

COMMUNICATION

Side-on phosphinoboryl platinum(II) complexes

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In this work, we report the synthesis of the first phosphinoboryl transition metal complexes, featuring a direct covalent bond between boron and phosphorus atoms. The oxidative addition of bromo(phosphino)boranes to platinum(0) compounds enabled the formation of platinum(II) complexes with unprecedented side-on coordination of the boryl ligand.

Transition metal boryl complexes have been extensively studied computationally and experimentally due to the strong σ -donors of Lewis acidic boryl ligands with minimal π -backbonding to the metal center^{1–13}. Many groundbreaking discoveries have been made since the first mention of boryls in the 1960s¹⁴. These complexes are well established and have been used as key intermediates in numerous reactions such as diboration^{15–23}, hydroboration^{24,25}, the activation of CO₂ and CS₂²⁶, and C–H borylation^{27–29}.

Several methods have been used for the preparation of mono-, bis-, and tris-transition-metal boryl complexes. A method widely used to obtain mono- and bis-boryl complexes is the oxidative addition of diboron^{22,23,30–33} (B–B) or borane^{34–37} (B–X, X = H or halogen) to low-valent metal centers to provide bis(boryl) and boryl complexes, respectively. Braunschweig reported iron, ruthenium, and platinum complexes bearing ferrocenyl(bromo)boryl ligands³⁸ as well as cationic platinum(II) boryl complexes^{39,40} demonstrating the high *trans* influence of the boryl group and applied *trans*-[(Cy₃P)₂Pt(Br){B(Mes)Br}] (Cy = cyclohexyl, Mes = mesityl) in the synthesis of base-free platinum(II) borylene complexes⁴¹. Furthermore, the trisboryl complexes [(Me₃P)₃Co(Bcat)₃]⁴² and [xant(PⁱPr₂)₂Ir(Bcat)₃] [Bcat = catecholboryl; xant(PⁱPr₂)₂ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene]⁴³ have also been investigated. Notably, complexes bearing PBP polydentate borane⁴⁴ and boryl ligands^{45–52} have found application in

hydrogen activation⁵³, as catalysts in the dehydrogenation of dimethylamine⁵⁴ and the hydrosilylation of aldehydes⁵⁵, and as pre-catalysts in ethylene polymerization⁵⁶ (Chart 1A). Interestingly, the cobalt(I) diphosphinoboryl complex underwent reversible double H₂ activation⁵⁷.

While platinum complexes bearing directly bonded low-valent P–B ligands have been previously described by Bourissou⁵⁸ with phosphinoborane (Chart 1B) and by Drover⁵⁹ and our group⁶⁰ with diphosphinoboranes, no transition metal boryl complexes with directly bonded boron and phosphorus centers have been reported to the best of our knowledge.

In this work, we synthesized and characterized the first platinum(II) complexes with a side-on bonded phosphinoboryl ligand featuring a direct B–P bond (Chart 1C). Recently, we used bromo(phosphino)boranes as substrates to synthesize phosphinoborinium^{61,62} and phosphinoborenium^{63,64} cations via bromide anion abstraction. The presence of reactive B–Br and B–P bonds in these boranes encouraged us to explore them as precursors for boryl ligands. Furthermore, we supposed that the introduction of a donor phosphanyl group to the boron atom will facilitate the side-on coordination of the boryl ligand to the transition metal center.

First, we tested the reactivity of *i*Pr₂N(Br)BPtBu₂ (**a**) with [(C₂H₄)Pt(PPh₃)₂] (**1**) in dichloromethane (Scheme 1). The reaction was initiated at –50 °C, after which the reaction mixture was gradually warmed to room temperature and stirred for 72 h. The reaction progress was monitored by ³¹P and ¹¹B NMR spectroscopy, with the near complete consumption of the starting materials upon reaction completion.

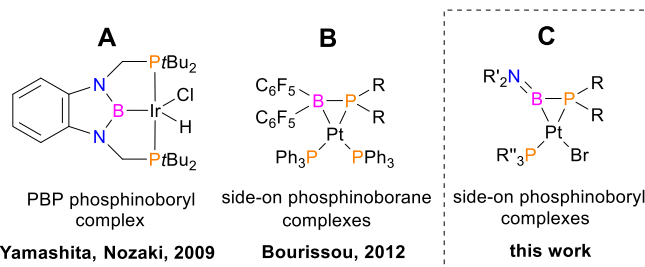
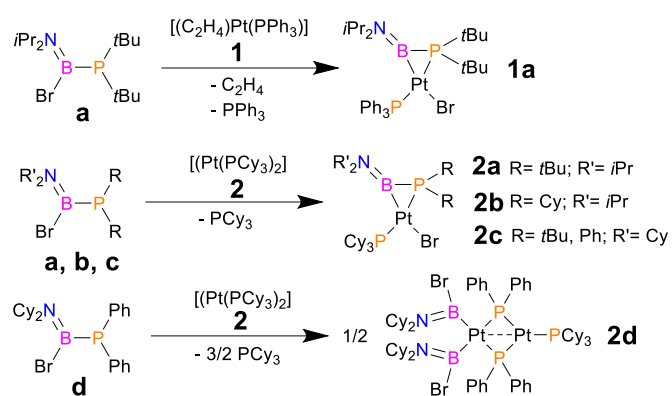


Chart 1. Structures of selected transition metal complexes with boron–phosphorus ligands.

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Scheme 1. Syntheses of platinum(II) complexes **1a** and **2a–2d**.

The desired phosphinoboryl Pt(II) complex (**1a**) was isolated as yellow crystals by diffusion crystallization from a toluene/pentane system at room temperature. The ^{31}P -NMR spectrum of **1a** displayed two doublets at 42.5 and -67.2 ppm with a $^2J_{PP}$ coupling constant of 265 Hz, which were respectively attributed to the phosphine ligand and tBu_2P fragment of the phosphinoboryl ligand. The large $^2J_{PP}$ coupling constant indicated that the phosphine ligand and the phosphorus atom of the phosphinoboryl group were positioned trans to each other. Both resonances exhibit platinum satellites, with coupling constants of 3314 Hz (PPh_3) and 1168 Hz ($iPr_2NB-PtBu_2$), confirming the coordination of the phosphorus atoms to the platinum(II) center. Notably, the ^{31}P NMR resonance of the phosphinoboryl ligand is significantly upfield shifted relative to the phosphorus resonance of the parent borane (-11.2 ppm). The ^{11}B NMR spectrum of **1a** showed a single broad resonance at 40.4 ppm, similar to the corresponding resonance of the borane (39.5 ppm), suggesting the presence of a tricoordinate boron atom. Furthermore, the oxidative addition of the B–Br bond of the parent bromo(phosphino)borane to the Pt(0) center was unambiguously confirmed by the X-ray diffraction (XRD) analysis of the crystals of **1a** (for the molecular structure of this complex, see Fig. S31).

Despite the successful isolation of the target complex **1a**, NMR analysis of the reaction mixture indicated the formation of several unidentified byproducts, explaining the low isolation yield of **1a** (18%). This finding encouraged us to search for more effective alternative metal precursors for side-on phosphinoboryl complexes. We turned our attention to $Pt(PCy_3)_2$ (**2**), which had been previously used as a substrate to synthesize numerous platinum boryl complexes.^{33–35,38–41} Unlike the reaction involving **1**, precursor **2** cleanly reacted with $iPr_2N(Br)BPtBu_2$ (**a**) in toluene.

Based on ^{31}P NMR spectroscopy, the reaction mixture contained only the target side-on phosphinoboryl complex **2a** and free PCy_3 as products (Fig. S13). This observation aligned with the proposed stoichiometry for the reaction of **2** with **a** (Scheme 1). The NMR spectroscopic features of **2a** were similar to those observed for **1a**, displaying a broad singlet in the ^{11}B NMR spectrum at 39.5 ppm and two coupled doublets with platinum satellites in the ^{31}P spectrum: $\delta = 40.3$ ppm (d, $^2J_{PP} = 239$ Hz, $^1J_{PtP} = 3148$ Hz, PCy_3); $\delta = -75.9$ ppm (bd, $^2J_{PP} = 239$ Hz, $^1J_{PtP} = 1080$ Hz, tBu_2P). Evaporating the solvent, dissolving the residue in

petroleum ether, and then storing the solution at -20 °C provided **2a** as yellow crystals with a 61% yield. The formation of **2a** was further confirmed by single-crystal XRD (Fig. 1).

To study the influence of the steric and electronic features of parent bromo(phosphino)boranes on the reaction outcomes of **2**, we conducted a series of analogous experiments with $iPr_2N(Br)BPtCy_2$ (**b**), $Cy_2N(Br)BPtBuPh$ (**c**), and $Cy_2N(Br)BPtPh_2$ (**d**). The boranes **b** and **c** reacted with **2** in a manner similar to **a**, producing only the desired side-on phosphinoboryl complexes (**2b**, **2c**) and free PCy_3 . The isolation yields of complexes **2b** and **2c** were 60% and 74%, respectively. NMR spectroscopic data and XRD analyses of **2b** and **2c** fully supported the formation of side-on phosphinoboryl complexes (see ESI for details, Figures S32 and S33).

In contrast to experiments with compounds **a–c**, phosphinoborane **d**, with less bulky and electron-withdrawing phenyl substituents on the phosphorus atom, reacted with **2** in toluene through the oxidative addition of the B–P bond instead of the B–Br bond to the metal fragment (Scheme 1). Evaporation of the solvent and crystallization from petroleum ether at -20 °C yielded **2d** as red crystals along with byproducts such as PCy_3 and the hydrido complex $[Br(H)Pt(PCy_3)_2]$ in a molar ratio of 2:4:1. The complex **2d** exhibited solubility in hydrocarbons similar to that of the byproducts, which prevented its purification via crystallization. X-ray analysis revealed that **2d** contained two Pt(II) centers connected by two bridging PPh_2 phosphido ligands (Fig. S34). Additionally, two Cy_2NBBr boryl ligands were coordinated to the first platinum atom, while one PCy_3 ligand completed the coordination sphere of the second platinum atom. The XRD results aligned with the $^{31}P\{^1H\}$ NMR data for **2d**, which displayed two coupled doublets ($^2J_{PP} = 80$ Hz): a highly deshielded resonance at 235.3 ppm with two sets of platinum satellites ($^1J_{Pt1P} = 979$ Hz, $^1J_{Pt2P} = 2780$ Hz) attributed to the bridging phosphido ligands, and a second resonance at 61.4 ppm for the PCy_3 ligand coupled only to one platinum center ($^1J_{Pt2P} = 2780$ Hz). Unlike **1a** and **2a–2c**, **2d** did not show any resonance in the ^{11}B NMR spectra despite the presence of two boryl ligands. The electron-withdrawing phenyl substituents on the phosphorus atom in the parent phosphinoborane facilitated the heterolytic cleavage of the B–P bond after the nucleophilic substitution of the electron-rich Pt(0) center onto the electrophilic boron atom and additionally stabilized the negative charge of the departing phosphido ligand. To our knowledge, compound **2d** is the first example of a transition metal complex containing both phosphido and boryl ligands.

All title phosphinoboryl complexes exhibited very similar structural features; therefore, they will be discussed in detail using the representative compound **2a** as an example (Fig. 1). The phosphinoboryl ligand coordinated to the Pt(II) center in a side-on manner *via* B1 and P1 atoms, forming a Pt1–B1–P1 triangle. Additionally, the phosphine and bromido ligands coordinated to the metal and were respectively positioned trans to the P1 and B1 atoms of the phosphinoboryl group. The geometry around the Pt1 atom was a distorted square planar, with the P2 and Br1 atoms deflected from the Pt1–B1–P1 plane in opposite directions by 0.411 and 0.321 Å, respectively.

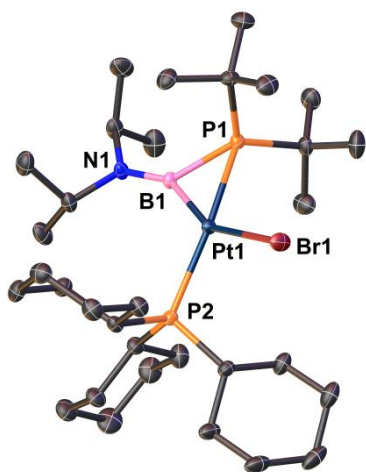


Figure 1. X-ray structure of complex **2a**. H-atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Due to the side-on coordination of the phosphinoboryl ligand, the B1–Pt1–P1 angle was acute, measuring $52.55(7)^\circ$, while the other angles around the Pt1 atom were obtuse, ranging from $93.75(2)^\circ$ to $112.10(7)^\circ$. The Pt1–B1 bond distance of 2.020 \AA was very close to analogous distances reported for aminoboryl platinum complexes.³⁴ The Pt1–P1 bond (2.286 \AA) was slightly shorter than the distance between Pt1 and the P2 atom of the PCy₃ ligand (2.323 \AA). Moreover, the B–P bond within the phosphinoboryl ligand ($1.921(3) \text{ \AA}$) was somewhat shorter than the expected length for a single covalent bond (1.96 \AA).⁶⁵ The B1 and N1 atoms exhibited planar trigonal geometries, with the sums of the angles around these atoms close to 360° . This is consistent with the significantly shortened B1–N1 bond distance ($1.385(3) \text{ \AA}$) and suggests π -donation from the N1 atom to the B1 atom. Furthermore, the Pt1–Br bond distance of 2.608 \AA was notably longer than the typical Pt–Br bond length (2.37 \AA),⁶⁵ which can be attributed to the strong trans effect of the phosphinoboryl ligand.

The electronic structure of **2a** was investigated through theoretical methods. According to our findings, the HOMO of **2a** was delocalized mainly at the Pt1–B1–P1 triangle in a bonding manner, with some contribution from the lone electron pair on the Br1 atom (of nonbonding character) (Fig. S36). The LUMO was also based on the Pt1–B1–P1 region (in a bonding manner) but with antibonding contributions between the Pt1–B1–P1 triangle and neighboring atoms (Fig. S36). According to natural bond orbital analysis, the largest positive charges were located on the P2 (+1.08), P1 (+0.57), and B1 (+0.50) atoms, whereas the platinum center carried only a slight positive charge (+0.13). The largest negative charges were found on the N1 (–0.81) and Br1 (–0.78) atoms. The phosphinoboryl ligand was stabilized by π -donation from the N1 atom to a formally empty, unhybridized p orbital of boron, consistent with the planar trigonal geometry around these atoms. The lone pair on the P1 atom interacted not only with the metal center, forming a dative bond but also, to a lesser extent, with the antibonding $\pi^*(\text{B1–N1})$ orbital, shortening the B1–P1 bond. The calculated 57% contribution of Pt to the $\sigma(\text{Pt1–B1})$ bond confirmed the covalent character of this bond. The ratio of boron p- to s-orbital contributions in the $\sigma(\text{Pt1–B1})$ bond was 1:1.82, indicating the strong σ -donor

properties of the phosphinoboryl ligand. These properties led to the strong trans effect of this ligand,⁶⁶ which manifested in a significant elongation of the Pt1–Br1 bond.

In conclusion, we developed a simple synthetic route for side-on phosphinoboryl complexes. The presence of reactive Pt–B and B–P bonds in these structures makes them promising candidates for applications in small molecule activation and catalysis.

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Conflicts of interest

There are no conflicts to declare

Data availability

The data supporting this article have been included as part of the ESI. Crystallographic data has been deposited at the CCDC under 2402129 (for **1a**), 2402130 (for **2**), 2402131 (for **2a**), 2402132 (for **2b**), 2402133 (for **2c**), 2402134 (for **2d**), and 2402135 (for **2H**).

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