Preparation and structure of *cis*-[Pt(BF$_2$)$_2$(PPh$_3$)$_2$]: the first crystallographically characterised complex containing the BF$_2$ ligand

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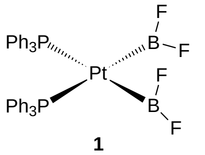
The platinum compound [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)] reacts with B$_2$F$_4$ affording the BF$_2$ complex *cis*-[Pt(BF$_2$)$_2$(PPh$_3$)$_2$] which is characterised by multinuclear NMR studies and X-ray crystallography.

A key step in many transition metal catalysed diboration reactions is oxidative addition of the B–B bond of a diborane(4) compound (R$_2$B–BR$_2$) to a low-valent transition metal centre affording a metal bis-boryl complex of the form L$_n$M(BR$_2$)$_2$.[1] Amongst the many studies which have been carried out,[1] one of the more thoroughly examined reactions, particularly in terms of this B–B bond oxidative addition step, has been the platinum catalysed diboration of alkynes described recently by the groups of Miyaura and Suzuki,[2] Smith[3] and Marder and Norman.[4] These and other studies[5,6] have resulted in a number of crystallographically characterised platinum bis-boryl species of the type *cis*-[Pt(BR$_2$)$_2$(PR′$_3$)$_2$]. In seeking to further explore the oxidative addition of B–B bonds to Pt^0, we examined the reaction between [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)] and diboron tetrafluoride, B$_2$F$_4$, and report herein the preparation and structural characterisation of the complex *cis*-[Pt(BF$_2$)$_2$(PPh$_3$)$_2$], the first example of a compound containing the BF$_2$ ligand.

The reaction between [Pt(PPh$_3$)$_2$(η-C$_2$H$_4$)][7] and a slight excess of B$_2$F$_4$[8] in toluene solution afforded, after work-up,† pale yellow crystals of the complex *cis*-[Pt(BF$_2$)$_2$(PPh$_3$)$_2$] **1**. The formula of **1** was evident from multinuclear NMR data‡ and the structure was confirmed by X-ray crystallography§ the results of which are shown in Fig. 1. The Pt centre in **1** adopts the expected square-planar coordination geometry (maximum atom deviation from the PtP$_2$B$_2$ mean plane is 0.025 Å) with the BF$_2$ groups in a *cis* configuration. Metric parameters of note are the Pt–B bond distances [Pt–B(1) 2.058(6) and Pt–B(2) 2.052(6) Å] together with the B–Pt–B [78.2(3)°] and P–Pt–P angles [99.4(1)°]. These values fall in or close to the range observed for other structurally characterised platinum(II) *cis* bis-boryl compounds[2–6] in which the boron atoms carry oxygen or sulfur substituents (Pt–B distances, B–Pt–B angles and non-chelate P–Pt–P anlges are in the range 2.03–2.076 Å, 73.0–81.0 and 100.38–107.14°, respectively).¶ There is no decisive crystallographic evidence for platinum-to-boron π-back-bonding in **1**.



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In **1**, the angles defined by the boron ligand planes and the mean platinum square plane are 81.1 and 87.4° for B(1) and B(2), respectively, therefore showing that the boryl ligands are essentially orthogonal to the platinum square plane [as observed for most platinum(II) *cis* bis-boryl complexes[2–6,9]]. Whether or not an electronic origin exists for the acute B–Pt–B angles (and large P–Pt–P angles) and/or the orientations of the boryl ligands is unclear at present, although we note that recent theoretical studies on model (PH$_3$)$_2$ platinum(II) *cis* bis-boryl complexes do reproduce the experimentally observed geometries.[10] Further insight into this matter, including the extent of any platinum-to-boron π-back-bonding, will have to await a more detailed theoretical analysis. The B$\cdots$B distance in**1** [2.591(9) Å] is also typical (*cf.* the range 2.514–2.667 Å for the complexes described in refs. 2–6); for comparison and the B–B bond distance in crystalline B$_2$F$_4$ is 1.67 Å.[11]

It is noteworthy that **1** is isoelectronic with the product of double oxidation of the η^2-alkene complex [Pt(PPh$_3$)$_2$(η-C$_2$F$_4$)] {whose arsine analogue, [Pt(AsPh$_3$)$_2$(η-C$_2$F$_4$)],[12] has been structurally characterised; C–C 1.447(18) Å} implying that such a complex would be a bis-carbene species, [Pt(PPh$_3$)$_2$(CF$_2$)$_2$]$^{2+}$, with a significantly longer, non-bonding C$\cdots$C interaction. The electronic requirements for this kind of alkene cleavage (as studied by Lappert and others; see ref. 13 and references therein) or its reverse, carbene coupling, have been examined by Hoffmann and coworkers.[13]

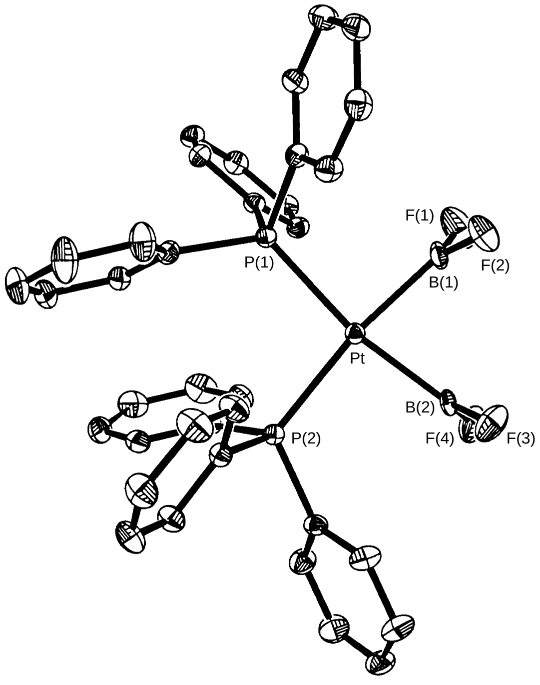

Fig. 1 A view of the molecular structure of **1** with key atoms labelled. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°): Pt–B(1) 2.058(6), Pt–B(2) 2.052(6), B(1)–F(1) 1.324(7), B(1)–F(2) 1.342(7), B(2)–F(3) 1.327(6), B(2)–F(4) 1.330(7); B(1)–Pt–B(2) 78.2(3), P(1)–Pt–P(2) 99.35(5), F(1)–B(1)–F(2) 110.6(5), Pt–B(1)–F(1) 124.6(5), Pt–B(1)–F(2) 124.7(4), F(3)–B(2)–F(4) 110.8(5), Pt–B(2)–F(3) 125.7(4), Pt–B(2)–F(4) 123.5(4).

To the best of our knowledge, there are no previous reports of metal–BF_2 complexes although we note that a number of BCl_2 (and some BBr_2 and BI_2) complexes have been described, but not structurally characterised, by Nöth and coworkers.[14] Further studies are in progress to examine the reactivity of B_2F_4 towards a range of transition metal compounds with a view to preparing further examples of complexes containing BF_2 ligands; we have recently structurally characterised the complex *cis*-[Pt(BF_2)$_2$(dppb)] [dppb = 1,2-bis(diphenylphosphino)butane] full details of which will be described in a future full paper.[15]

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Notes and References

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† A sample of [Pt(PPh_3)$_2$(η-C_2H_4)] (0.080 g, 0.011 mmol) was dissolved in toluene (5 cm^3) in a Young's tap tube after which the reaction flask was cooled in a liquid-nitrogen Dewar. A sample of B_2F_4 (*ca*. 0.03 mmol) was then condensed into the Young's tap tube and the contents allowed to warm to room temp. with stirring once the solvent had melted. A white precipitate formed at *ca*. −50 °C and once at room temp., stirring was continued for 30 min. After this time, the solvent volume was reduced slightly by vacuum and the reaction flask sealed under dinitrogen and cooled to −30 °C for *ca*. 24 h. The mother liquor was then removed by syringe and the remaining white solid dried under vacuum. Dissolution of this solid in CH_2Cl_2 (2 cm^3) afforded a cloudy pale yellow solution which was filtered affording a yellow filtrate to which a toluene overlayer (5 cm^3) was added. Solvent diffusion over a period of 7 days at −30 °C afforded pale yellow crystals of **1** (0.086 g, 97%) one of which was used for X-ray crystallography.

‡ *Spectroscopic data* for **1** (CD_2Cl_2): $^{31}P\{^1H\}$ NMR δ 24.3 (br t, $^1J_{PtP}$ 1607 Hz); $^{11}B\{^1H\}$ NMR δ 42.3; ^{19}F NMR δ −17.8 (br t, $^2J_{PtF}$ 1032 Hz); $^{13}C\{^1H\}$ NMR δ 134.4 (d, *o*-PPh_3, J_{PC} 12 Hz), 130.8 (s, *p*-PPh_3), 128.8 (d, *m*-PPh_3, J_{PC} 11 Hz), *ipso*-carbon not observed; ^1H NMR δ 7.32 (m, 18 H, PPh_3), 7.21 (m, 12 H, PPh_3). ^{31}P, ^{11}B and ^{19}F spectra were referenced to 85% H_3PO_4, $BF_3\cdot Et_2O$ and $BF_3\cdot Et_2O$ respectively. $C_{36}H_{30}B_2F_4P_2Pt$ requires C, 52.90; H, 3.70. Found C, 54.60; H, 3.90%. Mass spectrum (FAB), *m/z* 713 [Pt(PPh_3)$_2$]$^+$.

§ *Crystal data* for [Pt(PPh_3)$_2$(BF_2)$_2$]·0.5PhMe (**1**·0.5 PhMe): $C_{39.5}H_{34}B_2F_4P_2Pt$, M = 863.32, monoclinic, space group $P2_1/c$ (no. 14), a = 18.211(4), b = 9.5963(15), c = 20.422(3) Å, β = 90.617(14)°, U = 3568.7(11) Å^3, Z = 4, D_c = 1.607 Mg m^{-3}, λ = 0.71073 Å, μ = 4.070 mm^{-1}, $F(000)$ = 1700, T = 173(2) K. Data were collected on a Siemens SMART diffractometer for $1.99 < \theta < 27.57°$. The structure was solved by direct methods and refined by least-squares methods against all 8156 F^2 values with $F^2 > -3\sigma(F^2)$ to wR_2 = 0.0701 [R_1 = 0.0373 for 5825 data with $F^2 > 2\sigma(F^2)$]. Other crystals inspected (which were isostructural with **1**) showed signs of compositional disorder consistent with partial hydrolysis having occurred during recrystallisation leading to replacement of some BF_2 ligands by some B(OH)$_2$ or B(OH)F. CCDC 182/713.

¶ A preliminary presentation of the structure of the complex [Pt(PPh_3)$_2${B(OMe)$_2$}$_2$] reports Pt–B distances of 2.098(4) and 2.100(4) Å and B–Pt–B and P–Pt–P angles of 72.9(2) and 107.69(3)° respectively.[9]

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