Structural Aspect of Platinum Coordination Compounds: Part VI. Heteroborane Platinum Derivatives

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0. ABBREVIATIONS

cod	cyclooctadiene
dppe	bis(diphenylphosphino)ethane
dppb	bis(diphenylphosphino)butane
Et	ethyl
m	monoclinic
Me	methyl
or	orthorhombic
PEt_3	triethylphosphine
Ph	phenyl
PMe_3	trimethylphosphine
$P(Me)_2Ph$	dimethylphenylphosphine
$P(Ph)_3$	triphenylphosphine
tmnda	N,N,N',N'-tetramethylnaphthalene-1,8-diamine
tr	triclinic

1. INTRODUCTION

Platinum is a valuable and useful metal, and the chemistry of its compounds has been extensively investigated. The relationship between structure and chemistry is of major importance for applications ranging from industrial catalysis to biochemical activity. The kinetic inertness of Pt(II) complexes has led to their extensive use in investigations of geometric isomerism and reaction mechanism. A large number of structures are known for platinum coordination compounds, around two thousand five hundred, and many of these have already been correlated in our recent reviews /1-5/.

There are a series of platinum heteroboranes, and these are the subject of this review, including one hundred published structures analysed and classified in order to assist in understanding the stereochemical interactions in the coordination sphere of platinum. The structures have been classified according to the nuclearity (monomer, dimer, trimer), and are further subdivided within each set according to the coordination number of the platinum atom. The compounds have been listed and referenced in the order of increasing coordination number, increasing complexity of the coordination sphere and increasing atomic number of the principal coordinating atom of the ligand.

2. MONOMERIC COMPOUNDS

2.1 Coordination Numbers Four and Five

Crystallographic and structural data for over thirty platinum heteroboranes, four-coordinate (4) and five-coordinate (30), are collected in Table 1. Note that some authors include coordination Pt-B/C distances of over 240 pm, which we consider to be rather too long for a substantial σ-bond.

TABLE 1.

Crystallographic and Structural Data for Monomeric Pt(II) Heteroborane Compounds with Coordination Numbers Four and Five[a]

COMPOUND (colour)	**Cryst cl Sp.Grp Z**	**a [pm] b [pm] c [pm]**	**α [°] β [°] γ [°]**	**Chromo-phore**	**Pt-L [pm]**	**L-Pt-L [°]**	**Ref**
$Pt(PMe_2Ph)_2(\eta^2-C_2B_8H_{10})$ (yellow)	m I2/a 4	1824.8(2) 1016.8(2) 1328.2(3)	101.48(2)	PtC_2P_2 (B_2)	Cb 215.5(10) P 226.7(4) (B) 250.3(13,59)	C,C^b 98.1(4) P,P 91.5(2) P,C 92.8(4)	6
$Pt(PMe_2Ph)_2(\eta^3-C_2B_8H_9-2-Me)$ (yellow)	m $P2_1/n$ 4	947.6(1) 1547.7(3) 1804.0(3)	104.78(1)	PtC_2P_2 (B_2)	η^2,C 218.1(6,5) P 228.8(3,0) (B) 238.5(7,27)	C,C 107.2(3) P,P 94.3(1) C,P 111.7(3,6.4)	6
$Pt(PPh_3)_2(\eta^4-C_2B_6H_{10})$ (yellow)	tr $P\bar{1}$ 2	1103.5(4) 1142.0(3) 1615.4(5)	90.97(2) 92.89(3) 114.36(2)	PtC_2P_2	η^2,C 214.8(9,6) P 231.0(2,13)	C,C 94.8(3) P,P 93.72(7) C,P 85.9(3,1.9)	7
$Pt(PMe_3)_2(\eta^2-C_2B_8H_{10})$ (yellow)	tr $P\bar{1}$ 2	955.1(3) 1232.1(4) 1015.6(2)	107.37(2) 123.29(2) 91.87(2)	PtC_2P_2			8
$Pt(PMe_2Ph)_2(\eta^2-B_3H_7)$ (colourless)	m C2/c 8	1815.5(9) 1366.5(7) 1750.4(9)	107.25(6)	PtB_3P_2	η^2,B 216(4,3) 238(4) P 230.6(4,5)	B,B 52.9(12)^c P,P 96.2(1) B,P 105.6(8,11.3)	9
$Pt(PEt_3)_2(\eta^4-C_2B_5H_5-1,7-Me_2)^d$ (red)	m $P2_1/n$ 8	1802.1(12) 1641.3(5) 1873.1(12)	116.36(4)	PtB_3P_2	η^2,B 215.0(-,50) P 230.8(-,25)	P,P 105.5	10
$Pt(PEt_3)_2(\eta^2-C_2B_9-3,8-Me_2)^d$ (bright yellow)	or Pbca 16	1886.8(8) 1714.3(7) 3107(2)		PtP_2CB (B_3)	P 231.1(7,18) η^2,C 218(3) η^2,B 216(4) (B)247(4,4)	P,P 98.9(2)	11a
				PtP_2CB (B_3)	P 231.7(6,30) η^2,C 217(2) η^2,B 218(2) (B) 248(3,10)	P,P 99.3(2)	

$Pt(PMe_2Ph)_2(\eta^3\text{-}C_2B_9H_9\text{-}2,4\text{-}Me_2)$ (pale yellow)	tr $P\bar{1}$ 2	932.4(3) 1023.6(4) 1420.8(8)	100.40(4) 94.32(4) 98.95(3)	PtB_3P_2 (C_1)	η^3,B 226.2(9,8) P 227.6(2,27) (C) 244.7(8,5)	B,B 49.6(3)[c] P,P 97.30(7) B,P 95.9(2,3.1)	11b
$Pt(\eta^2\text{-dppe})(\eta^3\text{-}B_3H_7)$ (colourless)	m $P2_1/n$ 8	1604.9(4) 1539.5(4) 2107.5(5)	90.53(2)	PtB_3P_2	η^3,B 211.9(12) 216.7(13,7) η^2,P 230.0(2,4)	B,B 50.2(5,7) 89.7(5) P,P 85.3(1)[f]	12
$Pt(\eta^2\text{-dppb})(\eta^3\text{-}B_3H_7)$ (colourless)	m $P_{\bar{1}}$ 2	888.26(16) 1773.29(32) 955.20(17)	114.115(15)	PtB_3P_2	η^3,B 213.1(20) 219.3(14,1) η^2,P 232.0(2,6)	B,B 48.5(9,1.5)[c] 87.1(7) P,P 94.8(1)[f]	12
$Pt(PEt_3)_2(\eta^5\text{-}C_2B_4H_5)$ (yellow) at 215K	m $P2_1/a$ 4	1569.1(6) 1011.8(6) 1594.9(6)	115.76(3)	PtB_3P_2	η^3,B 212.9(10) 225.1(8,7) P 227.9(2,6)	B,B 46.6(4,0)[c] P,P 105.75(6) B,P 91.2(2,3) 124.8(2,3.4) 159.6(2,3.0)	13
$Pt(PEt_3)_2(\eta^5\text{-}C_2B_4H_4\text{-}2,3\text{-}Me_2)$[d] (yellow) at 215K	m $P2_1/n$ 8	1604.5(7) 1735.4(5) 1691.8(6)	117.11(3)	PtB_3P_2	η^3,B 223.3(16) 229.6(15,2) P 226.0(3,25)	B,B 45.1(7)[c] P,P 101.42(10) B,P 96.6(4,5.4) 149.3(5,2.2) 167.4(4)	13
				PtB_3P_2	η^3,B 226.1(19,10) 232.9(14) P 226.5(2,7)	B,B 44.6(6)[c] P,P 100.25(10) B,P 93.0(3,6.8) 141.3(3) 158.9(4,3.5)	
$Pt(PPh_3)_2(\eta^3\text{-}C_2B_9H_{11})$ (white)	m $P2_1/n$ 4	1433.9(3) 1495.9(3) 1852.5(4)	105.89(2)	PtB_3P_2	η^3,B 221.3(10) 223.5(10,5) P 232.2(4,3)	B,B 47.5(3,2)[c] 83.8(4) P,P 100.0(2) B,P 87.9(3,5.4) 127.9(3,4.1) 170.1(2,5.6)	14

TABLE 1. Continued

COMPOUND (colour)	Crys cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	Pt-L [pm]	L-Pt-L [°]	Ref
$Pt(PPh_3)_2(\eta^3\text{-}CB_7H_{11})$ (yellow)	tr P$\bar{1}$ 2	974.3(2) 1237.5(2) 1771.3(3)	95.26(1) 95.43(1) 110.10(11)	PtB_3P_2	η^3,B 220.3(8) 221.2(8,2) P 232.6(3,4)	B,B 46.8(3,1)^c 84.7(4) P,P 100.0(1) B,P 87.3(3,2.4) 129.1(3,1.1) 169.3(2,3.9)	15
$Pt(PPh_3)_2(\eta^3\text{-}NB_8H_{11})$ (white)	or $Pna2_1$ 4	1825.0(18) 1978.7(16) 1033.4(10)		PtB_3P_2			16
$Pt(PPh_3)_2(\eta^3\text{-}SB_7H_{10})$ (yellow)	m $P2_1/n$ 4	1152.2(5) 2000.5(5) 1639.8(4)	95.74(3)	PtB_3P_2	η^3,B 218.4(16) 223.2(15,10) P 231.8(4,2)	B,B 47.8(8,7)^c 84.5(6) P,P 98.0(2) B,P 88.4(4,2.1) 129.2(6,3.0) 170.5(5,9)	17
$Pt(PPh_3)_2(\eta^3\text{-}SB_8H_{10})$ (yellow)	m $P2_1/n$ 4	1333.6(4) 2103.4(5) 1454.5(3)	103.04(2)	PtB_3P_2	η^3,B 216.6(24) 222.1(19,17) P 232.4(5,7)	B,B 47.8(8,1)^c 88.4(5,3) P,P 98.1(2) B,P 128.4(6,8) 172.4(6,3)	17
$Pt(PMe_2Ph)(\eta^3\text{-}B_8H_{12})$ (pale yellow)	m C2/c 8	1977.1(8) 1302.5(4) 1977.3(4)	110.99(3)	PtB_3P_2	η^3,B 222.2(13) 224.0(14,6) P 230.5(3,1)	B,B 47.8(5,1)^c 87.0(5,7) P,P 95.0(1) B,P 129.0(4,11) 172.2(4,1.3)	18
$Pt(PMe_2Ph)_2(\eta^3\text{-}SeB_8H_{10})$ (colourless)	or $P2_1mm$ 2	693.5(1) 1004.8(2) 1741.3(2)		PtB_3P_2	η^3,B 214.7(10) 223.0(7,0) P 229.5(2,0)	B,B 47.5(2)^c 84.8(3) P,P 103.78(6) B,P 85.2(3,4) 126.00(7) 167.7(2)	19

Pt(PMe$_2$Ph)$_2$ (η^3-NB$_8$H$_{11}$) (pale yellow)	m C2/c 8	1940.8(3) 1318.5(2) 2017.7(3)	110.42(1)	PtB$_3$P$_2$	η^3,B 221.3(14,4) 222.6(14) P 230.6(5,2)	P,P 96.1(2)	20
Pt(PPh$_3$)$_2$ (η^3-SB$_8$H$_{10}$) (yellow)	m P2$_1$/n 4	1151.4(5) 2004.0(7) 1641.6(5)	95.68(3)	PtB$_3$P$_2$	η^3,B 221(2) 227(2) 278(2) P 232.1(4,3)	not given	21
Pt(PPh$_3$)$_2$ (η^3-CB$_8$H$_{12}$) (white)	m P2$_1$/n 4	1435.9(3) 1408.3(3) 1498.8(3)	105.37(1)	PtB$_3$P$_2$	η^3,B 218.9(9) 224.5(9,4) P 231.7(2,5)	P,P 98.70(2) B,P 88.9(2,4.2) 126.5(2,2.8) 171.3(3,4.1)	21,22
[Pt(PPh$_2$C$_6$H$_4$)$_2$ (η^3-CB$_8$H$_{10}$)] 0.5CHCl$_3$ (pale yellow) (at 253K)	tr_ P1 2	1046.6(6) 1374.7(5) 1509.8(8)	71.73(4) 87.34(4) 79.77(4)	PtB$_3$P$_2$	η^3,B 208(3) 220(3,3) P 229.7(7,2)	P,P 109.5(2) P,B 81.3(8,1) 121.9(8,2) 169.1(8,2)	23
Pt(η^2-dppe) (η^3-C$_2$B$_9$H$_{11}$)	m P2$_1$/n 4	1418.1(2) 2144.3(2) 1141.2(2)	99.83(1)	PtB$_3$P$_2$	η^3,B 225.3(3,2) 227.9(3) η^2,P 226.3(3,4)	P,P 84.7(1)^c P,B 93.5(2,1.4) 175.0(2,3.4)	24
Pt(PMe$_2$Ph) (η^3-C$_2$B$_9$H$_{11}$)^d (orange)	m P2$_1$/c 8	1273.87(5) 2170.62(12) 1797.93(11)	99.105(4)	PtB$_3$P$_2$ PtB$_3$P$_2$ (C)	η^3,B 226.3(7,3) P 226.5(1,5) η^3,B 226.5(7) 229.6(8,12) P 226.1(1,26) (C) 230.2(7)	P,P 92.33(6) P,P 93.11(6)	25
Pt(PMe$_2$Ph)$_2$ (η^3-OB$_8$H$_{10}$) (colourless) at 220(2)K	m C2/c 8	1926.79(15) 1516.21(8) 2008.67(13)	111.3530(5)	PtB$_3$P$_2$	η^3,B 219.8(7) 223.4(7,2) P 230.0(2,1)	P,P 95.73(6)	26
Pt(PMe$_2$Ph)$_2$ (η^3-B$_9$H$_{11}$ PMe$_2$Ph) (pale yellow) at 200K	tr_ P$_1$ 4	1011.04(8) 1034.56(6) 3170.9(3)	94.359(7) 91.684(7) 105.266(6)	PtB$_3$P$_2$	η^3,B 221.9(7,5) 225.3(6) P 231.6(2,5)	P,P 96.60(5)	26

TABLE 1. Continued

COMPOUND (colour)	Crystcl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	Pt-L [pm]	L-Pt-L [°]	Ref
Pt(PMe$_2$Ph)$_2$ (η^3-C$_2$B$_9$H$_{11}$)	m P2$_1$/n 4	1020.34(9) 1941.0(2) 1667.0(2)	94.160(7)	PtB$_3$P$_2$	η^3,B 226.7(9,11) 231.6(9) P 228.0(2,27)	P,P 95.02(8) P,B 97.0(2)	27
Pt(PEt$_3$)$_2$ (η^3-C$_2$B$_9$H$_{11}$) (bright orange)	m P2$_1$/n 4	937.5(4) 1598.5(3) 1603.3(7)	93.56(5)	PtB$_3$P$_2$	η^3,B 226.4(8) 228.0(3,3) P 228.0(2,5)	B,B 46.8(3,1)^c P,P 98 B,P 100.9(2,13.9) 135.46(21) 164.2(2,3.8)	28
[Pt(PEt$_3$)$_2$ (η^3-C$_2$B$_9$H$_{10}$-Ph-1)] 0.5CH$_2$Cl$_2$^{d} (dark orange)	or Pna2$_1$ 8	3335.4(7) 1026.0(2) 1740.0(4)		PtB$_3$P$_2$ PtB$_3$P$_2$	η^3,B 227.19(15) 229(2,[illegible]) P 228.0(4,[illegible]3) η^3,B 222.9(14) 228(2,0) P 228.0(4,11)	P,P 98.40(15) P,B 99.8(5,7.9) 138.0(4) 159.3(4,5.6) P,P 93.83(15) P,B 100.2(4,10.2) 136.5(4) 161.0(4,4.3)	29
Pt(PEt$_3$)$_2$ (η^3-C$_2$B$_9$H$_9$-1-Ph-2Me)	m P2$_1$/n 4	1103.8(6) 1619.22(20) 1638.1(5)	100.95(4)	PtB$_3$P$_2$	η^3,B 218.2(6) 227.4(6,2) P 229.62(14,10)	B,B 47.58(22,19)^c 73.85(21) P,P 97.81(5) B,P 94.3(2,3.3) 127.7(2,9.9) 167.5(2,3.6)	30
[Pt(PPh$_3$)$_2$ (η^3-C$_2$B$_9$H$_9$-1-Ph-2-Me)] 0.5CH$_2$Cl$_2$	tr P$\bar{1}$ 2	1026.4(5) 1220.6(3) 1934.0(3)	78.301(16) 81.149(21) 74.82(3)	PtB$_3$P$_2$	η^3,B 214.3(7) 230.8(8,17) P 230.4(2,10)	B,B 48.6(3,5)^c 71.9(3) P,P 98.50(5) B,P 94.9(2,2.9) 121.9(2,6) 166.0(2,2.7)	30

[Pt(PPh$_3$)$_2$ (η^3-C$_2$B$_9$H$_{11}$-1-Ph-2-Me)] unknown solvent	m $P2_1/n$ 4	1031.6(13) 2222.7(6) 1999.6(6)	89.86(6)	PtB$_3$P$_2$	η^3,B 217.1(17) 230.7(18,17) P 230.5(4,4)	B,B 47.3(6,1.1)^c 72.8(6) P,P 99.42(14) B,P 93.9(4,2.5) 122.6(5,2) 165.7(4,2.6)	30
Pt(PEt$_3$)$_2$ {η^4-C$_2$B$_8$H$_{10}$PEt$_3$} (pale yellow)	m $P2_1/c$ 4	978.13(16) 1231.2(3) 2061.9(3)	99.03(16)	PtB$_3$CP	η^4,B 217.5(10) 224.4(12,15) η^4,C 215.9(10) P 229.3(3)	B,B 47.8(4,2.2)^c B,C 42.3(4)^c B,P 120.6(3) 146.6 167.7(3) C,P 96.6(3)	31a
Pt(PEt$_3$)$_2$(H){η^2-C$_2$B$_4$H$_5$-μ-H}	m $P2_1/m$ 4	1097.0(4) 1158.7(3) 945.9(3)	114.47(2)	PtB$_2$P$_2$H	η^2,B 230.3(11) P 229.1(2,5) H 140	B,B 43.7(3)^c P,P 167.20(8) B,P 96.0(2,4.1)	31b
Pt(PMe$_2$Ph$_2$)(η^3-S$_2$B$_7$H$_7$) (pale yellow)	or $P2_12_12_1$ 4	893.5(1) 1502.5(1) 1822.6(1)		PtB$_2$P$_2$S	η^3,S 226.2(6,39) S 234.5(3) P 229.0(3,35)	B,B 89.2(2) P,P 98.4(1)	31c
Pt(PPh$_3$)$_2$(η^3-S$_2$B$_7$H$_7$) (pale yellow)	tr $P\bar{1}$ 2	1119.43(8) 1147.22(10) 1602.7(14)	89.468(7) 89.776(7) 64.367(5)	PtB$_2$P$_2$S	η^3,B 221.0(5) 233.5(5) S 234.93(11) P 231.5(1,34)	B,B 44.5(2)^c P,P 99.26(4) B,S 54.70(14)^c 88.87(13) B,P 112.30(14) 168.55(14) P,S 91.17(4) 141.47(14)	32

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Three-membered metallocyclic ring.

d. There are two crystallographic independent molecules.

e. Six-membered metallocyclic ring.

f. Seven-membered metallocyclic ring.

There are four derivatives in which one homobidentate borane chelates to platinum via two C atoms, with two PMe_2Ph /6/, PPh_3 /7/ or PMe_3 /8/ ligands completing a distorted square planar geometry about the Pt(II) atom.

The P-Pt-P bond angles range from 91.5(2)° to 94.3(1)°, and the C-Pt-C bond angles range from 94.8(3)° to 107.2(3)°. The mean Pt-P bond length increases with increasing size of the respective ligands in the order: 227.7(4) pm (PMe_2Ph) , 231.0(2) pm (PPh_3). The mean Pt-C bond distance of 216.5(10) pm is 12.3 pm shorter than the Pt-P mean value, as expected.

Thirty five-coordinate derivatives /9-32/ have a terdentate borane ligand, homodentate with three B atoms /9-30/, heterodentate with two B atoms and a S atom /31,32/. The remaining two coordination sites are occupied by P-donors, one being a homobidentate chelate /12/ and the others being pairs of monodentate ligands to create a PtB_3P_2 /9-30/ or PtB_2P_2S /31,32/ inner coordination sphere.

It is well known that two limiting stereochemistries may be distinguished for five-coordination, a square pyramid (coordination 4+1) and a trigonal bipyramid (3+2). In the platinum boranes neither of these appear to be involved, with the B atoms on one side of the platinum centre and the two P atoms on the other side. The structure of $Pt(\eta^2\text{-dppe})(\eta^3\text{-}B_3H_7)$ /12/ is shown in Figure 1 as an example. The triborane unit resides symmetrically disposed with respect to the dppe-Pt moiety, with the B atoms within bonding distance of the metal atom. The internal dihedral angle of the PtB_3 butterfly arrangement is 133.4°. The central B atom is closer to the Pt atom (211.9(12) pm) than the other two (217.3(12) and 216.0(3) pm). The dppe-Pt moiety is unexceptional, the methylene groups of the dppe chain being arranged above and below the PtB_3 plane. The P-Pt-P bite angle is 85.3(1)°.

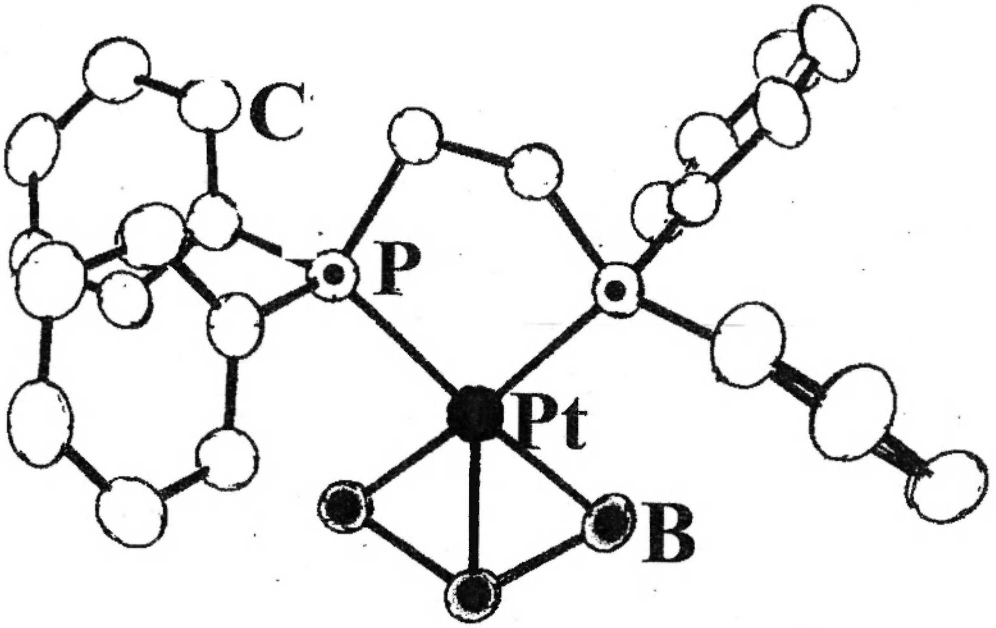

Fig. 1. Structure of $Pt(\eta^2\text{-dppe})(\eta^3\text{-}B_3H_7)$ [12

The B-Pt-B bite angles range from 44.6° to 51.0° (ave. 47.5°). The mean Pt-P bond distances increase in the order: 228 pm (PEt_3) < 229 pm (PMe_2Ph) < 231 pm (PPh_3), which follows the increasing size of the respective ligands. The mean Pt-P bond distances for the homobidentate P-donor ligands are 228 pm (dppe) < 232 pm (dppb). The former creates a five-membered and the latter a seven-membered metallocycle with mean P-Pt-P bite angles of 85.0° and 94.8°, respectively.

The boranes themselves can be classified into five structural and stoichiometrical groups which are: closo-boranes; nido-boranes; arachno-boranes; hippho-boranes and conjuncto-boranes. In the series of monomeric platinum heteroboranes with four- and five-coordination only three of these groups are found; closo- /6,8-10,13,17,24,25,29/, nido- /7,11,20-23,27,28,30/ and arachno-boranes /9,12,14,15,18,19,26,31,32/.

There are four examples where two crystallographically independent molecules differ mostly by degree of distortion /11,13,25,29/. The coexistence of two or more species like these is typical of the general class of distortion isomerism /33/.

2.2 Coordination Number Six

There are seventeen coloured derivatives in which the Pt(II) atom is six-coordinate, and their crystallographic and structural data are summarised in Table 2. Thirteen yellow derivatives /34-40a/ have a homo-tetradentate borane plus two P-donor ligands to give the PtB_4P_2 chromophore. The structure of bright yellow $Pt(PMe_3)_2(\eta^4\text{-}C_2B_6H_2)$ /34/ is shown in Figure 2 as an example. The compound exhibits C_2 molecular symmetry, having a

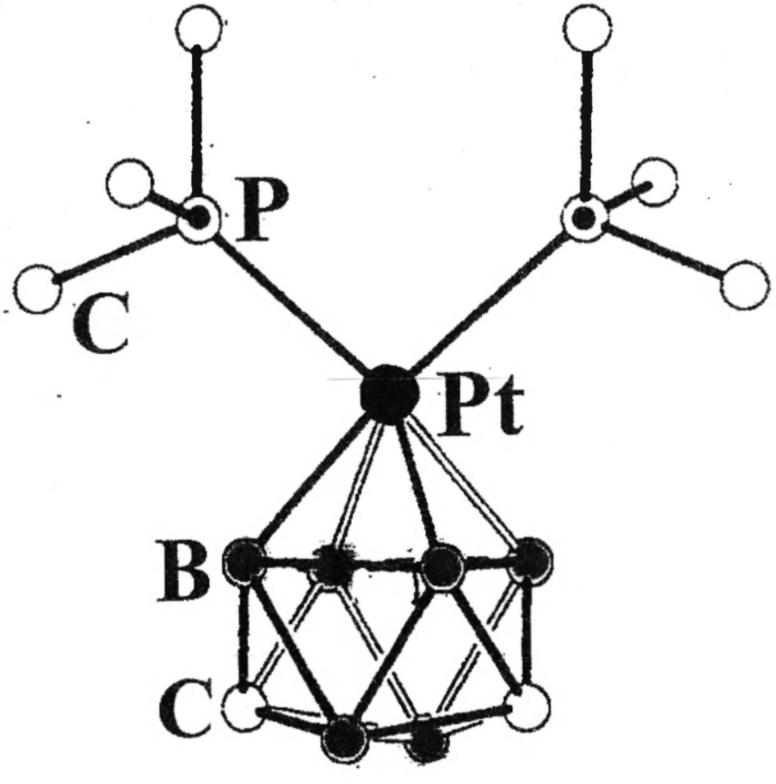

Fig. 2. Structure of $Pt(PMe_3)_2(\eta^4\text{-}C_2B_6H_2)$ [34]

TABLE 2

Crystallographic and Structural Data for Monomeric Platinum Heteroboranes with Coordination Number Six[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°], γ [°]	Chromophore	Pt-L [pm]	L-Pt-L [°]	Ref
$Pt(PMe_3)_2$ (η^4-$C_2B_6H_2$) (bright yellow)	m A2 2	571.6(2) 978.5(4) 1532.96(8)	94.24(3)	PtB_4P_2	η^4 B[b] 216(6,0) 217(5,0) P 245(1,0)	B,B[b] not given	34
α-$Pt(PMe_3)_2$ (η^4-C_2B_5-6,6'-Me_2) (bright yellow)	m A2/a 4	1200.2(5) 1041.5(7) 166.59(7)	102.47(3)	PtB_4P_2	η^4 B 219(3,0) 222(3) P 230.7(7)	not given	34
β-$Pt(PMe_3)_2$ (η^4-C_2B_5-6,6'-Me_2) (bright yellow)	m $P2_1/c$ 4	1189.2(4) 928.0(4) 1872.4(8)	106.17(3)	PtB_4P_2	η^4 B 220.5(10,15) 223(2,1) P 231.3(3,2)	B,B 50.6(5,3.1)[c] P,P 105.3(1) B,P 99.5(9,4.5)	34
$Pt(PEt_3)_2$ (η^4-$C_2B_7H_7$-1,6-Me_2) (pale yellow)	m $P2_1/a$ 4	1723(1) 1886(1) 1009.3(6)	126.96(4)	PtB_4P_2	η^4 B 222(1,4) 232(1,2) P 232.2(5,0)	B,B 49.1(6,44)[c] P,P 102.5(1) B,P 91.7(5,5.2) 111.4(3) 138.8(4,1.8) 160.1(4,4.1)	35
$Pt(PMe_2Ph)_2$ (η^4-$C_2B_9H_{10}$-1-Ph) (pale yellow)	m $P2_1/c$ 4	1040.8(3) 2584.7(5) 1099.3(3)	105.95(2)	PtB_4P_2	η^4 B 222.0(9,17) 227.5(8) P 229.8(2,1)	P,P 95.82(8)	36
$Pt(PMe_2Ph_2)$ (η^4-$C_2B_9H_{10}$-11-Ph) (pale yellow)	tr_ P1 2	1008.2(3) 1278.5(3) 1383.0(2)	122.10(2) 96.07(2) 94.23(2)	PtB_4P_2	η^4 B 223.0(5,19) 228.1(5) P 229.7(1,7)	P,P 97.70(4)	36
$Pt(PMe_2Ph_2)$ (η^4-$C_2B_9H_9$-1,11-Ph_2) (pale yellow)	tr_ P1 2	1106.0(4) 1299.7(4) 1329.3(3)	79.703(24) 80.314(24) 65.14(3)	PtB_4P_2	η^4 B 221.7(6,18) 229.3(6) P 228.9(1,3)	P,P 96.23(5)	36

Pt(PMe$_2$Ph)$_2$ (η^4-B$_{10}$H$_{11}$-8-Cl) (golden yellow)	m P2$_1$/n 4	978.9(2) 2674.3(7) 1079.6(2)	115.83(2)	PtB$_4$P$_2$	η^4,B 222.4(13,18) 230.7(13,36) P 234.0(3,15)	B,B 47.6(5,1.6)^c 85.7(5,3.3) P,P 96.1(1) B,P 90.5(3,7.8) 114.8(4) 138.0(3,5.1) 163.9(3)	37
Pt(PMe$_2$Ph)$_2$ (η^4-B$_{10}$H$_{12}$) (yellow)	m P2$_1$/n 4	1353.8(3) 1577.0(4) 1175.2(2)	94.94(2)	PtB$_4$P$_2$	η^4,B 222.0(5,6) 229.0(6,11) P 232.3(1,14)	B,B 46.8(2,1.6)^c 85.6(2,4.5) P,P 95.4(1) B,P 90.4(1,7.7) 114.1(2) 141.2(2,2.9) 169.3(1,6.9)	38
Pt(PMe$_2$Ph)$_2$ (η^4-B$_{10}$H$_{12}$ B$_{10}$H$_{12}$) (yellow)	m I2/a 8	2574.6(10) 954.1(4) 2707.0(6)	101.07(3)	PtB$_4$P$_2$	η^4,B 223.3(10,2) 232.1(11,4) P 233.8(3,3)	B,B 46.9(4,1.0)^c 85.4(4,4.4) P,P 95.4(1) B,P 89.7(3,7.6) 107.8(3) 144.9(3,6.3) 166.2(3,5.2)	38
Pt(PMe$_2$Ph)$_2$ (η^4-B$_9$H$_{10}$ B$_9$H$_{10}$) (yellow)	m P2$_1$/c 4	1544.4(2) 1068.2(3) 1981.9(3)	105.81(2)	PtB$_4$P$_2$	η^4,B 225(-,1) 233(-,2) P not given	not given	39
Pt(PMe$_2$Ph)$_2$ (η^4-B$_9$H$_{10}$ B$_9$H$_{10}$) (yellow)	m P2$_1$/c 4	968.3(1) 3128.4(6) 1055.9(1)	110.40(1)	PtB$_4$P$_2$	η^4,B 226(-,2) 235(-,1) P not given	not given	39
Pt(PEt$_3$)$_2$ {η^4-CB$_{10}$H$_{10}$-3-Te(Ph)CH$_2$Cl} (yellow)	m P2$_1$/c 4	1761.7(2) 1083.58(8) 1786.6(2)	97.036(11)	PtB$_4$P$_2$	η^4,B 224.0(6,5) 229.5(6,1) P 231.3(1,6)	B,B 48.0(2,1.3)^c 76.6(2,4.5) P,P 95.17(5) B,P 93.6(2,2.1) 115.5;142.2(3,4.7) 160.7(2,1.3)	40a

TABLE 2. Continued

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	Pt-L [pm]	L-Pt-L [°]	Ref
(PMe_2Ph) Pt(μ-η^2-$SCSNEt_2$) (η^4-$B_{10}H_{11}$) (yellow orange)	m $P2_1/n$ 4	1179.2(2) 1244.9(5) 1641.4(2)	 95.45(1)	PtB_4SP	η^4,B 217.1(6,2) 225.2(7,17) η^4,S 235.6(3) P 234.6(3)	B,B 48.7(2,1.1)^c 87.6(3,3.1) S,P 95.70(5) B,S 89.8(2,3)^d 126.6;174.9(1) B,P 88.0(2) 128.6(1,2.6) 174.2(1)	40b
[(PPh_3) Pt{η^4-SC(Ph)O} (η^4-$B_{10}H_9$-10-Ph)] $1.5CHCl_3$ (red)	m Cc 4	2885.1(5) 1161.5(2) 1999.2(4)	 127.42(1)	PtB_4SP	η^4,B 218.7(12) 220.6(11,2) 225.6(10) S 235.9(3) P 232.8(2)	B,B 47.9(4,9)^c 86.7(4,3.6) S,P 90.66(9) B,S 81.2^d; 107.1(3) 153.2(3,2.0) B,P 89.5;108.8(3) 156.4(4,6.3)	41
[(PPh_3) Pt{μ-η^2-SC(Ph)O} (η^4-$B_{10}H_{11}$)] $0.5CH_2Cl_2$^{e} (orange red)	m $P2_1/n$ 8	1164.2(2) 3322.5(3) 1631.2(4)	 93.21(4)	PtB_4SP	η^4,B 223(3,1) 226(4,1) S 233.0(7) P 235.2(6)	B,S 79.8(8)^d 103.5(9) 153.7(9,4.9) B,P 89.2(9) 113.8(8) 156.4(9,8) S,P 89.1(2)	42
				PtB_4SP	η^5,B 219(4,1) 222(3,1) η^5,S 234.0(7) P 234.6(7)	B,S 80.4(8)^d 108.5(9) 154.1(9,2.6) B,P 98.7(9,4.8) 138.8; 172.2(8) S,P 92.2(2)	

Pt(PMe$_2$Ph)$_2$ (η^4-C$_2$B$_9$H$_{10}$-1-Ph) (yellow)	m P2$_1$/c 4	1038.1(3) 2570.6(4) 1088.0(7)	104.57(4)	PtB$_3$P$_2$C	η^4,B 224.8(12,9) 231.3(12) η^4,C 232.6(10) P 226.9(3,19)	P,P 95.05(9)	36
Pt(PMe$_2$Ph)$_2$ (η^4-CC$_9$H$_{11}$) (pale yellow)	m P2$_1$/n 4	1186.8(1) 1554.1(2) 1344.1(2)	95.02(1)	PtB$_3$P$_2$C	η^4 B 226.4(8,20) 234.3(3) η^4,C 218.7(7) P 226.0(3)	B,B 47.7(2,1.2)^c 84.2(3) P,P 95.6(2) B,C 42.1(2)^c 85.3(3,4.7) B,P 94.3(3,3.2) 114.9; 143.2(2) 163.5(2) C,P 85.8; 175.9(2)	42b
Pt(PEt$_3$)$_2$ (η^4-C$_2$B$_8$H$_{12}$) (pale yellow)	or P2$_1$2$_1$2$_1$ 4	1482.5(4) 1013.67(13) 1611.93(15)		PtB$_3$P$_2$C	η^4,B 219.6(18,12) 231.3(14) η^4,C 214.5(10) P 233.4(3,30)	B,B 47.2(7,1.9)^c P,P 104.0(1) B,C 45.8(6)^c B,P 96.9(4,7.4) 113.1-143.1(5,1.8) P,C 95.9;157.6(4)	31a

Footnotes:

a. Where more than one chemically equivalent distance or angle is present the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Three-membered metallocyclic ring.

d. Five-membered metallocyclic ring.

e. There are two crystallographic independent molecules.

closo-polyhedral cage with geometry approximating a tricapped trigonal prism, whose low connectivity "cap" positions are occupied by the three heteroatoms.

Three orange/red derivatives /40-42/ have the PtB_4SP chromophore. In the first /40b/ a nido-7-platinaundecaborane has an exopolyhedral N,N-diethyldithiocarbamate ligand bridging the Pt and B(2) atoms to give a five-membered ring (PtBSCS). The tetrahapto Pt to borane bonding has a considerable twist distortion relative to other examples of this type without the metallocycle feature. The B-Pt-B bite angle is 90.1(2)°. The red cluster /41/ has a nido-eleven-vertex $\{PtB_{10}\}$ polyhedral skeleton and a five-membered (PtSCOB) ring of exopolyhedral cyclisation via one thiobenzoate unit. The Pt atom is bound to the thiobenzoate S atom, the PPh_3 P atom and four B atoms of the $\{PtB_{10}\}$ cage. The orange red cluster /42/ has a similar inner coordination sphere about the Pt atom. The B-Pt-S bite angles are 79.8(8)° /41/ and 80.4(8)° /42/.

The structure of yellow $Pt(PMe_2P)_2(\eta^4\text{-}C_2B_9H_{10}\text{-}1\text{-}Ph)$ /36/ shows that the borane coordinates to the Pt(II) atom via three B atoms and one C atom. Two PMe_2Ph ligands complete an inner coordination sphere about the Pt atom (PtB_3P_2C).

The data in Table 2 give a mean Pt-P bond distance increasing in the order: 231.5 pm (PMe_2Ph) < 232 pm (PEt_3) < 234 pm (PPh_3) < 235.5 pm (PMe_3); with an average value of 2.33 pm. It can be seen that the mean Pt-B bond distance of 225 pm, for boranes coordinating with four B atoms, is about 3 pm longer than those where one B atom is also bonded to an S /40/ or O /41/ atom of a bridging ligand. The mean B-Pt-B bite angle is 42.8°. Finally, the borane ligands are found in closo- /34/ and nido- /35-42/ polyhedral cages.

2.3 Coordination Number Seven

The crystallographic and structural data for ten coloured derivatives with a seven-coordinated Pt atom are summarised in Table 3. The structure of a red complex /43/ is shown in Figure 3, a complex of a macropolyhedral 16-vertex η^6-hexadecacarboranyl based on the structure of a conjuncto-borane. The borane consists of a nido-$\{PtB_7\}$ cluster and a nido-$\{PtB_{10}\}$ cluster conjoined with a Pt-B vector as the common edge.

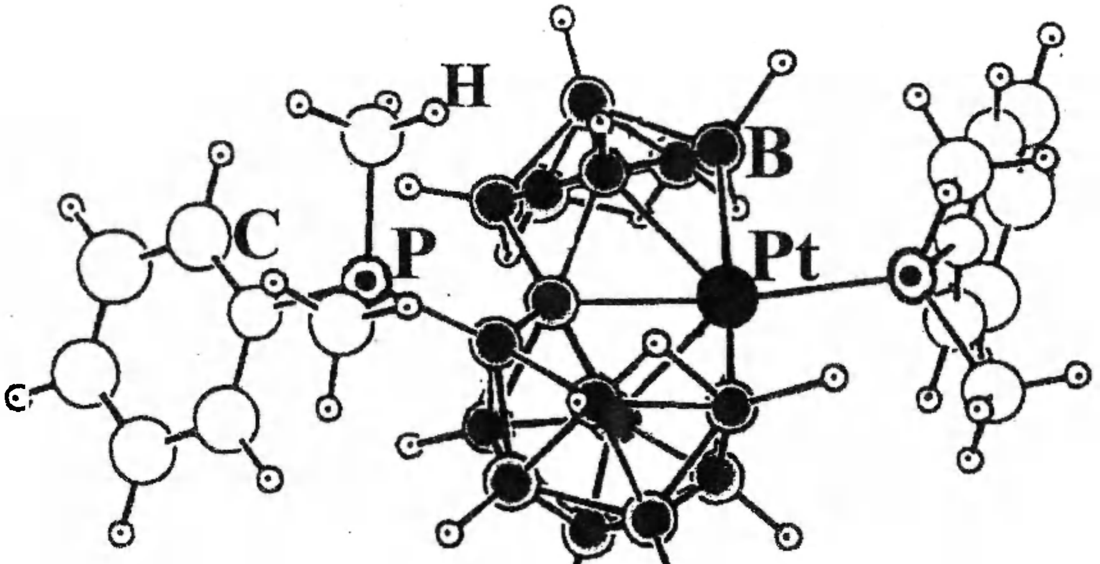

Fig. 3. Structure of $Pt(PMe_2Ph)(\eta^6\text{-}B_{16}H_{18}PMe_2Ph)$ [43]

TABLE 3.

Crystallographic and Structural Data for Monomeric Platinum Heteroboranes with Coordination Number Seven[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromo-phore	Pt-L [pm]	L-Pt-L [°]	Ref
$(PMe_2Ph)Pt(\eta^6$-$B_{16}H_{18}PMe_2Ph)$ (red)	m $P2_1$ 2	992.7(3) 1067.2(2) 1378.7(3)	 95.08(2)	PtB_5P	η^6,B[b] 223.8(12,9) 228.4(11,10) P 232.2(4)	B,B[b] 47.7(6,1.4)[c] 87.0(6,2.4) 119.7(4,12.0) 156.3(6,3.1) B,P 90.3(3,2.0) 101.6; 132.8(6,5.6) 173.4(3)	43,44
$Pt(PMe_2Ph)_2(\eta^5$-$B_{10}H_{10}PPh)$ (yellow)	tr $P\bar{1}$ 2	961.8(1) 1077.2(2) 1661.4(2)	108.67(2) 84.63(1) 115.96(1)	PtB_4P_3	η^5,B 227.8(6,23) η^5,P 235.8(3) P 231.3(3,9)	B,B 47.8(2,9)[c] 83.6(3,1.8) B,P 52.5(2,8) 91.6(2,9.3) 137.8(1,4.3) 170.4(1,4.7) P,P 97.2; 118.3(-,4.0)	45
$Pt(PMe_2Ph)_2(\eta^5$-$SB_{10}H_{10})$ (yellow)	m $P2_1/c$ 2	1183.72(10) 995.42(10) 2170.9(2)	 99.132(9)	PtB_4P_2S	η^5,B 223.9(3,9) 230.7(3,11) η^5,S 266.33(7) P 228.70(7) 230.21(7)	B,B 47.85(11,19)[c] B,S 47.99(8,41)[c] P,P 95.46(3)	46

TABLE 3. Continued

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	Pt-L [pm]	L-Pt-L [°]	Ref
$Pt(PEt_3)_2(\eta^5\text{-}SeB_{10}H_{10})$ (orange)	or Fdd2 16	5505.2(6) 1784.2(5) 1025.9(4)		PtB_4P_2Se	η^5,B 227(2,5) η^5 Se 267.6(2) P 231.4(4,3)	B,B 47.6(6,9)^c 82.0(6,6) B,Se 51.5(5,4)^c 88.0(5,2) B,P 94.9(5,9.1) 142.9(5,5.8) 164.0(5,7.6) P,P 98.5(2) P,Se 112.8(1,6.9)	19
$[Pt(PPh_3)_2(\eta^5\text{-}SeB_{10}H_{10})]\ CH_2Cl_2$ (orange)	tr $P\bar{1}$ 2	1283.7(3) 1453.4(2) 1189.8(3)	96.59(2) 107.31(2) 81.89(1)	PtB_4P_2Se	η^5 B 224.9(8,18) 230.5(7.6) η^5 Se 247.6(1) P 233.8(2,12)	B,B 47.1(2,9)^c 81.6(2,1.1) B,Se 51.9(2,1)^c 87.9(2,2) B,P 95.6(2,10.5) 147.9(2,10.3) 171.0(2) P,P 97.8(1) P,Se 86.2(2) 119.0(1)	47
$Pt(PEt_3)_2(\eta^5\text{-}TeB_{10}H_{10})$ (red)	m Cc 4	1038.7(2) 1722.7(4) 1444.7(3)	106.83(2)	PtB_4P_2Te	η^5,B 225.0(7,2) 229.4(9,2) η^5 Te 270.4(1) P 233.1(2,11)	B,B 47.6(3,5)^c 83.7(3,1.9) B,Te 56.7(2,1)^c 94.7(2,1) B,P 93.9(2,10.2) 139.2(2,8.3) 168.4(2,8.0)	48
$Pt(PMe_2Ph)_2(\eta^5\text{-}As_2B_9H_9)$ (red)	m $P2_1/c$ 4	1308.6(3) 1058.0(2) 1934.7(3)	104.45(2)	$PtB_3P_2As_2$	η^5 B 228.3(11,6) η^5,As 254.5(4) 265.5(4) P 229.7(4,3)	B,B 47.0(3,5)^c B,As 53.9(3,1.4)^c 92.0(3,1.1) As,As 57.4(3)^c P,P 96.5(2)	49

Pt(PEt$_3$) (SePh) (η^5-CB$_{10}$H$_{10}$SePh) (purple)	m P2$_1$/n 4	913.9(3) 1498.39(11) 2009.5(3)	98.85(2)	PtB$_4$CPSe	η^5,B 218.7(9,9) 225.5(9,24) η^5,C 223.0(7) Et$_3$P 233.0(2) PhSe 244.38(8)	B,B 49.2(3,2.2) 83.0(3,1.3) B,C 46.6(3,4)^c 82.0(3) B,P 95.8(2,0) 132.3(2,6) B,Se 122.4(2,20.9) 170.9(2) C,P 177.6(2) C,Se 96.8(2) P,Se 85.49(6)	40a
Pt(PEt$_3$) (SePh) {η^5-CB$_{10}$H$_{10}$-8-O(CH$_2$)$_4$Cl} (orange)	m P2$_1$/c 4	1124.52(1) 1199.71(13) 2047.5(3)	99.035(13)	PtB$_4$CPSe	η^5,B 220.0(6,15) 223.1(6,1) η^5,C 224.3(5) Et$_3$P 232.9(3) PhSe 241.25(6)	B,B 49.4(2,2.4)^c 83.3(2,9) B,C 46.4(2,1)^c 81.5(2,1) B,P 94.9(2,1.9) 132.0(2,4.1) B,Se 113.5(2,8) 155.5(2,9) C,P 174.06(13) C,Se 98.50(13) P,Se 85.39(4)	40a
Pt(PEt$_3$)$_2$(H) (η^4-SB$_9$H$_{10}$)	m C2/c 8	1638.7(6) 1013.8(5) 2927.6(8)	95.54	PtB$_3$P$_2$HS	η^4,B 220-225 η^4,S 243 H 166 P 237.5(-,15)	not given	50

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Five-membered metallocyclic ring.

The structure of a yellow cluster /45/ is based on a $PtB_{10}P$ icosahedron with the Pt and P atoms occupying adjacent positions. The compound appears to derive from the capping of the five-membered open face of the eleven-vertex nido-7-phospoaundecaborane cluster with the metal centre. The inner coordination sphere about the Pt(II) atom is PtB_4P_3.

There are four derivatives of composition $Pt(PR_3)_2(\eta^5\text{-}ZB_{10}H_{10})$, where R is PMe_2Ph and Z is S /46/, or PEt_3 and Se /19/, PPh_3 and Se /47/ or PEt_3 and Te /48/. All belong to the closo class. Crystals of the clusters exhibit conformational polymorphism and fluxional behaviour of the $Pt(PR_3)_2$ units in the closo-twelve-atom metallaheteroboranes with the $PtZB_{10}$ cage. The overall cage structure is a distorted dodecahedron in which the $Pt(PR_3)_2$ unit is bonded to a ZB_4 ring. The conformation of the PtP_2 unit over the ZB_4 face is essentially the same in each of the compounds /19,46-48/, and may be rationalised by consideration of the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO) interactions between the $Pt(PR_3)_2$ and $ZB_{10}H_{10}$ units /19/. The inner coordination sphere about each Pt(II) atom is PtB_4P_2Z, with Z defined as above.

A red derivative /49/ has a closo $PtAs_2B_9$ geometry giving a distorted icosahedron with the Pt and two As atoms forming one triangular face. The Pt(II) atom is surrounded by three B, two P and two As atoms.

There are two derivatives, purple and orange /40a/ both having $Pt(PEt_3)(SePh)$ moieties with the Pt atoms pentahapto coordinated by nido-7-CB_{10} cage frameworks. The cage of the purple compound incorporates another SePh group attached to a B atom in a site with respect to the {CBBBB} ring ligating the Pt atom. This is also the case for the incorporated $O(CH_2)_4Cl$ substituent in the orange derivative. Each Pt(II) atom adopts a PtB_4CPSe chromophore.

The molecular structure of $Pt(PEt_3)_2(H)(\eta^4\text{-}SB_9H_{10})$ /50/ has a Pt atom completing an eleven-atom icosahedral fragment and bonded to S, three B, and two P atoms together with a hydride ligand (PtB_3P_2HS).

The data in table 3 show platinum hexahapto coordinated by a conjuncto type of heteroborane /43,44/, and pentahapto coordinated by closo /19,45-49/ and nido /40a,50/ types of heteroborane. The mean Pt-B and Pt-Z distances for the pentahapto heteroboranes lengthen with increasing covalent radius of the Z atom in the order: 222 and 23.5 pm (C, 77 pm) < 233 and 266 pm (S, 102 pm) <227.5 and 267.5 pm (Se, 116 pm) < 228 and 270.5 pm (Te, 136 pm). The mean Pt-P bond distance increases in the order: 230.5 pm (PMe_2Ph) < 233.5 pm (PEt_3) < 234.0 pm (PPh_3).

There are three-membered metallocycles formed and the effect of both electronic and steric hindrance of the coordinating atom can be seen in the opening of the L-Pt-L bond angles. These angles open in the order: 46.5° (C,B) < 47.8° (B,B) < 48.0° (B,S) < 51.7° (B, Se) < 52.5° (B,P) < 54.0° (B,As) < 56.5° (B,Te) < 57.5° (As,As).

2.4. Coordination Number Eight (Sandwich)

There are seventeen derivatives with an eight-coordinate Pt atom in a sandwich environment, and these are listed in Table 4. The crystal structure of a golden yellow derivative /51/ reveals well separated $[PhCH_2NMe_3]^+$ cations and $[Pt(\eta^4\text{-}B10H12)_2]^{-2}$ anions. The latter resides on a crystallographic inversion centre, slightly but significantly distorted from C_{2h} point symmetry due to crystal packing. Molecular geometry calculations suggest that the $\{B_{10}H_{12}\}$ ligand does not fit particularly well with either a nido-$\{B_{10}H_{12}\}^{-2}$ or an arachno-$\{B_{10}H_{12}\}^{-4}$ formalism. The Pt atom is sandwiched by two $\{\eta^4\text{-}B_{10}H_{12}\}$ cage fragments (PtB_8).

Two orange derivatives /52/ are shown in Figure 4. One contains a [Pt(*anti*-η^4-$B_{18}H_{20})_2]^{-2}$ and the other a [Pt(*syn*-η^4-$B_{18}H_{20})_2]^{-2}$ anion. Each of the isomeric anions can be viewed as two nineteen-vertex subclusters ($PtB_{18}H_{20}$) joined via the common Pt vertex. In each case the subcluster itself can be viewed as a nido-platinundecaboranyl and a nido-decaboranyl unit fused by one B-B edge in common. The nido-platinadecaboranyl description implies a η^4 Pt-borane bonding mode.

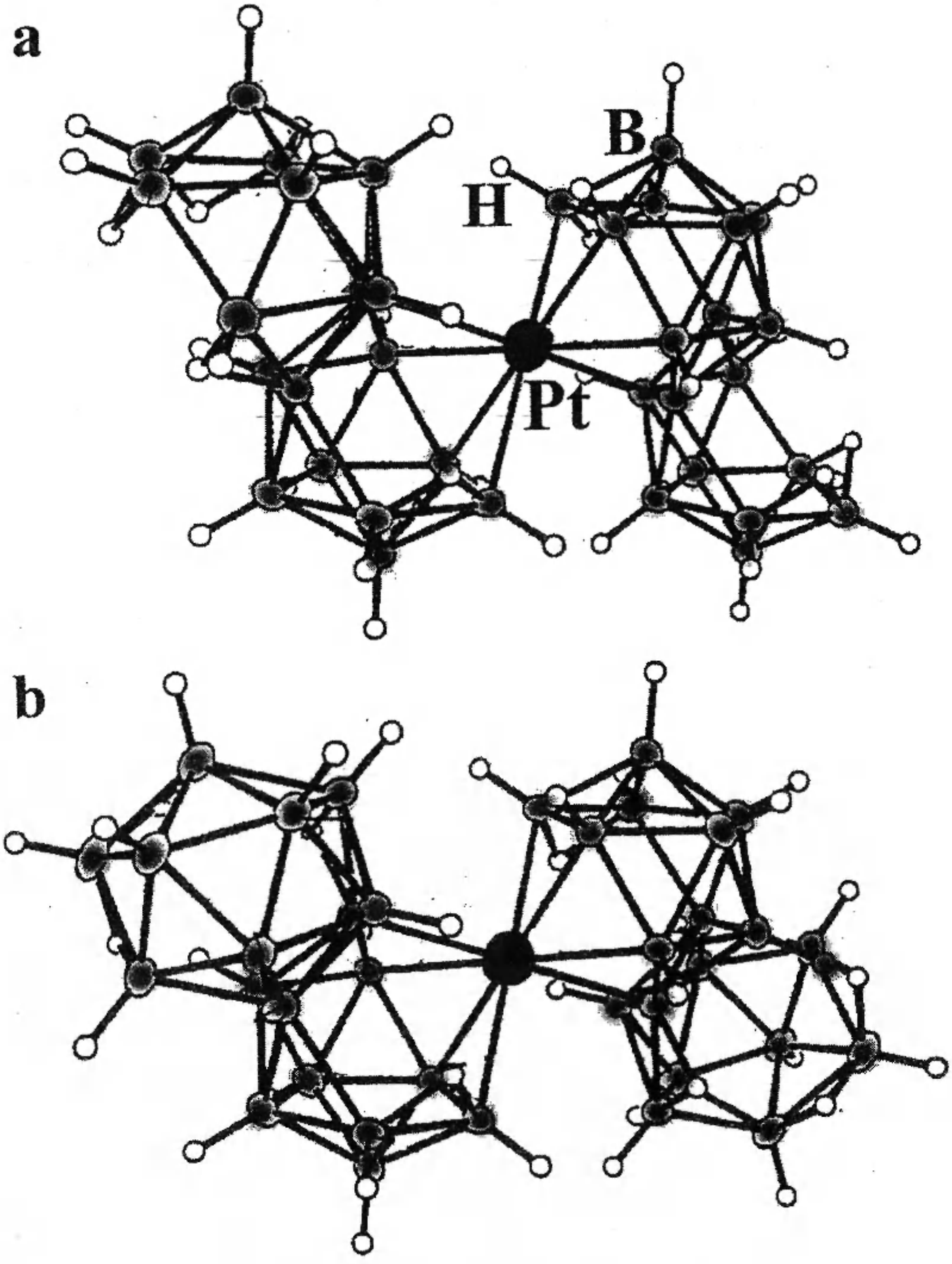

**Fig. 4. (a) Structure of [Pt(anti-η^4-$B_{18}H_{20})_2]^{-2}$
(b) Structure of [Pt(syn-η^4-$B_{18}H_{20})_2]^{-2}$ [52]**

TABLE 4.

Crystallographic and Structural Data for Monomeric Platinum Heteroboranes with Coordination Number Eight and Higher (Sandwiched)[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	Pt-L [pm]	L-Pt-L [°]	Ref
$(PhCH_2NMe_3)_2$ $[Pt(\eta^4\text{-}B_{10}H_{12})_2]$ (golden yellow) at 185(1)K	tr_ P1 1	902.3(3) 1044.0(4) 1117.2(3)	111.55(3) 108.794(24) 101.29(3)	PtB_8	η^4,B[b] 222.3(3,8) 228.5(3,11)	B,B[b] 47.19(12,1.27)[c]	51
$(NEt_4)_2$ [Pt(anti-η^4-$B_{10}H_{12})_2$] (orange)	m $P2_1/c$ 2	1056.46(9) 1081.28(9) 2039.60(13)	104.232(6)	PtB_8	η^4,B 223.9(3,9) 235.3(3,63)	not given	52
$(tmndaH)_2$ [Pt(syn-η^4-$B_{18}H_{20})_2$] (orange)	tr_ P1 1	1064.2(2) 1105.60(14) 1220.12(13)	88.058(10) 84.150(11) 85.995(10)	PtB_8	η^4,B 222.8(4,3) 231.3(4,11)	not given	52
$(ppn)_2$ [Pt{η^4-$(C_5H_{11})_2B_{10}H_{10}\}_2$] (golden yellow)	m $P2_1/c$ 4	1528.4(3) 1883.4(2) 1779.1(2)	110.43(1)	PtB_8	η^4,B 224.1(11,31) 238.5(11,15)	not given	53
$Pt(PMe_2Ph)$ (η^7-$B_{26}H_{26}PMe_2Ph$) (blue-red) at 223(2)K	m $P2_1/c$ 4	2433.44(2) 1044.36(1) 1428.12(2)	99.701(1)	PtB_7P	η^7,B 220.0(10,20) 226.6(11,11) 233.4(11) P 237.7(2)	not given	54
$Pt(PMe_2Ph)_2$ (Cl) (η^5-$CB_{10}H_{11}$) (yellow)	m $P2_1/c$ 4	1184.4(2) 1308.2(1) 1638.5(1)	98.67(1)	PtB_4P_2CCl	η^5,B 223.0(3,4) 225.4([illegible]) η^5,C 224.0(2) P 233.99(6) 241.62(6) Cl 244.69(6)	P,C 98.84(6) 162.39(6) P,Cl 84.11(2,23) C,Cl 98.47(6)	55
Pt(η^4-cod) {η^4-CHB_2C_2(Me)(Et)$_4$} (pale yellow)	or Pcmn 4	1077.7(1) 1393.7(4) 1393.1(3)		PtC_5B_2	η^4,C 222.4(8,18) η^4,C 220.2(5) η^4,B 238.8(7)	not given	56
Pt(η^3-cod) {η^5-CHB_2C_2(Me)(Et)$_4$} (pale yellow)	m $P2_1/n$ 4	1113.5(3) 1407.0(5) 1313.8(40)	90.12(2)	PtC_5B_2	η^3,C 192.6(16) 215.6(16,29) η^5,C 209.3(13) 231.5(14,16) η^5,B 238.4(17,17)	not given	56

Pt{η^4-cod}{η^4-$C_{12}B_2H_{10}$} (pale yellow)	m $P2_1/c$ 8	873.4(5) 1409.8(7) 3187.8(16)	95.79(4)	PtC_2B_2	C 239.2-243.0(7) B 234.3(8,9)	not given	57
Pt{η^4-$C_2B_7H_9$-9-Me}$_2$ (red-orange)	m C2/c 4	655.4(3) 2059.0(3) 1334.9(3)	103.48(3)	PtC_2B_4	η^4,C 208.0(17,11) 220.8(18,43) η^4,B 228.3(19,4) 234.8(18,40)	not given	58
Pt{η^4-$C_3B_7H_9$-8-Me}$_2$ (red-orange)	m $P2_1/c$ 6	1789.8(3) 1034.8(1) 1412.7(2)	108.12(3)	PtC_4B_4	η^4,C 211.0(8,12) 219.2(7,18) η^4,B 227.5(8,25) 232.1(9,14)	not given	58
Pt(PMe$_2$Ph)$_2${η^6-$C_2B_8H_9$-2-Me}	m $P2_1/n$ 4	947.6(1) 1547.7(3) 1804.0(3)	104.78(1)	$PtB_4C_2P_2$	η^6,B 238.5(7,17) η^6,C 218.1(6,5) P 228.8(3,0)	not given	59
Pt(PMe$_2$Ph)$_2${η^6-$C_2B_8H_{10}$}	m I2/a 4	1824.8(2) 1016.8(2) 1328.2(3)	101.48(2)	$PtB_4C_2P_2$	η^6,B 249.8(13,64) η^5,C 215.5(10,0) P 226.7(4,0)	not given	59
Pt{P(OMe)$_3$}$_2${η^6-$C_2B_8H_{10}$} (white)	m C2/c 4	1330.9(2) 1093.6(1) 1516.5(1)	107.81(1)	$PtB_4C_2P_2$	η^6,B 255.2(7) η^6,C 213.5(6) P not given	C,C 97.4(3)	60
Pt{P(OMe)$_3$}$_2${η^6-$C_2B_8H_9$-2-Ph} (white)	m $P2_1/n$ 4	1054.5(2) 1739.9(3) 1315.9(2)	93.81(1)	$PtB_4C_2P_2$	η^6,B 239.6(6) η^6,C 220.1(5) P not given	C,C 106.1(3)	60
Pt(H)(PEt$_3$)$_2${η^5-$CB_{10}H_{11}$} (colourless)	m $P2_1/c$ 4	1865.6(3) 1587.7(3) 1839.2(3)	116.467(11)	PtB_4P_2HC	η^5,B 221.7(9) 226.0(14,19) η^5,C 230.5(10) P 236.2(2,2) H 159.6	P,P 98.6(1) P,H 85.9(1,8)	61
Pt{η^5-$C_2B_9H_{11}$}$_2$	or $P2_12_12_1$ 4	1083.6(6) 1200.9(7) 1314.2(6)		PtB_6C_4	η^5,B 220(1) η^5,C 224(1)	not given	62

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Three-membered metallocyclic ring.

A golden yellow derivative /53/ contains ppn$^+$ cations and $[Pt(\eta^4-(C_5H_{11})B_{10}H_{10})_2]^{-2}$ anions. The complex is composed of two decaborane cages, each bonded in a η^4 fashion to the Pt atom, which is a common vertex in two 11-vertex cages. Consistent with the nido-electron count of each cage, the cage frameworks are based on an icosahedron missing one vertex. The Pt atom sits on a crystallographic centre of symmetry, and the two cages are symmetry related.

The structure of a blue-red cluster /54/ consists of a nido-eleven-vertex $\{PtB_{10}\}$ subcluster fused, with a $\{PtB_2\}$ triangular face in common, to another such moiety which is itself fused to a nido-ten-vertex $\{B_{10}\}$ subcluster, with a $\{B_2\}$ edge in common. The Pt atom is, surprisingly, not in an open face site.

In a yellow cluster /55/ the Pt atom is coordinated on one side by the open {CBBBB} pentagonal face of the nido-7-$CB_{10}H_{11}$ cage, and on the other side by a Cl atom and two PPh_2Ph molecules.

There are three pale yellow derivatives /56,57/ in which η^4-cyclooctadiene with a η^4-heteroborane form a sandwich about the Pt centre with an inner coordination sphere of PtC_6B_2. Another two red-orange derivatives /58/ have a pair of heteroboranes in η^4-fashion, forming a staggered sandwich configuration about each Pt atom (PtC_4B_4).

An inner coordination sphere of $PtB_4C_2P_2$ is found in four derivatives /59,60/. A η^6-carborane-metal bonding is seen with a remarkable flexing of the 10-vertex η^6-$\{C_2B_8H_9X\}$ moiety between extreme nido and arachno 10-vertex geometries. Two PX_3 (X = Me_2Ph /59/ or OMe /60/) complete the inner coordination sphere about the Pt atoms.

The open face of the nido-$CB_{10}H_{11}$ cage in a colourless derivative /61/ is pentahapto (B_4C) coordinated to the Pt atom. Two PEt_3 ligands with a hydrido ligand complete the coordination about the Pt(II) atom (PtB_4P_2HC). In another derivative /62/, a Pt(IV) atom is coordinated in a symmetrical sandwich between two planar pentagonal fragments (C_2B_3) of the σ-carbonyl anions, with a dihedral angle of 173°.

3. DI- and TRIMERIC COMPOUNDS

There are sixteen coloured dimeric platinum heteroboranes, for which the relevant data are shown in Table 5. The structure of a yellow dimer /63/ consists of a four-vertex Pt_2B_2 and an eight-vertex Pt_2B_6 subcluster conjoined at a common Pt-Pt edge, as shown in Figure 5. There is an essentially linear P-Pt-Pt-L axis to which the B_6 and B_2 subclusters are appended: P(1)-Pt(1)-Pt(2) 174.8(1)°, P(2)-Pt(2)-Pt(1) 178.3(1)°. The Pt(II)-Pt(II) bond distance of 262.1(1)° is the shortest found in the heteroborane platinum chemistry.

In another yellow dimer /64/ there is also an essentially linear P-Pt-Pt-P axis to which two equivalent B_6 subclusters are appended: P-Pt-Pt' and P'-Pt'-P 175.5(1)°. The Pt(II)-Pt(II) bond distance of 264.4(1) pm is somewhat longer than in the previous case /63/. The cage of a yellow dimer /8/ is related to a nido icosahedral geometry, having a substantially flatter open face. The second Pt atom lies outside the polyhedral framework and is involved in a 3-centre interaction with B (Pt-B 208(3) pm) and another Pt atom (Pt-Pt 282.0(2) pm. In another yellow dimer /66/, the twelve-vertex closo-diplatinadodecaborane is seen to be based on a closed $\{Pt_2B_{10}\}$ icosahedron, with the metal atoms adjacent to a nido or "slipped" closo geometry. The interplatinum distance of 286.3(2) pm suggests reasonable strong bonding.

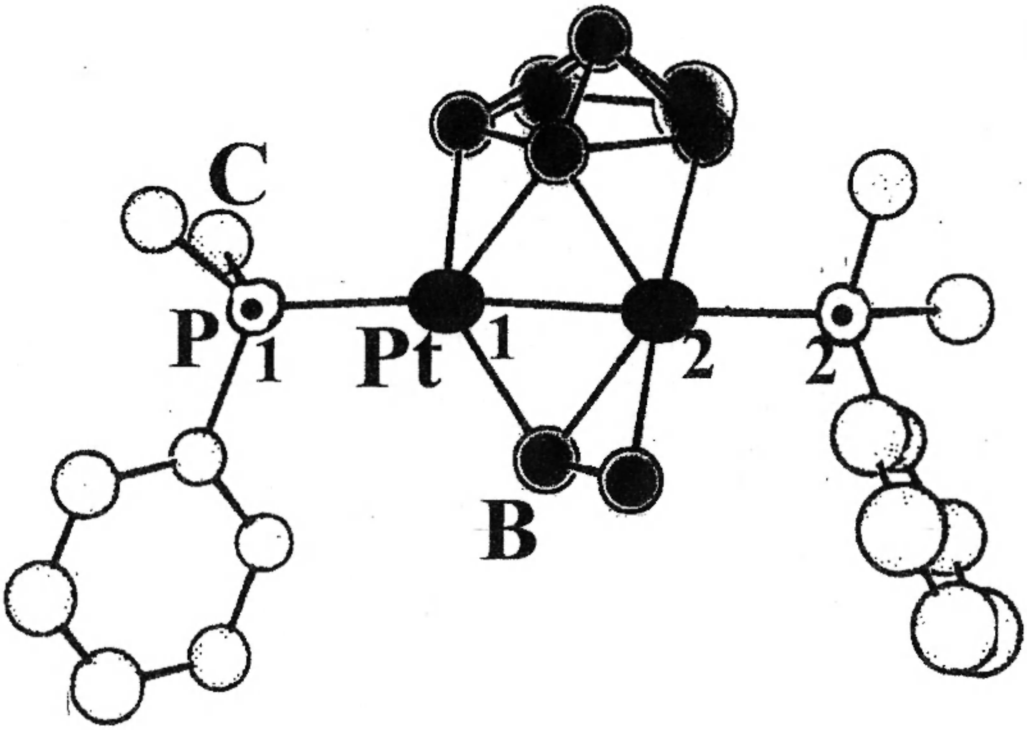

Fig. 5. Structure of $Pt_2(PMe_2Ph)_2(\eta^3\text{-}B_2H_5)(\eta^3\text{-}B_6H_9)$ [63]

The basic $\{Pt_2B_{16}\}$ cluster of a dark orange example /67/ consists of a closo twelve-vertex $\{1,2\text{-}Pt_2B_{10}\}$ unit and a nido nine-vertex $\{2,3\text{-}Pt_2B_6\}$ unit, conjoined with the closed triangular Pt_2B faces in common. The Pt-Pt distance is 291.2(4) pm. The molecule of another dimer /10/ has a cage which can be described as a tricapped trigonal prism in which the metal atoms vector is a capping linkage. The Pt-Pt distance is rather long (302.98(10) pm), but lies roughly perpendicular to the two sets of P_2Pt planes.

In the red dimer /8/ the $Pt_2C_2B_5$ cage has the geometry of a highly distorted trigonal prism, tricapped with two C atoms and one B atom. The Pt-Pt distance is 305.1(4) pm. The structure of a yellow dimer /68/ consists of a nine-vertex n-arachno framework, obtained by removal of two adjacent vertices of connectivity (six and four, respectively) from an eleven-vertex closo octahedron. The {(dppe)Pt} moieties are located at the 6 and 8 positions in the n-arachno B_9H_{15} framework, each replacing a BH group and a bridging H atom.

In another red dimer /40a/ two TePh groups bridge the Pt(1) and Pt(2) atoms, with Pt(1) carrying PEt_3 and η^5-2-$CB_{10}H_{11}$ ligands while Pt(2) carries a TeH and PEt_3 group. In the bridge system the Pt(1)-Te(1) and Pt(1)-Te(2) bond lengths of 272.20(6) and 270.54(6) pm are perceptibly longer than the Pt(2)-Te(1) and Pt(2)-Te(2) values of 261.75(6) and 261.13(7) pm, respectively. This may result from the Pt atoms having different formal oxidation states with Pt(1) at 4 and Pt(2) at 2.

TABLE 5.

Crystallographic and Structural Data for Monomeric Di-and Trimeric Platinum Heteroboranes[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	Pt-L [pm]	Pt-Pt[pm] Pt-L-Pt[°]	L-Pt-L [°]	Ref
$(PMe_2Ph)_2Pt_2(\mu\text{-}\eta^3\text{-}B_3H_5)(\mu\text{-}\eta^3\text{-}B_6H_9)$ (yellow)	m $P2_1$ 2	1618.3(9) 1330.3(7) 592.3(3)	 93.62(4)	PtB_3PPt^I PtB_4PPt^I	μB^b 220.3(28,22) B 217.4(25) P 228.8(5) μB 217.6(25,18) B 226.1(25,17) P 229.2(5)	262.1(1) B 73.6(9,1)	B,B^b 48.5(9)^c 105.5; 141.3(9) B,P 88.9; 127.2(7,2.8) B,B 49.3(9,1.0)^c 107.4, 135.4(9.1.0) B,P 87.2(6,9) 126.3(8,1.2)	63
$(PMe_2Ph)_2Pt_2(\mu\text{-}\eta^3\text{-}B_6H_9)_2$ (yellow)	m $P2_1/c$ 2	1014.0(2) 586.8(2) 2316.9(6)	 91.65(2)	PtB_4PPt^I	μB 220.1(9,23) B 222.5(10,3) P 230.2(2)	254.4(1) B 73.8(3)	B,B 43.4(4,5)^c 106.2(3) 137.1(3,4.3) 168.9(4) B,P 53.3(2,1.0) 90.2(3,4.6) 126.8(2,3.8)	64
$\{(\eta^5\text{-}C_2B_9H_9\text{-}7,8\text{-}Me_2)\text{-}Pt\}_2\{\mu\text{-}\eta^2\eta^4C(H)C(Ph)C(H)C(Ph)\}$ (red)	tr $P\bar{1}$ 4	1331.7(2) 1678.3(4) 1728.9(4)	64.94(2) 83.31(2) 78.58(2)	$PtC_6B_3Pt^I$ $PtC_4B_3Pt^I$	η^5,C 225.2(21,11) η^5,B 215.4(32) 219.3(25,1) μC 217.0(16) 233.0(15) C 225.2(19,8) η^5,C 228.2(26,47) η^5,B 216.0(24) 227.5(30,34) η^2,μC 204.3(22,20)	278.2(1) C 80.7(7,2.4)	not given μC,μC 80.2(7)	65
$(Me_3P)_2Pt(\mu\text{-}\eta^4\text{-}B_8H_{10})Pt(PMe_3)_2$ (yellow)	m A2/a 8	2914.3(16) 1005.8(7) 2193.5(7)	 90.54(4)	PtP_2BPt^I $PtB_2C_2P_2Pt^I$	μB 208(3)	282.0(2)		8

$(PMe_2Ph)_2ClPt_2\{\mu$-$\mu\,\eta^5$-$B_{10}H_9(PMe_2Ph)\}$ (yellow)	m $P2_1/c$ 4	11887.6(3) 2170.4(3) ?	97.93(2)	$PtB_4P_2Pt^t$ $PtB_{[illegible]}ClPPt^t$	μB 232.9(8,26) B 222.1(9,9) P 232.7(4,5) μB 227.4(8,58) B 218.2(8,11) Cl 238.9(4) P 231.7(4)	286.3(2)		66
$(PMe_2P)_2Pt_2\{\mu$-$\mu B_{16}H_{15}(C_6H_4Me)(PMe_2Ph)\}$ (dark orange)	m $P2_1/n$ 4	1069.4(2) 3210.5(5) 1252.5(2)	90.99(1)	PtB_6PPt^t	μB 219.3(20,26) B 220.9(20,51) 229.6(20,23) P 231.5(6,0)	291.2(4)		67
$(PEt_3)_4Pt_2\{\mu$-η^5-$C_2B_4H_4$-Me_2-4,5$\}$	or Pbca 8	1726.7(2) 2016.1(4) 2308.6(3)		PtB_2P_2C PtB_3P_2	μB 221.9(19) B 225(3) C 220(2) P 231.4(6,70) μB 221.3(18) B 223(3,3) P 232.6(6,4)	302.98(10)	P,P 102.9(2) P,P 101.1(2)	10
$(PEt_3)_4Pt_2\{\mu$-η^6-$C_2B_5H_7\}$ (red)	m $P2_1$ 2	1007.8(5) 1854.1(1) 1264.8(5)	126.54(5)	$PtC_2B_2P_2$		305.1(4)		8
$[(\eta^2$-dppe$)_2Pt_2\{\mu$-η^5-$B_{[illegible]}H_{11}\}]\,0.5Et_2O$ (yellow)	tr $P\bar{1}$ 2	1289.18(1) 1571.53(1) 1786.79(2)	97.118(1) 94.409(2) 108.92(1)	PtB_3P_2 PtB_4P_2	μB 219.9(9,9) B 219.[illegible](0) P 228.2(2,4) μB 229.8(9,31) B 226.5(9,38) P 229.2(2,3)		P,P 85.83(8)^d μB,P 167.5(3) B,P 174.5(2) P,P 84.97(7)^d μB,P 152.1(2) B,P 170.3(2)	68
$(PEt_3)(TePh)Pt(\mu$-$TePh)_2Pt(PEt_3)(\eta^5$-$CB_{10}H_{11})$ (deep red)	m $P2_1/c$ 4	2205.0(5) 1002.3(2) 2142.2(4)	115.40(2)	$Pt^{II}Te_3P$ $Pt^{IV}B_5Te_2P$	μTe 261.44(7,31) Te 262.25(7) P 228.4(2) η^5,B 220.3(3) 223.9(7,13) μTe 271.37(6,83) P 239.2(7)	Te 97.50(2,28)	μTe,μTe 82.89(2) μTe,Te 94.68(2) 177.23(2) μTe,P 94.79(4) 176.91(4) Te,P 87.60(4) B,B 108.7(2) Te,Te 79.24(2) B,Te 83.6(2)-168.4(2) Te,P 92.08(4,3.58)	40a

TABLE 5. Continued

COMPOUND (colour)	Crystal Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	Pt-L [pm]	Pt-Pt[pm] Pt-L-Pt[°]	L-Pt-L [°]	Ref
$(PEt_3)_2Pt\{\mu-\eta^4-CB_{10}H_{10}\ \mu(H)-CB_{10}H_{10}-\eta^4\}\ Pt(PEt_3)_2$ (green)	tr_ P1 2	1019.5(1) 1358.2(3) 1805.6(2)	95.97(1) 93.07(1) 103.43(2)	PtB_4P_2 (C)	η^4,B 225.0(6,24) 231.6(5) P 234.2(2,36) (C) 241.5(7,22)		B,B 47.8(2,1.2)^c 78.7(3,2.7) P,P 96.63(5,15) B,P 92.2(2,4.8) 117.9-138.2(2) 169.1(2,4.6)	55
$(PMe_2Ph)_2Pt\{\mu-\eta^4:\eta^5-(CB_{10}H_{10})_2\}\ Pt(PMe_2Ph)_2$ (deep purple)	tr_ P1 2	998.18(8) 1444.5(2) 1971.6(2)	94.543(6) 96.23(1) 105.250(7)	PtB_4P_2 (C) PtB_4P_2C	η^4,B 224.0(6,3) 227.2(6,3) P 233.8(2,4) (C) 238.0(5) B 224.2(6,6) C 220.4(5) P 234.4(2,24)		P,P 95.43(5) P,P 94.66(5)	55
$(PMe_2Ph)_2Pt\{\mu-\eta^3-B_8H_{10}\}\ Pt(PMe_2Ph)_2$ (colourless)	m C2/c 4	1376.2(3) 1510.5(4) 1921.0(3)	92.69(2)	PtB_3P_2	η^3,B 220.3(5) 224.3(5,2) P 230.4(1,1)		B,B 46.8(2,6)^c 86.6(1,1.7) P,P 97.7(1) B,P 89.6(1) 129.4(1,4.2) 170.2(1,2.2)	18
$[(PMe_2Ph)_2Pt\{\mu-\eta^4:\eta^4-B_{16}H_{17}\}Pt(\eta^4-B_{10}H_{11}PME_2Ph)]\ 0.5C_6H_{14}$ (orange) (at 160K)	m $P2_1/n$ 4	1479.03(4) 1305.95(3) 2834.31(7)	90.452(2)	PtB_3HP_2 PtB_8	η^3 B 232.6(6,31) η^3 H 184(6) P 229.9(1,26) η^4,B 222.3(6,25) 228.2(6,14)		not given	69
$(PMe_2Ph)_2Pt\{\mu-\eta^4:\eta^4-B_{18}H_{16}\}\ Pt(PMe_2Ph)_2$ (bottle green)	tr_ P1 2	1430.3(3) 1435.3(5) 1314.3(3)	103.63(3) 96.85(3) 66.70(3)	PtB_4P_2	η^4,B 224(-,2) 229(-,4) P not given		not given	39

$(\eta^3\text{-}C_8H_{13})Pt\{\mu\text{-}\eta^5\text{:}\eta^5\text{-}CH\,B_2C_3(Me)_4\}Pt(\eta^4\text{-}C_8H_{12})$	m $P2_1/a$ 4	1409.0(3) 991.2(4) 1765.6(8)	107.00(2)	PtC_6B_2	η^3,C 210.2(15,22) $\eta^5\mu$,C 212.8(13) 237.0(13,3) $\eta^5\mu$B 234.4(16,6)	379.7(1) C not given B not given	not given	56
				PtC_3B_2	η^4,C 217.0(15,27) $\eta^5\mu$C 231.6(15,17) $\eta^5\mu$B 224.1(17,2)			
$[(PMe_2Ph)_4Pt_3B_{14}H_{16}]\,CH_2Cl_2$ (dark green)	m $P2_1/c$ 4	1249.0(3) 3732.6(8) 1072.0(2)	104.92(2)	PtB_4P_2	μ_3B 218.6(17) μB 227.9(17,29) B 223.3(17) P 233.3(4,9)	301.2(1) 337.6(1) B 86.6(6) 123.1(7) 132.5(8) 146.3(1)	P,P 97.60(2) μ_3B,P 97.5(5) 158.3(5) μB,P 91.6(4,6.3) 143.7; 174.8(5) B,P 97.9(5) 134.8(5)	44 70
				PtB_5P	μ_3B 212.6(17) μB 237.9(17) B 227.2(17,15) P 231.0(4)		μ_3B,μB 78.3(6) μ_3B,B 47.9(6)[c] 90.4(6,4.0) μ_3B,P 175.5(3) μB,P 49.0(4) B,P 91.2(5) 123.1(5)	
				PtB_5P	μ_3B 212.3(16) μB 223.5(17) B 228.3(18,21) P 228.8(4)		μ_3B,B 91.5(6,6.0) B,B 123.9(6) μ_3B,P 172.3(5) μB,P 133.1(4) B,P 93.7(4,6.7) 123.6(4)	

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Three-membered metallocyclic ring.

d. Five-membered metallocyclic ring.

The structure of a green dimer /55/ is shown in Figure 6. The molecule has two $Pt(PEt_3)_2(\&-CB_{10}H_{10})$ units bridged by an I atom (B(x)-I = 2167(2) pm, B(y)-I = 219.7(6) pm and B(x)-I-B(y) = 112.1(3)°/. Moreover, in both halves of the molecule the boron atoms linked to the I atom are in a β-site with respect to the C atom in the {CBBBB} ring ligating the Pt atoms.

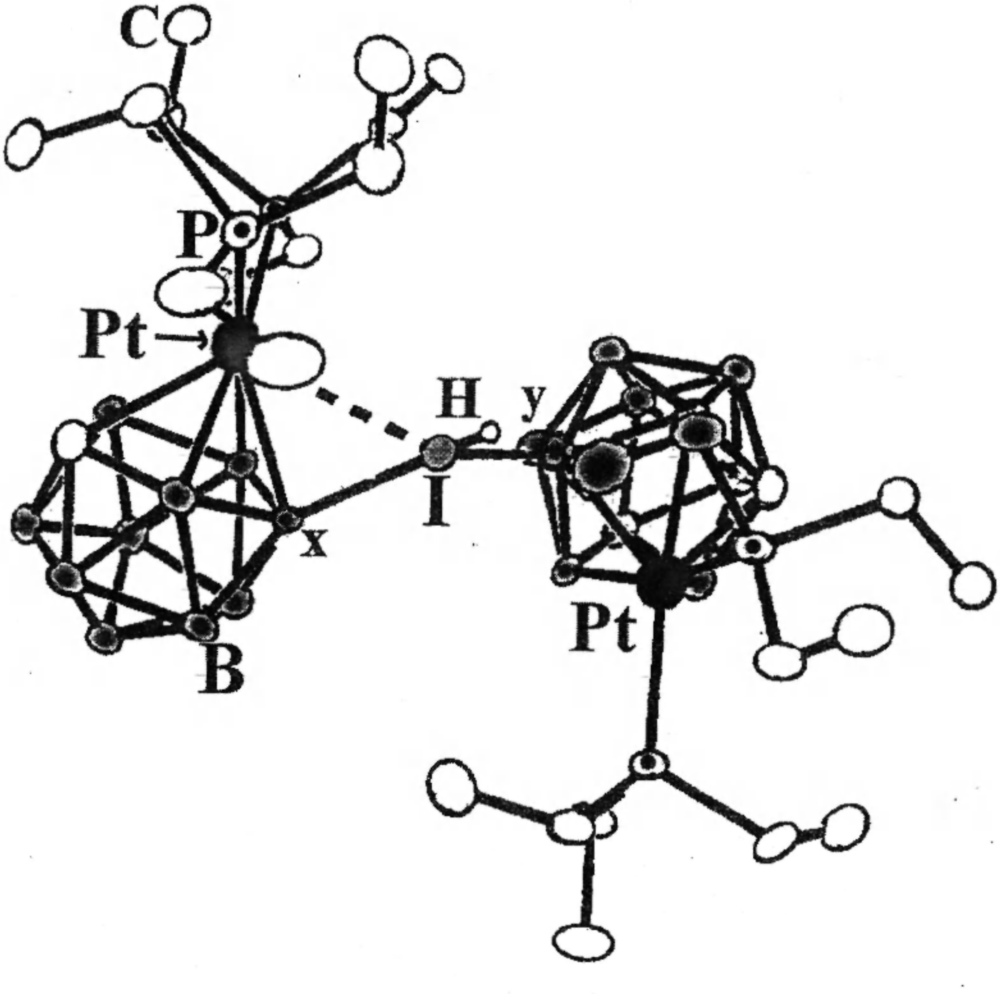

Fig. 6. Structure of $Pt_2(PEt_3)_4\{I(H)(CB_{10}H_{10})_2\}$ [55]

The molecular structure of a colourless dimer /18/ is that of an arachno-diplatina-decaborane which features a bis(trihapto)B_8 unit. The gross structure can be seen as an open faced ten-vertex cluster with a six atom open face.

The structure of an orange dimer /69/ is shown in Figure 7. The structure appears as a three-cluster assembly based on two nido eleven-vertex $\{PtB_{10}\}$ clusters, and a nido eight-vertex $\{B_8\}$ subcluster which is fused to the central $\{PtB_{10}\}$ unit with a common two-boron edge B(2)-B(5).

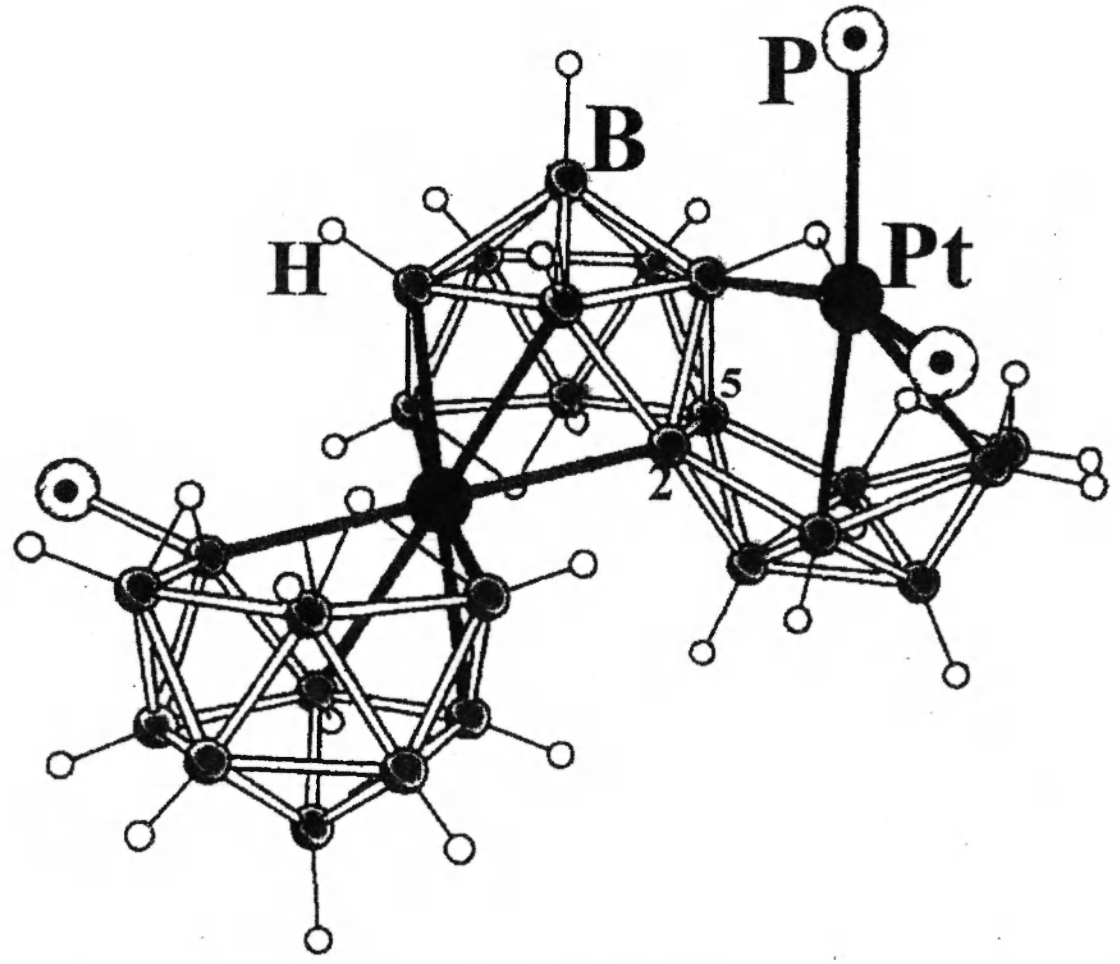

Fig. 7. Structure of [$(PMe_2Ph)_2Pt(B_{16}H_{17})Pt(B_{10}H_{11}.PMe_2Ph)$] [69]

A dark green trimer /70/ is the only example of its type and its structure is shown in Figure 8. The gross heavy atom cluster structure comprises a 17-vertex polyhedral configuration with a seven-membered {PtB_2PtB_3} open face [Pt(10), B(9), B(8), Pt(7), B(5'), B(4'), B(9')], but with an otherwise deltahedral framework. The structure can be interpreted in terms of two fused subclusters: (i) an arachno-type nine-vertex 6',8'-Pt_2B_7 moiety which has its Pt(7)-B(7')-Pt(10) atoms in common, and (ii) a nido-type eleven-vertex 2,7,10-Pt_3B_8 moiety distorted somewhat from the idealised [$B_{11}H_{14}$]$^-$ configuration due to accommodation of the larger Pt atoms. The Pt(2)-Pt(7) distance of 301.2(1) pm is about 36.4 pm shorter than the Pt(7)-Pt(10) distance of 337.6(1) pm.

In this series there are four types of heteroborane from a bonding point of view, ter-, tetra- penta- and hexadentate. The mean Pt-B bond distance increases in the order: 221.5 pm (ter-) < 223.5 pm (penta-) < 224 pm (hexa-) < 227 pm (tetradentate). There are three types of P donor ligands, PMe_2Ph, PEt_3 and η^2-dppe. The mean Pt-P bond length increases in the order: 228.5 pm (η^2-dppe) < 231 pm (PMe_2Ph) < 231.5 pm (PEt_3).

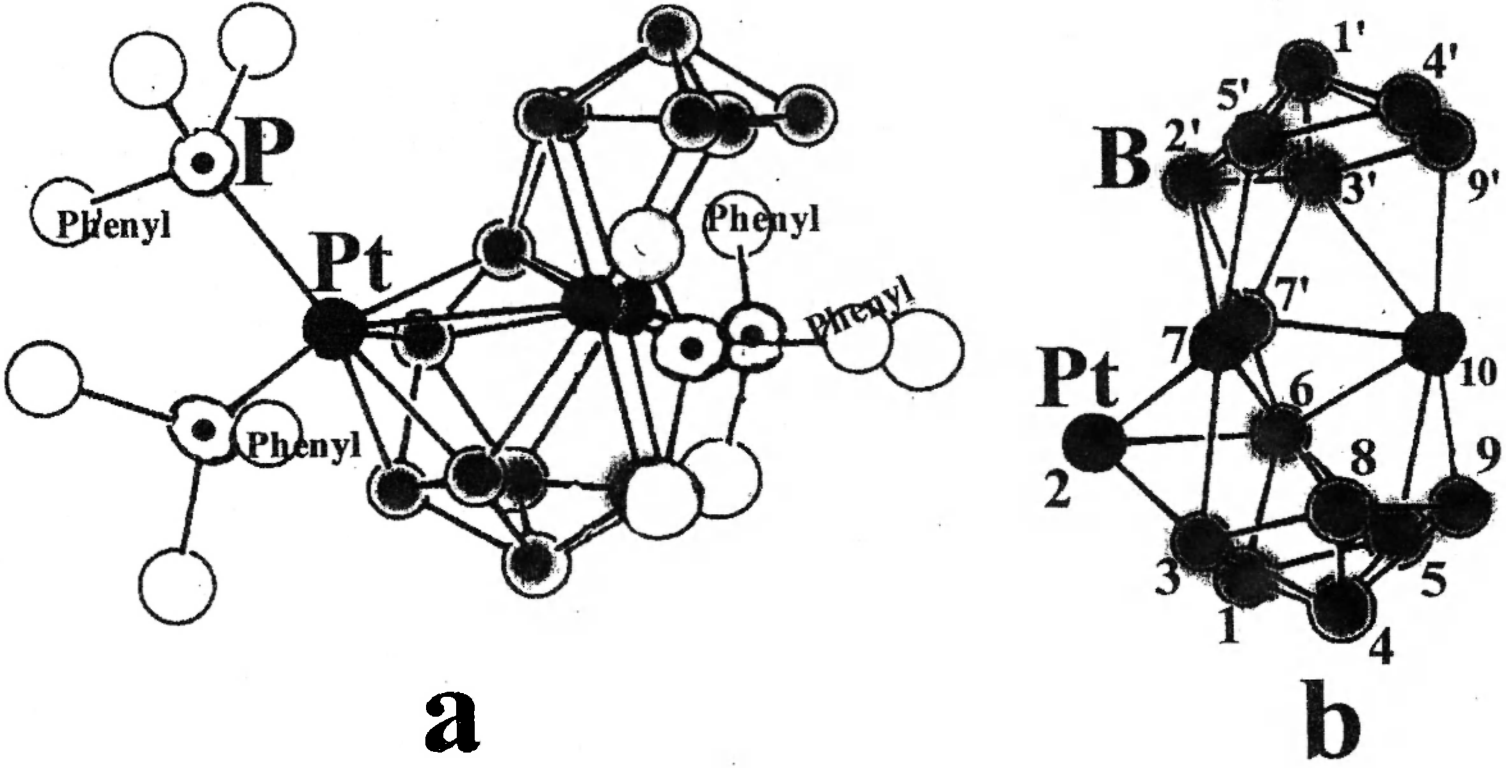

Fig. 8. (a) Structure of $[(PMe_2Ph)_4Pt_3(B_{14}H_{16})]$
(b) From new angle with organo-P ligands omitted for clarity [70]

4. CONCLUSIONS

This review identifies eighty three monomeric, sixteen dimeric and one trimeric platinum heteroboranes. The valence state Pt(II) is found in all but one example /40a/, which contains a mixed valence situation of Pt(II) and Pt(IV) atoms. The Pt atoms are four-, five-, six-, seven- and eight-coordinated, the latter having a sandwich configuration. The heteroborane moieties are bi- to hepta-dentate. The P-donor ligands are predominantly PMe_2Ph with some examples of PPh_3, PEt_3 and PMe_3 examples. The most common space group is monoclinic (72 examples) with some triclinic (18) and orthorhombic (10).

From the five well known borane classes only four are found in the chemistry of platinum: closo- /6,8,10,13,17,19,24,25,29,34,45-49,55,66/, nido- /7,11,20-23,27,28,30,35-42,50-55,59,54,69/, arachno- /9,12, 14,15,18, 19,26,44,59,68,70/, and conjuncto- /39,43,56/.

The shortest Pt(II)-Pt(II) bond distance of 262.1(1) pm is found in a dimer /56/. It is 39.1 pm shorter than that found in the trimer /62/ of 301.2(1) pm.

One example /34/ exists in two isomeric forms, differing mostly by degree of distortion. Another five derivatives /11,13,25,29,41/ contain two crystallographically independent molecules, also differing mostly by degree of distortion. All are typical examples of distortion isomerism /33/.

Despite the increasing availability of data retrieval systems, the location of relevant material is not always simple. One problem is the choice of key words for indexes, resulting in effective invisibility of some material of structural importance. Some original papers lack appropriate information, as evident from the gaps in the review Tables. Some material is only available as supplementary material. We hope that this summary will serve a function by gathering together relevant available material and delineating areas of interest. Related reviews of organoplatinum and heterometallic clusters are currently in progress.

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