co-ordinatively unsaturated metal–ligand fragments to $C\equiv M$ (M = Mo or W) bonds in molecules of the type $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (**A**, Scheme 1) has led to the synthesis of numerous di- or poly-nuclear metal compounds with linkages between molybdenum or tungsten and other transition elements. This preparative methodology originated a decade ago with studies on reactions of the species $[W(\equiv CC_6H_4\text{-}Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with zerovalent platinum compounds. Thus with $[Pt(C_2H_4)(PMe_2Ph)_2]$ the *p*-tolylmethylidyne-tungsten reagent affords the dimetal compound $[WPt(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$.[2] Since this reaction was first reported, several tungsten and molybdenum reagents of type **A** have been employed as precursors in related syntheses.[3,4]

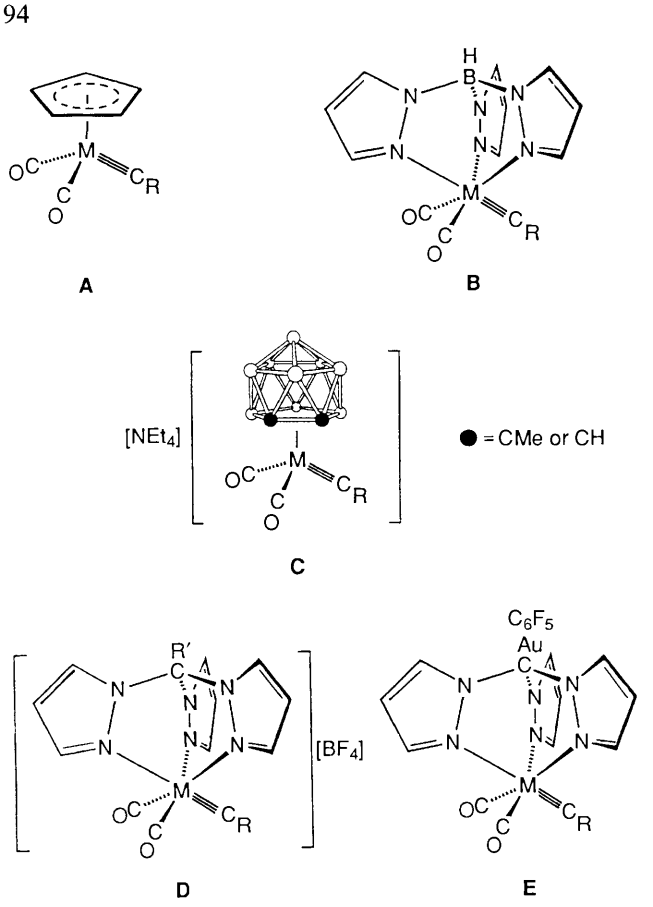
The scope of this route to compounds having bonds between different transition elements was greatly extended with the discovery that new reagents with $C\equiv M$ bonds could be prepared by replacing the cyclopentadienyl ligand present in molecules of type **A** with the groups $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate][5] or $\eta^5\text{-}C_2B_9H_9R_2$ (R = H or Me).[1,6,7] The presence of the $HB(pz)_3$ and $\eta^5\text{-}C_2B_9H_9R_2$ ligands in species of types **B** and **C** (Scheme 1) greatly influences the nature of the products obtained in reactions with low-valent metal–ligand fragments. Consequently, the structures of the di- or poly-nuclear metal compounds formed are often very different from those resulting from the use of molecules of type **A** as precursors. It is for these and other reasons that this area of study has produced many molecules with novel structures.

Recently this field has been further extended by the synthesis of alkylidyne-molybdenum and -tungsten complexes of types **D** and **E**, in which tris(pyrazol-1-yl)methane ring systems ligate the metal atoms.[8] The salts $[M(\equiv CR)(CO)_2\{HC(pz)_3\}][BF_4]$ (M = W, R = Me, **1a**, C_6H_4Me-4, **1b** or $C_6H_3Me_2$-2,6, **1c**; M = Mo, R = C_6H_4Me-4, **1d**)[8a] contain the six-electron donor $HC(pz)_3$ [tris(pyrazol-1-yl)methane]. The complexes **1** react with various bases, for example NaOEt, LiMe or LiBu, in thf (tetrahydrofuran) to afford at low temperatures the unstable zwitterionic species $[\overset{+}{M}(\equiv CR)(CO)_2\{\overset{-}{C}(pz)_3\}]$, which can be captured by addition of the Lewis-acid fragment AuC_6F_5 to yield the neutral compounds $[M(\equiv CR)(CO)_2\{(C_6F_5)AuC(pz)_3\}]$ **2**.[8b] The latter contain the five-electron donor ligand $(C_6F_5)AuC(pz)_3$, demonstrating an isolobal mapping between molecules of types **B** and **E** (Scheme 1). Both the salts **1** and the neutral compounds **2** afford a variety of mixed-metal complexes upon treatment with low-valent metal–ligand fragments, and hence add to the battery of reagents now available for preparing compounds with bonds between tungsten or molybdenum and other metals.

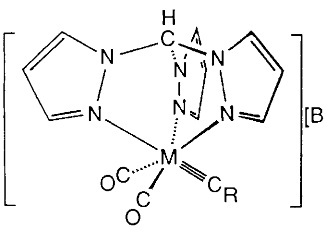
The chemistry of the neutral complexes **2** is more attractive than that of the salts **1** since the former are more soluble, and afford reaction products readily purified by column chromatography. However, the usefulness of the reagents **2** is somewhat inhibited by the need to use the reagent $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) in their synthesis and the observation that in some reactions the C–Au bonds in the compounds **2** are cleaved, a feature discussed further below. For these reasons we have prepared the new alkylidynetungsten complexes $[W(\equiv CR)(CO)_2\{(F_3B)C(pz)_3\}]$ (R = Me, **3a** or C_6H_4Me-4, **3b**), containing the five-electron $(F_3B)C(pz)_3$ donor group, and we have studied some reactions of these reagents with low-valent metal complexes.

Results and Discussion

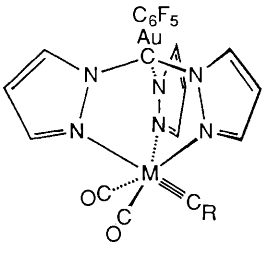
Treatment of thf solutions of the salts **1a** or **1b** at −78 °C



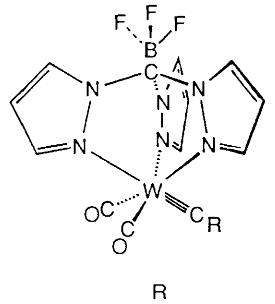
Scheme 1 M = Mo or W, R = alkyl or aryl, R′ = H or Me



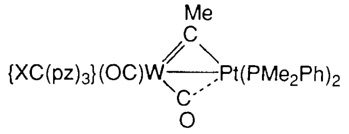
	M	R
1a	W	Me
1b	W	C_6H_4Me-4
1c	W	$C_6H_3Me_2$-2,6
1d	Mo	C_6H_4Me-4



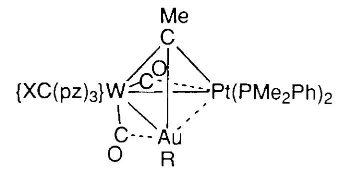
	M	R
2a	W	Me
2b	W	C_6H_4Me-4
2c	W	$C_6H_3Me_2$-2,6
2d	Mo	C_6H_4Me-4



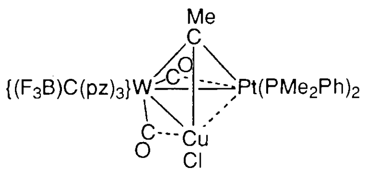
	R
3a	Me
3b	C_6H_4Me-4



	X
4a	BF_3
4b	$Au(C_6F_5)$



	X	R
5a	BF_3	Cl
5b	BF_3	C_6F_5
5c	$Au(C_6F_5)$	C_6F_5
5d	BF_3	$Mn(CO)_5$



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with LiBu affords the aforementioned zwitterionic intermediate $[\overset{+}{W}(\equiv CR)(CO)_2\{\overset{-}{C}(pz)_3\}]$, which can be captured by addition of an excess of $BF_3{\cdot}Et_2O$ to yield the compounds $[W(\equiv CR)(CO)_2\{(F_3B)C(pz)_3\}]$ (R = Me, **3a** or C_6H_4Me-4, **3b**). In these products, characterised by the data given in Tables 1 and 2, the bridgehead carbon atom carries a BF_3 group.

Compound **3a** may be prepared by a simpler procedure which avoids using the salt **1a**. Treatment of $HC(pz)_3$ in thf with LiBu, followed immediately by $BF_3{\cdot}Et_2O$, yields the salt $Li[(F_3B)C(pz)_3]$, characterised from the NMR data (see Experimental section). The latter with $[W(\equiv CMe)Br(CO)_4]$ in thf affords complex **3a**. The overall yield (*ca.* 35–40%) of the desired product by this method is lower than that (*ca.* 70%) obtained using compound **1a** as the precursor. However, the latter has first to be prepared from $[W(\equiv CMe)Br(CO)_4]$ and $HC(pz)_3$, in the presence of $TlBF_4$.[8a]

As expected, in their IR spectra the compounds **3** display two strong CO stretching bands, and for **3a** the absorptions occur at 1988 and 1897 cm^{-1}. These may be compared with those for compound **2a**[8b] at 1985 and 1894 cm^{-1}, and those for the complex $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$[5a] at 1983 and 1899 cm^{-1}. The ^1H NMR spectra of the compounds **3** (Table 2) are very similar to those of **2**[8b] except that the resonances attributed to the H^5 nuclei of the pyrazolyl rings of the former are broadened. This feature may be attributed to the proximity of the boron nuclei at the bridgehead site. In the ^{13}C-$\{^1H\}$ NMR spectra of complexes **3a** and **3b** there are diagnostic peaks for the ligated carbon atoms of the alkylidyne groups at δ 302.4 and 290.8 ppm, respectively. Again, these values correspond closely with those observed in the spectra of **2a** (δ 301.6), **2b** (290.0)[8b] and $[W(\equiv CR)(CO)_2\{HB(pz)_3\}]$ [R = Me (δ 295.2) or C_6H_4Me-4 (284.8 ppm)].[5a]

The reaction in thf between compound **3a** and $[Pt(nb)(PMe_2Ph)_2]$ (nb = norbornene = bicyclo[2.2.1]heptene), generated *in situ* from $[Pt(nb)_3]$ and PMe_2Ph, afforded the expected dimetal compound $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ **4a**, data for which are given in Tables 1–3. Compound **4a** is an analogue of the product $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ **4b**, obtained from the reagent **2a** and $[Pt(nb)(PMe_2Ph)_2]$. However, it is noteworthy that the synthesis of **4b** is accompanied by the

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

Compound	Colour	Yield (%)	$\nu_{max}(CO)$[b]/cm^{-1}	Analysis (%) C	H	N
3a $[W(\equiv CMe)(CO)_2\{(F_3B)C(pz)_3\}]$	Yellow	72[c]	1988s, 1897s	30.0 (30.7)	2.3 (2.2)	14.6 (15.3)
3b $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{(F_3B)C(pz)_3\}]$	Yellow	79	1988s, 1902s	38.1 (38.5)	2.9 (2.6)	12.9 (13.5)
4a $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$	Red	78	1889s, 1787m (br)	34.4 (35.3)	3.5 (3.4)	7.8 (8.2)
5a $[WPtAuCl(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$	Green	82	1925s, 1766m	29.1 (28.8)	3.0 (2.7)	6.5 (6.7)
5b $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$	Green	63	1918s, 1766m	30.8 (31.2)	2.5 (2.5)	5.8 (6.1)
5d $[WMnPtAu(\mu_3\text{-}CMe)(CO)_7(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$	Green	43	2054m, 1951s, 1906w, 1766w (br)	29.4 (29.8)	2.5 (2.4)	5.8 (6.0)
6 $[WPtCuCl(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$	Brown	69	1891s, 1777m	32.6 (32.2)	3.4 (3.1)	7.4 (7.5)
7a $[WPt(\mu\text{-}CMe)(CO)_2(cod)\{(F_3B)C(pz)_3\}]$	Red	12	1926s, 1740m (br)	31.6 (31.1)	2.9 (2.8)	10.2 (9.9)
7b $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)\{(F_3B)C(pz)_3\}]$	Red	74	1936s, 1746	36.5 (36.3)	3.2 (3.0)	9.4 (9.1)
8a $[WPt_2(\mu_3\text{-}CMe)(CO)_2(cod)_2\{(F_3B)C(pz)_3\}]$	Orange	37	1775s, 1711m	30.6 (31.2)	3.3 (3.1)	7.0 (7.3)
8b $[WPt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)_2\{(F_3B)C(pz)_3\}]$	Yellow	42	1788s, 1724m	34.4 (35.1)	3.5 (3.3)	6.4 (6.8)
9a $[W_2Pt(\mu\text{-}CMe)_2(CO)_4\{(F_3B)C(pz)_3\}_2]$	Red	39	1967m (sh), 1946s, 1804m	26.2 (26.1)	1.9 (1.9)	13.2 (13.0)
9b $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{(F_3B)C(pz)_3\}_2]$	Red	56	1976s, 1954s, 1809m	33.9 (33.3)	2.4 (2.2)	11.9 (11.7)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2. [c] Yield is *ca.* 35–40% when prepared from $Li[(F_3B)C(pz)_3]$ (see Experimental section).

formation of the trimetal compound $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(C_6F_5)AuC(pz)_3\}]$ **5c**. The latter species results from addition of an $Au(C_6F_5)$ fragment to **4b**, and implies cleavage of the C–$Au(C_6F_5)$ bond in **2a** during the course of reaction. This feature in the reactivity patterns of the reagents **2** was mentioned in the Introduction.

The IR spectrum of compound **4a** displays two CO stretching bands at 1889 and 1787 cm^{-1}. The low frequency of the latter strongly implies that one of the CO ligands asymmetrically bridges the W–Pt bond. Similar, IR bands are shown by compound **4b** (1886 and 1785 cm^{-1}),[8b] and by the related species $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2\{HB(pz)_3\}]$ [$\nu_{max}(CO)$ at 1914 and 1764 cm^{-1}].[5a] Evidently the two CO ligands in **4a** undergo site exchange in solution on the NMR time-scale, since in the $^{13}C\text{-}\{^1H\}$ NMR spectrum (Table 2) only one CO resonance at δ 229.2 ppm is observed. A diagnostic doublet resonance for the μ-C group is seen at δ 353.0 ppm [*J*(PC) 57 Hz]. The $^{31}P\text{-}^{13}C$ coupling involves the PMe_2Ph ligand transoid to the μ-C atom. The corresponding data for complex **4b** are δ 352.5 ppm [*J*(PC) 53 Hz]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of compound **4a** (Table 3) shows the pattern expected for the presence of a *cis*-$Pt(PMe_2Ph)_2$ group. Two resonances are observed, both doublets with ^{195}Pt satellite peaks, at δ 4.8 [*J*(PP) 20, *J*(PtP) 2095] and −7.2 ppm [*J*(PP) 20, *J*(PtP) 1357 Hz].

Compound **4a** can be used to prepare trimetal complexes. Thus treatment of CH_2Cl_2 solutions of **4a** with the compounds [AuR(tht)] (R = Cl or C_6F_5) affords the species $[WPtAuR(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ (R = Cl, **5a** and C_6F_5, **5b**), respectively. Similarly, addition of CuCl to a CH_2Cl_2 solution of complex **4a** gives $[WPtCuCl(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ **6**. Compound **5b** is closely related to the previously prepared species **5c**, referred to above, the structure of which has been established by X-ray diffraction.[8b] In the trimetal core the long Pt ··· Au separation [2.932(1) Å] implies at most only weak metal–metal bonding, and the structure is best viewed as being of the 'butterfly' type, with the Pt and Au atoms occupying the wing-tip sites and the μ_3-C–W bond forming the body of the butterfly. It is likely that the structures of the related compounds **5a**, **5b** and **6** described herein are basically similar, since all members of this family of cluster compounds have 44 valence electrons. Trimetal species with the core structure μ_3-CWPtM (M = Cu or Au) and 44 valence electrons would be expected to adopt a butterfly arrangement of the kind found for **5c**, and established by X-ray diffraction for the cation of the salt $[WPtAu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][PF_6]$ [Pt ··· Au 2.956(2) Å].[9]

The NMR data for the species **5a**, **5b** and **6** are in agreement with the formulations proposed. The $^{13}C\text{-}\{^1H\}$ NMR spectra of **5a** and **5b** were informative, with characteristic resonances for the μ_3-C nuclei occurring at δ 296.5 and 310.5 ppm, respectively. Both signals are doublets [*J*(PC) 60 Hz], due to coupling with a phosphorus atom of one PMe_2Ph ligand, presumably lying transoid to the alkylidyne carbon. Two CO peaks are seen in each spectrum, as expected. In the spectrum of compound **5a** the CO signal at δ 236.9 ppm (Table 2) is a doublet [*J*(PC) 10 Hz], and shows weak $^{195}Pt\text{-}^{13}C$ coupling (18 Hz). This resonance may, therefore, be assigned to the carbonyl ligand semi-briding the W–Pt bond. Unfortunately compound **6** was too insoluble to measure its $^{13}C\text{-}\{^1H\}$ NMR spectrum. However, the ^1H NMR spectra of all three complexes **5a**, **5b** and **6** displayed all the expected resonances.

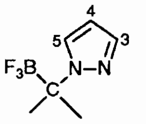
The $^{31}P\text{-}\{^1H\}$ NMR spectra (Table 3) of compounds **5a**, **5b** and **6** showed two singlet resonances for the *cis*-$Pt(PMe_2Ph)_2$ groups. The absence of $^{31}P\text{-}^{31}P$ coupling is not unusual, since if observed for a *cis*-PtP_2 moiety it is usually weak. Each resonance showed ^{195}Pt satellite peaks, and the signal with the larger $^{195}Pt\text{-}^{31}P$ coupling may be assigned to the PMe_2Ph ligand transoid to the Pt–W bond.

The Cl atom in compound **5a** may be replaced by an $Mn(CO)_5$ group by treatment with $Na[Mn(CO)_5]$ in thf. The resulting product $[WMnPtAu(\mu_3\text{-}CMe)(CO)_7(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ **5d**, was characterised by the data given in Tables 1–3. A similar reaction between complex **6** and $Na[Mn(CO)_5]$ failed to give a stable product.

Reactions between the compounds **3** and $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene) or $[Pt(nb)_3]$ were next investigated. In thf at ambient temperatures, complex **3a** and $[Pt(cod)_2]$ gave a mixture of the three compounds $[WPt(\mu\text{-}CMe)(CO)_2(cod)\{(F_3B)C(pz)_3\}]$ **7a**, $[WPt_2(\mu_3\text{-}CMe)(CO)_2(cod)_2\{(F_3B)C(pz)_3\}]$ **8a** and $[W_2Pt(\mu\text{-}CMe)_2(CO)_4\{(F_3B)C(pz)_3\}_2]$ **9a**, which were readily separated by column chromatography on alumina. The corresponding reaction between complex **3b** and $[Pt(cod)_2]$ afforded two products: $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)\{(F_3B)C(pz)_3\}]$ **7b** and $[WPt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)_2\{(F_3B)C(pz)_3\}]$ **8b**. However, if this reaction is carried out in thf at 50 °C the compound $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{(F_3B)C(pz)_3\}_2]$ **9b** is formed, in addition to the two species **7b** and **8b**. Although it was not possible to separate compounds **8b** and **9b** by chromatography, the latter could be obtained readily from the reaction between **3b** and $[Pt(nb)_3]$. It was also shown that compound **8b** could be prepared in good yield by treating **7b** with $[Pt(cod)_2]$. Data for the compounds **7**, **8**, **9a** and **9b** are given in Tables 1 and 2.

It is interesting to compare the formation and structures of compounds **7**, **8**, **9a** and **9b** with the products obtained from

Table 2 Hydrogen-1 and carbon-13 NMR data for the complexes[a]



Complex	^{1}H (δ)	^{13}C (δ)[b]
3a	2.38 (s, 3 H, Me), 6.29 (m, 1 H, H^4), 6.36 (m, 2 H, H^4), 7.73 [d, 1 H, H^3, *J*(H^{3}H^4), 2], 8.03 [d, 2 H, H^3, *J*(H^{3}H^4) 2], 8.35 (m, 1 H, H^5), 8.39 (m, 2 H, H^5)	302.4 (C≡W), 221.8 (CO), 145.7, 144.6, 135.9, 106.7 ($C_3H_3N_2$), 38.6 (Me)
3b	2.30 (s, 3 H, Me-4), 6.33 (m, 1 H, H^4), 6.38 (m, 2 H, H^4), 7.12, 7.31 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8], 7.78 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.09 [d, 2 H, H^3, *J*(H^{3}H^4) 2], 8.41 (m, 3 H, H^5)	290.8 (C≡W), 222.6 (CO), 147.1 [C^1(C_6H_4)], 145.8–106.8 ($C_3H_3N_2$ and C_6H_4), 21.7 (Me-4)
4a	1.49 [d, 6 H, MeP, *J*(PH) 12, *J*(PtH) 21], 1.94 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 11], 2.67 (m, 3 H, Me), 6.24 (m, 2 H, H^4), 6.39 (m, 1 H, H^4), 7.29–7.71 (m, 12 H, H^3 and Ph), 8.13 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.39 (s, 2 H, H^5), 8.45 (s, 1 H, H^5)	353.0 [d, μ-C, *J*(PC) 57], 229.2 (CO), 145.4–106.3 ($C_3H_3N_2$ and Ph), 41.7 [d, Me, *J*(PC) 7], 17.9 [d, MeP, *J*(PC) 28, *J*(PtC) 22], 15.6 [d, MeP, *J*(PC) 24, *J*(PtC) 12]
5a	1.45 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 18], 1.60 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 19], 1.86 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 12], 2.00 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 12], 2.54 (m, 3 H, Me), 6.06, 6.39, 6.49 (m × 3, 3 H, H^4), 6.89 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 7.34–7.81 (m, 10 H, Ph), 8.24 (s, 1 H, H^5), 8.33 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.44 (s, 1 H, H^5), 8.46 (s, 1 H, H^5), 8.70 [d, 1 H, H^3, *J*(H^{3}H^4) 2]	296.5 [d, μ_3-C, *J*(PC) 60], 236.9 [d, CO, *J*(PC) 10, *J*(PtC) 18], 222.3 (CO), 148.1–106.4 ($C_3H_3N_2$ and Ph), 40.6 [d, C*Me*, *J*(PC) 5], 19.2 [d, MeP, *J*(PC) 29], 18.1 [d, MeP, *J*(PC) 33], 16.1 [d, MeP, *J*(PC) 31], 11.0 [d, MeP, *J*(PC) 24]
5b	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) 12], 1.99 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 12], 2.58 (m, 3 H, Me), 6.03, 6.41, 6.48 (m × 3, 3 H, H^4), 6.79 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 7.29–7.73 (m, 10 H, Ph), 8.25 (s, 1 H, H^5), 8.36 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.46 (s, 2 H, H^5), 8.84 [d, 1 H, H^3, *J*(H^{3}H^4) 2]	310.5 [d, μ_3-C, *J*(PC) 58], 237.2, 223.2 (CO), 147.3–106.3 ($C_3H_3N_2$ and Ph), 41.0 [d, C*Me*, *J*(PC) 5], 18.8 [d, MeP, *J*(PC) 19], 18.3 [d, MeP, *J*(PC) 21], 15.6 [d, MeP, *J*(PC) 29], 11.1 [d, MeP, *J*(PC) 26]
5d	1.40 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 17], 1.80 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 19], 1.90 [d, 3 H, MeP, *J*(PH), 8, *J*(PtH) 11], 1.97 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 12], 2.48 (m, 3 H, Me), 5.91 (m, 1 H, H^4), 6.46 (m, 2 H, H^4), 6.54 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 7.31–7.80 (m, 10 H, Ph), 8.19 (s, 1 H, H^5), 8.31 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.44 (s, 2 H, H^5), 8.77 [d, 1 H, H^3, *J*(H^{3}H^4) 2]	306.1 [d, μ_3-C, *J*(PC) 59], 236.5 [d, WCO, *J*(PC) 5], 224.5 (WCO), 221.4 (MnCO), 145.8–105.9 ($C_3H_3N_2$ and Ph), 39.0 (Me), 19.0 [d, MeP, *J*(PC) 27], 18.5 [d, MeP, *J*(PC) 27], 14.6 [d, MeP, *J*(PC) 29], 10.7 [d, MeP, *J*(PC) 27]
6[c]	1.39 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 17], 1.71 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 19], 1.89 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 11], 2.05 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 12], 2.36 (m, 3 H, Me), 6.09, 6.40, 6.48 (m × 3, 3 H, H^4), 6.79 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 7.30–7.80 (m, 10 H, Ph), 8.28 (m, 2 H, H^3 and H^5), 8.38 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.45, 8.48 (s × 2, 2 H, H^5)	
7a	2.30–2.75 [m, 8 H, CH_2(cod)], 3.16 [s, 3 H, Me, *J*(PtH) 2], 4.75–5.35 [m, 4 H, CH(cod)], 6.29 (m, 2 H, H^4), 6.39 (m, 1 H, H^4), 7.61 [d, 2 H, H^3, *J*(H^{3}H^4) 2], 8.04 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.40 (m, 3 H, H^5)	330.1 (μ-C), 230.4 (CO), 145.8–106.5 ($C_3H_3N_2$), 108.7 [CH(cod), *J*(PtC) 51], 93.0 [CH(cod), *J*(PtC) 60], 36.0 (Me), 31.4, 29.4 [CH_2(cod)]
7b	2.25–2.75 [m, 8 H, CH_2(cod)], 2.32 (s, 3 H, Me), 4.45–5.35 [m, 4 H, CH(cod)], 6.16 (m, 2 H, H^4), 6.42 (m, 1 H, H^4), 6.52, 7.05 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8], 7.48 [d, 2 H, H^3 *J*(H^{3}H^4) 2], 8.03 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.34 (s, 2 H, H^5), 8.42 (s, 1 H, H^5)	318.8 [μ-C, *J*(PtC) 376], 230.1 [CO, *J*(PtC) 36], 153.6 [C^1(C_6H_4)], 145.6–106.1 ($C_3H_3N_2$ and C_6H_4), 107.0 [CH(cod), *J*(PtC) 57], 94.7 [CH(cod), *J*(PtC) 58], 30.3, 29.7 [CH_2(cod)], 20.7 (Me-4)
8a	2.25–2.65 [m, 16 H, CH_2(cod)], 2.96 [s, 3 H, Me, *J*(PtH) 2], 4.50–5.10 [m, 8 H, CH(cod)], 6.18 (m, 2 H, H^4), 6.46 (m, 1 H, H^4), 7.46 [d, 2 H, H^3, *J*(H^{3}H^4) 2], 8.36 (s, 2 H, H^5), 8.41, 8.42 (s × 2, 2 H, H^3 and H^5)	242.9 (CO), 232.4 (μ_3-C), 147.2–89.2 [$C_3H_3N_2$ and CH(cod)], 34.6, 32.8, 28.4, 25.9 [CH_2(cod)], 27.1 (Me)
8b	2.17 (s, 3 H, Me), 2.22–2.75 [m, 16 H, CH_2(cod)], 4.45–5.46 [m, 8 H, CH(cod)], 5.72, 6.64 [(AB)$_2$, 4 H, C_6H_4, *J* (AB) 8], 6.07 (m, 2 H, H^4), 6.50 (m, 1 H, H^4), 7.38 [d, 2 H, H^3, *J*(H^{3}H^4) 2], 8.37 (s, 2 H, H^5), 8.40 (s, 1 H, H^5), 8.48 [d, 1 H, H^3, *J*(H^{3}H^4) 2]	241.1 [CO, *J*(PtC) 9], 229.5 [μ_3-C, *J*(PtC) 142], 148.5–106.9 (C_6H_4 and $C_3H_3N_2$), 110.7, 105.9, 101.0, 87.6 [CH(cod)], 34.7, 33.1, 28.7, 26.3 [CH_2(cod)], 20.3 (Me)
9a	2.98 (s, 3 H, Me), 6.34, 6.44, 6.49 (m × 3, 3 H, H^4), 7.94 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.03 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.12 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.42 (s, 1 H, H^5), 8.49 (s, 2 H, H^5)	315.0 (μ-C), 228.8, 221.4 (CO), 145.6–106.9 ($C_3H_3N_2$), 40.2 (Me)
9b	2.30 (s, 3 H, Me), 6.07, 6.31, 6.47 (m × 3, 3 H, H^4), 6.86, 7.07 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8], 6.91 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 7.98 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.07 [d, 1 H, H^3, *J*(H^{3}H^4) 2], 8.37, 8.43, 8.48 (s × 3, 3 H, H^5)	302.7 (μ-C), 225.9, 223.3 (CO), 151.0 [C^1(C_6H_4)], 144.8–106.2 ($C_3H_3N_2$ and C_6H_4), 21.2 (Me-4)

[a] Chemical shifts (δ) in ppm, 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 ppm). [c] Carbon-13 spectrum not recorded due to insolubility of the complex.

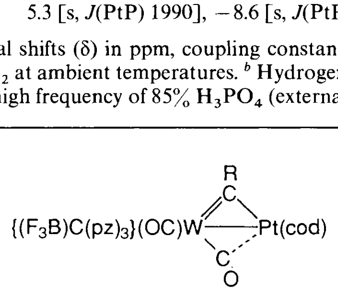
reactions studied previously. Compounds **9a** and **9b** are analogues of the complexes [$W_2Pt(\mu\text{-}CR)_2(CO)_4\{(C_6F_5)AuC(pz)_3\}_2$] (R = Me, **9c** or C_6H_4Me-4, **9d**), prepared from reactions between the reagent **2a** or **2b** and [Pt(nb)$_3$], respectively. All four compounds **9a**–**9d** belong to a large family of tri-metal complexes of formulation [$WPt_2(\mu\text{-}CR)_2(CO)_4L_2$] [R = alkyl or aryl; L = η-C_5H_5, η-C_5Me_5 or HB(pz)$_3$],[10] of which the paradigm molecule is [$WPt_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2$].[11] These species have been used extensively as precursors to cluster compounds with chains or rings of metal atoms,[12] and it is hoped that the complexes **9** can be used for this purpose also.

Reactions between [Pt(cod)$_2$] and the reagents [W(≡CR)(CO)$_2$L] [R = alkyl or aryl; L = η-C_5H_5, η-C_5Me_5 or

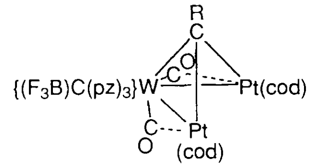
Table 3 Phosphorus-31 NMR spectra for the complexes[a]

Complex	^{31}P (δ)[b]
4a	4.8 [d, J(PP) 20, J(PtP) 2095], −7.2 [d, J(PP) 20, J(PtP) 1357]
5a	−1.0 [s, J(PtP) 2026], −13.6 [s, J(PtP) 1460]
5b	0.6 [s, J(PtP) 2019], −13.3 [s, J(PtP) 1470]
5d	−1.9 [s, J(PtP) 2024], −12.5 [s, J(PtP) 1448]
6	5.3 [s, J(PtP) 1990], −8.6 [s, J(PtP) 1450]

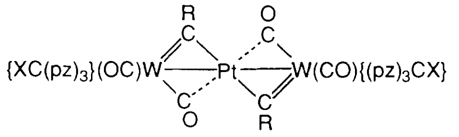
[a] Chemical shifts (δ) in ppm, coupling constants in Hz; measurements in CD_2Cl_2 at ambient temperatures. [b] Hydrogen-1 decoupled, chemical shifts to high frequency of 85% H_3PO_4 (external) taken as positive.



	R
7a	Me
7b	C_6H_4Me-4



	R
8a	Me
8b	C_6H_4Me-4



	X	R
9a	BF_3	Me
9b	BF_3	C_6H_4Me-4
9c	$Au(C_6F_5)$	Me
9d	$Au(C_6F_5)$	C_6H_4Me-4

HB(pz)$_3$] in general result in facile displacement of both cod ligands from platinum, with formation of the trimetal compounds [$W_2Pt(\mu$-CR$)_2(CO)_4L_2$]. Hence the isolation of dimetal complexes akin to the compounds **7** is unusual. However, reactions between the salts [X][W(≡CR)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)] and [Pt(cod)$_2$] in thf afford the complexes [X][WPt(μ-CR)(CO)$_2$(cod)(η^5-$C_2B_9H_9Me_2$)] [X = P(CH_2Ph)Ph_3, R = C_6H_4Me-4; X = NEt_4, R = Ph], the anions of which are structurally similar to the neutral complexes **7**.[13]

Formation of the products **8** was also unexpected. As mentioned above, complex **8b** is readily prepared by addition of a Pt(cod) fragment to **7b**, and it is therefore very likely that formation of the species **8** in the reaction mixtures involves the intermediacy of the dimetal compounds **7**. The complexes **8** are structurally related to the previously reported species [WPt_2(μ$_3$-CC_6H_4Me-4)(CO)$_4$(PMePh_2)$_2$(η-C_5H_5)], obtained by treating toluene solutions of [WPt(μ-CC_6H_4Me-4)(CO)$_2$(PMePh_2)$_2$(η-C_5H_5)] with CO.[14]

The spectroscopic data for the new compounds **7**, **8**, **9a** and **9b** are in accord with the formulations proposed. The IR spectra of the complexes **7** show two CO stretching bands, one of which is in the terminal region (**7a**, 1926; **7b**, 1936 cm^{-1}) and the other in the asymmetrically bridging region (**7a**, 1740; **7b**, 1746 cm^{-1}). Similarly, the compounds **8** display two CO stretching bands (Table 1), but for these species both absorptions are in the asymmetrically bridging region. Indeed, an X-ray diffraction study of the compound [WPt_2(μ$_3$-CC_6H_4Me-4)(CO)$_4$(PMePh_2)$_2$(η-C_5H_5)], mentioned above, revealed that the W–Pt bonds were each semi-bridged by a carbonyl group.[14] The complexes **9a** and **9b** both show three CO stretching bands in their IR spectra (Table 1), and the pattern observed is similar to that found previously for several compounds of this structural type.[10b]

The ^{13}C-{^{1}H} NMR spectra of the complexes **7** display diagnostic signals for the μ-C nuclei at δ 330.1, **7a**, and 318.8 ppm, **7b**. The spectrum of the latter was of sufficient quality to reveal ^{195}Pt satellite peaks [J(PtC) 376 Hz]. Only one CO resonance is observed (Table 2) in the spectrum of both compounds, and this must indicate dynamic behaviour in solution involving site exchange of the carbonyl ligands.

The ^{1}H and ^{13}C-{^{1}H) NMR data for the compounds **8** are given in Table 2. In the ^{13}C-{^{1}H} NMR spectra peaks at δ 232.4, **8a**, and 229.5 ppm, **8b**, are assigned to the μ$_3$-C nucleus. These shifts are relatively shielded for triply bridging alkylidyne-carbon atoms. However, the assignment is supported by the observation of ^{195}Pt–^{13}C coupling (142 Hz) on the resonance at 229.5 ppm for **8b**.

The ^{13}C-{^{1}H} NMR spectra of complexes **9a** and **9b** also show diagnostic resonances for the μ-C groups at δ 315.0 and 302.7 ppm, respectively. These signals are very similar to those observed for the μ-C nuclei in the spectra of **9c** (δ 314.6) and **9d** (303.1 ppm).[8b] The ^{1}H NMR spectra of the compounds **7**, **8**, **9a** and **9b** display all the expected resonances for the groups present.

Finally, the ^{11}B-{^{1}H} and ^{19}F-{^{1}H} NMR spectra of all the new compounds were measured. As expected, the BF_3 groups gave rise to quartet resonances in the ^{11}B-{^{1}H} spectra in the range δ −0.08 to −0.57 ppm [J(BF) 39 Hz], and correspondingly quartet resonances appear also in the ^{19}F-{^{1}H} spectra at *ca* δ −140 ppm [J(BF) 39 Hz]. The compound **5b** containing a C_6F_5 group showed diagnostic resonances in its ^{19}F-{^{1}H} NMR spectrum for this group at δ −114.4 [d, 2 F, J(FF) 24], −160.6 [t, 1 F, J(FF) 24 Hz] and −162.8 ppm (m, 2 F).

The results described in this paper show that the new alkylidynetungsten complexes **3** significantly add to the variety of precursors (Scheme 1) now available for the synthesis of mixed-metal compounds, based on the methodology of adding metal–ligand fragments to C≡M bonds. Moreover, it is noteworthy that the (F_3B)C(pz)$_3$ group present in the reagents **3**, and in the compounds obtained from them, is closely related to the HB(pz)$_3$ ligand, for which a very extensive chemistry has been developed.[15] Further studies will reveal whether the new five-electron donor group (F_3B)C(pz)$_3$ will also play a significant role in transition-metal complex chemistry.

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. Fluorine-19 and boron-11 NMR chemical shifts are positive to high frequency of CCl_3F (external) and BF_3·Et_2O (external), respectively, with measurements in CD_2Cl_2. The compounds **1a**, **1b**,[8a] [AuCl(tht)], [Au(C_6F_5)(tht)],[16] [Pt(nb)$_3$] and [Pt(cod)$_2$][17] were prepared as described previously. The reagent BF_3·Et_2O was obtained from Aldrich Chemical Co. Analytical data for the new complexes are given in Table 1.

Preparation of the Complexes [W(≡CR)(CO)$_2${(F_3B)-

$C(pz)_3\}]$.—(*i*) A thf (100 cm^3) solution of compound **1a** (0.75 g, 1.32 mmol), cooled to −78 °C, was treated first with LiBu (1.39 mmol, 0.87 cm^3 of a 1.6 mol dm^{-3} solution in hexane), followed immediately by $BF_3{\cdot}Et_2O$ (0.30 cm^3, 2.44 mmol). The mixture was stirred while it was slowly warmed to room temperature. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (15 cm^3) and chromatographed. Elution with CH_2Cl_2–hexane (3:2) removed an orange fraction. Slow removal of solvent *in vacuo* from the eluate gave yellow *microcrystals* of $[W(\equiv CMe)(CO)_2\{(F_3B)C(pz)_3\}]$ **3a** (0.52 g).

The complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{(F_3B)C(pz)_3\}]$ **3b** (0.38 g), was similarly obtained from **2b** (0.50 g, 0.78 mmol), LiBu (0.83 mmol) and $BF_3{\cdot}Et_2O$ (1.46 mmol).

(*ii*) A thf (15 cm^3) solution of $HC(pz)_3$ (0.50 g, 2.34 mmol) at −78 °C was treated with LiBu (2.40 mmol), followed immediately by $BF_3{\cdot}Et_2O$ (1.0 cm^3, 8.13 mmol). The resulting white suspension was allowed to warm slowly to room temperature, whereupon an orange solution formed. Solvent was removed *in vacuo*, and the residue was redissolved in thf (*ca.* 5 cm^3) and cooled to −78 °C for 1 h. The supernatant liquid was removed with a syringe, and the cream solid thus obtained was dried *in vacuo* for 12 h to afford the salt $Li[(F_3B)C(pz)_3]{\cdot}thf$ (0.45 g, 54%). NMR $[(CD_3)_2CO]$: ^1H, δ 6.23 (m, 3 H, H^4), 7.41 [d, 3 H, H^3, $J(H^3H^4)$ 2 Hz] and 8.18 (s, 3 H, H^5); $^{13}C\text{-}\{^1H\}$, δ 139.5, 132.5 and 104.4 ppm. Resonances due to a thf molecule were also observed.

This reagent may be prepared *in situ* and used to make $[W(\equiv CMe)(CO)_2\{(F_3B)C(pz)_3\}]$ **3a**. The compound $[W(\equiv CMe)Br(CO)_4]$ (1.42 g, 3.52 mmol) in thf (50 cm^3) at *ca.* 15 °C was treated with a thf (15 cm^3) solution of $Li[(F_3B)C(pz)_3]$, obtained from $HC(pz)_3$ (0.75 g, 3.50 mmol), LiBu (3.50 mmol) and $BF_3{\cdot}Et_2O$ (9.80 mmol). The mixture was stirred for 24 h. Removal of solvent *in vacuo*, followed by dissolution of the residue in CH_2Cl_2 (5 cm^3) and column chromatography, eluting with CH_2Cl_2–hexane (4:1), gave a single yellow fraction. Slow removal of solvent *in vacuo* afforded complex **3a** (0.66 g).

Reactions of the Compounds $[W(\equiv CR)(CO)_2\{(F_3B)C(pz)_3\}]$ (R = Me *or* C_6H_4Me-4).—(*i*) A thf (20 cm^3) solution of complex **3a** (0.25 g, 0.46 mmol) was treated with a thf (10 cm^3) solution of $[Pt(nb)(PMe_2Ph)_2]$ (0.50 mmol), prepared *in situ* from $[Pt(nb)_3]$ (0.24 g, 0.50 mmol) and PMe_2Ph (1.0 mmol). The reaction mixture was stirred for 4 h, solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (3 cm^3) and chromatographed at −10 °C. Elution with CH_2Cl_2–light petroleum (3:2) removed a single red eluate which was collected. Slow removal of solvent *in vacuo* gave red *microcrystals* of $[WPt(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ **4a** (0.36 g).

(*ii*) A CH_2Cl_2 (15 cm^3) solution of complex **4a** (0.25 g, 0.25 mmol) was treated with $[AuCl(tht)]$ (0.09 g, 0.28 mmol). The mixture was stirred for 15 min, although reaction occurred immediately. Solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 (3 cm^3) and chromatographed at −15 °C. Elution with CH_2Cl_2–light petroleum (3:1) removed a single green band. Slow removal of solvent *in vacuo* from this eluate gave green *microcrystals* of $[WPtAuCl(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ **5a** (0.26 g).

The compound $[WPtAu(C_6F_5)(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ **5b** (0.22 g), was similarly obtained from $[Au(C_6F_5)(tht)]$ (0.13 g, 0.28 mmol) and the complex **4a** (0.25 g, 0.25 mmol).

(*iii*) A freshly prepared thf (10 cm^3) solution of complex **5a** (0.30 g, 0.24 mmol) at −50 °C was treated with $Na[Mn(CO)_5]$ (*ca.* 1.2 mmol) in the same solvent (10 cm^3). The mixture was warmed slowly to room temperature, solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (3 cm^3) and chromatographed at −10 °C. Elution with CH_2Cl_2–light petroleum (3:1) removed a single green fraction. Slow removal of solvent *in vacuo* afforded green *microcrystals* of $[WMnPtAu(\mu_3\text{-}CMe)(CO)_7(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ **5d** (0.15 g).

(*iv*) The complex $[WPtCuCl(\mu_3\text{-}CMe)(CO)_2(PMe_2Ph)_2\{(F_3B)C(pz)_3\}]$ **6** was prepared from **4a** (0.20 g, 0.20 mmol) and CuCl (0.03 g, 0.30 mmol) in CH_2Cl_2 (15 cm^3). The mixture was filtered through a Celite pad (3 × 2 cm), hexane (15 cm^3) was added, and the solvent mixture was then slowly removed *in vacuo* to yield brown *microcrystals* of compound **6** (0.15 g).

(*v*) Compound **3a** (0.15 g, 0.27 mmol) in thf (15 cm^3) was treated with solid $[Pt(cod)_2]$ (0.34 g, 0.82 mmol). The mixture was stirred until an IR spectrum indicated that the sample of **3a** used had been consumed (*ca.* 4–6 h). 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 eluted with CH_2Cl_2–light petroleum (2:3). Two red bands separated, and further elution with CH_2Cl_2–light petroleum (4:1) removed a third (yellow) fraction. The three eluates were collected individually and solvent was removed slowly *in vacuo* from each to yield in order of elution red *microcrystals* of $[WPt(\mu\text{-}CMe)(CO)_2(cod)\{(F_3B)C(pz)_3\}]$ **7a** (0.03 g), red *microcrystals* of $[W_2Pt(\mu\text{-}CMe)_2(CO)_4\{(F_3B)C(pz)_3\}_2]$ **9a** (0.07 g), and orange *microcrystals* of $[WPt_2(\mu_3\text{-}CMe)(CO)_2(cod)_2\{(F_3B)C(pz)_3\}]$ **8a** (0.12 g), respectively.

(*vi*) Using the same procedure, compound **3b** (0.17 g, 0.27 mmol) in thf (15 cm^3) was treated with solid $[Pt(cod)_2]$ (0.34 g, 0.82 mmol). Work up of the reaction mixture in a manner similar to that described above gave red *microcrystals* of $[WPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)\{(F_3B)C(pz)_3\}]$ **7b** (0.18 g) and yellow *microcrystals* of $[WPt_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(cod)_2\{(F_3B)C(pz)_3\}]$ **8b** (0.03 g).

The yield of compound **8b** can be increased by treating **7b** (0.25 g, 0.27 mmol) with $[Pt(cod)_2]$ (0.15 g, 0.36 mmol) in thf (10 cm^3) at 40 °C for 2 h. Column chromatography and working up as described above gave red *microcrystals* of unreacted **7b** (0.07 g) and yellow *microcrystals* of complex **8b** (0.19 g).

A thf (15 cm^3) solution of the reagent **3b** (0.20 g, 0.32 mmol) was treated portionwise with $[Pt(nb)_3]$ (0.08 g, 0.16 mmol), and the mixture was stirred for *ca.* 15 h. Solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 (3 cm^3) and the resulting solution was chromatographed. Elution with CH_2Cl_2–hexane (4:1) removed a red band. Slow removal of solvent *in vacuo* from the eluate afforded red *microcrystals* of $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{(F_3B)C(pz)_3\}_2]$ **9b** (0.13 g).

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