A Base-stabilized Iodoborylene Complex of Platinum(II)

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The first base-stabilized iodoborylene platinum complex was prepared through the addition of 4-picoline (4-Pic) to a suspension of an iodo-bridged binuclear iodoboryl complex. An X-ray structure determination of the title compound has characterized the molecular structure as *cis*-[Pt{BI(4-Pic)}I_2(PCy_3)]. The bond lengths lie in the expected range for neutral, base-stabilized borylene complexes. The strong *trans* influence of the borylene moiety is reflected in the longer Pt–I distance for the iodo ligand opposite the borylene, compared to that opposite the phosphine ligand.

Key words: Boron, Borylene, Base Stabilization, Iodine, Transition Metal Complex

Introduction

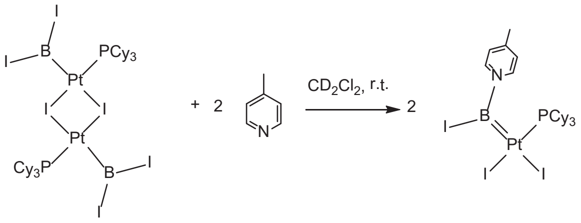
Although transition metal borylene complexes [1 – 3] are by now well-known species, only a few distinct classes of these molecules have been prepared, and many challenges still exist in their synthesis. For instance, terminal borylene complexes have only been synthesized with either strongly π-basic or sterically demanding substituents: the smallest alkyl borylene substituent known to stabilize a terminal borylene complex is *tert*-butyl, while for aryl groups it is mesityl and duryl. One other glaring paucity in the synthesis of borylene complexes can be found with the haloborylenes. While for heavier group 13 analogs, monovalent element halides can act as terminal ligands (*e. g.* the terminal iodogallylene of Aldridge and coworkers [4]), terminal haloborylenes are completely unknown and even bridging haloborylene complexes are rare [1 – 3, 5 – 8]. In 2009 and 2010 the groups of Aldridge and Andrews isolated long-anticipated fluoroborylene complexes [9 – 12]. However, the former required bridging over two metals, and the latter, while terminal, were isolated only in a matrix at 5 K.

Iodoborylene complexes, either as base-stabilized, bridging or terminal examples, have until now been completely unknown. A theoretical study on terminal haloborylenes of the form [M(BX)(η^5-C_5H_5)$(CO)_2$] (M = Mn, Re; X = F, Cl, Br, I) from 2011 indicated that heavier halides result in shorter and stronger M=B bonds. However, the very poor orbital overlap between boron and iodine may lead to strong Lewis acidity of the boron atom and necessitate the addition of a base to stabilize the complexes. Interestingly, while base-stabilized bromoborylenes are known [13], none have been structurally authenticated. Herein, we describe the isolation and characterization of a base-stabilized iodoborylene complex of divalent platinum, the first preparation of an iodoborylene of any sort.

Results and Discussion

The bis(iodo)-bridged diiodoborylcomplex [Pt(BI_2)(μ-I)(PCy_3)$]_2$ [14] was seen as an excellent candidate for the addition of Lewis bases, given the two bridging iodo ligands. Addition of a Lewis base to this complex could conceivably have led to interesting diiodoboryl complexes with mutually *trans* neutral ligands, and possibly provided a convenient route to mixed-ligand boryl complexes. However, the reaction of yellow crystals of suspended [Pt(BI_2)(μ-I)(PCy_3)$]_2$ in CD_2Cl_2 with two equivalents of 4-picoline (4-Pic) resulted instead in a red solution of the mononuclear, base-stabilized iodoborylene complex *cis*-[Pt{BI(4-Pic)}I_2(PCy_3)], **1** (Scheme 1). Filtration and evaporation of the solvent provided analytically pure red crystals of **1** (53 %).

A signal shifted to higher frequency with respect to the starting material [6] in the $^{31}P\{^1H\}$ NMR spectrum was detected at $\delta = 30.3$ ppm ($^1J_{P-Pt} = 4794$ Hz). A broad signal in the $^{11}B\{^1H\}$ spectrum appears at $\delta = 35.7$ ppm, suggesting a significant amount of boryl



Scheme 1. The synthesis of base-stabilized iodoborylene **1**.

character of the boron-centered ligand. The aryl protons of 4-Pic appear as two multiplet signals representing two protons each at 10.10 and 7.62 ppm, lying in the typical range of the aryl resonances of boron-bound 4-Pic substituents in cationic base-stabilized borylene complexes of the general formula *trans*-[Pt{BR(4-Pic)}Br(PCy$_3$)$_2$]$^+$ [15 – 17], while the signal for the three methyl protons was found at 2.58 ppm.

Compound **1** crystallizes in an orthorhombic crystal system in the space group *Pbca* with $Z = 8$. The molecular structure (Fig. 1) shows a square-planar, *cis*-configurated geometry for the complex. The boron atom of the borylene ligand is *sp*^{2}-hybridized and features an anionic iodo and a neutral 4-Pic substituent, similar to other base-stabilized borylene ligands [18 – 21]. Formally, **1** results from the attack of the base at the boron atom inducing a boron-to-platinum halide shift. The Pt–B distance of **1** (197.7(3) pm) is significantly shorter than in cationic base-stabilized borylene ligands of Pt [1 – 3]. However, this effect could be due to the lack of charge and the influence of the two iodo ligands in **1**, as its Pt–B distance is statistically equivalent to that of its closest relative, the base-stabilized borylene *cis*-[Pt{BFc(4-Pic)}Br$_2$(PCy$_3$)] (198.8(3) pm) [15 – 17]. The B–N separation (156.4(4) pm) lies in the typical range of cationic base-stabilized borylene platinum complexes (*e. g.* *trans*-[Pt{B(Pip)(4-Pic)}Br(PCy$_3$)$_2$][BAr$^f_4$]: 156.5(5) pm, Pip = C$_5$H$_{10}$N, Ar^f = 3,5-C$_6$H$_3$(CF$_3$)$_2$) [21] and the B–I3 distance (219.6(3) pm) is similar to those in *trans*-[Pt(BI$_2$)I(PCy$_3$)$_2$] (**2**) (218.9(7) and 218.5(8) pm) [14]. The B–Pt–I2 angle is 70.1(2)°, and the distance between the boron atom and the platinum-bound iodo ligand next to the boron atom has a value of B–I2 272.8 pm. The sum of the covalent radii of the elements concerned is 223(4) pm, ruling out a covalent interaction. The Pt–I1 bond length in *trans* disposition to the borylene ligand is about 3 % longer (274.91(3) pm) than the Pt–I2 distance in *trans* disposition to the PCy$_3$ ligand (266.99(4) pm), indicating both the strong *trans* influence of the borylene ligand and its similarity to known boryl ligands [17, 19 – 21].

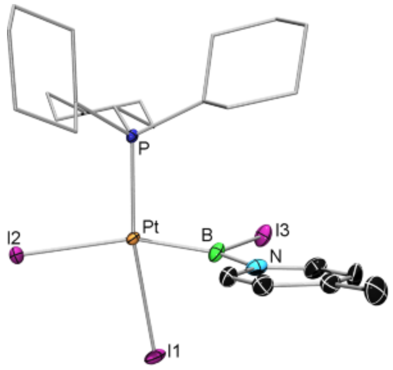


Fig. 1 (color online). Molecular structure of *cis*-[Pt{BI(4-Pic)}I$_2$(PCy$_3$)] (**1**) in the crystal. Displacement ellipsoids represent 50 % probability. For clarity, the ellipsoids of the cyclohexyl substituents as well as one molecule of CH$_2$Cl$_2$ are not displayed. Selected bond lengths (pm) and angles (deg): Pt–B 197.7(3), Pt–P 225.04(7), Pt–I1 274.91, Pt–I2 266.99(4), B–I3 219.6(3), B–N 156.4(4); B–Pt–I1 163.37(10), P–Pt–I2 169.03(2), B–Pt–P 99.5(1), B–Pt–I2 70.1(1), I1–Pt–I2 93.462(9).

In summary, the first example of an iodoborylene complex was prepared by a remarkably simple route, the addition of 4-picoline to a binuclear platinum(II) diiodoboryl complex. The complex has been structurally and spectroscopically characterized, and its Pt–B distance reflects a bonding situation somewhere between a single and double bond.

Experimental Section

*cis-[Pt{BI(4-Pic)}I$_2$(PCy$_3$)] (**1**)*

To a yellow suspension of crystalline [Pt(BI$_2$)(μ-I)(PCy$_3$)]$_2$ (100 mg, 57.7 mol) in 0.5 mL CD$_2$Cl$_2$, a solution of 4-picoline was added under vigorous stirring (10.0 mg, 107 mol). During the addition, most of the solid dissolved, and a red solution was formed. The remaining solids were filtered off, and the solution was covered with hexanes. A crystalline red sample of **1** was obtained in 53 % yield (58.3 mg). – ^{1}H NMR (500.13 MHz, CD$_2$Cl$_2$, 296.5 K): δ = 10.10 (m, 2H, Pic), 7.62 (m, 2H, Pic), 2.58 (s, 3H, Me-4-Pic), 2.45 – 2.37 (m, 3H, Cy), 2.05 – 1.54 (m, 24H, Cy), 1.20 – 1.08 (m, 6H, Cy). – ^{13}C{^{1}H} NMR (125.77 MHz, CD$_2$Cl$_2$, 296.8 K): δ = 161.0 (s, C$_{\text{para}}$, 4-Pic), 150.9 (s, C$_{\text{ortho}}$, Pic), 127.1 (s, C$_{\text{meta}}$, 4-Pic), 37.7 (m, C1, Cy), 30.4 (br s, C3/5, Cy), 27.6 (m, C2/6, Cy), 26.2 (s, C4, Cy), 22.5 (s,

CH_3, Me-4-Pic). – ^{11}B{^{1}H} NMR (160.47 MHz, CD_2Cl_2, 296.5 K): $\delta = 35.7$. – ^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, 296.8 K): $\delta = 30.3$ (s, $^1J_{\mathrm{P-Pt}} = 4794$ Hz). – Elemental analysis for $C_{24}H_{40}BI_3NPPt{\cdot}CH_2Cl_2$: calcd. C 28.72 (28.73); found H 4.04 (4.05); N 1.52 (1.34) %.

Crystal structure determination

The crystal data of **1** were collected on a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror monochromated MoK_α radiation. The structure was solved using Direct Methods, expanded using Fourier techniques and refined with the SHELX software package [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations.

Crystal data for **1**: $C_{25}H_{42}BCl_2I_3NPPt$, $M_r = 1045.07$, orange block, $0.31 \times 0.27 \times 0.17$ mm^3, orthorhombic space group *Pbca*, $a = 16.326(2)$, $b = 16.583(2)$, $c = 23.842(4)$ Å, $V = 6455.0(16)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd.}} = 2.15$ g·cm^{-3}, $\mu = 7.4$ mm^{-1}, $F(000) = 3920$, $T = 100(2)$ K, $R_1 = 0.0250$, $wR^2 = 0.0535$, 9799 independent reflections [$2\theta \leq 61.04°$] and 308 refined parameters, $\Delta\rho_{\mathrm{fin}}$ (max / min) = 1.608 / -2.151 e Å^{-3}.

CCDC 927832 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[1] H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924 – 3957.

[2] H. Braunschweig, R. D. Dewhurst, V. H. Gessner, *Chem. Soc. Rev.* **2013**, doi: 10.1039/c3cs35510a.

[3] C. E. Anderson, H. Braunschweig, R. D. Dewhurst, *Organometallics* **2008**, *27*, 6381 – 6389.

[4] N. D. Coombs, W. Clegg, A. L. Thompson, D. J. Willock, S. Aldridge, *J. Am. Chem. Soc.* **2008**, *130*, 5449 – 5451.

[5] H. Braunschweig, M. Müller, *Chem. Ber.* **1997**, *130*, 1295 – 1298.

[6] P. Bissinger, H. Braunschweig, F. Seeler, *Organometallics* **2007**, *26*, 4700 – 4701.

[7] K. K. Pandey, H. Braunschweig, R. D. Dewhurst, *Eur. J. Inorg. Chem.* **2011**, 2045 – 2056.

[8] H. Braunschweig, K. Radacki, D. Rais, F. Seeler, K. Uttinger, *J. Am. Chem. Soc.* **2005**, *127*, 1386 – 1387.

[9] D. Vidovic, S. Aldridge, *Angew. Chem. Int. Ed.* **2009**, *48*, 3669 – 3672.

[10] X. Wang, B. O. Roos, L. Andrews, *Angew. Chem. Int. Ed.* **2010**, *49*, 157 – 160.

[11] X. Wang, B. O. Roos, L. Andrews, *Chem. Commun.* **2010**, *46*, 1646 – 1648.

[12] H. Braunschweig, R. D. Dewhurst, *Angew. Chem. Int. Ed.* **2010**, *49*, 3412 – 3414.

[13] H. Braunschweig, K. Radacki, K. Uttinger, *Organometallics* **2008**, *27*, 6005 – 6012.

[14] H. Braunschweig, K. Radacki, K. Uttinger, *Inorg. Chem.* **2007**, *46*, 8796 – 8800.

[15] H. Braunschweig, P. Brenner, K. Radacki, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2089 – 2092.

[16] H. Braunschweig, K. Radacki, K. Uttinger, *Chem. Eur. J.* **2007**, *13*, 7858 – 7866.

[17] H. Braunschweig, P. Brenner, A. Müller, K. Radacki, D. Rais, K. Uttinger, *Chem. Eur. J.* **2007**, *13*, 7171 – 7176.

[18] G. J. Irvine, C.E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Angew. Chem. Int. Ed.* **2000**, *39*, 948 – 950.

[19] C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Organometallics* **2002**, *21*, 4862 – 4872.

[20] H. Braunschweig, K. Radacki, D. Rais, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2005**, *44*, 5651 – 5654.

[21] H. Braunschweig, K. Radacki, K. Uttinger, *Organometallics* **2008**, *27*, 6005 – 6012.

[22] G. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.