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FULL PAPER

Phosphine exchange reactions involving *cis*-[Pt(PPh$_3$)$_2$(Bcat)$_2$] (cat = 1,2-O$_2$C$_6$H$_4$) and the oxidative addition of 1,2-B$_2$Cl$_2$(NMe$_2$)$_2$ to Pt^0

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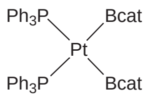
The reaction between the platinum(II) bis(boryl) complex *cis*-[Pt(PPh$_3$)$_2$(Bcat)$_2$] (cat = 1,2-O$_2$C$_6$H$_4$) and the tertiary phosphines PMe$_3$, PEt$_3$, PMe$_2$Ph, PMePh$_2$ and dcpe [1,2-bis(dicyclohexylphosphino)ethane] and the phosphite P(OEt)$_3$ afforded the new complexes *cis*-[Pt(PR$_3$)$_2$(Bcat)$_2$] (PR$_3$ = PMe$_3$, PEt$_3$, PMe$_2$Ph or PMePh$_2$), *cis*-[Pt(dcpe)(Bcat)$_2$] and *cis*-[Pt{P(OEt)$_3$}$_2$(Bcat)$_2$]. With PCy$_3$ the mixed phosphine species *cis*-[Pt(PCy$_3$)(PPh$_3$)(Bcat)$_2$] is the major product and was characterised by X-ray crystallography. With P(OMe)$_3$ reductive elimination of B$_2$(cat)$_2$ and the formation of platinum(0) products occurs exclusively whereas with dmpe [1,2-bis(dimethylphosphino)ethane] the only identifiable product is the platinum(II) species [Pt(dmpe)$_2$]Cl$_2$. With dppm [bis(diphenylphosphino)methane] a reaction occurs to give a product assigned the structure *cis*-[Pt(dppm)(Bcat)$_2$] or [Pt$_2$(dppm)$_2$(Bcat)$_4$] but two binuclear products were isolated as minor products, namely [Pt$_2$(PPh$_3$)(μ-dppm)$_2$(Bcat)(μ-Bcat)] and [Pt$_2$(κ^1-dppm)(μ-dppm)$_2$(Bcat)(μ-Bcat)]. Both compounds were characterised by X-ray crystallography and shown to contain unusual semi-bridging Bcat groups. The reaction between [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)] and the diborane(4) compound 1,2-B$_2$Cl$_2$(NMe$_2$)$_2$ is also described which results in B–B bond oxidative addition yielding *cis*-[Pt(PPh$_3$)$_2${BCl(NMe$_2$)}$_2$] and a complex to which this bis(boryl) subsequently rearranges, namely *trans*-[PtCl(PPh$_3$)$_2${BCl(NMe$_2$)}]. Both of these complexes were characterised by X-ray crystallography and have geometries typical of *cis*-bis(boryl) and *trans*-boryl chloride complexes respectively.

The platinum catalysed addition of diborane(4) compounds to the C–C/C–O multiple bonds present in alkenes,[1] alkynes,[2] 1,3-dienes,[3] α,β-unsaturated ketones[4] and allenes[5] (diboration) is now well established. Key intermediates in these reactions are platinum(II) bis(boryl) complexes formed by oxidative addition of the B–B bond of the diborane(4) compound to a platinum(0) centre[1–6] and many examples of complexes with the general formula *cis*-[Pt(PR$_3$)$_2$(BR′$_2$)$_2$] have now been isolated and structurally characterised.[2b,c,e,3b,7–9] As part of a study of the chemistry of platinum(II) bis(boryl) complexes, with the ultimate aims of developing better diboration catalysts, gaining further insight into the mechanism of diboration catalysis and probing further the nature of the Pt–B bond, we have carried out exploratory studies involving phosphine exchange reactions with the complex *cis*-[Pt(PPh$_3$)$_2$(Bcat)$_2$] **1** (cat = 1,2-O$_2$C$_6$H$_4$). This study builds on preliminary work which established that no dissociation of PPh$_3$ occurs at room temperature in solution (at least on the timescale associated with ^{31}P NMR spectroscopy) although the chelating diphosphines dppe [1,2-bis(diphenylphosphino)ethane] and dppb [1,2-bis(diphenylphosphino)butane] did substitute both PPh$_3$ ligands yielding the complexes [Pt(dppe)(Bcat)$_2$] **2** and [Pt(dppb)(Bcat)$_2$] **3**.[2e] We also describe herein the reaction of the diborane(4) compound 1,2-B$_2$Cl$_2$(NMe$_2$)$_2$, which has recently been shown to undergo reactions giving rise to metal complexes containing diboran(4)yl [–B(NMe$_2$)BCl(NMe$_2$)][10] and borylene [B(NMe$_2$)] ligands,[11] with [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)].

For a report dealing with related phosphine substitution reactions involving the rhodium complex [RhCl(PPh$_3$)$_2$(Bcat)$_2$] see ref. 12.

Results and discussion

As stated above and described in ref. 2(*e*), compound **1** reacts with 1 equivalent of either dppe or dppb affording **2** and **3** respectively in essentially quantitative yield. Compound **1** reacts similarly with 1 equivalent of dcpe [1,2-bis(dicyclohexylphosphino)ethane] in toluene affording **4**, NMR data for which are presented in Table 1 (data for compounds **1**–**3** are also given for comparison). In all cases, the ^{31}P-{^{1}H} resonances are broad, due to the presence of the quadrupolar boron nucleus *trans* to phosphorus, whilst the small |$^1J_{\mathrm{Pt-P}}$| values are as expected for *cis* co-ordination about platinum(II) but also reflect the large *trans* influence of the boryl group.[9c] The ^{11}B-{^{1}H} resonances occur in the region δ 47–55 consistent with other platinum boryl compounds.[9c]



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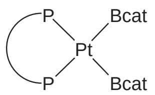


2 PP = dppe; **3** PP = dppb; **4** PP = dcpe

In contrast to the reactions of compound **1** with dppe, dppb and dcpe, that in toluene with 1 equivalent of the more basic diphosphine dmpe [1,2-bis(dimethylphosphino)ethane] was more complicated. After precipitation of all products from toluene by addition of hexane (only PPh$_3$ remained in solution) and redissolving in CD$_2$Cl$_2$, analysis by ^{31}P-{^{1}H} NMR spectroscopy revealed, in addition to traces of unchanged **1**, three resonances with approximately equal intensities each with platinum satellites, one of which (δ_{P} 26.5; $^1J_{\mathrm{Pt-P}}$ = 2397 Hz) is attributed to the ionic platinum(II) compound [Pt(dmpe)$_2$]Cl$_2$ by comparison with data given in ref. 14 (δ_{P} 29.0; $^1J_{\mathrm{Pt-P}}$ = 2352 Hz). We propose that the chloride counter ion derives from the NMR solvent since we observed that [Pt(dmpe)$_2$]Cl$_2$ was formed as the sole product when an excess of dmpe was added to a solution of [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)] in CD$_2$Cl$_2$ at room

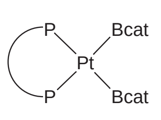
Table 1 The ^{31}P-{^{1}H} and ^{11}B-{^{1}H} NMR data for [Pt(P)$_2$(Bcat)$_2$] compounds[a]

Compound	θ/° ($\tilde{\nu}$[b]/cm^{-1})	Solvent	δ_P ($^1J_{Pt-P}$/Hz)	δ_B
1 *cis*-[Pt(PPh$_3$)$_2$(Bcat)$_2$]	145 (2068.9)	CDCl$_3$	28.7 (1616)	47.0
2 *cis*-[Pt(dppe)(Bcat)$_2$][c]	125	C$_6$D$_6$–thf	57.8 (1454)	48.9
3 *cis*-[Pt(dppb)(Bcat)$_2$][c]		C$_6$D$_6$–thf	21.6 (1589)	48.9
4 *cis*-[Pt(dcpe)(Bcat)$_2$]	142	CH$_3$C$_6$H$_5$	78.1 (1404)	54.5
5 *cis,cis*-[Pt$_2$(μ-dppm)$_2$(Bcat)$_4$][d,e]	121	CD$_2$Cl$_2$	17.3 (1522)	47.5
8 *cis*-[Pt(PMe$_3$)$_2$(Bcat)$_2$]	118 (2064.1)	CD$_2$Cl$_2$	−17.2 (1398)	47.9
9 *cis*-[Pt(PEt$_3$)$_2$(Bcat)$_2$]	132 (2061.7)	C$_6$D$_6$	18.0 (1564)	49.6
10 *cis*-[Pt(PMe$_2$Ph)$_2$(Bcat)$_2$][e,f,g]	122 (2065.3)	C$_6$D$_6$	−5.5 (1537)	48.4
11 *cis*-[Pt(PMePh$_2$)$_2$(Bcat)$_2$][d]	136 (2067.0)	CD$_2$Cl$_2$	9.2 (1594)	47.0
12 *cis*-[Pt{P(OEt)$_3$}$_2$(Bcat)$_2$][e,g]	108 (2077.0)	CD$_2$Cl$_2$	149.9 (2824)	48.0
13 *cis*-[Pt(PCy$_3$)(PPh$_3$)(Bcat)$_2$]	170 (2056.4)	CD$_3$C$_6$D$_5$	36.6 (1713); 23.7 (1564)	48.8
14 *cis*-[Pt(PPh$_3$)$_2${BCl(NMe$_2$)}$_2$]		CD$_3$C$_6$D$_5$	30.4 (1434)	50.8
15 *trans*-[PtCl(PPh$_3$)$_2${BCl(NMe$_2$)}]		CD$_3$C$_6$D$_5$	25.8 (3188)	36.4

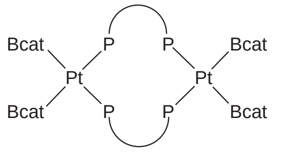
[a] The δ (^{31}P) values reported in ppm with positive shifts downfield relative to 85% H$_3$PO$_4$ at 161.3 (400), 121.5 (300) and 36.1 MHz (90), δ (^{11}B) values in ppm with positive shifts downfield relative to BF$_3$·OEt$_2$ at 128.4 (400), 96.3 (300) and 28.6 MHz (90). [b] Ligand (PR$_3$) cone angle and electronic parameter {$\nu = \nu_{CO}(A_1)$ of [Ni(CO)$_3$L] in CH$_2$Cl$_2$} from ref. 13. [c] Ref. 2(*e*). [d] At −90 °C. [e] Contained unchanged compound **1**. [f] At −55 °C. [g] Contained decomposition products.

temperature, although the presence of traces of DCl cannot be ruled out as a source of chloride. The remaining ^{31}P signals (δ_P 22.3; $^1J_{Pt-P}$ = 3837 Hz; δ_P 36.4; $^1J_{Pt-P}$ = 2041 Hz) arise from compounds which we have not been able to identify. The ^{11}B-{^{1}H} NMR spectrum, however, showed no signals consistent with the presence of a platinum boryl complex although a resonance corresponding to the diborane(4) compound B$_2$(cat)$_2$ was observed indicating the likely reductive elimination of the boryl groups in **1**. Signals due to the compounds B$_2$(cat)$_3$ and [B(cat)$_2$]$^-$, which are often associated with the decomposition of metal–Bcat complexes, were also observed however.[2e,9c]

The reaction of compound **1** in dichloromethane with 1.1 equivalent of dppm [bis(diphenylphosphino)methane] resulted in an orange-red solution (compounds **1**–**4** are colourless or pale yellow) for which only an extremely broad resonance at about δ −8 was seen in the ^{31}P-{^{1}H} spectrum. No platinum satellites were observed but on cooling to −90 °C the spectrum resolved into two major resonances, each with platinum satellites, one corresponding to unchanged **1** and the other (δ_P 17.3; $^1J_{Pt-P}$ = 1522 Hz) characteristic of a new platinum *cis*-bis(boryl) complex **5** [in the presence of an excess of dppm (2.6 equivalents) only **5** was observed]. Additional resonances were also observed at −90° C arising from free PPh$_3$ and dppm together with signals due to traces of other unidentified products. One possible structure for **5** is equivalent to the known structures of **2** and **3**, *i.e.* *cis*-[Pt(dppm)(Bcat)$_2$] **5a**, although in view of the known propensity of dppm to act as a bridging ligand and the observed ^{31}P chemical shift[15] a binuclear structure is more likely, *i.e.* *cis,cis*-[Pt$_2$(μ-dppm)$_2$(Bcat)$_4$] **5b**; the Bcat groups would be expected to be *cis* as observed in the mononuclear examples. The ^{11}B-{^{1}H} NMR spectrum of the reaction mixture at room temperature contained a broad resonance [δ_B 46.9 (C$_7$D$_8$); 47.5 (CD$_2$Cl$_2$)] also consistent with the presence of a metal boryl species.[9c]



5a



5b

PP = dppm

However, crystallisation from the orange-red reaction solution did not afford crystals of compound **5** but rather yielded small quantities of two new materials, one red and the other orange which were both characterised by X-ray crystallography and shown to be [Pt$_2$(PPh$_3$)(μ-dppm)$_2$(Bcat)(μ-Bcat)] **6** (Fig. 1) and [Pt$_2$(κ^1-dppm)(μ-dppm)$_2$(Bcat)(μ-Bcat)] **7** (Fig. 2) respectively; both crystallise as solvates (see Experimental section). Selected bond lengths and angles are given in Table 2. Although both structures are affected by disorder, the basic features of their geometries are well established.

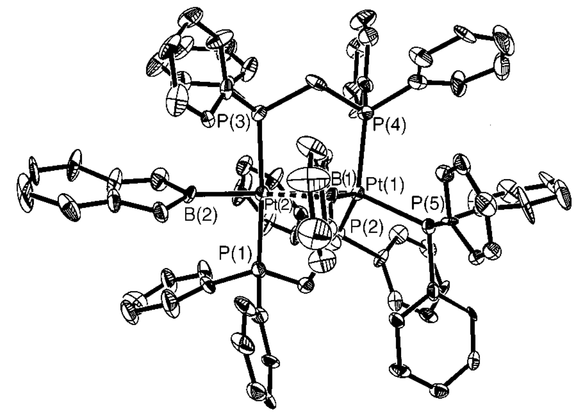


Fig. 1 A view of the molecular structure of compound **6** with key atoms labelled. Ellipsoids are drawn at the 30% probability level and hydrogen atoms have been omitted for clarity. The peculiar nature of some of the ellipsoids is a consequence of disorder problems discussed in the Experimental section.

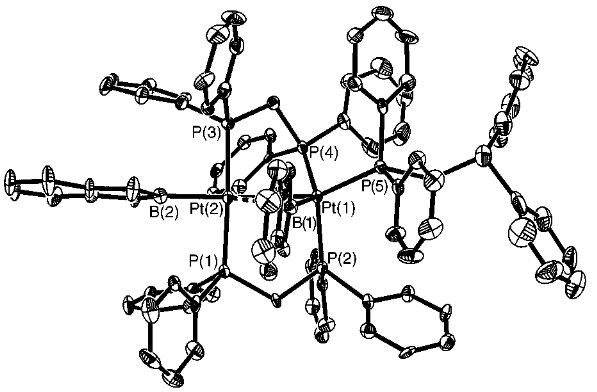


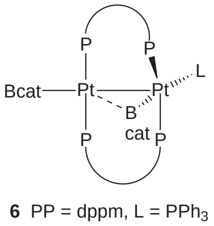
Fig. 2 A view of the molecular structure of compound **7** with key atoms labelled. Ellipsoids are drawn at the 30% probability level and hydrogen atoms have been omitted for clarity.

The two structures are very similar and comprise a Pt$_2$P$_5$B$_2$ core in which the diplatinum moiety [**6**, Pt(1)–Pt(2) 2.7719(13); **7**, 2.7690(8) Å] is bridged by two dppm ligands. In **6**, Pt(1) is also bonded to a PPh$_3$ group whereas in **7** this platinum is linked to one phosphorus of a third dppm ligand, a κ^1-binding mode. The other platinum atom, Pt(2), in both structures

Table 2 Selected bond lenghts (Å) and angles (°) for compounds **6** and **7**

	6	**7**
Pt(1)–Pt(2)	2.7719(13)	2.7690(8)
Pt(1)–B(1)	2.12(2)	2.14(2)
Pt(2)–B(1)	2.49(2)	2.51(2)
Pt(2)–B(2)	2.04(2)	2.06(2)
Pt(1)–P(2)	2.309(5)	2.305(3)
Pt(1)–P(4)	2.334(5)	2.304(3)
Pt(1)–P(5)	2.297(5)	2.303(3)
Pt(2)–P(1)	2.284(5)	2.281(3)
Pt(2)–P(3)	2.302(5)	2.290(3)
B(2)–Pt(2)–Pt(1)	175.2(6)	175.5(4)
B(2)–Pt(2)–P(1)	87.6(6)	88.7(4)
B(2)–Pt(2)–P(3)	88.5(6)	88.8(4)
B(2)–Pt(2)–B(1)	137.7(8)	136.9(5)
P(1)–Pt(2)–P(3)	171.5(2)	172.43(12)
B(1)–Pt(2)–P(1)	98.8(6)	99.4(4)
B(1)–Pt(2)–P(3)	89.1(6)	87.2(4)
Pt(1)–B(1)–Pt(2)	73.5(7)	72.7(5)
Pt(2)–Pt(1)–B(1)	129.0(7)	131.5(4)
Pt(2)–Pt(1)–P(2)	83.32(14)	95.51(8)
Pt(2)–Pt(1)–P(4)	96.04(16)	120.18(12)
Pt(2)–Pt(1)–P(5)	103.1(2)	100.63(12)
B(1)–Pt(1)–P(2)	129.0(7)	96.6(4)
B(1)–Pt(1)–P(4)	97.5(7)	96.6(4)
B(1)–Pt(1)–P(5)	91.4(6)	89.8(4)
P(2)–Pt(1)–P(4)	121.6(2)	120.18(12)
P(2)–Pt(1)–P(5)	103.1(2)	114.66(12)
P(4)–Pt(1)–P(5)	109.6(2)	100.63(12)

carries a terminal Bcat group [**6**, Pt(2)–B(2) 2.04(2); **7**, 2.06(2) Å] whilst the second Bcat group bridges the two platinum centres albeit quite asymmetrically [**6**, Pt(1)–B(1) 2.12(2), Pt(2)–B(1) 2.49(2); **7**, 2.14(2), 2.51(2) Å]. In terms of the Pt–B distances, the values for the Pt(2)–B(2) and Pt(1)–B(1) bonds are typical of platinum boryl bond lengths in a range of platinum bis(boryls),[9c] the latter slightly longer, whereas the Pt(2)–B(1) distance is considerably longer. This observation together with the Pt–Pt bond distances is consistent with a description of **6** and **7** as bis(dppm) bridged platinum(I) dimers in which each platinum carries a terminal Bcat group. In addition, one platinum, Pt(1), is attached to a third two-electron donor ligand (PPh_3 in **6** and a κ^1-dppm in **7**) which results in the Bcat group on that platinum tilting towards the second platinum centre such that a semi-bridging attachment mode is adopted. As far as the geometries around each platinum are concerned, Pt(2) is almost ideally square planar if the long Pt(2)–B(1) bond is ignored [maximum atom deviations from the mean plane are 0.0996 (**6**) and 0.0918 Å (**7**)] whereas Pt(1) adopts an irregular five-co-ordinate geometry. The two boron trigonal planes and the mean square plane around Pt(2) are essentially orthogonal.



6 PP = dppm, L = PPh_3
7 PP = dppm, L = κ^1-dppm

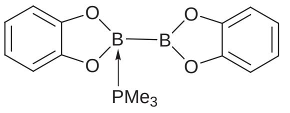
The formulas of compounds **6** and **7** are such that the total valence electron count for the Pt^I_2 unit is 32 and in this sense they are rather unusual. Of the numerous known examples of complexes containing the $Pt_2(dppm)_2$ core, representative examples for comparison are the Pt^{II}_2 compounds $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ (A frame, 32 e$^-$, $\text{Pt}\overset{0}{-}\text{Pt}$; the character above the Pt–Pt bond denotes the formal bond order),[16] $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ (A frame, 30 e$^-$, $\text{Pt}\overset{0}{-}\text{Pt}$),[17] *trans*, *trans*-$[Pt_2(CN)_4(\mu\text{-dppm})_2]$ (32 e$^-$, $\text{Pt}\overset{0}{-}\text{Pt}$),[18] *cis*, *cis*-$[Pt_2Me_4(\mu\text{-dppm})_2]$ (32 e$^-$, $\text{Pt}\overset{0}{-}\text{Pt}$)[19] and $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$ [so-called V frame, 32 e$^-$, $\text{Pt}\overset{1}{-}\text{Pt}$ 2.769(1) Å],[20] the Pt^I_2 compounds $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [30 e$^-$, $\text{Pt}\overset{1}{-}\text{Pt}$ 2.651(1) Å][21] and $[Pt_2H(\kappa^1\text{-dppm})(\mu\text{-dppm})_2][PF_6]$ [30 e$^-$, $\text{Pt}\overset{1}{-}\text{Pt}$ 2.769(1) Å][22] and the Pt^0_2 compound $[Pt_2(\mu\text{-dppm})_3]$ (32 e$^-$, $\text{Pt}\overset{0}{-}\text{Pt}$).[23] With the exception of the Pt^{II}_2 compound $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$ which is described as having a donor–acceptor Pt–Pt bond, only the Pt^I_2 compounds have platinum–platinum (single) bonds. Of the two Pt^I_2 dimers mentioned above, the complex $[Pt_2H(\kappa^1\text{-dppm})(\mu\text{-dppm})_2][PF_6]$ bears most resemblance to **6** and **7** (H^- and $Bcat^-$ are formally analogous) and structurally the $Pt_2(dppm)_2(P)$ core is similar in all three structures. However, the hydride compound has only 30 valence electrons and contains no bridging ligand. In the other complex, $[Pt_2Cl_2(\mu\text{-dppm})_2]$, a terminal chloride is present on each platinum *trans* to the Pt–Pt bond. A structure similar to this, *i.e.* $[Pt_2(\mu\text{-dppm})_2(Bcat)_2]$, is an interesting possibility for a product from the reaction described here and might arise from reductive elimination of $B_2(cat)_2$ from structure **5b** described earlier. We propose, however, that in view of the known high *trans* influence of boryl ligands[9c] and the similarly high *trans* influence of the Pt–Pt bond,[19] a structure such as $[Pt_2(\mu\text{-dppm})_2(Bcat)_2]$ is not favourable and that in order to avoid this mutually *trans* alignment of Pt–B and Pt–Pt bonds one boryl group tips into a *cis*, and ultimately semi-bridging, position thereby generating a vacant co-ordination site at that platinum centre which is filled by a phosphine ligand; PPh_3 in **6** and dppm in **7**. In principle, this might also happen with the other boryl group thereby generating a 34 electron complex $[Pt_2(\mu\text{-dppm})_2(P)_2(Bcat)_2]$ but it is likely that there would be problems of steric conjestion associated with this structure. At this stage, however, it would be unwise to speculate further on precisely what is happening in the reaction between **1** and dppm, but the isolation of complexes containing a bridging boryl group is certainly unusual. The only other example of which we are aware is the rhodium complex $[Rh_2(\mu\text{-}H)_2H(dippe)_2(\mu\text{-Bcat})]$ [dippe = 1,2-bis(diisopropylphosphino)ethane], a 30 e$^-$ complex.[24]

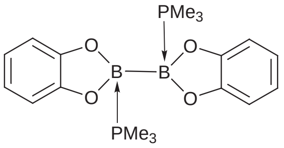
The reactions between compound **1** and two equivalents of a number of monodentate phosphines and phosphites in dichloromethane according to eqn. (1) were also studied. The

$$\begin{array}{ll} cis\text{-}[Pt(PPh_3)_2(Bcat)_2] + 2\,PR_3 \longrightarrow & \\ \qquad\quad \mathbf{1} \qquad\qquad\qquad cis\text{-}[Pt(PR_3)_2(Bcat)_2] + 2\,PPh_3 & (1) \end{array}$$

8, $PR_3 = PMe_3$;
9, $PR_3 = PEt_3$;
10, $PR_3 = PMe_2Ph$;
11, $PR_3 = PMePh_2$;
12, $PR_3 = P(OEt)_3$

compound *cis*-$[Pt(PMe_3)_2(Bcat)_2]$ **8** was formed cleanly when two equivalents of PMe_3 were added (Table 1) but with an excess of PMe_3 some reductive elimination of $B_2(cat)_2$ was evident with concomitant formation of platinum(0) products. At first sight this observed reductive elimination was surprising since a more basic phosphine such as PMe_3 should favour the higher oxidation state, in this case Pt^{II}, in any reductive elimination/oxidative addition equilibrium. However, a more detailed analysis of the ^{31}P and ^{11}B NMR spectra revealed the presence of the mono and bis adducts of $B_2(cat)_2$, namely $[B_2(cat)_2(PMe_3)]$ and $[B_2(cat)_2(PMe_3)_2]$ formed from the reaction between an excess of PMe_3 and $B_2(cat)_2$. Their formation was confirmed in a separate experiment in which PMe_3 was added to a $CHCl_3$ solution of $B_2(cat)_2$ and spectroscopic data for both products are given in the Experimental section. Mono and bis adducts of diborane(4) compounds with two-electron donor





ligands, including phosphines, have been observed previously as described in ref. 25.†

The reaction between compound **1** and either PEt_3, PMe_2Ph or $PMePh_2$ in dichloromethane afforded the compounds *cis*-$[Pt(PEt_3)_2(Bcat)_2]$ **9**, *cis*-$[Pt(PMe_2Ph)_2(Bcat)_2]$ **10** and *cis*-$[Pt(PMePh_2)_2(Bcat)_2]$ **11** as the major products although small quantities of some other platinum–phosphine species were also evident. Thus with PMe_2Ph small amounts of the mixed phosphine platinum(0) complex $[Pt(PPh_3)_2(PMe_2Ph)_2]$ [which has been previously reported:[26] $\delta_P(CH_3CN)$ 15.1, −38.3, $^1J_{Pt-P} =$ 3779, 3900 Hz, *cf.* δ_P 14.6, −39.8, $^1J_{Pt-P} = 3774$, 3802 Hz from ref. 26] were observed. Decomposition products such as $[Pt(PPh_3)_2(PMe_2Ph)_2]$ are not unexpected in reactions such as those described here, however, in view of the known sensitivity of metal boryl compounds in solution; see for example ref. 12. In the case of compound **11**, ^{31}P NMR spectroscopy showed a characteristic broad signal with ^{195}Pt satellites (Table 1) and a similarly characteristic platinum boryl resonance was observed in the ^{11}B NMR spectrum. Only at −90 °C, however, was the ^{31}P spectrum clearly resolved since at room temperature even a trace excess of $PMePh_2$ resulted in very broad signals due, presumably, to phosphine exchange processes. Similar observations were made for some related rhodium complexes.[12] With less than two equivalents of $PMePh_2$, the ^{31}P spectrum showed only **11** and unchanged **1** with no evidence for a mixed phosphine species.

When the phosphite ligand $P(OEt)_3$ was used the boryl complex *cis*-$[Pt\{P(OEt)_3\}_2(Bcat)_2]$ **12** was produced as the major product together with minor amounts of $[Pt\{P(OEt)_3\}_4]$ (δ_P 128.6, $^1J_{Pt-P} = 5386$ Hz)[27] and some unchanged **1**. The use of $P(OMe)_3$, however, resulted exclusively in the rapid formation of $[Pt\{P(OMe)_3\}_4]$ (δ_P 133.4, $^1J_{Pt-P} = 5403$ Hz) with no new platinum(II) bis(boryl) complex evident; $B_2(cat)_2$ was observed in the ^{11}B-$\{^1H\}$ NMR spectrum.

In the reaction between compound **1** and two equivalents of PCy_3 in toluene the mixed phosphine compound *cis*-$[Pt(PCy_3)(PPh_3)(Bcat)_2]$ **13** was produced [eqn. (2)] as evidenced

$$\underset{\mathbf{1}}{[Pt(PPh_3)_2(Bcat)_2]} + 2\,PCy_3 \longrightarrow \underset{\mathbf{13}}{[Pt(PCy_3)(PPh_3)(Bcat)_2]} + PPh_3 + PCy_3 \quad (2)$$

by the presence of two broad resonances in the ^{31}P-$\{^1H\}$ NMR spectrum each with platinum satellites (δ_P 36.6, 23.7, $^1J_{Pt-P} = 1713, 1564$ Hz). Additional resonances (δ_P 9.2 and −5.8) indicated that both PCy_3 and PPh_3 were also present as "unbound" ligands consistent with the formula of **13** and the reaction stoichiometry. The chemically inequivalent boryl ligands were not resolved by ^{11}B-$\{^1H\}$ NMR which displayed only a single broad resonance at δ_B 48.8. Even in the presence of excess of PCy_3 no evidence of a bis-PCy_3 boryl complex was observed.

Slow diffusion of hexane into a toluene solution of compound **13** resulted in a colourless crystalline precipitate containing free PPh_3 and **13**. The structure of **13** was confirmed by X-ray crystallography (Fig. 3) selected bond lengths and angles for which are given in Table 3. The structure of **13** adopts the expected square planar co-ordination geometry around the platinum centre (maximum atom deviation from the PtP_2B_2 mean plane is 0.0614 Å) with the boryls in a *cis* configuration and oriented approximately perpendicular to the platinum square plane [B(1) 74.8° and B(2) 70.2°]. In most respects the structure differs in no significant way from those of other platinum(II) *cis*-bis(boryls),[2b,c,e,3b,7–9] but there is still some discussion in the literature as to the extent of any platinum to boron π-back bonding[9c] and having an unsymmetrical species such as **13** where each Bcat group is *trans* to a different phosphine could therefore offer some structural data relevant to this matter. The two Pt–B bond lengths, however, are the same within experimental error [Pt(1)–B(1) 2.044(4), Pt(1)–B(2) 2.050(4) Å] although the two Pt–P distances are slightly different [Pt(1)–P(1) 2.3824(11), Pt(1)–P(2) 2.3456(10) Å] with that to the PCy_3 ligand being the longer. Thus, whatever factors influence the Pt–P bond lengths, there is clearly no effect on the *trans* Pt–B distances and therefore, by implication, the extent of any Pt–B π bonding at least on the basis of bond lengths.

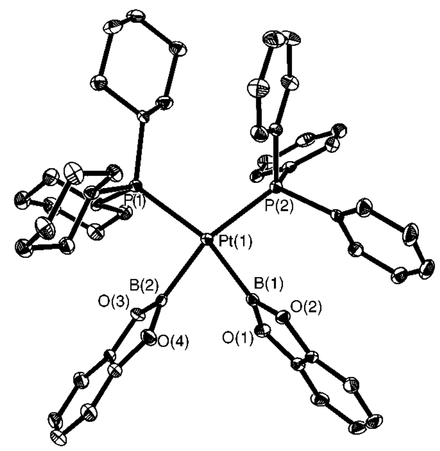


Fig. 3 A view of the molecular structure of compound **13** with key atoms labelled. Details as in Fig. 2.

Table 3 Selected bond lengths (Å) and angles (°) for compound **13**

Pt(1)–B(1)	2.044(4)	Pt(1)–P(1)	2.3824(11)
Pt(1)–B(2)	2.050(4)	Pt(1)–P(2)	2.3456(10)
B(1)–Pt(1)–B(2)	73.3(2)	B(2)–Pt(1)–P(1)	90.84(12)
B(1)–Pt(1)–P(1)	163.91(12)	B(2)–Pt(1)–P(2)	163.10(12)
B(1)–Pt(1)–P(2)	90.13(12)	P(1)–Pt(1)–P(2)	105.84(4)

As a conclusion to this section on phosphine substitution reactions it is useful to look for any apparent trends. Clearly the chelating diphosphines all readily substitute PPh_3 in a manner consistent with the chelate effect. The phosphines dppe, dppb and dcpe all do this cleanly to afford new *cis*-bis(boryls), whereas dmpe leads to extensive decomposition involving the solvent, and dppm results in products which reflect the propensity of this diphosphine to act as a bridging ligand. With regard to the monodentate tertiary phosphine ligands, all of those studied substitute both PPh_3 ligands with the exception of PCy_3, the latter possibly due to steric effects. Small amounts of decomposition products are evident in many cases comprising platinum(0) species and boron compounds such as $B_2(cat)_3$ and $[B(cat)_2]^-$. Reductive elimination of $B_2(cat)_2$ does not seem to be a major process consistent with the expectation that more basic phosphines should favour the Pt(II) product. In the case of the reaction with PMe_3, however, the products of reductive elimination are seen although this is most likely due to the fact that the $B_2(cat)_2$ produced is removed from the system through

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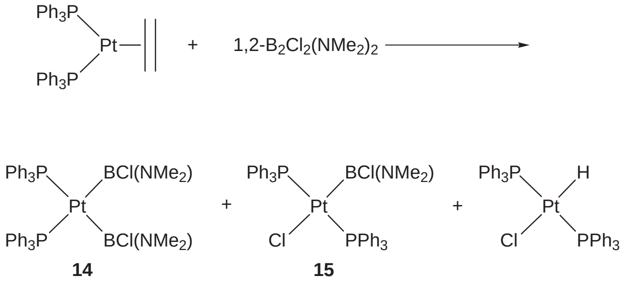
† Diborane(4) compounds with diolate groups have previously only been observed to form adducts with nitrogen bases such as amines and pyridines whereas the more Lewis acidic dithiolate derivatives form adducts with phosphine ligands as well.[25b] The PMe_3 adducts of $B_2(cat)_2$ are therefore the first reported adducts of a diolate diborane(4) compound with a phosphine. We should note, however, that in ref. 25(a), it was mentioned in a concluding sentence that $B_2(cat)_2$ showed no evidence for adduct formation with PMe_3, an assertion which is now clearly seen to have been in error.

formation of adducts with PMe_3; the other phosphines studied here do not form adducts with this diborane(4) compound. In the case of the two phosphites studied, their enhanced π-acceptor capabilities should serve to stabilise the homoleptic platinum(0) complexes observed thereby accounting for the observed facile elimination of $B_2(cat)_2$ particularly in the case of $P(OMe)_3$.

As mentioned above in the discussion of Pt–B π bonding in compound **13**, this feature of the bonding in metal boryls remains unresolved and one which this study was, in part, designed to address. Most of the platinum boryls sructurally characterised to date have involved either diolate or dithiolate groups bonded to the boron,[2b,c,e,3b,7,9] although the BF_2 complex described in ref. 8 is an exception. In order to extend the range of boryl substituents we looked at the oxidative addition reaction of 1,2-$B_2Cl_2(NMe_2)_2$ with $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$. Oxidative addition of this diborane(4) compound to metal centres has been little studied, although recent work by Braunschweig and co-workers[10,11] has established that it is an effective source of diboran(4)yl and borylene ligands in certain cases.

The reaction between $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ and one equivalent of 1,2-$B_2Cl_2(NMe_2)_2$ in toluene or benzene was monitored by ^{31}P NMR spectroscopy which revealed the presence of new products in addition to substantial amounts of unchanged starting materials. With an excess of 1,2-$B_2Cl_2(NMe_2)_2$ (≈3.5 equivalents) all of the platinum starting material was consumed and three new products were formed as shown in Scheme 1 although the distribution of these products changed over time.



Scheme 1

One of the three products was identified as the known compound *trans*-$[PtH(Cl)(PPh_3)_2]$ (δ_P 28.6, $^1J_{Pt-P} = 3022$ Hz)[2e] whilst NMR spectroscopic data (Table 1) for the other two were consistent with the formulas *cis*-$[Pt(PPh_3)_2\{BCl(NMe_2)\}_2]$ **14** and *trans*-$[PtCl(PPh_3)_2\{BCl(NMe_2)\}]$ **15**. Compound **14** is present as the major species early in the reaction but after prolonged reaction times **15** starts to dominate. The amount of the hydride *trans*-$[PtH(Cl)(PPh_3)_2]$ present does not change over time indicating that this is probably a side product possibly resulting from some initial degree of hydrolysis but since the mechanism of this reaction, particularly the apparent transformation of **14** into **15**, is unclear, any further speculation is unwarranted. The ^1H NMR spectra for both **14** and **15** show two sets of methyl resonances consistent with hindered rotation about the B–N bonds.

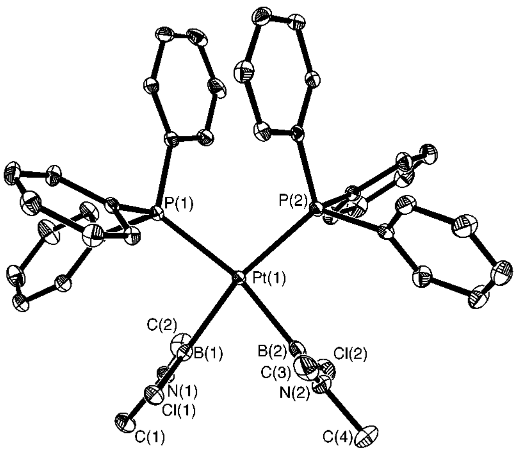


Fig. 4 A view of the molecular structure of compound **14** with key atoms labelled. Details as in Fig. 2.

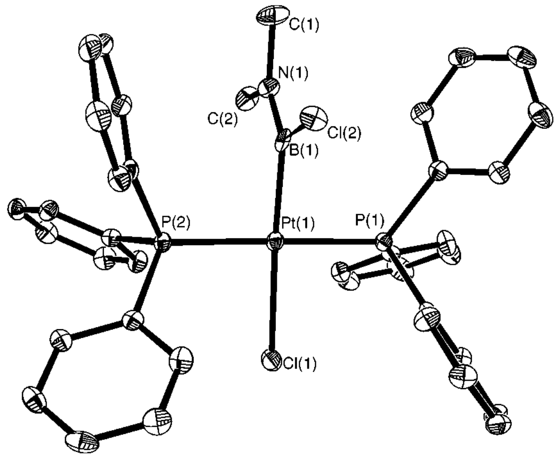


Fig. 5 A view of the molecular structure of compound **15** with key atoms labelled. Details as in Fig. 2. Only the major component of the disorder associated with the $BCl(NMe_2)$ ligand is shown.

Table 4 Selected bond lengths (Å) and angles (°) for compound **14**

Pt(1)–B(1)	2.084(3)	B(1)–N(1)	1.378(4)
Pt(1)–B(2)	2.076(4)	B(2)–N(2)	1.379(5)
Pt(1)–P(1)	2.3445(8)	B(1)–Cl(1)	1.861(4)
Pt(1)–P(2)	2.3382(7)	B(2)–Cl(2)	1.854(4)
B(1)–Pt(1)–B(2)	75.15(13)	Pt(1)–B(1)–N(1)	128.7(3)
B(1)–Pt(1)–P(1)	92.48(9)	Pt(1)–B(1)–Cl(1)	117.0(2)
B(1)–Pt(1)–P(2)	167.31(9)	Cl(1)–B(1)–N(1)	114.3(2)
B(2)–Pt(1)–P(1)	167.63(9)	Pt(1)–B(2)–N(2)	127.6(3)
B(2)–Pt(1)–P(2)	92.23(9)	Pt(1)–B(2)–Cl(2)	117.5(2)
P(1)–Pt(1)–P(2)	100.13(3)	Cl(2)–B(2)–N(2)	114.8(3)

Table 5 Selected bond lengths (Å) and angles (°) for compound **15**

Pt(1)–B(1)	2.075(10)	Pt(1)–P(1)	2.291(2)
Pt(1)–Cl(1)	2.470(2)	Pt(1)–P(2)	2.288(2)
B(1)–Pt(1)–Cl(1)	175.9(2)	Cl(1)–Pt(1)–P(1)	87.79(4)
B(1)–Pt(1)–P(1)	90.4(2)	Cl(1)–Pt(1)–P(2)	91.82(4)
B(1)–Pt(1)–P(2)	89.9(2)	P(1)–Pt(1)–P(2)	178.73(5)

Crystals of both compounds **14** and **15** were obtained from toluene–hexane mixtures and the structures of both were determined by X-ray crystallography. Views of the two structures are shown in Figs. 4 and 5 and selected bond lengths and angles are presented in Tables 4 and 5. Compound **14** (Fig. 4), which crystallises as a toluene solvate, adopts a structure typical for this class of bis(boryl) compound[2b,c,e,3b,7–9] for which the notable parameters are the distances Pt(1)–B(1) 2.084(3) and Pt(1)–B(2) 2.076(4) Å and the angles B(1)–Pt(1)–B(2) 75.15(13) and P(1)–Pt(1)–P(2) 100.13(3)° all of which lie within previously observed ranges.[9c] All non-hydrogen atoms in each boryl ligand are essentially coplanar, allowing for B–N π overlap, these planes being nearly orthogonal to the mean platinum square plane [dihedral angles: B(1), 86.5°; B(2), 80.1°]. The structures of platinum(II) *cis*-bis(boryls) have been discussed in detail [see ref. 9(*c*) and refs. therein] and no further comment will be made here except to note that the Pt–B bond lengths are not significantly different from those observed in a range of diolate substituted species.[9c] On this basis, there is no real structural evidence to indicate whether the $BCl(NMe_2)$ boryl group is any better or worse as a π acceptor than other types of boryl ligands. Indeed, in a range of structures with differing boryl substituents and various phosphines, the Pt–B distances all lie within a fairly narrow range[9c] which might be taken as evidence for little Pt–B π bonding although small differences in extent may not be reflected in significant bond length variations.

The structure of compound **15** (Fig. 5) is similar to that of *trans*-[PtCl(PPh$_3$)$_2$(Bcat)].[7] In **14** the boryl groups avoid a mutually *trans* configuration due to their high *trans* influence but in **15** the presence of the weaker *trans* influence chloride allows for the observed *trans* configuration. In contrast to *trans*-[PtCl(PPh$_3$)$_2$(Bcat)] which has quite a short Pt–B bond [2.008(8) Å],[7] the Pt–B bond in **15** [Pt(1)–B(1) 2.075(10) Å] is closer to those bonds found in **14**. Some care should be exercised in discussing the metric parameters associated with the boryl (and chlorine) group in **15**, however, due to a degree of disorder associated with the orientation of the boryl group as discussed in the Experimental section.

In conclusion, we have shown that the phosphine ligands in compound **1** are labile and readily substituted by a range of more basic monodentate tertiary phosphines and diphosphines. Whilst it has previously been demonstrated that platinum bis(boryls) with chelating diphosphines are not active diboration catalysts, consistent with the active catalytic species having only one bound phosphine,[2e] compounds such as **8**–**12** and particularly **13** are currently being examined for their effectiveness in catalysing the diboration of alkynes and other unsaturated species. These studies together with results which demonstrate that **14** is a very effective catalyst precursor for the addition of 1,2-B$_2$Cl$_2$(NMe$_2$)$_2$ to alkynes will form the basis of a future report. In terms of any structural insight into the nature of the Pt–B bond in platinum(II), *cis*-bis(boryls), the results described here for **13** and **14**, together with the results of previous structural studies,[9c] show that the Pt–B bond lengths as well as the orientations of the boryl ligands with respect to the platinum square plane show little variation as a function of the groups bound to boron or the nature of the phosphine bound to platinum.

Experimental

General procedures

Except where indicated all operations were carried out under dry dinitrogen or argon atmospheres using standard Schlenk and vacuum line techniques. All non-deuteriated solvents used were distilled over appropriate drying agents prior to use. Deuteriated solvents were dried over molecular sieves and degassed by three freeze–pump–thaw cycles under nitrogen.

High field NMR spectra were recorded using a JEOL GX-400 spectrometer [^{11}B-{^{1}H} at 128.4 MHz and ^{31}P-{^{1}H} at 161.3 MHz], a JEOL Lambda 300 spectrometer [^{11}B-{^{1}H} at 96.3 MHz and ^{31}P-{^{1}H} at 121.5 MHz] or a JEOL EX-90 spectrometer [^{11}B-{^{1}H} at 26.8 MHz and ^{31}P-{^{1}H} at 36.1 MHz]. Chemical shifts are reported in ppm relative to external or internal (JEOL EX-90) BF$_3$·Et$_2$O and 85% H$_3$PO$_4$.

Compound **1**[2e] was prepared from the reaction between [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)][28] and B$_2$(cat)$_2$.[29] The compound 1,2-B$_2$Cl$_2$(NMe$_2$)$_2$ was prepared according to the literature method.[30] The phosphines dppm, dmpe, dcpe and PCy$_3$ were used as purchased without further purification, while PMe$_3$, PEt$_3$, PMe$_2$Ph, PMePh$_2$, P(OEt)$_3$ and P(OMe)$_3$ were distilled under argon and stored over molecular sieves (3 Å).

Liquid phosphines and phosphites were as added as stock solutions (EX-90) or neat *via* micro-syringe (Lambda 300, GX-400) depending on the instrumentation for characterisation. Typical reactions are described below. Unless otherwise indicated, the presence of trace amounts of diborane(4) decomposition products were apparent in the ^{11}B-{^{1}H} NMR spectra of several solutions due to reactions with trace amounts of atmospheric moisture or oxygen. The ^{31}P-{^{1}H} and ^{11}B-{^{1}H} NMR data for all new complexes are given in Table 1.

Preparations and reactions

***cis*-[Pt(dcpe)(Bcat)$_2$] 4.** Samples of compound **1** (0.100 g, 0.095 mmol) and dcpe (0.040 g, 0.095 mmol) were transferred to a 10 cm^3 Young's tap NMR tube and dissolved in toluene (≈2 cm^3) resulting in a pale yellow solution. The solution was analysed by ^{31}P-{^{1}H} and ^{11}B-{^{1}H} NMR spectroscopy which showed essentially quantitative conversion into **4**. The reaction solution was then layered with hexane (≈3.0 cm^3) but solvent diffusion at room temperature afforded only oils and incomplete separation of PPh$_3$; no analytically pure samples of **4** were obtained. The reaction between **1** and dmpe was carried out similarly. Precipitation of the products directly from toluene afforded a white solid which was redissolved in CD$_2$Cl$_2$ and analysed by ^{31}P NMR spectroscopy.

The reaction between compound 1 and dppm. Samples of compound **1** (0.150 g, 0.143 mmol) and dppm (0.062 g, 0.161 mmol, 1.1 equivalents) were added to a 5 cm^3 Young's tap NMR tube and dissolved in CD$_2$Cl$_2$ (≈0.75 cm^3) resulting in an orange solution which became red over time. Analysis by ^{31}P-{^{1}H} and ^{11}B-{^{1}H} NMR spectroscopy at room temperature and −90 °C (see text for details) showed the presence of **5** as the major product. The reaction solution was then layered with hexane (≈3 cm^3) and solvent diffusion over a period of days at room temperature afforded red crystals of **6** and minor quantities of orange crystals of **7**. When 2.6 molar equivalents of dppm were used larger quantities of **7** were obtained but in neither reaction were the yields of **6**/**7** high although crystals of each compound were suitable for X-ray crystallography. Compound **5** could not be isolated as a solid (see Table 1 for NMR data) and obtaining satisfactory analytical data and NMR spectra for **6** and **7** was hampered by low yields and the fact that both compounds crystallised together making separation difficult.

***cis*-[Pt(PMePh$_2$)$_2$(Bcat)$_2$] 11.** A sample of compound **1** (0.100 g, 0.095 mmol) was transferred to a 5 cm^3, Young's tap NMR tube and dissolved in CD$_2$Cl$_2$ (≈0.75 cm^3) to which PMePh$_2$ (36 μL, 0.19 mmol) was added *via* syringe resulting in an orange solution. Analysis by ^{31}P-{^{1}H} and ^{11}B-{^{1}H} NMR spectroscopy revealed the presence of **11** in essentially quantitative yield although attempts at crystallisation did not afford analytically pure samples as only oily products were obtained. The reactions with PMe$_3$, PEt$_3$, PMe$_2$Ph, P(OEt)$_3$ and P(OMe)$_3$ were performed similarly, NMR data for which are given in Table 1 and, where appropriate, in the text. In the case of the reaction with PMe$_3$ evidence for the presence of the PMe$_3$ adducts of B$_2$(cat)$_2$ was obtained when an excess of PMe$_3$ was used. These adducts were also prepared by addition of two equivalents of PMe$_3$ to B$_2$(cat)$_2$ in CHCl$_3$: NMR, [B$_2$(cat)$_2$(PMe$_3$)], ^{11}B-{^{1}H} δ 37.6 (B) and −14.6 (Me$_3$P→B), ^{31}P-{^{1}H} −12.2; [B$_2$(cat)$_2$(PMe$_3$)$_2$], ^{11}B-{^{1}H} δ 1.5, ^{31}P-{^{1}H} δ −4.5.

***cis*-[Pt(PCy$_3$)(PPh$_3$)(Bcat)$_2$] 13.** Samples of compound **1** (0.075 g, 0.071 mmol) and PCy$_3$ (0.044 g, 0.157 mmol) were added to a 10 cm^3 Young's tap NMR tube and dissolved in CD$_3$C$_6$D$_5$ (≈3 cm^3) resulting in a pale yellow suspension which was gently warmed until all solids had dissolved. Analysis by ^{31}P-{^{1}H} and ^{11}B-{^{1}H} NMR spectroscopy showed essentially quantitative conversion into **13**. Addition of an overlayer of *n*-hexane (≈3 cm^3) and subsequent solvent diffusion at room temperature afforded intimate mixtures of of PPh$_3$ and **13** which prevented obtaining satisfactory elemental analytical data.

The reaction between [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)] and 1,2-B$_2$Cl$_2$(NMe$_2$)$_2$. A sample of [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)] (0.100 g, 0.134

Table 6 Selected crystallographic details for the complexes **6**·CH_2Cl_2, **7**·0.15 C_6H_{14}·0.69 CH_2Cl_2, **13**, **14**·0.5 $CD_3C_6D_5$ and **15**

	6·CH_2Cl_2	**7**·0.15 C_6H_{14}·0.69 CH_2Cl_2	**13**	**14**·0.5 $CD_3C_6D_5$	**15**
Empirical formula	$C_{81}H_{69}B_2Cl_2O_4P_5Pt_2$	$C_{88.61}H_{77.54}B_2Cl_{1.38}O_4P_6Pt_2$	$C_{48}H_{56}B_2O_4P_2Pt$	$C_{43.5}H_{45.5}B_2Cl_2N_2P_2Pt$	$C_{38}H_{36}BCl_2NP_2Pt$
Formula weight	1743.91	1853.14	975.58	945.87	845.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	47.493(13)	22.880(4)	16.752(3)	11.2268(10)	10.865(5)
b/Å	12.601(3)	14.210(2)	12.174(2)	12.0715(14)	12.093(6)
c/Å	24.635(7)	26.731(4)	22.850(2)	17.3490(30)	14.228(5)
α/°				85.897(8)	95.819(6)
β/°	96.442(14)	114.248(10)	111.428(10)	72.861(10)	92.523(10)
γ/°				69.461(8)	105.637(6)
V/Å^3	14651(7)	7924(2)	4337.9(11)	2102.6(5)	1786.1(13)
T/K	173(2)	173(2)	173(2)	173(2)	173(2)
Z	8	4	4	2	2
μ/mm^{-1}	4.047	3.746	3.352	3.572	4.195
Total reflections	33762	60301	27083	21868	14303
Independent reflections	11470	12447	9917	9499	5583
R_{int}	0.1854	0.1562	0.0517	0.0315	0.0478
$R1$ [$I > 2\sigma(I)$] (data)	0.0823 (5148)	0.0656 (7765)	0.0356 (7258)	0.0240 (8089)	0.0307 (4722)
Extinction coefficient	—	0.00014(2)	0.00020(2)	0.00051(7)	—

mmol) was placed into a scintillation vial to which a solution of 1,2-$B_2Cl_2(NMe_2)_2$ (0.080 g, 0.443 mmol) in C_6D_6 (or $CD_3C_6D_5$, $CH_3C_6H_5$) (≈1 cm^3) was added *via* pipette. The resulting solution was then stirred for one hour and transferred to a NMR tube and analysed by $^{31}P-\{^1H\}$ and $^{11}B-\{^1H\}$ NMR spectroscopy after which it was transferred to a clean scintillation vial. Colourless crystals of **14** and **15** suitable for X-ray crystallography were obtained by slow diffusion of *n*-hexane (≈10 cm^3) into the reaction mixture over a period of three days at room temperature. Satisfactory elemental analysis could not be obtained due to the co-crystallisation of the two products. ^1H NMR: for **14** ($CD_3C_6D_5$), δ 7.58 (m, 12 H, PPh_3), 6.92 (m, 18 H, PPh_3), 2.87 (s, 6 H, NMe_2) and 2.57 (s, 6 H, NMe_2); for **15** (C_6D_6), δ 7.96 (m, 12 H, PPh_3), 7.05 (m, 18 H, PPh_3), 2.46 (s, 3 H, NMe_2) and 1.91 (s, 3 H, NMe_2); for *trans*-[PtH(Cl)(PPh_3)$_2$] (C_6D_6), δ 7.86 (m, 12 H, PPh_3), 7.03 (m, 18 H, PPh_3) and −15.3 (dt, 1 H, $^1J_{Pt-H}$ 1163, $^2J_{P-H}$ 12 Hz); ^{31}P and ^{11}B NMR data are given in Table 1.

X-Ray crystallography

Crystals were mounted in inert oil under a stream of argon and transferred to the cold gas stream of the diffractometer. Crystallographic data for compounds **6**, **7**, **13**, **14** and **15** (**6**, **7** and **14** as solvates) are presented in Table 6. Measurements were made on a Siemens SMART CCD area detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω, with the total data set being more than a hemisphere in each case. Absorption corrections were applied, based on multiple and symmetry equivalent measurements. The structures were solved and refined by standard methods.[31]

The high values of R_{int} for complexes **6** and **7** are probably caused by loss of solvent from the crystals prior to mounting on the diffractometer. No crystal decay was observed over the data collection period in either case. The crystal structure of **6** contains 2 solvent molecules of dichloromethane (deuteriated), one of which is disordered over an inversion centre and the other exists in two different orientations. The crystal structure of **7** contains disordered hexane and dichloromethane (deuteriated) in the ratio 0.15:0.69. The consequences of the disordered solvent in these structures are evident in the displacement parameters of atoms in the Bcat ligands which are themselves somewhat disordered. The crystal structure of **14** contains toluene which is disordered over an inversion centre. That of **15** shows two orientations of the BCl(NMe_2) ligand, related by a 180° rotation about the Pt–B bond, which are disordered in the ratio 0.76:0.24. A second position for the *trans* chloride could not be located in the difference map.

CCDC reference number 186/1386.

See http://www.rsc.org/suppdata/dt/1999/1687/ for crystallographic files in .cif format.

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