

# Oxidative addition of boron–boron, boron–chlorine and boron–bromine bonds to platinum(0)<sup>1</sup>

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## Abstract

The synthesis and spectroscopic characterisation of the new diborane(4) compounds  $B_2(1,2-O_2C_6Cl_4)_2$  and  $B_2(1,2-O_2C_6Br_4)_2$  are reported together with the diborane(4) *bis*-amine adduct  $[B_2(\text{calix})(\text{NHMe}_2)_2]$  (calix = Bu<sup>t</sup>calix[4]arene). B–B bond oxidative addition reactions between the platinum(0) compound  $[Pt(PPh_3)_2(\eta-C_2H_4)]$  and the diborane(4) compounds  $B_2(1,2-S_2C_6H_4)_2$ ,  $B_2(1,2-O_2C_6Cl_4)_2$  and  $B_2(1,2-O_2C_6Br_4)_2$  are also described which result in the platinum(II) *bis*-boryl complexes *cis*- $[Pt(PPh_3)_2\{B(1,2-S_2C_6H_4)\}_2]$ , *cis*- $[Pt(PPh_3)_2\{B(1,2-O_2C_6Cl_4)\}_2]$  and *cis*- $[Pt(PPh_3)_2\{B(1,2-O_2C_6Br_4)\}_2]$  respectively, the former two having been characterised by X-ray crystallography. In addition, the platinum complex  $[Pt(PPh_3)_2(\eta-C_2H_4)]$  reacts with  $XB(1,2-O_2C_6H_4)$  (X = Cl, Br) affording the *mono*-boryl complexes *trans*- $[PtX(PPh_3)_2\{B(1,2-O_2C_6H_4)\}]$  as a result of oxidative addition of the B–X bonds to the Pt(0) centre; the chloro derivative has been characterised by X-ray crystallography. © 1998 Elsevier Science S.A.

## 1. Introduction

A key mechanistic feature of the transition metal catalysed diboration of alkenes [1], alkynes [2–6] and 1,3-dienes [7] is the oxidative addition of the B–B bond in diborane(4) compounds ( $R_2B-BR_2$ ) to a low-valent transition metal centre resulting in metal boryl species,  $M-BR_2$ . Such species have also been implicated in the palladium catalysed cross-coupling of diborane(4) compounds with haloarenes [8,9], and crystallographically characterised examples of metal boryls resulting from B–B bond oxidative addition to tungsten(II) [10,11],

iron(0) [12], cobalt(0) [13], rhodium(I) [14–16], iridium(I) [17] and platinum(0) [3,4,6] centres have now been described. Structurally characterised examples of metal boryls also include complexes of tantalum [18], tungsten [19], manganese [20], iron [21], rhodium [22] and iridium [23–26].

In addition to complexes deriving from B–B bond oxidative addition, a number of related studies have focussed on the oxidative addition of Si–Si, Ge–Ge, Sn–Sn, B–Si, B–Sn, Si–Cl, Si–Br, P–Se, S–S and Se–Se bonds to either palladium(0) or platinum(0) centres (and, in the case of Si–Cl, iridium(I))<sup>3</sup>. Herein we describe further studies of the oxidative addition of B–B bonds to platinum(0) together with examples of B–Cl and B–Br bond oxidative addition reactions.

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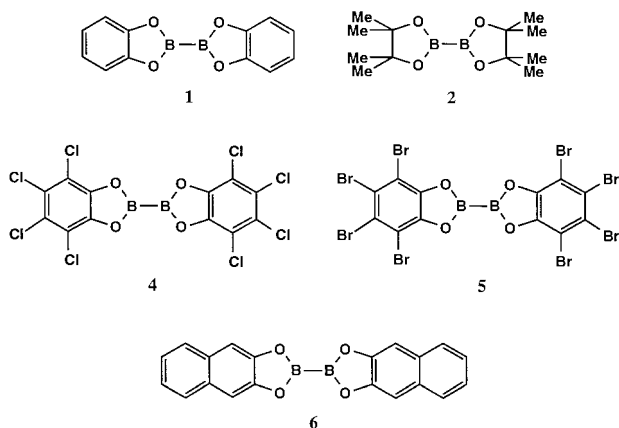
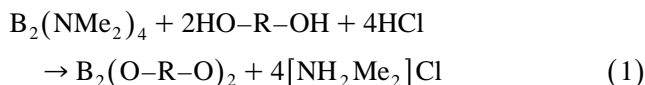
<sup>1</sup> Dedicated to Professor Ken Wade on the occasion of his 65th birthday and in recognition of his outstanding contributions to the understanding of the chemistry of boron.

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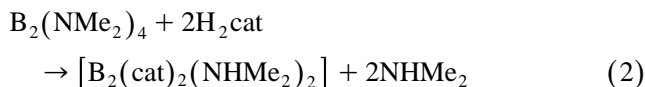
<sup>3</sup> For selected examples, see the following: for Si–Si, Ref. [27]; for Ge–Ge, Ref. [28]; for Sn–Sn, Ref. [29]; for B–Si, Ref. [30]; for B–Sn, Ref. [31]; for Si–Br, Ref. [32]; for Si–Cl, Ref. [33]; for P–Se, Ref. [34]; for S–S and Se–Se, Ref. [35].

## 2. Results and discussion

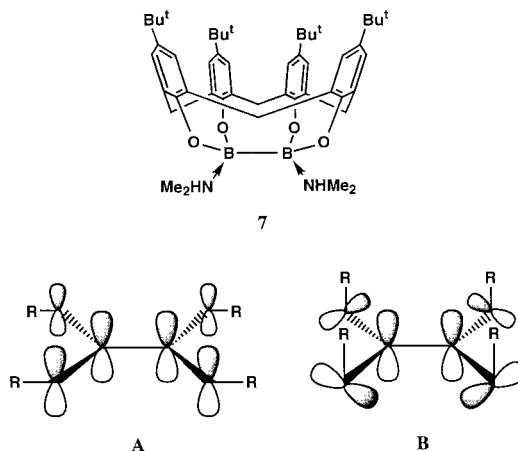
The diborane(4) compounds which have been most studied with respect to metal catalysed diboration and B–B bond oxidative addition reactions are the catecholate and pinacolate species  $B_2(1,2-O_2C_6H_4)_2$  (**1**) [36,37] and  $B_2(OCMe_2CMe_2O)_2$  (**2**) [38], although the substituted catecholate derivatives  $B_2(1,2-O_2-3-MeC_6H_3)_2$ ,  $B_2(1,2-O_2-4-MeC_6H_3)_2$ ,  $B_2(1,2-O_2-4-Bu^tC_6H_3)_2$ ,  $B_2(1,2-O_2-3,5-Bu^tC_6H_2)_2$  and  $B_2(1,2-O_2-3-MeOC_6H_3)_2$  have also been characterised in addition to the thiocatecholate compound  $B_2(1,2-S_2C_6H_4)_2$  (**3**) [36,37]. The synthetic route to all of the catecholate and thiocatecholate species mentioned here has been described in detail in Ref. [36] and is summarised in Eq. (1). Herein, we provide synthetic and spectroscopic data for two new compounds of this class, namely the tetrahalocatecholate species  $B_2(1,2-O_2C_6Cl_4)_2$  (**4**) and  $B_2(1,2-O_2C_6Br_4)_2$  (**5**). An attempted preparation of the diborane(4) compound  $B_2(1,2-O_2C_{10}H_6)_2$  (**6**), derived from  $B_2(NMe_2)_4$  and naphthalene-1,2-diol, was hampered by its extreme insolubility.



In all of the catecholate or thiocatecholate diborane(4) compounds mentioned above, the initial reaction between  $B_2(NMe_2)_4$  and the catechol or thiocatechol proceeds to afford *bis*-amine adducts of the form  $[B_2(cat)_2(NHMe_2)_2]$  (cat = general catecholate group) according to Eq. (2), the role of the HCl in Eq. (1) thus being to remove both free and coordinated amine,  $NHMe_2$ , as the ammonium salt  $[NH_2Me_2]Cl$  [36]. In general, the alkoxy diborane(4) compounds such as **2** and  $B_2(OCH_2CMe_2CH_2O)_2$  [36] are insufficiently Lewis acidic at the boron centre to coordinate amine.



An interesting example of a tetraaryloxy diborane(4) compound which appears to be unstable in the absence of coordinated amine, however, is  $[B_2(calix)(NHMe_2)_2]$  (**7**) derived from the reaction between  $B_2(NMe_2)_4$  and  $Bu^tcalix[4]arene$ . Spectroscopic and analytical data for **7** were fully consistent with the structure shown in the diagram, but the attempted preparation of the uncomplexed diborane(4) compound by addition of HCl (as in Eq. (1)) resulted only in degradation products such as  $Bu^tcalix[4]arene$  itself; no boron containing species could be identified. One explanation for the apparent instability of the desired compound  $B_2(calix)$  relates to the likely inability of the calix oxygens to act as  $\pi$ -donors to the diboron unit. Thus, in the absence of substantial steric protection, diborane(4) compounds are only stable in the presence of efficient  $\pi$ -donor groups where the contact atoms are generally-nitrogen, oxygen, sulphur or fluorine (see structure **A**)<sup>4</sup>. Whilst four oxygen atoms would be present in  $B_2(calix)$ , the orientation of the organyl groups to which they are attached is such that the  $\pi$ -donor orbitals on the oxygen atoms are not in the correct orientation to overlap effectively with the boron centres (**B**). We assume therefore that as a result of this absence of efficient oxygen  $\pi$ -donation, the desired compound  $B_2(calix)$  is too unstable to be isolated.



The diborane(4) compounds **3–5** all react cleanly and quantitatively with the platinum(0) complex  $[Pt(PPh_3)_2(\eta-C_2H_4)]$  to afford the platinum(II) *bis*-boryls, *cis*- $[Pt(PPh_3)_2\{B(1,2-S_2C_6H_4)_2\}]$  (**8**), *cis*- $[Pt(PPh_3)_2\{B(1,2-O_2C_6Cl_4)_2\}]$  (**9**) and *cis*- $[Pt(PPh_3)_2\{B(1,2-O_2C_6Br_4)_2\}]$  (**10**), spectroscopic and analytical data for which were consistent with the expected structures. Additionally, both **8** and **9** were characterised by X-ray crystallography, the results of which

<sup>4</sup> For a recent review of diborane(4) compounds, see [39].

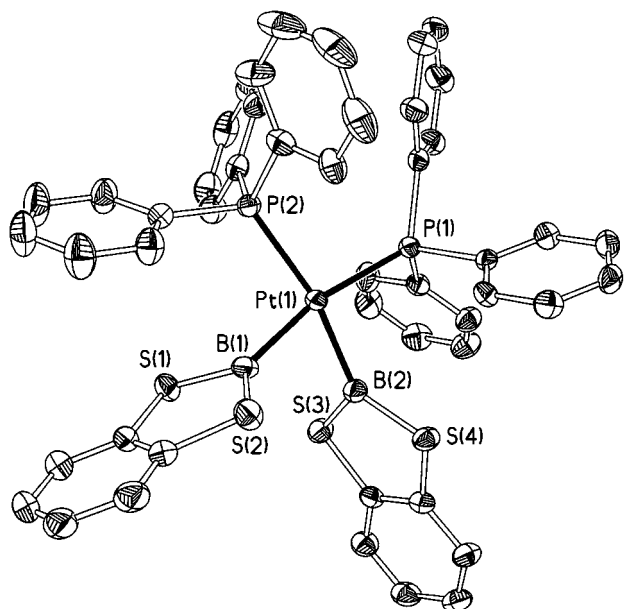


Fig. 1. A view of the molecular structure of compound **8** with key atoms labelled and H atoms omitted. Ellipsoids are drawn at the 50% level.

are shown in Figs. 1 and 2 respectively; selected bond lengths and angles are given in Table 1.

The structures of both **8** and **9** adopt the expected square planar coordination geometry around the platinum centre (maximum atom deviations from the PtP<sub>2</sub>B<sub>2</sub> mean plane are 0.121 and 0.037 Å, respectively) with the boryl groups in a *cis*-configuration. Metric parameters of note are the Pt–B bond distances (**8**, av. 2.065 and **9** av. 2.04 Å) together with the B–Pt–B (**8**, 78.5(2) and **9**, 79.9(8)°) and P–Pt–P angles (**8**, 100.38(3) and **9**, 100.8(2)°). All of these parameters are similar to those found in the other structurally characterised platinum (II) *cis*, *bis*-boryl compounds [Pt(PPh<sub>3</sub>)<sub>2</sub>{B(OCMe<sub>2</sub>CMe<sub>2</sub>O)}<sub>2</sub>] [**3**], [Pt(PPh<sub>3</sub>)<sub>2</sub>{B(1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] [**4,6**], [Pt(PPh<sub>3</sub>)<sub>2</sub>{B(1,2-O<sub>2</sub>-4-Bu<sup>t</sup>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>] [**6**], [Pt(dppe){B(1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] [**6**] and [Pt(dppb){B(1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] [**6**], for which the Pt–B distances range from 2.031 to 2.076 Å, the B–Pt–B angles fall in the relatively narrow range of 75.3–81.0° and the P–Pt–P angles range from 100.72 to 107.14°. In the compound with the chelating diphosphine ligand dppe, the P–Pt–P angle (85.36°) is somewhat reduced as expected.

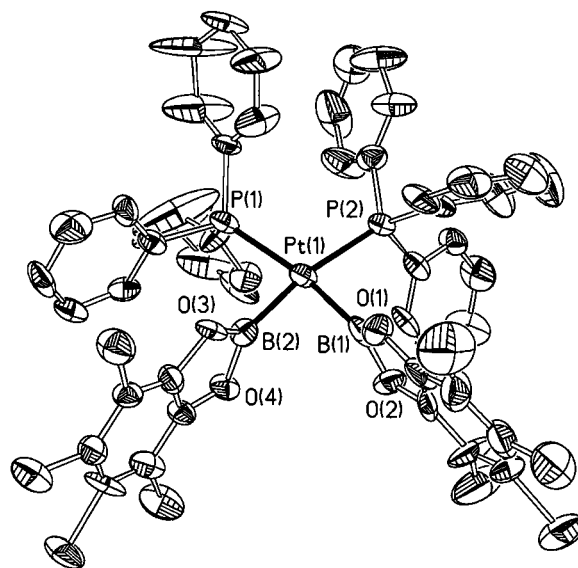
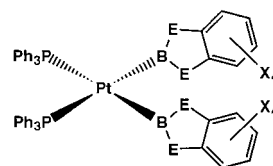


Fig. 2. A view of the molecular structure of compound **9** with key atoms labelled and H atoms omitted. Ellipsoids are drawn at the 50% level.

[**6**], [Pt(dppe){B(1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] [**6**] and [Pt(dppb){B(1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] [**6**], for which the Pt–B distances range from 2.031 to 2.076 Å, the B–Pt–B angles fall in the relatively narrow range of 75.3–81.0° and the P–Pt–P angles range from 100.72 to 107.14°. In the compound with the chelating diphosphine ligand dppe, the P–Pt–P angle (85.36°) is somewhat reduced as expected.



**8**, E = S, X = H; **9**, E = O, X = Cl; **10**, E = O, X = Br

Table 1  
Selected bond lengths (Å) and angles (°) for compounds **8**, **9** and **11**

| <b>8</b>                    | <b>9</b>                  | <b>11</b>                  |
|-----------------------------|---------------------------|----------------------------|
| Bond lengths                |                           |                            |
| Pt(1)–B(1), 2.056(4)        | Pt(1)–B(1), 2.04(2)       | Pt(1)–B(1), 2.008(8)       |
| Pt(1)–B(2), 2.075(4)        | Pt(1)–B(2), 2.03(2)       | Pt(1)–Cl(1), 2.4446(14)    |
| Pt(1)–P(1), 2.3954(9)       | Pt(1)–P(1), 2.354(5)      | Pt(1)–P(1), 2.2993(14)     |
| Pt(1)–P(2), 2.3369(9)       | Pt(1)–P(2), 2.369(5)      | Pt(1)–P(2), 2.2964(14)     |
| B(1)–S(1), 1.805(4)         | B(1)–O(1), 1.47(2)        | B(1)–O(1), 1.399(9)        |
| B(1)–S(2), 1.829(4)         | B(1)–O(2), 1.40(3)        | B(1)–O(2), 1.414(9)        |
| B(2)–S(3), 1.802(4)         | B(2)–O(3), 1.37(2)        |                            |
| B(2)–S(4), 1.810(4)         | B(2)–O(4), 1.49(2)        |                            |
| Bond angles                 |                           |                            |
| B(1)–Pt(1)–B(2), 78.5(2)    | B(1)–Pt(1)–B(2), 80.0(8)  | B(1)–Pt(1)–Cl(1), 178.8(2) |
| P(1)–Pt(1)–P(2), 100.38(3)  | P(1)–Pt(1)–P(2), 100.8(2) | P(1)–Pt(1)–P(2), 179.63(6) |
| B(1)–Pt(1)–P(1), 167.07(12) | B(1)–Pt(1)–P(1), 168.9(6) | B(1)–Pt(1)–P(1), 89.5(2)   |
| B(1)–Pt(1)–P(2), 92.54(12)  | B(1)–Pt(1)–P(2), 90.1(6)  | B(1)–Pt(1)–P(2), 90.2(2)   |
| B(2)–Pt(1)–P(1), 88.73(11)  | B(2)–Pt(1)–P(1), 89.2(6)  | Cl(1)–Pt(1)–P(1), 91.57(6) |
| B(2)–Pt(1)–P(2), 167.34(11) | B(2)–Pt(1)–P(2), 169.8(6) | Cl(1)–Pt(1)–P(2), 88.72(6) |

Clearly B–Pt–B angles less than  $90^\circ$  and P–Pt–P angles greater than  $90^\circ$  are standard for this type of *cis,bis*-boryl complex although at this time, the origin of the particularly acute B–Pt–B angles remains unclear. Steric factors certainly favour such a distortion in that whilst  $\text{PPh}_3$  is a very three-dimensional ligand, the boryl groups are much more two-dimensional such that when they are oriented approximately perpendicular to the platinum square plane, they are probably able approach one another quite closely. In the complexes mentioned above [3,4,6], the interplanar angles between the boron trigonal plane and the mean square plane around the platinum centres range from  $71.3$  to  $88.8^\circ$  (with the exception of one  $\text{B}(1,2\text{-O}_2\text{C}_6\text{H}_4)$  group in  $[\text{Pt}(\text{dppe})\{\text{B}(1,2\text{-O}_2\text{C}_6\text{H}_4)\}_2]$  for which the angle is  $55.1^\circ$ ); in **8** and **9**, the corresponding interplanar angles are  $78.2$  and  $74.2^\circ$  for **8** and  $78.1$  and  $80.9^\circ$  for **9**. Whether or not an electronic origin exists for the acute B–Pt–B angles and/or the orientations of the boryl ligands is also unclear although we note that a recent theoretical study by Sakaki and Kikuno [40] on model  $(\text{PH}_3)_2$  platinum(II) *cis,bis*-boryl complexes does reproduce the experimentally observed geometries, although no explicit comment is made concerning the B–Pt–B angles and the boryl ligand orientations<sup>5</sup>. Any further insight into this matter will have to await a more detailed theoretical analysis, but appreciable  $\text{B}\cdots\text{B}$  interactions would seem to be relatively unimportant, however, in the view of the long  $\text{B}\cdots\text{B}$  distances:  $\text{B}\cdots\text{B}$  distances are  $2.613$  Å for **8** and  $2.62$  Å for **9** and range from  $2.514$  to  $2.667$  Å for the complexes described in Refs. [3,4,6]; for comparison, the B–B bond distance in **1** is  $1.678(3)$  Å.

In considering the nature of metal boryls in more detail, the *cis*-configuration observed for the platinum(II) complexes is also found in all other structurally characterised examples of metal *bis*-boryls (and *tris*-boryls) and is presumed to be due to the high *trans* influence of the boryl group. It is of interest to note that the *bis*-silyl, germyl and stannyl complexes of platinum(II), which result from the oxidative addition of Si–Si, Ge–Ge and Sn–Sn bonds respectively [27–29] are also *cis*, but in cases where Si–X (X = halide) bond oxidative addition has occurred, the resulting  $[\text{PtX}(\text{PR}_3)_2(\text{SiR}'_3)]$  complexes adopt a *trans* geometry. These data are consistent with a relative ordering of *trans* influence for the various ligands as  $\text{BR}_2 \approx \text{SiR}_3 > \text{PR}_3 > \text{X}$  (the large *trans* influence of the boryl ligand and its effect on Ir–P bond lengths has been discussed for the complex *cis, mer*- $[\text{IrCl}(\text{PMe}_3)_3\{\text{B}(1,2\text{-O}_2\text{C}_6\text{H}_4)\}_2]$  in Ref. [17]) and we should therefore expect that a complex with the general formula

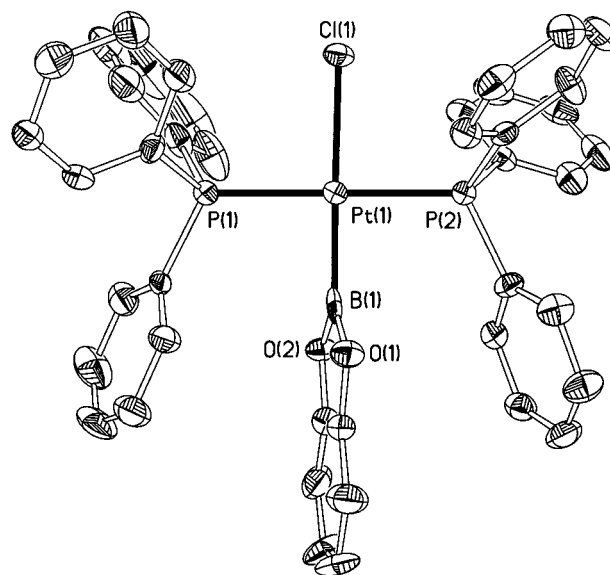


Fig. 3. A view of the molecular structure of compound **11** with key atoms labelled and H atoms omitted. Ellipsoids are drawn at the 50% level.

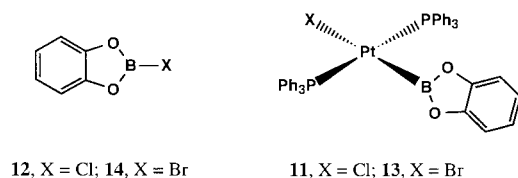
$[\text{PtX}(\text{PR}_3)_2(\text{BR}'_2)]$  would also have a *trans* geometry. This expectation was confirmed in the synthesis and structural characterisation of the complex  $[\text{PtCl}(\text{PPh}_3)_2\{\text{B}(1,2\text{-O}_2\text{C}_6\text{H}_4)\}]$  (**11**).

Compound **11** was prepared<sup>6</sup> from the reaction between  $[\text{Pt}(\text{PPh}_3)_2(\eta\text{-C}_2\text{H}_4)]$  and  $\text{ClB}(1,2\text{-O}_2\text{C}_6\text{H}_4)$  (**12**) in high yield as a colourless crystalline material, the structure of which was established by X-ray crystallography. The results of this study are shown in Fig. 3 with selected bond lengths and angles given in Table 1. The structure of **11** clearly reveals a square planar platinum centre (maximum deviation from the  $\text{Pt}_2\text{BCl}$  plane =  $0.008$  Å) with the boryl and chloride ligands adopting a *trans* configuration; none of the interbond angles deviate significantly from idealised values. The Pt–B distance ( $2.008(8)$  Å) is slightly shorter than the Pt–B distances described above for the platinum(II) *bis*-boryls in line with chloride having a smaller *trans* influence than  $\text{PPh}_3$ . Consistent with this observation is the fact that the Pt–P bond lengths in **11** are also slightly shorter than those in **8** and **9** for example (Table 1). Also noteworthy is the conformation about the Pt–B bond such that the plane of the boryl ligand is almost perpendicular ( $78.3^\circ$ ) to the platinum square plane. As with complexes **8** and **9**, this orientation is undoubtedly the one which minimises intramolecular steric interactions although, in line with the discussion above for the

<sup>5</sup> Possible electronic factors influencing observed boryl ligand orientations have been discussed in Refs. [19,21].

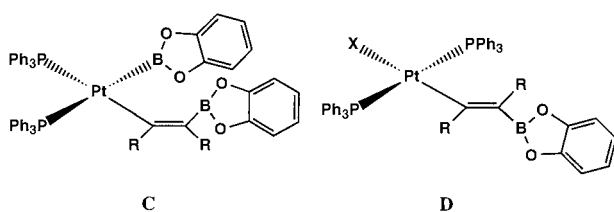
<sup>6</sup> Two prior reports of oxidative addition of B–X bonds to Pt(0) triphenylphosphine complexes have appeared, but only IR and elemental analysis data were used to suggest the formulation; no NMR data or X-ray structural results were presented [41,42].

bis-boryls, electronic factors which favour this orientation may also be important. The bromo compound  $[\text{PtBr}(\text{PPh}_3)_2\{\text{B}(1,2\text{-O}_2\text{C}_6\text{H}_4)\}]$  (**13**) was prepared similarly from the reaction between  $[\text{Pt}(\text{PPh}_3)_2(\eta\text{C}_2\text{H}_4)]$  and  $\text{BrB}(1,2\text{-O}_2\text{C}_6\text{H}_4)$  (**14**) and spectroscopic data for **13** were consistent with a structure analogous to that of **11**.



As mentioned in Section 1, platinum(0) complexes are efficient catalysts for alkyne diboration in which it is thought that initial oxidative addition of the B–B bond to the platinum centre is followed by dissociation of a phosphine ligand. Coordination of the alkyne and subsequent insertion into one of the Pt–B bonds then affords a  $\sigma$ -vinyl species as shown in **C** (although in none of the reactions studied so far has a species such as **C** been isolated or even directly observed) [2–6]. Subsequent reductive elimination of a B–C bond then regenerates the Pt(0) centre and affords *cis*-1,2-diborylalkenes, *cis*- $\text{R}(\text{BR}'_2)\text{C}=\text{C}(\text{BR}'_2)\text{R}$ .

The fact that intermediates such as **C** have not been detected implies that reductive B–C bond elimination is relatively fast, but in compounds such as **11** or **13** it may be possible to characterise a product such as **D** (shown with two phosphines) containing a  $\sigma$ -vinyl group as subsequent reductive elimination of a C–X bond is expected to be slower particularly in view of the likely *trans* disposition of the vinyl and X groups. A similar situation was observed in the related system involving the platinum silyl complexes *trans*- $[\text{PtX}(\text{PEt}_3)_2(\text{SiMe}_3)]$  (X = Br, I) which interestingly, react with the alkynes  $\text{RC}\equiv\text{CR}$  (R = Ph, Pr) to afford the *E*-vinyl species *trans*- $[\text{PtX}(\text{PEt}_3)_2\{E\text{-C}(\text{R})=\text{C}(\text{R})(\text{SiMe}_3)\}]$  [43,45].



Preliminary in situ NMR studies of the reaction between **11** and  $\text{EtO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Et}$  at  $60^\circ\text{C}$  in  $\text{CDCl}_3$  solution, however, have not shown evidence for alkyne insertion. Rather, it seems that B–Cl reductive elimination may be taking place (i.e. B–Cl oxidative addition may well be reversible) in that the complex

$[\text{Pt}(\text{PPh}_3)_2(\eta\text{-EtO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Et})]$  [44] has been identified as a significant product. As the reductive elimination process may be accelerated by the electron withdrawing nature of this alkyne and the final alkyne  $\pi$ -complex is stabilized by this as well, further examinations of the reactions of **11** and **13** with electron donating alkynes are in progress and will be reported in due course.

## 3. Experimental

### 3.1. General procedures

All reactions were performed using standard Schlenk or glove box techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were distilled from appropriate drying agents immediately prior to use (sodium-benzophenone for  $\text{Et}_2\text{O}$ ,  $\text{CaH}_2$  for chlorinated solvents and sodium or sodium-benzophenone for toluene and hexanes). Microanalytical data were obtained at the University of Bristol. NMR spectra were recorded on JEOL GX 270, JEOL GX 400, JEOL Lambda 300 and Bruker WP 200 spectrometers and were referenced to  $\text{Me}_4\text{Si}$ ,  $\text{Me}_4\text{Si}$ , 85%  $\text{H}_3\text{PO}_4$  and  $\text{BF}_3\cdot\text{Et}_2\text{O}$  for  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  nuclei, respectively. Mass spectra (high and low resolution) were obtained in the EI mode on a Micromass Autospec spectrometer.

### 3.2. Preparations

$\text{B}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)_2$  (**4**): A solution of  $\text{B}_2(\text{NMe}_2)_4$  (0.120 g, 0.6 mmol) in  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ) was added to a solution of dry tetrachlorocatechol (0.33 g, 1.53 mmol) in  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ) at room temperature resulting in the immediate formation of a white precipitate. The mixture was stirred for 12 h after which time the solid was allowed to settle whereupon the  $\text{Et}_2\text{O}$  was removed by syringe. After washing with  $\text{Et}_2\text{O}$  ( $2 \times 5 \text{ cm}^3$ ), the solid was pumped to dryness. To this dry solid,  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ) was added followed by a solution of HCl in  $\text{Et}_2\text{O}$  (1.3  $\text{cm}^3$  of a 1.0 M solution) and the resulting slurry was then stirred at room temperature for 18 h. After this time, the solvent volume was reduced by vacuum to about 5  $\text{cm}^3$  and toluene (15  $\text{cm}^3$ ) was added. The resulting suspension was then warmed to about  $60^\circ\text{C}$  and filtered through Celite, the remaining solid being washed with warm toluene ( $2 \times 10 \text{ cm}^3$ ) and the clear, colourless filtrates combined. After reduction of the filtrate volume to about 8  $\text{cm}^3$  and cooling to  $-30^\circ\text{C}$ , compound **4** was obtained as a white powder (0.25 g, 63%).

Spectroscopic data for **4**: Mass spectrum,  $m/z$  514 ( $\text{M}^+$ , 100%). Hrms,  $\text{HC}_{12}\text{B}_2\text{Cl}_8\text{O}_4$  requires 507.756, found 507.755 with correct isotope pattern. Elemental analysis,  $\text{C}_{12}\text{B}_2\text{Cl}_8\text{O}_4$  requires C, 28.10, found C, 28.60.

$B_2(1,2-O_2C_6Br_4)_2$  (**5**): Compound **5** was prepared in a similar manner to **4** from  $B_2(NMe_2)_4$  and dry tetrabromocatechol with typical yields of about 50%.

Spectroscopic data for **5**: Mass spectrum,  $m/z$  870 ( $M^+$ , 100%) with correct isotope pattern. Elemental analysis,  $C_{12}B_2Br_8O_4$  requires C, 16.70, found C, 17.65.

Compounds **4** and **5** are both very insoluble in common solvents requiring the use of hot toluene as means of extraction from the crude reaction mixture; isolated yields are thus rather low and it was also not possible to obtain satisfactory  $^{11}B$  NMR spectra for this reason. Since tetrachlorocatechol and tetrabromocatechol are usually hydrates, it is important that these are dried prior to use in order to avoid hydrolysis of  $B_2(NMe_2)_4$  [45].

$[B_2(calix)(NHMe_2)_2]$  (**7**): A solution of  $B_2(NMe_2)_4$  (0.33 g, 1.69 mmol) in toluene (5  $cm^3$ ) was added to a suspension of  $Bu^t calix[4]arene$  (1.10 g, 1.69 mmol) in toluene (30  $cm^3$ ) and the resulting suspension refluxed for 4 h. After this time, all volatiles were removed by vacuum affording **7** as a toluene solvate as an analytically pure white solid in essentially quantitative yield (1.26 g, 100%).

Spectroscopic data for **7**: NMR:  $^1H$  ( $CDCl_3$ )  $\delta$  7.08 (d, 4H, aryl C–H,  $^4J_{HH} = 2.5$  Hz), 6.85 (d, 4H, aryl C–H,  $^4J_{HH} = 2.5$  Hz), 4.75 (d, 2H,  $CH_2$ ,  $^2J_{HH} = 12.4$  Hz), 4.10 (d, 2H,  $CH_2$ ,  $^2J_{HH} = 14.4$  Hz), 3.35 (d, 2H,  $CH_2$ ,  $^2J_{HH} = 14.4$  Hz), 3.25 (d, 2H,  $CH_2$ ,  $^2J_{HH} = 12.4$  Hz), 2.85 (s, 12H,  $NHMe_2$ ), 2.50 (br s, 2H,  $NHMe_2$ ), 1.15 (s, 36H,  $CMe_3$ );  $^{13}C$ - $\{^1H\}$  ( $CDCl_3$ )  $\delta$  148.7, 143.6, 130.4, 128.1, 125.9, 124.2 (aryl C), 36.8 ( $NHMe_2$ ), 35.4 ( $CMe_3$ ), 34.0 ( $CH_2$ ), 31.4 ( $CMe_3$ ), 30.8 ( $CH_2$ );  $^{11}B$ - $\{^1H\}$  ( $CDCl_3$ )  $\delta$  20.5 (br s). Mass spectrum,  $m/z$  754 ( $M^+ - 2H$ , 100%). Hrms,  $C_{48}H_{64}B_2N_2O_4$  requires 754.507, found 754.505. Elemental analysis,  $C_{48}H_{64}B_2N_2O_4$  requires C, 77.85; H, 8.80; N, 3.30, found C, 78.70; H, 8.90; N, 3.20.

$[Pt(PPh_3)_2\{B(1,2-S_2C_6H_4)\}_2]$  (**8**): Samples of  $[Pt(PPh_3)_2(\eta-C_2H_4)]$  (0.171 g, 0.228 mmol) and **3** (0.069 g, 0.228 mmol) were dissolved in toluene (5  $cm^3$ ) resulting in the immediate formation of a white precipitate. After stirring at room temperature for 15 min, the mixture was allowed to settle and the solvent was removed by filtration. The resulting white solid was then washed with hexanes (5  $cm^3$ ) and dried by vacuum (0.192 g, 82%). Crystals suitable for X-ray diffraction

Table 2

Crystallographic data for the complexes **8**, **9** and **11**

| Compound  | 8 · 0.5 toluene                           | 9 · 2.0 toluene                              | 11                        |
|---|---|--|---------------------------|
| Formula   | $C_{48}H_{38}B_2P_2PtS_4 \cdot 0.5C_7H_8$ | $C_{48}H_{30}B_2Cl_8O_4P_2Pt \cdot 2OC_7H_8$ | $C_{42}H_{34}BClO_2P_2Pt$ |
| <i>M</i>  | 1067.7                                    | 1417.2                                       | 874.0                     |
| Crystal system  | triclinic                                 | triclinic                                    | orthorhombic              |
| Space group   | $P\bar{1}$                                | $P\bar{1}$                                   | <i>Pbca</i>               |
| <i>a</i> (Å)  | 9.6914(7)                                 | 14.648(8)                                    | 11.5686(12)               |
| <i>b</i> (Å)  | 11.7173(9)                                | 15.789(6)                                    | 23.389(3)                 |
| <i>c</i> (Å)  | 22.718(2)                                 | 16.600(5)                                    | 26.790(3)                 |
| $\alpha$ (°)  | 75.262(2)                                 | 106.70(5)                                    | 90                        |
| $\beta$ (°)   | 84.697(2)                                 | 101.82(4)                                    | 90                        |
| $\gamma$ (°)  | 68.990(3)                                 | 116.42(3)                                    | 90                        |
| <i>V</i> (Å <sup>3</sup> )                              | 2329.1(3)                                 | 3036(2)                                      | 7248.8(13)                |
| <i>F</i> (000)  | 1066                                      | 1408   | 3456                      |
| <i>Z</i>  | 2   | 2  | 8                         |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )          | 1.523                                     | 1.550  | 1.602                     |
| $\mu$ (mm <sup>-1</sup> )                               | 3.30                                      | 2.76   | 4.07                      |
| Crystal size (mm)                                       | 0.50 × 0.44 × 0.16                        | 0.20 × 0.20 × 0.20                           | 0.14 × 0.12 × 0.10        |
| <i>T</i> (K)  | 160(2)                                    | 173(2)                                       | 160(2)                    |
| $\theta_{max}$ (°)                                      | 28.4                                      | 25.0   | 25.0                      |
| Max. indices <i>hkl</i>                                 | 12, 14, 30                                | 17, 18, 19                                   | 14, 29, 35                |
| Reflections measured                                    | 14452                                     | 14114  | 35004                     |
| Unique reflections                                      | 10059                                     | 10047  | 6375                      |
| <i>R</i> <sub>int</sub>                                 | 0.0432                                    | 0.0888                                       | 0.1143                    |
| Transmission  | 0.418–0.835                               | 0.100–0.292                                  | 0.457–0.612               |
| Weighting <i>a, b</i>                                   | 0.0329, 4.8269                            | 0.139, 0.0                                   | 0.0082, 18.2721           |
| Refined parameters                                      | 563                                       | 628  | 443                       |
| <i>R</i> <sub>w</sub> (all data) <sup>a</sup>           | 0.082                                     | 0.292  | 0.080                     |
| <i>R</i> (data with $F^2 > 2\sigma(F^2)$ ) <sup>b</sup> | 0.031 (9600)                              | 0.108 (5099)                                 | 0.035 (4251)              |
| Goodness of fit on $F^2$                                | 1.16                                      | 0.970  | 1.185                     |
| Extinction <i>x</i>                                     | 0.0003(2)                                 | —  | 0.000024(11)              |
| Max, min. electron density (eÅ <sup>-3</sup> )          | +1.90, -1.67                              | +3.52, -3.99                                 | +1.26, -0.85              |

<sup>a</sup> $R_w = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$ .<sup>b</sup> $R = \sum|F_o| - |F_c| / \sum|F_o|$ .

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8** (5 cm<sup>3</sup> toluene).  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

|       | <i>x</i>     | <i>y</i>    | <i>z</i>   | $U(\text{eq})$ |
|-------|--------------|-------------|------------|----------------|
| Pt(1) | 16888.57(14) | −281.82(11) | 7273.52(5) | 20.56(5)       |
| B(1)  | 18395(4)     | −1890(4)    | 7776(2)    | 25.6(8)        |
| S(1)  | 17985.8(10)  | −3003.5(8)  | 8413.2(4)  | 28.7(2)        |
| S(2)  | 20399.3(11)  | −2350.6(9)  | 7678.0(5)  | 33.8(2)        |
| C(1)  | 19824(4)     | −3938(3)    | 8661(2)    | 28.5(7)        |
| C(2)  | 20946(5)     | −3634(4)    | 8317(2)    | 32.2(8)        |
| C(3)  | 22437(5)     | −4309(4)    | 8488(2)    | 42.2(10)       |
| C(4)  | 22759(5)     | −5276(5)    | 9012(2)    | 48.2(12)       |
| C(5)  | 21637(6)     | −5581(4)    | 9355(2)    | 46.3(11)       |
| C(6)  | 20161(5)     | −4920(4)    | 9182(2)    | 38.1(9)        |
| B(2)  | 17227(5)     | −1524(4)    | 6722(2)    | 24.7(7)        |
| S(3)  | 16391.4(12)  | −2720.1(9)  | 6907.0(4)  | 30.9(2)        |
| S(4)  | 18282.3(11)  | −1621.0(8)  | 6024.8(4)  | 28.4(2)        |
| C(7)  | 17062(4)     | −3407(3)    | 6290(2)    | 26.3(7)        |
| C(8)  | 17935(4)     | −2887(3)    | 5869(2)    | 25.3(7)        |
| C(9)  | 18489(4)     | −3379(4)    | 5358(2)    | 32.1(8)        |
| C(10) | 18201(4)     | −4410(4)    | 5287(2)    | 33.8(8)        |
| C(11) | 17365(5)     | −4951(4)    | 5717(2)    | 35.7(9)        |
| C(12) | 16788(5)     | −4453(4)    | 6213(2)    | 32.8(8)        |
| P(1)  | 15254.4(9)   | 1327.3(8)   | 6515.8(4)  | 20.5(2)        |
| C(13) | 14048(4)     | 640(3)      | 6285(2)    | 23.8(7)        |
| C(14) | 13991(4)     | 457(4)      | 5710(2)    | 30.0(8)        |
| C(15) | 13067(5)     | −141(4)     | 5604(2)    | 37.4(9)        |
| C(16) | 12198(5)     | −537(4)     | 6057(2)    | 38.5(9)        |
| C(17) | 12234(5)     | −342(4)     | 6628(2)    | 41.7(10)       |
| C(18) | 13161(5)     | 228(4)      | 6744(2)    | 35.5(9)        |
| C(19) | 13888(4)     | 2874(3)     | 6603.1(15) | 23.6(7)        |
| C(20) | 12382(4)     | 3269(4)     | 6468(2)    | 32.9(8)        |
| C(21) | 11408(5)     | 4460(4)     | 6520(2)    | 39.8(10)       |
| C(22) | 11911(5)     | 5262(4)     | 6709(2)    | 40.1(10)       |
| C(23) | 13409(5)     | 4881(4)     | 6841(2)    | 38.7(9)        |
| C(24) | 14390(4)     | 3699(3)     | 6783(2)    | 30.9(8)        |
| C(25) | 16274(4)     | 1847(3)     | 5851.2(15) | 21.5(6)        |
| C(26) | 15546(4)     | 2746(3)     | 5339(2)    | 27.8(7)        |
| C(27) | 16349(5)     | 3143(4)     | 4846(2)    | 30.8(8)        |
| C(28) | 17897(4)     | 2648(4)     | 4858(2)    | 29.9(8)        |
| C(29) | 18638(4)     | 1761(4)     | 5367(2)    | 30.0(8)        |
| C(30) | 17832(4)     | 1358(3)     | 5863(2)    | 24.5(7)        |
| P(2)  | 16470.9(10)  | 743.5(8)    | 8065.5(4)  | 22.4(2)        |
| C(31) | 17387(4)     | −100(3)     | 8807(2)    | 27.0(7)        |
| C(32) | 16629(5)     | −317(5)     | 9346(2)    | 42.7(10)       |
| C(33) | 17423(6)     | −949(6)     | 9892(2)    | 57.6(15)       |
| C(34) | 18945(6)     | −1354(5)    | 9898(2)    | 54.0(13)       |
| C(35) | 19709(5)     | −1159(5)    | 9365(2)    | 49.1(12)       |
| C(36) | 18923(5)     | −530(4)     | 8823(2)    | 37.0(9)        |
| C(37) | 14501(4)     | 1156(4)     | 8241(2)    | 27.3(7)        |
| C(38) | 14003(5)     | 137(4)      | 8378(2)    | 34.4(8)        |
| C(39) | 12504(5)     | 334(5)      | 8474(2)    | 40.8(10)       |
| C(40) | 11482(5)     | 1551(5)     | 8433(2)    | 41.7(10)       |
| C(41) | 11959(5)     | 2566(5)     | 8292(2)    | 41.0(10)       |
| C(42) | 13466(4)     | 2370(4)     | 8197(2)    | 32.3(8)        |
| C(43) | 17023(4)     | 2114(3)     | 7923(2)    | 29.1(7)        |
| C(44) | 16591(5)     | 2997(4)     | 8279(2)    | 43.9(10)       |
| C(45) | 17158(6)     | 3971(4)     | 8153(3)    | 57.9(15)       |
| C(46) | 18178(6)     | 4041(4)     | 7693(3)    | 56.2(14)       |
| C(47) | 18634(6)     | 3158(5)     | 7352(2)    | 51.0(12)       |
| C(48) | 18055(4)     | 2203(4)     | 7461(2)    | 33.7(8)        |
| C(49) | 16143(9)     | 4833(7)     | 9596(3)    | 63(3)          |
| C(50) | 16816(8)     | 3533(8)     | 9702(4)    | 68(3)          |
| C(51) | 16202(10)    | 2752(6)     | 10118(4)   | 74(3)          |

Table 3 (continued)

|       | <i>x</i>  | <i>y</i> | <i>z</i> | $U(\text{eq})$ |
|-------|-----------|----------|----------|----------------|
| C(52) | 14914(11) | 3270(10) | 10428(4) | 83(4)          |
| C(53) | 14241(9)  | 4569(11) | 10322(4) | 76(3)          |
| C(54) | 14855(9)  | 5351(7)  | 9906(4)  | 71(3)          |
| C(55) | 14130(16) | 6753(7)  | 9792(7)  | 121(8)         |

were obtained by recrystallisation from toluene/hexanes mixtures.

Spectroscopic data for **8**: NMR: <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.36 (m, 12H, PPh<sub>3</sub>, and 4H, S<sub>2</sub>C<sub>6</sub>-3,6-H<sub>4</sub>), 7.06 (m, 18H, PPh<sub>3</sub>), 6.88 (m, 4H, S<sub>2</sub>C<sub>6</sub>-4,5-H<sub>4</sub>); <sup>13</sup>C-{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>) δ 145.7 (br m, S<sub>2</sub>-1,2-C<sub>6</sub>H<sub>4</sub>), 134.1 (m, *o*-PPh<sub>3</sub>), 129.4 (s, *p*-PPh<sub>3</sub>), 127.6 (m, *m*-PPh<sub>3</sub>), 124.3 (s, S<sub>2</sub>-4,5-C<sub>6</sub>H<sub>4</sub>), 122.7 (s, S<sub>2</sub>-3,6-C<sub>6</sub>H<sub>4</sub>), PPh<sub>3</sub> *ipso* carbons not observed; <sup>11</sup>B-{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>) δ 72 (br s); <sup>31</sup>P-{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>) δ 28.0 (br s, <sup>1</sup>J<sub>PtP</sub> = 1600 Hz). Elemental analysis, C<sub>48</sub>H<sub>38</sub>B<sub>2</sub>P<sub>2</sub>PtS<sub>4</sub> requires C, 56.45; H, 3.75, found C, 56.55; H, 3.65.

[Pt(PPh<sub>3</sub>)<sub>2</sub>{B(1,2-O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>2</sub>}] (**9**): A suspension of **4** (0.050 g, 0.097 mmol) in toluene (20 cm<sup>3</sup>) was gently warmed until most of the solid had dissolved. A solution of [Pt(PPh<sub>3</sub>)<sub>2</sub>(ηC<sub>2</sub>H<sub>4</sub>)] (0.073 g, 0.097 mmol) in toluene (5 cm<sup>3</sup>) was then added and the resulting mixture stirred at room temperature for 2 h. After this time the solvent volume was reduced by vacuum to about 5 cm<sup>3</sup> and the reaction solution cooled to −30°C. After 3 days, white crystals of **9** (0.048 g, 40%) had formed, some of which were suitable for X-ray diffraction.

Spectroscopic data for **9**: NMR: <sup>1</sup>H (CDCl<sub>3</sub>) δ 7.4–7.0 (m, 30H, PPh<sub>3</sub>); <sup>11</sup>B-{<sup>1</sup>H} (CDCl<sub>3</sub>) δ 51.5 (br s); <sup>31</sup>P-{<sup>1</sup>H} (CDCl<sub>3</sub>) δ 26.3 (br s, <sup>1</sup>J<sub>PtP</sub> = 1608 Hz). Elemental analysis, C<sub>48</sub>H<sub>30</sub>B<sub>2</sub>O<sub>4</sub>P<sub>2</sub>PtCl<sub>8</sub> requires C, 46.75; H, 2.45, found C, 47.25; H, 2.90.

[Pt(PPh<sub>3</sub>)<sub>2</sub>{B(1,2-O<sub>2</sub>C<sub>6</sub>Br<sub>4</sub>)<sub>2</sub>}] (**10**): Compound **10** was prepared in an identical manner to **9** from [Pt(PPh<sub>3</sub>)<sub>2</sub>(ηC<sub>2</sub>H<sub>4</sub>)] and **5** and with similar yields (55%).

Spectroscopic data for **10**: NMR: <sup>11</sup>B-{<sup>1</sup>H} (CDCl<sub>3</sub>) δ 48.0 (br s); <sup>31</sup>P-{<sup>1</sup>H} (CDCl<sub>3</sub>) δ 26.0 (br s, <sup>1</sup>J<sub>PtP</sub> = 1614 Hz). Elemental analysis, C<sub>48</sub>H<sub>30</sub>B<sub>2</sub>O<sub>4</sub>P<sub>2</sub>PtBr<sub>8</sub> requires C, 36.30; H, 1.90, found C, 38.00; H, 2.10.

[PtCl(PPh<sub>3</sub>)<sub>2</sub>{B(1,2-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)}] (**11**): Samples of [Pt(PPh<sub>3</sub>)<sub>2</sub>(ηC<sub>2</sub>H<sub>4</sub>)] (0.100 g, 0.134 mmol) and **12** (0.025 g, 0.160 mmol) were dissolved in toluene (5 cm<sup>3</sup>) which resulted in the immediate formation of a white precipitate. After stirring for 1.5 h, the reaction mixture was filtered and the white solid was washed with toluene (2 cm<sup>3</sup>) affording **11** (0.090 g, 78%). Crystals suitable for X-ray diffraction were obtained by layering hexanes over a CDCl<sub>3</sub> solution.

Spectroscopic data for **11**: NMR: <sup>1</sup>H (CDCl<sub>3</sub>) δ 7.72 (m, 12H, PPh<sub>3</sub>), 7.24 (m, 18H, PPh<sub>3</sub>), 6.57 (m, 2H, O<sub>2</sub>C<sub>6</sub>-3,6-H<sub>4</sub>), 6.49 (m, 2H, O<sub>2</sub>C<sub>6</sub>-4,5-H<sub>4</sub>); <sup>13</sup>C-{<sup>1</sup>H}

Table 4

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9** ( $20 \text{ cm}^3 \text{ CH}_3\text{C}_6\text{H}_5$ ).  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

|       | <i>x</i>  | <i>y</i> | <i>z</i> | <i>U</i> (eq) |
|-------|-----------|----------|----------|---------------|
| Pt(1) | 1915(1)   | 2307(1)  | 4207(1)  | 38(1)         |
| O(1)  | 1408(11)  | 2016(11) | 2196(8)  | 49(3)         |
| O(2)  | −109(11)  | 835(10)  | 2345(8)  | 52(4)         |
| O(3)  | 3244(10)  | 1465(9)  | 3422(7)  | 37(3)         |
| O(4)  | 1768(10)  | 190(9)   | 3529(8)  | 39(3)         |
| B(1)  | 981(22)   | 1691(19) | 2853(15) | 46(6)         |
| B(2)  | 2372(16)  | 1304(17) | 3679(14) | 36(5)         |
| Cl(1) | −2522(7)  | −751(7)  | 881(5)   | 129(3)        |
| Cl(2) | −2694(8)  | −670(7)  | −1031(5) | 135(4)        |
| Cl(3) | −633(8)   | 912(7)   | −1216(4) | 117(3)        |
| Cl(4) | 1658(8)   | 2398(7)  | 493(5)   | 118(3)        |
| Cl(5) | 1038(6)   | −2135(4) | 3082(5)  | 82(2)         |
| Cl(6) | 2629(6)   | −2660(4) | 2325(4)  | 79(2)         |
| Cl(7) | 4707(5)   | −881(5)  | 2270(4)  | 75(2)         |
| Cl(8) | 5085(5)   | 1389(4)  | 2826(4)  | 62(2)         |
| P(1)  | 3181(4)   | 2875(4)  | 5665(3)  | 38(1)         |
| P(2)  | 1125(4)   | 3316(4)  | 4567(3)  | 36(1)         |
| C(1)  | 4119(16)  | 2405(14) | 5639(11) | 38(4)         |
| C(2)  | 3815(16)  | 1431(14) | 5536(14) | 53(6)         |
| C(3)  | 4476(19)  | 1023(16) | 5399(14) | 59(6)         |
| C(4)  | 5508(22)  | 1646(19) | 5436(13) | 59(6)         |
| C(5)  | 5847(20)  | 2680(19) | 5539(16) | 73(7)         |
| C(6)  | 5168(16)  | 3031(17) | 5630(14) | 51(5)         |
| C(7)  | 2492(14)  | 2340(18) | 6366(13) | 52(6)         |
| C(8)  | 3059(30)  | 2539(32) | 7215(19) | 224(29)       |
| C(9)  | 2495(31)  | 2115(35) | 7752(19) | 214(29)       |
| C(10) | 1339(34)  | 1409(26) | 7303(25) | 126(15)       |
| C(11) | 869(23)   | 1154(19) | 6459(24) | 82(8)         |
| C(12) | 1395(16)  | 1579(16) | 5977(16) | 58(6)         |
| C(13) | 4119(16)  | 4278(13) | 6304(12) | 40(5)         |
| C(14) | 4662(37)  | 4749(22) | 7195(19) | 199(25)       |
| C(15) | 5549(44)  | 5852(20) | 7628(19) | 254(34)       |
| C(16) | 5710(21)  | 6433(16) | 7183(16) | 74(7)         |
| C(17) | 5141(19)  | 5943(17) | 6278(16) | 81(8)         |
| C(18) | 4357(19)  | 4891(19) | 5848(15) | 80(8)         |
| C(19) | 1668(16)  | 4365(16) | 5696(13) | 49(5)         |
| C(20) | 1520(24)  | 4047(21) | 6382(17) | 90(9)         |
| C(21) | 1953(32)  | 4844(31) | 7302(18) | 120(14)       |
| C(22) | 2457(28)  | 5857(28) | 7478(20) | 115(13)       |
| C(23) | 2605(23)  | 6131(21) | 6792(19) | 101(11)       |
| C(24) | 2155(19)  | 5430(18) | 5885(17) | 78(8)         |
| C(25) | 1143(16)  | 3997(14) | 3830(13) | 41(5)         |
| C(26) | 420(22)   | 4301(20) | 3638(17) | 74(8)         |
| C(27) | 435(26)   | 4810(24) | 3086(22) | 103(11)       |
| C(29) | 1973(21)  | 4728(18) | 2884(16) | 69(7)         |
| C(30) | 1950(18)  | 4201(15) | 3473(15) | 56(6)         |
| C(31) | −339(16)  | 2500(14) | 4418(12) | 39(5)         |
| C(32) | −879(16)  | 2951(16) | 4748(13) | 47(5)         |
| C(33) | −1987(19) | 2308(21) | 4591(17) | 72(7)         |
| C(34) | −2524(24) | 1236(22) | 4096(18) | 82(8)         |
| C(34) | 1239(27)  | 4991(21) | 2739(22) | 101(10)       |
| C(35) | 1979(18)  | 829(19)  | 3830(17) | 64(7)         |
| C(36) | −889(17)  | 1434(15) | 3968(13) | 44(5)         |
| C(38) | −341(22)  | 769(20)  | 1464(12) | 65(8)         |
| C(39) | −1369(20) | 100(20)  | 732(14)  | 84(9)         |
| C(40) | −1409(25) | 182(22)  | −92(15)  | 81(9)         |
| C(41) | −516(29)  | 879(24)  | −155(16) | 82(9)         |
| C(42) | 486(21)   | 1506(21) | 580(15)  | 70(7)         |
| C(43) | 561(21)   | 1476(17) | 1383(13) | 53(6)         |
| C(44) | 3258(16)  | 554(15)  | 3161(11) | 42(5)         |
| C(45) | 2365(15)  | −191(14) | 3223(12) | 35(4)         |

Table 4 (continued)

|        | <i>x</i> | <i>y</i>  | <i>z</i>  | <i>U</i> (eq) |
|--------|----------|-----------|-----------|---------------|
| C(46)  | 2178(20) | −1206(16) | 2992(12)  | 61(7)         |
| C(47)  | 2889(20) | −1398(15) | 2666(13)  | 54(6)         |
| C(48)  | 3794(17) | −626(16)  | 2628(12)  | 47(5)         |
| C(49)  | 3993(14) | 393(14)   | 2871(12)  | 37(4)         |
| C(101) | 2924(56) | 8043(50)  | 9945(29)  | 310(38)       |
| C(102) | 3573(35) | 8614(32)  | 9494(38)  | 229(25)       |
| C(103) | 3271(43) | 8727(39)  | 8600(34)  | 194(20)       |
| C(104) | 2187(28) | 8224(27)  | 8207(22)  | 112(10)       |
| C(105) | 1420(31) | 7620(31)  | 8579(25)  | 139(13)       |
| C(106) | 1990(37) | 7671(36)  | 9455(36)  | 174(18)       |
| C(107) | 1200(53) | 6940(51)  | 9763(47)  | 349(42)       |
| C(201) | 6015(51) | 4543(56)  | 10324(30) | 386(49)       |
| C(202) | 5232(43) | 3482(62)  | 10000(45) | 353(43)       |
| C(203) | 5028(41) | 2775(45)  | 9156(49)  | 834(162)      |
| C(204) | 5606(51) | 3129(50)  | 8635(32)  | 695(120)      |
| C(205) | 6389(43) | 4191(54)  | 8960(30)  | 269(30)       |
| C(206) | 6593(42) | 4898(42)  | 9804(34)  | 500           |
| C(207) | 7682(56) | 5945(46)  | 10294(57) | 500           |

( $\text{CDCl}_3$ )  $\delta$  149.1 (t,  $\text{O}_2$ -1,2- $\text{C}_6\text{H}_4$ ,  $^3J_{\text{PtC}} = 36$  Hz), 134.5 (m, *o*- $\text{PPh}_3$ ), 131.4 (t, *ipso*- $\text{PPh}_3$ ,  $^1J_{\text{PC}} = 29$  Hz), 130.2 (s, *p*- $\text{PPh}_3$ ), 128.0 (t, *m*- $\text{PPh}_3$ ,  $^3J_{\text{PC}} = 11$  Hz), 119.9 (s,  $\text{O}_2$ -4,5- $\text{C}_6\text{H}_4$ ), 110.6 (s,  $\text{O}_2$ -3,6- $\text{C}_6\text{H}_4$ );  $^{11}\text{B}$ -{ $^1\text{H}$ } ( $\text{CDCl}_3$ )  $\delta$  28.7 (br s);  $^{31}\text{P}$ -{ $^1\text{H}$ } ( $\text{CDCl}_3$ )  $\delta$  23.5 (s,  $^1J_{\text{P1P}} = 2869$  Hz). Elemental analysis,  $\text{C}_{42}\text{H}_{34}\text{BClO}_2\text{P}_2\text{Pt}$  requires C, 57.70; H, 3.90, found C, 58.15; H, 3.80.

[PtBr( $\text{PPh}_3$ ) $_2$ {B(1,2- $\text{O}_2\text{C}_6\text{H}_4$ )}] (**13**): Samples of [Pt( $\text{PPh}_3$ ) $_2$ ( $\eta$ - $\text{C}_2\text{H}_4$ )] (0.128 g, 0.17 mmol) and **14** (0.051 g, 0.26 mmol) were dissolved in toluene (5  $\text{cm}^3$ ) which resulted in the immediate formation of a white precipitate. After stirring for 1.5 h, the reaction mixture was cooled to  $-40^\circ\text{C}$  and left to stand overnight. After this time, the reaction mixture was filtered and washed with hexanes (5  $\text{cm}^3$ ) affording **13** as a white powder (0.135 g, 87%).

Spectroscopic data for **13**: NMR:  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  7.71 (m, 12H,  $\text{PPh}_3$ ), 7.22 (m, 18H,  $\text{PPh}_3$ ), 6.53 (m, 4H,  $\text{O}_2\text{C}_6\text{H}_4$ );  $^{13}\text{C}$ -{ $^1\text{H}$ } ( $\text{CDCl}_3$ )  $\delta$  149.1 (s,  $\text{O}_2$ -1,2- $\text{C}_6\text{H}_4$ ), 134.6 (m, *o*- $\text{PPh}_3$ ), 131.7 (t, *ipso*- $\text{PPh}_3$ ,  $^1J_{\text{PC}} = 29$  Hz), 130.2 (s, *p*- $\text{PPh}_3$ ), 128.1 (m, *m*- $\text{PPh}_3$ ), 120.0 (s,  $\text{O}_2$ -4,5- $\text{C}_6\text{H}_4$ ), 119.7 (s,  $\text{O}_2$ -3,6- $\text{C}_6\text{H}_4$ );  $^{11}\text{B}$ -{ $^1\text{H}$ } ( $\text{CDCl}_3$ )  $\delta$  30.9 (br s);  $^{31}\text{P}$ -{ $^1\text{H}$ } ( $\text{CDCl}_3$ )  $\delta$  22.8 (s,  $^1J_{\text{P1P}} = 2844$  Hz).

### 3.3. X-ray crystallography

Crystallographic data for **8**, **9** and **11**, the former two as toluene solvates, are presented in Table 2; atomic positional parameters are listed in Tables 3–5, respectively. Measurements were made on Siemens SMART CCD area detector diffractometers with Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$   $\text{\AA}$ ) [46]. Intensities were integrated [46] from several series of exposures, each exposure covering  $0.3^\circ$  in  $\omega$ , and the total data set being more



Table 5

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **11**.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

|       | <i>x</i>   | <i>y</i>   | <i>z</i>   | $U(\text{eq})$ |
|-------|------------|------------|------------|----------------|
| Pt(1) | 3909.6(2)  | 1656.68(9) | 1373.53(9) | 20.48(8)       |
| Cl(1) | 3900.5(15) | 1612.3(7)  | 461.9(5)   | 29.8(3)        |
| B(1)  | 3900(7)    | 1678(3)    | 2123(3)    | 29.3(16)       |
| O(1)  | 4837(4)    | 1546.0(18) | 2432.2(17) | 29.7(11)       |
| O(2)  | 2940(4)    | 1829.3(17) | 2421.2(16) | 27.3(10)       |
| C(1)  | 4452(7)    | 1619(3)    | 2914(2)    | 30.7(15)       |
| C(2)  | 3308(7)    | 1787(3)    | 2902(3)    | 30.5(16)       |
| C(3)  | 2690(8)    | 1897(3)    | 3334(3)    | 44(2)          |
| C(4)  | 3295(8)    | 1821(3)    | 3767(3)    | 48(2)          |
| C(5)  | 4446(9)    | 1665(4)    | 3802(3)    | 58(2)          |
| C(6)  | 5043(8)    | 1559(3)    | 3351(3)    | 47(2)          |
| P(1)  | 4090.9(13) | 2635.5(6)  | 1360.4(7)  | 21.6(3)        |
| C(7)  | 2967(6)    | 2931(3)    | 967(3)     | 33.7(16)       |
| C(8)  | 1852(7)    | 2760(3)    | 1040(4)    | 59(2)          |
| C(9)  | 954(9)     | 2980(4)    | 758(6)     | 98(4)          |
| C(10) | 1212(12)   | 3366(5)    | 376(5)     | 111(4)         |
| C(11) | 2322(12)   | 3534(4)    | 293(4)     | 88(3)          |
| C(12) | 3211(9)    | 3320(3)    | 580(3)     | 55(2)          |
| C(13) | 5415(6)    | 2924(2)    | 1101(2)    | 25.0(15)       |
| C(14) | 5907(6)    | 2676(3)    | 671(3)     | 41.1(19)       |
| C(15) | 6828(7)    | 2930(3)    | 435(3)     | 50(2)          |
| C(16) | 7319(7)    | 3421(3)    | 630(3)     | 44(2)          |
| C(17) | 6869(6)    | 3668(3)    | 1054(2)    | 31.6(16)       |
| C(18) | 5929(5)    | 3418(2)    | 1290(2)    | 25.6(14)       |
| C(19) | 3971(6)    | 3008(2)    | 1952(2)    | 23.0(14)       |
| C(20) | 4790(6)    | 2909(3)    | 2321(3)    | 33.4(17)       |
| C(21) | 4723(8)    | 3170(3)    | 2786(3)    | 47(2)          |
| C(22) | 3819(8)    | 3536(3)    | 2883(3)    | 55(2)          |
| C(23) | 2993(8)    | 3647(3)    | 2524(4)    | 56(2)          |
| C(24) | 3063(6)    | 3386(3)    | 2054(3)    | 37.6(18)       |
| P(2)  | 3736.5(13) | 678.8(6)   | 1391.0(6)  | 21.0(3)        |
| C(25) | 2400(5)    | 383(3)     | 1125(2)    | 25.1(15)       |
| C(26) | 2047(6)    | –159(3)    | 1265(3)    | 35.9(18)       |
| C(27) | 1046(7)    | –389(3)    | 1060(3)    | 45(2)          |
| C(28) | 400(7)     | –86(3)     | 721(3)     | 43(2)          |
| C(29) | 759(6)     | 453(3)     | 581(3)     | 43(2)          |
| C(30) | 1769(6)    | 696(3)     | 780(3)     | 32.8(16)       |
| C(31) | 4921(5)    | 362(3)     | 1046(2)    | 23.3(15)       |
| C(32) | 5999(5)    | 628(3)     | 1075(2)    | 27.3(15)       |
| C(33) | 6936(6)    | 409(3)     | 813(3)     | 33.2(17)       |
| C(34) | 6795(6)    | –70(3)     | 516(3)     | 34.1(17)       |
| C(35) | 5732(6)    | –324(3)    | 476(3)     | 36.0(18)       |
| C(36) | 4804(6)    | –123(3)    | 747(3)     | 31.8(17)       |
| C(37) | 3776(6)    | 351(3)     | 2008(2)    | 24.5(14)       |
| C(38) | 4691(6)    | 13(3)      | 2173(3)    | 33.9(16)       |
| C(39) | 4731(7)    | –177(3)    | 2665(3)    | 39.5(19)       |
| C(40) | 3863(7)    | –41(3)     | 2993(3)    | 39.4(17)       |
| C(41) | 2929(6)    | 278(3)     | 2830(3)    | 31.8(16)       |
| C(42) | 2870(6)    | 472(3)     | 2341(2)    | 29.6(16)       |

than a hemisphere in each case. Absorption corrections were applied, based on multiple and symmetry equivalent measurements [47]. The structures were solved variously by heavy atom and direct methods and refined by least-squares on  $F^2$  values for all reflections, with weighting  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$ , where  $P = (F_o^2 + 2F_c^2)/3$ . An isotropic extinction parameter  $x$  was refined for **8** and **11**, whereby  $F_c' = F_c/(1 +$

$0.001 x F_c^2 \lambda^3 / \sin 2\theta)^{1/4}$ . For **8** and **11**, some restraints were applied to anisotropic displacement parameters in ligand substituents showing highly anisotropic behaviours and hence possible unresolved disorder and for disordered toluene solvent in **8**. For **9**, the toluene solvates were refined subject to positional restraints with isotropic atoms, the ring carbons of one of toluene being constrained to regular hexagonal geometry. Isotropic hydrogen atoms were constrained with a riding model. The largest features in the final difference syntheses were close to Pt atoms and disordered groups.

Additional material available from the Cambridge Crystallographic Data Centre comprises atomic coordinates and displacement parameters and complete bond lengths and angles.

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