Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 59.[1] Reactions of the Alkylidyne Compounds $[M(\equiv CR)(CO)_2\{HB(pz)_3\}]$ [M = Cr, Mo, or W, R = C_6H_4Me-4; M = W, R = Me, $HB(pz)_3$ = Hydrotris(pyrazol-1-yl)borate] with d^{10} Complexes; Crystal Structure of $[PtW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ *

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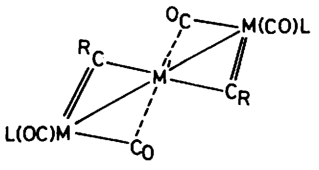
Treatment of the compound $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ [$\{HB(pz)_3\}$ = hydrotris(pyrazol-1-yl)-borate] with $[Ni(cod)_2]$ (cod = cyclo-octa-1,5-diene) or $[Pt(C_2H_4)_3]$ affords the trimetal complexes $[M'W_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ (M' = Ni or Pt). Similarly, reactions between the species $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (M = Cr, Mo, or W) and $[Pt(C_2H_4)_3]$ yield the related compounds $[PtM_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{HB(pz)_3\}_2]$. The molecular structure of $[PtW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ has been established by *X*-ray diffraction. The molecule has a nearly linear W–Pt–W spine [172.8(1)°], with mean Pt–W separations of 2.716 Å. Each metal–metal bond is bridged by an ethylidyne group [mean values μ-C–W 1.885, μ-C–Pt 2.040 Å] and semi-bridged by a carbonyl ligand [W–C–O 166°]. The dihedral angle between the two dimetallacyclopropene rings is 79°. Each tungsten atom carries a terminally bound CO ligand and a $HB(pz)_3$ group. If the metal–metal bonds are ignored, each tungsten is in a *pseudo*-octahedral environment defined by the three nitrogen atoms of its associated $HB(pz)_3$ ligand, the two CO groups and a μ-CMe fragment. A gold salt $[AuW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2][PF_6]$ has been obtained by treating $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ with [AuCl(tht)] (tht = tetrahydrothiophene) in the presence of $TlPF_6$. Reactions between the complexes $[M(\equiv CR)(CO)_2\{HB(pz)_3\}]$ (M = Cr, Mo, or W, R = C_6H_4Me-4; M = W, R = Me) and $[Pt(C_2H_4)\{P(OMe)_3\}_2]$ give dimetal compounds $[PtM(\mu\text{-}CR)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$, but only the ethylidyne-bridged platinum–tungsten compound is reasonably stable in solution. A molybdenum–platinum salt formulated as $[PtMo\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}][BF_4]$ has also been prepared. Spectroscopic data for the new compounds are reported.

Among the earliest reactions studied[2] which demonstrated that the C≡W group in the tolylmethylidynetungsten compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ could function as a 'ligand' were those involving the reagents $[Ni(cod)_2]$ (cod = cyclo-octa-1,5-diene), $[Pd(\eta\text{-}C_7H_{10})_3]$ (C_7H_{10} = bicyclo[2.2.1]-heptene) and $[Pt(C_2H_4)_3]$.[3] The products are the trimetallic complexes $[M'W_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [M' = Ni (**1a**), Pd (**1b**), or Pt (**1c**)]. The palladium compound (**1b**) proved to be a very labile species, unsuitable for further syntheses. However, the nickel and platinum complexes are stable, as are the related trimetal compounds (**1d**)—(**1o**).[4] Hence these species have been employed in the preparation of complexes with chains and rings of metal atoms.[5]

In this paper we describe an extension of this area of chemistry using the recently prepared[6,7] compounds $[M(\equiv CR)(CO)_2\{HB(pz)_3\}]$ [M = Cr, Mo, or W, R = C_6H_4Me-4; M = W, R = Me; $HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate] to obtain further examples of complexes of type (**1**). Also included herein is a description of some related dimetal species synthesised in the expectation that the presence of the hydrotris(pyrazol-1-yl)borate group might lead to differences in properties compared with analogous compounds containing the ligands $\eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$.[8]



	M'	M	R	L
(**1a**)	Ni	W	C_6H_4Me-4	$\eta\text{-}C_5H_5$
(**1b**)	Pd	W	C_6H_4Me-4	$\eta\text{-}C_5H_5$
(**1c**)	Pt	W	C_6H_4Me-4	$\eta\text{-}C_5H_5$
(**1d**)	Ni	W	Me	$\eta\text{-}C_5H_5$
(**1e**)	Ni	W	Ph	$\eta\text{-}C_5H_5$
(**1f**)	Ni	W	Me	$\eta\text{-}C_5Me_5$
(**1g**)	Ni	W	Ph	$\eta\text{-}C_5Me_5$
(**1h**)	Ni	W	C_6H_4Me-4	$\eta\text{-}C_5Me_5$
(**1i**)	Ni	Mo	C_6H_4Me-4	$\eta\text{-}C_5H_5$
(**1j**)	Pt	W	Me	$\eta\text{-}C_5H_5$
(**1k**)	Pt	W	Ph	$\eta\text{-}C_5H_5$
(**1l**)	Pt	W	Me	$\eta\text{-}C_5Me_5$
(**1m**)	Pt	W	Ph	$\eta\text{-}C_5Me_5$
(**1n**)	Pt	W	C_6H_4Me-4	$\eta\text{-}C_5Me_5$
(**1o**)	Pt	Mo	C_6H_4Me-4	$\eta\text{-}C_5H_5$
(**1p**)	Ni	W	Me	$HB(pz)_3$
(**1q**)	Pt	W	Me	$HB(pz)_3$
(**1r**)	Pt	W	C_6H_4Me-4	$HB(pz)_3$
(**1s**)	Pt	Cr	C_6H_4Me-4	$HB(pz)_3$
(**1t**)	Pt	Mo	C_6H_4Me-4	$HB(pz)_3$

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* 1,2;2,3-Di-μ-carbonyl-1,3-dicarbonyl-1,2;2,3-di-μ-(ethylidyne)-1,3-bis[hydrotris(pyrazol-1-yl)borato]platinumditungsten(2 *Pt–W*).

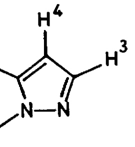
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

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

Compound	Colour	Yield (%)	$\nu_{max.}(CO)$[b]/cm^{-1}	Analysis (%) C	H	N
(1p) $[NiW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$	Purple	60	1 933vs, 1 788m	31.5 (30.7)	3.0 (2.6)	15.8 (16.5)
(1q) $[PtW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$	Red	85	1 956 (sh), 1 931vs, 1 792m	27.9 (27.0)	2.5 (2.3)	14.4 (14.5)
(1r) $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{HB(pz)_3\}_2]$	Red	86	1 966 (sh), 1 937vs, 1 795m, 1 740m	34.1 (34.9)	2.6 (2.6)	13.2 (12.9)
(1s) $[PtCr_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{HB(pz)_3\}_2]$	Green	50	[c]1 998s, 1 979vs, 1 830m, 1 817m	43.1 (43.7)	3.7 (3.3)	15.1 (16.1)
(1t) $[PtMo_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{HB(pz)_3\}_2]$	Dark red	75	1 985vs, 1 961vs, 1 818m, 1 805m	39.7 (40.3)	2.8 (3.0)	14.7 (14.9)
(2d) $[AuW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2][PF_6]$	Yellow	80	2 013vs, 1 929vs	23.1 (24.0)	2.1 (2.0)	12.7 (12.9)
(3d) $[PtW(\mu\text{-}CMe)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$	Red	30	1 903vs, 1 768m	24.1 (24.7)	3.6 (3.3)	9.0 (9.1)
(3e) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$	Red	20	1 907vs, 1 770m			
(3f) $[PtCr(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$	Brown	15	1 903vs, 1 770m			
(3g) $[PtMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$	Red	40	1 926vs, 1 771m			
(4b) $[PtMo\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2\{P(OMe)_3\}_2\text{-}\{HB(pz)_3\}][BF_4]$	Green	93	1 955vs, 1 872vs	29.0 (30.0)	3.6 (3.6)	7.5 (8.4)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2 unless otherwise stated. [c] In hexane.

Table 2. Hydrogen-1 ^{13}C, and ^{195}Pt n.m.r. data[a] for the trimetal complexes



Complex	^1H (δ)[b]	^{13}C (δ)[c]	^{195}Pt (δ)[d]
(1p)	2.80 (s, 6 H, μ-CMe), 6.22 (m, 6 H, H^4), 7.69 (m, 8 H, H^3 or H^5), 8.07 (s, 4 H, H^3 or H^5)	316.4 [μ-C, J(WC) 166], 230.1 (CO), 225.0 [CO, J(WC) 160], 145.1—106.4 ($C_3H_3N_2$), 41.6 (Me)	
(1q)	3.03 (s, 6 H, μ-CMe), 6.25 (m, 6 H, H^4), 7.72 (m, 8 H, H^3 or H^5), 7.95 (br, 4 H, H^3 or H^5)	310.3 [μ-C, J(PtC) 700, J(WC) 153], 229.9 (CO), 224.6 [CO, J(WC) 180], 145.1—106.5 ($C_3H_3N_2$), 40.0 (Me)	1 468 [J(WPt) 117]
(1r)	2.33 (s, 6 H, Me-4), 6.27 (m, 6 H, H^4), 6.96, 7.26 [$(AB)_2$, 8 H, C_6H_4, J(AB) 8], 7.69 (m, 8 H, H^3 or H^5), 7.98 (m, 4 H, H^3 or H^5)	313.6 [μ-C, J(PtC) 720, J(WC) 160], 229.0 (CO), 224.9 [CO, J(WC) 143], 145.6—105.6 (C_6H_4 and $C_3H_3N_2$), 21.6 (Me-4)	1 610 [J(WPt) 107]
(1s)	[e]2.35 (s, 6 H, Me-4), 5.82, 6.07, 6.39 (s × 3, 2 H, H^4), 6.95, 7.05 [$(AB)_2$, 8 H, C_6H_4, J(AB) 7], 7.62 (s, 2 H, H^3 or H^5), 7.64 (s, 4 H, H^3 or H^5), 7.67 (s, 2 H, H^3 or H^5), 7.78 (s, 2 H, H^3 or H^5), 8.30 (s, 2 H, H^3 or H^5)	[f]337.7 [μ-C, J(PtC) 716], 237.7, 232.7 (CO), 151.8—104.8 (C_6H_4 and $C_3H_3N_2$), 21.8 (Me-4)	1 661
(1t)	2.33 (s, 6 H, Me-4), 6.25 (m, 6 H, H^4), 6.95, 7.27 [$(AB)_2$, 8 H, C_6H_4, J(AB) 8], 7.69 (m, 8 H, H^3 or H^5), 7.99 (m, 4 H, H^3 or H^5)	310.7 [μ-C, J(PtC) 694], 229.4, 225.1 (CO), 145.6—105.6 (C_6H_4 and $C_3H_3N_2$), 22.1 (Me-4)	1 342
(2d)	3.00 (s, 6 H, μ-CMe), 6.29 (m, 6 H, H^4), 7.67 (m, 8 H, H^3 or H^5), 7.97 (s, 4 H, H^3 or H^5)	277.8 [μ-C, J(WC) 154], 217.1 [CO, J(WC) 179], 147.8—106.6 ($C_3H_3N_2$), 42.1 (Me)	

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz; measurements at room temperature, unless otherwise stated. [b] Measured in $CDCl_3$, unless otherwise stated. [c] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of $SiMe_4$; measurements in CD_2Cl_2–CH_2Cl_2. [d] Chemical shifts are to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz; measurements in $CDCl_2$–CH_2Cl_2. [e] Measured in CD_2Cl_2. [f] Measured at −50 °C.

Results and Discussion

Treatment of a tetrahydrofuran (thf) solution of $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ with $[Ni(cod)_2]$ afforded the purple trimetal complex $[NiW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ **(1p)**. Similar reactions between the compounds $[M(\equiv CR)(CO)_2\{HB(pz)_3\}]$ (M = Cr, Mo, or W, R = C_6H_4Me-4; M = W, R = Me) and $[Pt(C_2H_4)_3]$ in light petroleum yielded the related complexes $[PtM_2(\mu\text{-}CR)_2(CO)_4\{HB(pz)_3\}_2]$ **(1q)**—**(1t)**. These new compounds were characterised by the data given in Tables 1 and 2. In particular, the $^{13}C\text{-}\{^1H\}$ n.m.r spectra showed characteristic resonances in the range *ca.* 310—338 p.p.m. for alkylidyne-carbon nuclei bridging a metal–metal bond, as found previously in the spectra of compounds **(1a)**—**(1o)**.[4] The alkylidyne-carbon resonance for the nickel compound **(1p)** at δ 316.4 p.p.m. showed ^{183}W satellite peaks with J(WC) = 166 Hz. In the spectrum of the related compound **(1f)** the μ-*C*Me signal is at 326.1 p.p.m. with J(WC) 174 Hz. Interestingly, the $^{13}C\text{-}\{^1H\}$ spectrum of the cyclopentadienyl complex **(1d)** could not be measured, due to its instability in solution. Evidently the $HB(pz)_3$ and $\eta\text{-}C_5Me_5$ ligands stabilise the NiW_2 species compared with the $\eta\text{-}C_5H_5$ group. In the $^{13}C\text{-}\{^1H\}$ n.m.r. of the platinum-containing compounds **(1q)**—**(1t)** the μ-C signals display ^{195}Pt satellite peaks [J(PtC) *ca.* 700 Hz]. This coupling is somewhat smaller than those observed in the spectra of analogous complexes containing $\eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$ ligands: *e.g.* **(1n)**, J(PtC) 786 Hz, compared with 720 Hz for **(1r)**.

The $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectra of **(1q)**—**(1t)** show resonances in the range δ 1 342—1 661 p.p.m., with J(WPt) 107—117 Hz. The corresponding data for the platinum–tungsten species with $\eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$ ligands are δ 1 685—1 740 p.p.m., with J(WPt) 166—196 Hz.[4]

In the previous studies[2] the molecular structures of **(1a)** and

Table 3. Selected internuclear distances (Å) and angles (°) for $[PtW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ (**1q**)

W(1)–C(5)	1.888(8)	W(2)–C(7)	1.882(8)	Pt–W(1)	2.713(1)	Pt–W(2)	2.720(1)
Pt–C(5)	2.034(8)	Pt–C(7)	2.045(9)	C(5)–C(6)	1.48(1)	C(7)–C(8)	1.49(1)
W(1)–C(1)	1.974(9)	W(2)–C(2)	1.993(9)	W(1)–C(3)	1.993(10)	W(2)–C(4)	1.982(8)
C(1)–O(1)	1.20(1)	C(2)–O(2)	1.18(1)	C(3)–O(3)	1.15(1)	C(4)–O(4)	1.16(1)
W(1)–N(11)	2.262(7)	W(1)–N(21)	2.222(8)	W(1)–N(31)	2.213(7)	W(2)–N(41)	2.216(7)
W(2)–N(51)	2.265(7)	W(2)–N(61)	2.234(9)	Pt···C(1)	2.25(1)	Pt···C(2)	2.30(1)

W(1)–Pt–W(2)	172.8(1)	W(1)–Pt–C(5)	44.0(2)	W(2)–Pt–C(5)	139.9(2)	W(1)–Pt–C(7)	140.8(2)
W(2)–Pt–C(7)	43.7(2)	C(5)–Pt–C(7)	133.8(3)	Pt–W(1)–C(1)	54.6(3)	Pt–W(1)–C(3)	84.3(3)
C(1)–W(1)–C(3)	91.9(4)	Pt–W(1)–C(5)	48.5(2)	C(1)–W(1)–C(5)	102.2(4)	C(3)–W(1)–C(5)	90.8(4)
Pt–W(1)–N(11)	139.9(2)	C(1)–W(1)–N(11)	85.5(3)	C(3)–W(1)–N(11)	94.5(3)	C(5)–W(1)–N(11)	170.5(3)
Pt–W(1)–N(21)	105.6(2)	C(1)–W(1)–N(21)	96.2(3)	C(3)–W(1)–N(21)	169.7(3)	C(5)–W(1)–N(21)	93.7(3)
N(11)–W(1)–N(21)	79.8(3)	Pt–W(1)–N(31)	139.9(2)	C(1)–W(1)–N(31)	165.5(3)	C(3)–W(1)–N(31)	89.3(3)
C(5)–W(1)–N(31)	92.2(3)	N(11)–W(1)–N(31)	80.0(3)	N(21)–W(1)–N(31)	81.2(3)	Pt–W(2)–C(2)	55.9(3)
Pt–W(2)–C(4)	86.8(3)	C(2)–W(2)–C(4)	87.4(4)	Pt–W(2)–C(7)	48.7(3)	C(2)–W(2)–C(7)	104.5(4)
C(4)–W(2)–C(7)	91.2(3)	Pt–W(2)–N(41)	104.7(2)	C(2)–W(2)–N(41)	94.3(3)	C(4)–W(2)–N(41)	167.2(3)
C(7)–W(2)–N(41)	100.7(3)	Pt–W(2)–N(51)	144.4(2)	C(2)–W(2)–N(51)	88.9(3)	C(4)–W(2)–N(51)	86.8(3)
C(7)–W(2)–N(51)	166.4(4)	N(41)–W(2)–N(51)	80.5(3)	Pt–W(2)–N(61)	137.7(2)	C(2)–W(2)–N(61)	166.4(3)
C(4)–W(2)–N(61)	93.4(3)	C(7)–W(2)–N(61)	89.1(3)	N(41)–W(2)–N(61)	81.9(3)	N(51)–W(2)–N(61)	77.6(3)
W(1)–C(1)–O(1)	164.3(8)	W(2)–C(2)–O(2)	167.4(8)	W(1)–C(3)–O(3)	176.7(8)	W(2)–C(4)–O(4)	177.0(8)
Pt–C(5)–W(1)	87.5(3)	Pt–C(5)–C(6)	117.1(6)	W(1)–C(5)–C(6)	153.9(7)	Pt–C(7)–W(2)	87.6(4)
Pt–C(7)–C(8)	116.5(6)	W(2)–C(7)–C(8)	155.9(7)				

(**1c**) were established by *X*-ray diffraction. An *X*-ray diffraction study was therefore carried out on compound (**1q**), for which suitable crystals were available, in order to obtain comparative structural data. The results are summarised in Table 3, and the molecular structure is shown in the Figure.

The data confirm that the molecule has a W–Pt–W spine with each metal–metal bond bridged by an ethylidyne group, and semi-bridged by one CO ligand. The various mean internuclear separations and angles for (**1q**) are very similar to those previously found[2] for (**1c**) (in parentheses): Pt–W 2.716 (2.713), μ-C–W, 1.885 (1.91), μ-C–Pt, 2.040 (2.015), Pt···CO 2.27 (2.33 Å); Pt–μ-C–W 87.6 (87.6), W–μ-C–O, 166 (167°). The W–Pt–W spine of (**1q**) [172.8(1)°] deviates somewhat less from linearity than that of (**1c**) [165.5(0)°]. Moreover, the dihedral angle between the two dimetallacyclopropene rings in (**1q**) (79°) is appreciably less than that in (**1c**) (97°).

The band in the i.r. spectrum of (**1q**) at 1 792 cm^{-1} may be assigned to the semi-bridging CO groups revealed by the *X*-ray diffraction study. In the i.r. spectra of (**1j**) and (**1l**) these bands are at 1 817 and 1 793 cm^{-1}, respectively.[4]

In the alkylidynetungsten compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{B(pz)_4\}]$ the C≡W distance is 1.821(7) Å.[6] Making the reasonable assumption that the carbon–tungsten triple bond in the related species $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ would be of very similar length, this dimension is perceptibly shorter than that found in (**1q**) (mean 1.885 Å), as expected. In (**1q**) each tungsten centre carries a linearly bound CO ligand, and a $HB(pz)_3$ group. The dimensions of the $W\{HB(pz)_3\}$ fragments are similar to those previously observed,[6,8] and call for no comment. If the metal–metal bonds are ignored, the tungsten atoms show *pseudo*-octahedral geometry. Thus for the W(1) atom: N(11), N(31), C(1), and C(5) are coplanar, with C(3)–W(1)–N(21) 170°, while for the W(2) atom: N(51), N(61), C(2), and C(7) are coplanar, with C(4)–W(2)–N(41) 167°. The terminal carbonyl groups, C(3)O(3) and C(4)O(4), each lie almost perpendicular to the metal–metal bonds [C(3)–W(1)–Pt 84.3(3), C(4)–W(2)–Pt 86.8(3)°]. The ethylidyne groups are on the same side of the W–Pt–W spine, with the angle C(5)–Pt–C(7) 133.8(3)°.

We have previously reported[9] the copper, silver, and gold salts $[MW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2][X]$ (**2**, M = Cu or Au, X = PF_6; M = Ag, X = BF_4) in which the M^+ (d^{10}) cations are 'complexed' by two $(\eta\text{-}C_5H_5)(OC)_2W\equiv CC_6H_4Me\text{-}4$

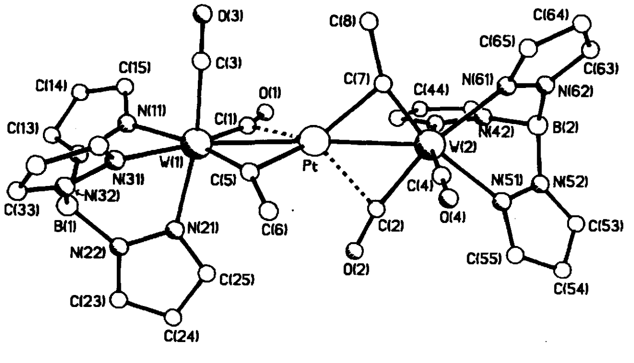
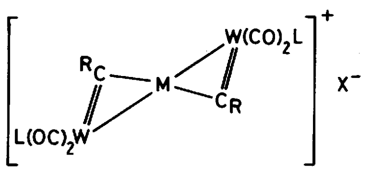
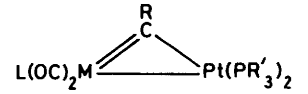


Figure. The molecular structure of $[PtW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ (**1q**) showing the atom-numbering scheme



	M	R	L	X
(**2a**)	Cu	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$	PF_6
(**2b**)	Ag	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$	BF_4
(**2c**)	Au	$C_6H_4Me\text{-}4$	$\eta\text{-}C_5H_5$	PF_6
(**2d**)	Au	Me	$HB(pz)_3$	PF_6



	M	R	PR'$_3$	L
(**3a**)	W	Me	PMe_3	$\eta\text{-}C_5H_5$
(**3b**)	W	$C_6H_4Me\text{-}4$	PMe_2Ph	$\eta\text{-}C_5H_5$
(**3c**)	W	$C_6H_4Me\text{-}4$	PMe_3	$HB(pz)_3$
(**3d**)	W	Me	$P(OMe)_3$	$HB(pz)_3$
(**3e**)	W	$C_6H_4Me\text{-}4$	$P(OMe)_3$	$HB(pz)_3$
(**3f**)	Cr	$C_6H_4Me\text{-}4$	$P(OMe)_3$	$HB(pz)_3$
(**3g**)	Mo	$C_6H_4Me\text{-}4$	$P(OMe)_3$	$HB(pz)_3$

groups. It was therefore of interest to establish whether a similar salt could be formed from an alkylidynetungsten species containing a hydrotris(pyrazol-1-yl)borate ligand. Treatment of a thf solution of $[\mathrm{W(\equiv CMe)(CO)_2\{HB(pz)_3\}}]$ with $[\mathrm{AuCl(tht)}]$ (tht = tetrahydrothiophene), in the presence of $\mathrm{TlPF_6}$, afforded the yellow salt $[\mathrm{AuW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2}][\mathrm{PF_6}]$ (**2d**), data for which are given in Tables 1 and 2. The $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum of (**2d**) shows a resonance for the bridging alkylidyne-carbon nuclei at δ 277.8 p.p.m. [J(WC) 154 Hz]. The corresponding chemical shift for (**2c**) is 295.8 p.p.m. with J(WC) 153 Hz.[9]

The i.r. spectrum of (**2d**) shows two bands (2 013 and 1 929 cm^{-1}) in the terminal CO region. The peaks in the spectrum of (**2c**) (at 2 024 and 1 969 cm^{-1}) are at somewhat higher frequency, as expected if the $\mathrm{4\text{-}MeC_6H_4C\equiv W(CO)_2(\eta\text{-}C_5H_5)}$ group is a less strong donor group to $\mathrm{Au^I}$ than the $\mathrm{MeC\equiv W(CO)_2\{HB(pz)_3\}}$ fragment. An *X*-ray diffraction study[9] on (**2c**) revealed that both CO ligands are terminally bound to the tungsten atoms, in contrast with the structures of (**1a**), (**1c**), and (**1q**) in which two strongly semi-bridging carbonyl groups are present.

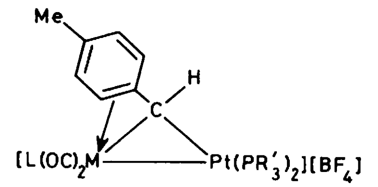
In common with (**2c**), the salt (**2d**) shows in its $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum only one CO group resonance [(**2c**), δ 211.8; (**2d**), 217.1 p.p.m.], and this must reflect site-exchange of these groups at room temperature on the n.m.r. time-scale. Like (**2c**), compound (**2d**) does not appear to dissociate readily in solution, in contrast with (**2a**) and (**2b**). Indeed, the copper salt (**2a**), while stable as a solid, is completely dissociated in thf, and is only stable in non-donor solvents such as $\mathrm{CH_2Cl_2}$ for short periods.[9]

Attempts to obtain a neutral complex from (**2d**) by treatment with $\mathrm{NaBH_4}$ or $\mathrm{K[BH(CHMeEt)_3]}$ were unsuccessful. Reactions with these reagents produced only gold mirrors.

An important feature of the chemistry of the complexes $[\mathrm{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)}]$ ($\mathrm{R = C_6H_4Me\text{-}4}$ or Me) is their ability to displace ethylene from the reagents $[\mathrm{Pt(C_2H_4)(PR'_3)_2}]$ (R′ = alkyl or aryl) to form stable dimetal compounds $[\mathrm{PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)}]$.[10] Typical of several known species of this type are the complexes (**3a**) and (**3b**), which have an extensive derivative chemistry. Previously we reported[6] the preparation of the compound $[\mathrm{PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2\{HB(pz)_3\}}]$ (**3c**) obtained by treating $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}}]$ with $[\mathrm{Pt(C_2H_4)(PMe_3)_2}]$. In view of this result, reactions between the complexes $[\mathrm{M(\equiv CR)(CO)_2\{HB(pz)_3\}}]$ (M = Cr or Mo, $\mathrm{R = C_6H_4Me\text{-}4}$; M = W, R = Me) and the reagents $[\mathrm{Pt(C_2H_4)(PR'_3)_2}]$ (R′ = Me or Et) and $[\mathrm{Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}}]$ were investigated. Surprisingly, the only products obtained were the trimetal complexes (**1q**), (**1s**), and (**1t**). Evidently if dimetal compounds with M–Pt (M = Cr, Mo, or W) bonds are formed the $\mathrm{PR'_3}$ or $\mathrm{P(cyclo\text{-}C_6H_{11})_3}$ groups are subsequently displaced by an $\mathrm{RC\equiv M(CO)_2\{HB(pz)_3\}}$ fragment. The latter apparently functions as a better ligand towards $\mathrm{Pt^0}$ than do the tertiary phosphines.

Since the stability of dimetal compounds of the type $[\mathrm{PtM(\mu\text{-}CR)(CO)_2(PR'_3)_2\{HB(pz)_3\}}]$ is likely to be strongly influenced by the relative σ-donor and π-acceptor properties of the group $\mathrm{PR'_3}$, reactions with the reagent $[\mathrm{Pt(C_2H_4)\{P(OMe)_3\}_2}]$, generated *in situ* from $[\mathrm{Pt(cod)_2}]$, were studied. It was thought that if the alkylidyne{hydrotris(pyrazol-1-yl)borato}metal compounds were relatively strong σ donors *via* their C≡W bonds towards $\mathrm{Pt^0}$, the presence of π-acceptor $\mathrm{P(OMe)_3}$ groups in a $\mathrm{Pt\{P(OMe)_3\}_2}$ fragment might afford kinetically stable dimetal compounds.

Treatment of $[\mathrm{W(\equiv CMe)(CO)_2\{HB(pz)_3\}}]$ with $[\mathrm{Pt(C_2H_4)\{P(OMe)_3\}_2}]$ in light petroleum gave a chromatographically separable mixture of (**1q**) and the red complex $[\mathrm{PtW(\mu\text{-}CMe)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}}]$ (**3d**). Data for the latter are given in Table 1. Compound (**3d**) decomposes in solution affording the trimetal compound (**1q**) and $[\mathrm{Pt\{P(OMe)_3\}_4}]$. Hence the formation of (**1q**) in the synthesis of (**3d**) is explained. Although decomposition of (**3d**) in solution prevented measurement of meaningful ^{1}H and $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. data, the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum (in $\mathrm{CDCl_3}$) could be recorded. Resonances characteristic[10] for a *cis*-$\mathrm{Pt\{P(OMe)_3\}_2}$ fragment were observed as two doublet signals at δ 12.2 [J(PP) 17, J(PtP) 4 180] and 13.7 p.p.m. [J(PP) 17, J(PtP) 5 400, J(WP) 39 Hz], respectively. The corresponding data for (**3c**) are δ −12.1 [J(PP) 10, J(PtP) 3 793] and −20.9 p.p.m. [J(PP) 10, J(PtP) 2 849 Hz].[6]



	M	$\mathrm{PR'_3}$	L
(**4a**)	W	$\mathrm{PMe_3}$	$\mathrm{\eta\text{-}C_5H_5}$
(**4b**)	Mo	$\mathrm{P(OMe)_3}$	$\mathrm{HB(pz)_3}$

Reactions between $[\mathrm{Pt(C_2H_4)\{P(OMe)_3\}_2}]$ and $[\mathrm{M(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}}]$ (M = Cr, Mo, or W) afforded the compounds $[\mathrm{PtM(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}}]$ (**3e**)—(**3g**). The chromium-containing species (**3f**) was formed only in low yield, and the reactions producing (**3e**) and (**3g**) also afforded the trimetal compounds (**1r**) and (**1t**), respectively. The three compounds (**3e**)—(**3g**) were characterised only *via* their i.r. spectra (Table 1), since satisfactory microanalytical data could not be obtained.

We have previously reported that protonation of (**3a**) with $\mathrm{HBF_4{\cdot}Et_2O}$ affords the salt $[\mathrm{PtW\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$ (**4a**), the formulation of which was established by an *X*-ray diffraction study.[11] In view of this result, it seemed possible that one or other of the species (**3d**)—(**3g**) might be protonated to give a stable derivative. Reaction between (**3d**) and $\mathrm{HBF_4{\cdot}Et_2O}$ in diethyl ether led to decomposition of the dimetal compound and release of $[\mathrm{W(\equiv CMe)(CO)_2\{HB(pz)_3\}}]$. However, treatment of (**3g**) with $\mathrm{HBF_4{\cdot}Et_2O}$ afforded the green salt $[\mathrm{PtMo\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}}][\mathrm{BF_4}]$ (**4b**) in essentially quantitative yield. This salt was more robust than (**3g**) and hence microanalytical data could be obtained (Table 1), and the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum measured in $\mathrm{CD_2Cl_2}$. The spectrum confirmed the presence of the *cis*-$\mathrm{Pt\{P(OMe)_3\}_2}$ group with two doublet resonances at δ 8.3 [J(PP) 17, J(PtP) 3 977] and 10.8 p.p.m. [J(PP) 17, J(PtP) 5 382 Hz]. Unfortunately ^{1}H and $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectra of (**4b**) could not be recorded, due to decomposition, and hence formulation of the salt as being structurally akin to (**4a**) rests on the analytical, i.r., and $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. data.

The results described herein show that in their respective reactions with d^{10} complexes, the compounds $[\mathrm{M(\equiv CR)(CO)_2\{HB(pz)_3\}}]$ (M = Cr, Mo, or W, $\mathrm{R = C_6H_4Me\text{-}4}$; M = W, R = Me) display both similarities and differences compared with related species with $\mathrm{\eta\text{-}C_5H_5}$ or $\mathrm{\eta\text{-}C_5Me_5}$ ligands. Thus the ready formation of the reactively stable trimetal compounds (**1p**)—(**1t**) and (**2d**) is in common with the previous studies leading to (**1a**)—(**1o**) and (**2c**). However, with compounds of type (3) the situation is complicated, relative stabilities presumably depending on the electronic and steric properties of the fragments [CR, $\mathrm{W(CO)_2L}$, and $\mathrm{PR'_3}$] ligating the platinum atom.

As mentioned above, an analogue of (**3a**) containing an $\mathrm{HB(pz)_3}$ ligand could not be isolated whereas (**3d**), with $\mathrm{P(OMe)_3}$ instead of $\mathrm{PMe_3}$ groups present, could be prepared.

This is qualitatively explicable if it is assumed that the $MeC{\equiv}W(CO)_2\{HB(pz)_3\}$ fragment is a superior σ donor and weaker π acceptor than $MeC{\equiv}W(CO)_2(\eta\text{-}C_5H_5)$, so that excess electron density at the Pt centre is relieved by back-bonding to the $P(OMe)_3$ ligands. The latter would be superior in this respect to PMe_3. Similarly, the relative stability sequence (**3c**) > (**3d**) > (**3e**) may be due to the fragment $4\text{-}MeC_6H_4C{\equiv}W(CO)_2\{HB(pz)_3\}$ being a poorer σ donor and better π acceptor than $MeC{\equiv}W(CO)_2\{HB(pz)_3\}$. Steric effects are also likely to play a role. The $HB(pz)_3$ group is significantly larger than C_5H_5,[12] although the cone angles for $P(OMe)_3$ (107°) and PMe_3 (118°) are not appreciably different.

Experimental

The experimental procedures employed and the instrumentation used have been described earlier.[4] Phosphorus-31 chemical shifts (p.p.m.) are positive to high frequency of 85% H_3PO_4 (external). Light petroleum refers to that fraction of b.p. 40—60 °C. The compound $[Ni(cod)_2]$ was purchased from Strem Chemicals Inc., and $[Pt(cod)_2]$[13] and $[AuCl(tht)]$[14] were prepared as described elsewhere, as were the alkylidyne compounds $[M({\equiv}CR)(CO)_2\{HB(pz)_3\}]$ (M = Cr, Mo, or W, R = $C_6H_4\text{-}Me\text{-}4$; M = W, R = Me).[6,7] Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Trimetal Complexes $[NiW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ *and* $[PtM_2(\mu\text{-}CR)_2(CO)_4\{HB(pz)_3\}_2]$ (M = Cr, Mo, *or* W, R = $C_6H_4Me\text{-}4$; M = W, R = Me).—*Method* (*i*). A thf (10 cm^3) solution of $[W({\equiv}CMe)(CO)_2\{HB(pz)_3\}]$ (0.15 g, 0.30 mmol) was treated with solid $[Ni(cod)_2]$ (0.04 g, 0.15 mmol). After stirring the mixture for 2 h at room temperature, solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (*ca.* 5 cm^3) and chromatographed on an alumina column (*ca.* 2 × 10 cm). Elution with dichloromethane–light petroleum (1:4) removed first a yellow band containing $[W({\equiv}CMe)(CO)_2\{HB(pz)_3\}]$ (0.05 g), and then a dark red eluate. Removal of solvent *in vacuo* afforded purple *microcrystals* of $[NiW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ (**1p**) (0.09 g).

Method (*ii*). A light petroleum (50 cm^3) solution of $[Pt(C_2H_4)_3]$ (0.50 mmol) was generated *in situ* at 0 °C from $[Pt(cod)_2]$ and treated with $[W({\equiv}CMe)(CO)_2\{HB(pz)_3\}]$ (0.48 g, 1.00 mmol) in the same solvent (60 cm^3). After stirring (30 min), solvent was decanted, and the residue washed with light petroleum (3 × 10 cm^3) and dried *in vacuo* giving red *microcrystals* of $[PtW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ (**1q**) (0.49 g).

Method (*iii*). In a similar manner, $[Pt(C_2H_4)_3]$ at 0 °C in light petroleum (15 cm^3) was treated with $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.10 g, 0.20 mmol) in the same solvent (15 cm^3). A red precipitate appeared after *ca.* 5 min. After stirring for 30 min, solvent was removed with a syringe and the residue was washed with light petroleum (3 × 5 cm^3) and dried *in vacuo* to afford red *microcrystals* of $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{HB(pz)_3\}_2]$ (**1r**) (0.10 g).

Method (*iv*). A light petroleum (20 cm^3) solution of $[Pt(C_2H_4)_3]$ (0.15 mmol), prepared *in situ* from $[Pt(cod)_2]$ in the usual manner,[4] was treated with $[Cr({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.13 g, 0.30 mmol) in the same solvent (80 cm^3). After stirring the mixture for 10 min, solvent was removed *in vacuo*. The dark green residue was dissolved in CH_2Cl_2 (3 cm^3), and chromatographed on alumina. Elution with dichloromethane–light petroleum (1:2) gave a green eluate, which after removal of solvent yielded *microcrystals* of $[PtCr_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{HB(pz)_3\}_2]$ (**1s**) (0.08 g).

Method (*v*). Similarly, $[Pt(C_2H_4)_3]$ (0.25 mmol) in light petroleum (15 cm^3) at 0 °C with $[Mo({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.23 g, 0.50 mmol) also in light petroleum (10 cm^3) gave, after chromatography on alumina, eluting with dichloromethane–light petroleum (1:4), red *microcrystals* of $[PtMo_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4\{HB(pz)_3\}_2]$ (**1t**) (0.20 g).

Synthesis of the Salt $[AuW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2][PF_6]$.—A thf (10 cm^3) solution of $[W({\equiv}CMe)(CO)_2\{HB(pz)_3\}]$ (0.60 g, 1.2 mmol) was treated with solid $[AuCl(tht)]$ (0.20 g, 0.60 mmol) and $TlPF_6$ (0.20 g, 0.60 mmol). The mixture was stirred for 30 min, after which it was filtered through a Celite column (*ca.* 3 × 10 cm) affording a yellow solution. Solvent was reduced in volume to *ca.* 5 cm^3, and Et_2O (20 cm^3) was slowly added, precipitating yellow *microcrystals* of $[AuW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2][PF_6]$ (**2d**) (0.60 g).

Preparation of the Compounds $[PtM(\mu\text{-}CR)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$ (M = Cr, Mo, *or* W,R = $C_6H_4Me\text{-}4$; M = W, R = Me).—*Method* (*i*). The compound $[Pt(C_2H_4)\{P(OMe)_3\}_2]$ (0.90 mmol) was prepared *in situ* from $[Pt(cod)_2]$ in light petroleum (100 cm^3) saturated with ethylene at 0 °C. The platinum complex prepared in this manner[10] was added to $[W({\equiv}CMe)(CO)_2\{HB(pz)_3\}]$ (0.43 g, 0.90 mmol) in the same solvent (100 cm^3). A red precipitate appeared, and the mixture was stirred for 15 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (2 cm^3) and chromatographed on an alumina column (*ca.* 3 × 10 cm). Elution with dichloromethane–light petroleum (1:4) gave a red eluate containing compound (**1q**) (0.62 g, 60%), followed by a dark red solution. Removal of solvent to a volume of *ca.* 5 cm^3, with cooling to −70 °C, gave red *microcrystals* of $[PtW(\mu\text{-}CMe)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$ (**3d**) (0.27 g). After *ca.* 30 min, solutions of (**3d**) in CH_2Cl_2 afford complex (**1q**) and $[Pt\{P(OMe)_3\}_4]$.

Method (*ii*). In a similar manner, the compound $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$ (**3e**) (0.10 g) was prepared from $[Pt(C_2H_4)\{P(OMe)_3\}_2]$ (0.50 mmol) and $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.25 g, 0.50 mmol). The reaction also produced compound (**1r**) (*ca.* 0.16 g), and unreacted $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (*ca.* 0.05 g).

Method (*iii*). A light petroleum (50 cm^3) solution of $[Pt(C_2H_4)\{P(OMe)_3\}_2]$ (0.50 mmol) was added to $[Cr({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.20 g, 0.50 mmol) in the same solvent (100 cm^3) at 0 °C. After stirring for 1 h, solvent was removed *in vacuo*. The residue was dissolved in the minimum quantity of CH_2Cl_2 (*ca.* 2 cm^3) and chromatographed on an alumina column (3 × 15 cm). Elution with dichloromethane–light petroleum (1:4) afforded in the first eluate $[Cr({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.10 g), and from the second eluate brown *microcrystals* of $[PtCr(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$ (**3f**) (0.04 g).

Method (*iv*). Similarly, $[Pt(C_2H_4)\{P(OMe)_3\}_2]$ (0.40 mmol) in light petroleum (50 cm^3) was added to $[Mo({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.20 g, 0.40 mmol) in light petroleum (50 cm^3). After stirring for 4 h at room temperature, solvent was removed, the residue dissolved in CH_2Cl_2 (*ca.* 2 cm^3), and chromatographed. Elution with dichloromethane–light petroleum (1:4) gave fractions from which $[Mo({\equiv}CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.03 g), (**1t**) (0.18 g), and red oily *microcrystals* of $[PtMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$ (**3g**) (0.14 g) were obtained.

Protonation of $[PtMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}]$ (**3g**).—A Et_2O (10 cm^3) solution of (**3g**) (0.04 g, 0.04 mmol) was treated with excess of $HBF_4{\cdot}Et_2O$ (25 μl, 0.09 mmol), affording a green precipitate. Solvent was removed with a syringe, and the residue washed with Et_2O (3 × 5 cm^3) to give green *microcrystals* of $[PtMo\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2\{P(OMe)_3\}_2\{HB(pz)_3\}][BF_4]$ (**4b**) (0.038 g).

Crystal Structure Determination of $[PtW_2(\mu\text{-}CMe)_2(CO)_4\{HB(pz)_3\}_2]$ (**1q**).—A suitable spherical crystal (*ca.* 0.2 mm) of

Table 4. Atomic positional parameters (fractional co-ordinates) (× 10^4) for (**1q**), with estimated deviations in parentheses

Atom	*x*	*y*	*z*
Pt	4 223(1)	338(1)	1 156(1)
W(1)	5 538(1)	2 113(1)	793(1)
W(2)	3 274(1)	−1 492(1)	1 571(1)
C(1)	6 061(11)	1 785(8)	1 338(3)
O(1)	6 595(9)	1 833(7)	1 669(2)
C(2)	5 168(10)	−1 588(8)	1 344(3)
O(2)	6 308(8)	−1 864(7)	1 238(2)
C(3)	3 668(11)	3 099(9)	845(3)
O(3)	2 570(8)	3 665(7)	856(2)
C(4)	2 074(11)	−2 158(8)	1 092(3)
O(4)	1 426(9)	−2 582(6)	812(2)
C(5)	4 262(9)	752(7)	612(2)
C(6)	3 593(11)	−173(8)	324(2)
C(7)	2 474(10)	101(8)	1 449(2)
C(8)	1 380(11)	1 159(9)	1 448(3)
B(1)	8 271(13)	3 254(9)	348(3)
N(11)	7 215(8)	3 716(6)	920(2)
N(12)	8 257(9)	4 008(7)	700(2)
C(13)	9 168(11)	4 925(9)	864(4)
C(14)	8 718(12)	5 270(10)	1 188(3)
C(15)	7 517(11)	4 492(8)	1 206(3)
N(21)	7 678(8)	1 266(6)	659(2)
N(22)	8 619(8)	1 880(7)	463(2)
C(23)	9 737(11)	1 115(10)	390(3)
C(24)	9 498(11)	4(10)	533(3)
C(25)	8 208(10)	124(8)	697(2)
N(31)	5 374(8)	2 870(6)	221(2)
N(32)	6 642(9)	3 299(7)	95(2)
C(33)	6 161(14)	3 722(9)	−260(3)
C(34)	4 579(12)	3 577(10)	−368(3)
C(35)	4 144(12)	3 063(8)	−59(3)
B(2)	3 165(17)	−2 901(11)	2 393(3)
N(41)	4 609(9)	−1 183(7)	2 148(2)
N(42)	4 376(11)	−1 864(8)	2 451(2)
C(43)	5 403(16)	−1 492(12)	2 750(3)
C(44)	6 312(15)	−579(12)	2 653(3)
C(45)	5 775(12)	−401(10)	2 275(3)
N(51)	3 684(9)	−3 476(6)	1 759(2)
N(52)	3 631(10)	−3 849(7)	2 115(2)
C(53)	3 901(15)	−5 048(10)	2 144(4)
C(54)	4 142(15)	−5 487(11)	1 803(4)
C(55)	4 028(13)	−4 473(9)	1 579(3)
N(61)	1 337(10)	−1 826(7)	1 878(2)
N(62)	1 557(11)	−2 404(7)	2 217(2)
C(63)	167(16)	−2 591(9)	2 308(3)
C(64)	−976(15)	−2 097(10)	2 039(4)
C(65)	−206(11)	−1 641(9)	1 772(3)

(**1q**) was grown from dichloromethane–light petroleum (1:5). Diffracted intensities were collected on a Nicolet *P*3*m* diffractometer at room temperature using the ω—2θ scan mode ($2.9 \leqslant 2\theta \leqslant 55°$).

Crystal data. $C_{26}H_{26}B_2N_{12}O_4PtW_2$, $M = 1\,155.0$, monoclinic, $a = 8.737(2)$, $b = 10.843(2)$, $c = 36.345(5)$ Å, $\beta = 101.44(1)°$, $U = 3\,375(1)$ Å^3, $Z = 4$, $D_m = 2.24$ g cm^{-3}, $D_c = 2.27$ g cm^{-3}, $F(000) = 2\,135$, space group $P2_1/n$ (no. 14, non-standard setting), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 111.78 cm^{-1}.

Data were corrected for Lorentz and polarisation effects and an empirical correction was applied for *X*-ray absorption based on an ellipsoidal model with azimuthal scan data.[15] Of 7 456 unique reflections, 4 827 had $I \geqslant 3\sigma(I)$, and only these were used in the structure solution and refinement. The structure was solved by conventional heavy-atom and electron-density difference methods, and was refined by blocked-cascade, full-matrix least-squares methods, with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included at fixed positions (B–H and C–H, 0.960 Å) with isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameters of the attached carbon or boron atoms. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.000\,2|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $> \pm 1$ e Å^{-3} and those located were near the metal atoms. Refinement converged at $R = 0.035$ ($R' = 0.033$). Scattering factors were from ref. 16. All computations were carried out on a Data General 'Eclipse' computer with the SHELXTL system of programs.[15] The atomic co-ordinates are listed in Table 4.

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