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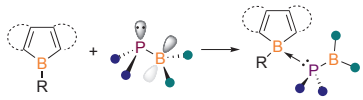
Addition of a Phosphinoboronate Ester to Borole and Borafluorene



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Dedicated to Professor Donald Matteson and in memory of the late Professor Stephen Westcott in recognition of their contributions to organoboron chemistry.

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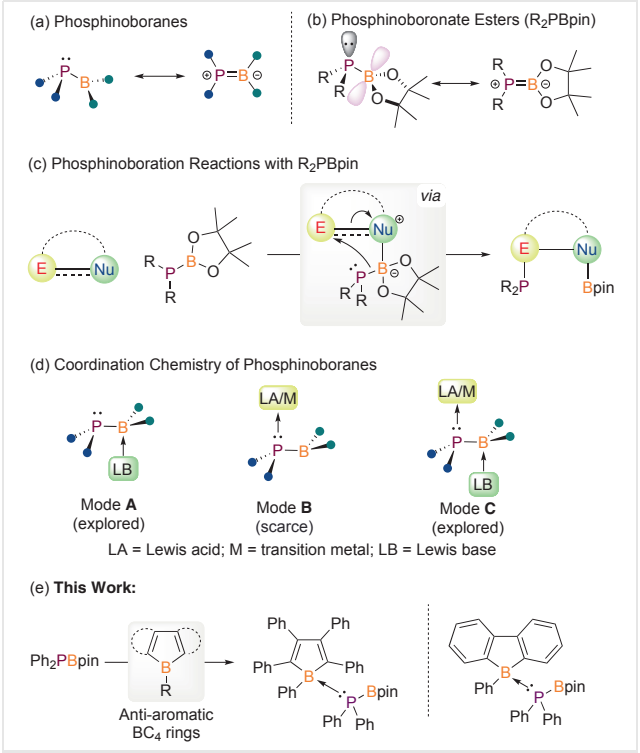
Abstract The additions of the phosphinoboronate ester Ph_2PBpin to an antiaromatic borole and a borafluorene is reported. The Lewis acid/base adducts are obtained in excellent yields and represent the first P-donor adducts of Ph_2PBpin.

Key words pinacol diphenylphosphinoboronate, boroles, borafluorenes, antiaromaticity, Lewis acid

Phosphinoboranes[1–3] ($R_2P–BR_2$) feature trivalent and tricoordinate P and B atoms linked covalently and are valence isoelectronic with aminoboranes ($R_2N–BR_2$; Scheme 1a).[1,3–4] In species with alkyl or aryl substituents on boron, dimerization typically occurs;[1,5–7] however, if there is sufficient steric bulk or the boron atom is disubstituted with alkoxy groups, dimerization is precluded. These monomers can be viewed as frustrated Lewis pairs. In 2014, phosphinoboronate esters R_2PBpin (R = Ph, Cy; pin = pinacolato) (Scheme 1b) were disclosed;[8] these enabled effective phosphinoborations in which a phosphine and a borane moiety are introduced onto a substrate through addition across an unsaturated bond. This single-step transformation is effective for an array of organic substrates that includes aldehydes, ketones, aldimines, α,β-unsaturated carbonyls, heteroallenes, diazobenzenes, diazomethanes, pyridines, and CO_2 (Scheme 1c).[9–18]

Despite the phosphinoboration reaction gaining attraction in synthesis, its mechanism is not well understood. The coordination chemistry of phosphinoboranes presents insight into whether they act as Lewis acids, Lewis bases, or ambiphiles. In phosphinoboranes, three Lewis acid/base binding modes are possible: binding of a Lewis base to the boron center (Mode **A**; Scheme 1d), binding of the phosphorus atom to a Lewis acid (Mode **B**), and a combination of



Scheme 1 (a) Phosphinoborane structure, (b) Phosphinoboronate esters (R_2PBpin), (c) Phosphinoboration reaction with R_2PBpin, (d) Literature reports on the coordination chemistry of phosphinoboranes, (e) Phosphinoboronate esters (R_2PBpin): this work.

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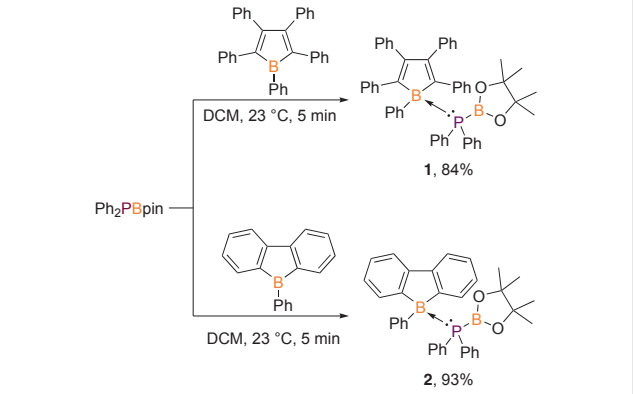
both types of interaction (Mode **C**). Within these, Modes **A** and **C**, in which the boron atom acts as a Lewis acid, have been widely explored,[7,19–36] whereas reports on the phosphorus atom acting as a Lewis base (Mode **B**) are scarce.[6,21,37]

Proposed mechanisms for the phosphinoboration addition to organic substrates have been in line with the aforementioned coordination chemistry of boron acting as a Lewis acid. In the literature, it has been suggested that the substrate acts as a nucleophile to coordinate to the boron center to form an activated borate intermediate. In the borate intermediate, the phosphorus center is rendered more nucleophilic and the B–P bond is weakened, enabling it to rupture and add across an unsaturated bond (Scheme 1c). Recently, it was demonstrated that tributylphosphine can catalyze phosphinoboration across C≡C triple bonds, further suggesting that boron activation is occurring.[38] In Ph_2PBpin, despite the presence of tricoordinate boron and phosphorus centers, there is negligible π-dative interaction between the phosphorus lone pair and the p-orbital on the boron.[8] X-ray diffraction confirmed that the phosphorus atom is pyramidal [sum of angles = 310.0(6)°], in accordance with calculations. To date, neither the nucleophilicity nor the coordination chemistry of the phosphorus atom has been investigated.

Because the donor ability of the phosphine in Ph_2PBpin is diminished, we hypothesized that reactions with strong Lewis acids might furnish stable adducts (Mode **B**). Boroles and 9-borafluorenes both contain a central unsaturated BC_4 ring that is rendered highly Lewis acidic due to its antiaromatic state.[39–42] To understand the coordination chemistry of phosphinoboranes and to provide insight into possible reaction mechanisms, we report the reactions of Ph_2PBpin with pentaphenyl-1*H*-borole and 9-phenyl-9-borafluorene.

Treatment of Ph_2PBpin with pentaphenyl-1*H*-borole or 9-phenyl-9-borafluorene at 23 °C in dichloromethane led to P–B adducts **1** and **2**, respectively, in excellent yields (Scheme 2). The reaction progress could be monitored by the immediate color change from dark blue (borole) or yellow (9-phenyl-9-borafluorene) to colorless, indicating the consumption of the central unsaturated BC_4 ring.

In the $^{11}B\{^1H\}$ NMR spectra of the reaction mixtures, the broad peaks for tricoordinate boron centers of pentaphenyl-1*H*-borole (δ = 64.5 ppm) and 9-phenyl-9-borafluorene (δ = 65.4 ppm) disappeared while new peaks emerged in the tetracoordinate region at δ = –5.2 and –9.3 ppm, respectively. The chemical shifts for the Bpin moiety appeared at δ = 30.8 and 30.9 ppm, respectively, shifted slightly upfield from that of Ph_2PBpin (δ = 34.0 ppm). The $^{31}P\{^1H\}$ NMR signals for **1** and **2** appeared at δ = –34.2 and –35.2 ppm, respectively, shifted downfield from that of Ph_2PBpin (δ = –63.5 ppm). Furthermore, the molecular structures of these B–P adducts were unambiguously determined from X-ray diffraction studies on single crystals;[43] that is, the phosphorus atom of Ph_2PBpin coordinated to the boron center of the



Scheme 2 Reaction of Ph_2PBpin with pentaphenyl-1*H*-borole and 9-phenyl-9-borafluorene

borole ring (Figure 1). Upon coordination, the P(1)–B(2) bonds of the Ph_2PBpin elongate slightly [**1**: 1.953(2) Å, **2**: 1.9432(18) Å, cf. free Ph_2PBpin: 1.9274(14) Å]. The dative P(1)–B(1) bonds were slightly longer than the P–B bond in the phosphinoboronate diester [**1**: 2.001(2) Å, **2**: 2.0047(19) Å]. Phosphine adducts of borafluorene or boroles have rarely been reported in the literature.[44–45] The analogous P(1)–B(1) bond length in pentaphenylborole·PH_2Ph is 1.983(3) Å, slightly shorter than donor bonds in **1** and **2**.[46] In the bulkier adduct of PCy_3 with 1-bromotetraphenyl-1*H*-borole, the P(1)–B(1) bond length is comparable [2.0156(19) Å].[45]

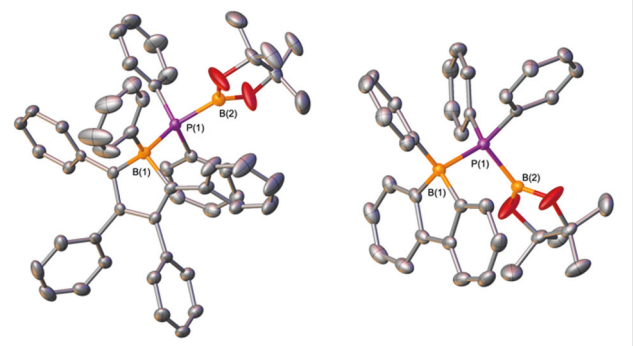


Figure 1 Solid-state structures of **1** and **2**. Ellipsoids are depicted at the 50% probability level and hydrogen atoms are omitted for clarity. For disordered atoms, only the component with the highest occupancy is shown. Selected bond lengths (Å) and angles (°) of **1**: B(1)–P(1) 2.001(2), P(1)–B(2) 1.953(2), B(1)–P(1)–B(2) 119.68(1); **2**: B(1)–P(1) 2.0047(19), P(1)–B(2) 1.9432(18), B(1)–P(1)–B(2) 107.42(8).

The results of these studies provide insight into the mechanism of phosphinoboration reactions in which Lewis acid–base adducts are proposed to be formed by coordination of oxygen to Ph_2PBpin (i.e., O→B),[8,38] increasing the P–B bond length and activating it for subsequent phosphorus transfer. Because of the high reactivity of these intermediates, characterization by NMR or X-ray crystallography has

been elusive. In the current study, reversing the polarity (P→B in **1** and **2**) forms the complementary tetracoordinate boron and reveals a concomitant increase in the P–B bond length of Ph_2PBpin, which is consistent with P–B bond activation in phosphinoboration reactions.

Boroles have diverse reactivity modes due to the presence of a Lewis acidic boron center, diene groups, and an antiaromatic state. In reactions with polar substrates, 1,4-addition across a diene or B–C bond rupture of the endocyclic bond can occur.[46–52] To investigate the potential for these reactivity modes in addition to adduct formation, **1** and **2** were heated to 70 °C in C_6D_6 for 24 hours, with no change in their NMR spectra. Further heating at 100 °C in toluene for 16 hours resulted in a complex mixture. Therefore, our studies indicate selective P–B adduct formation.

In conclusion, we report the reaction of Ph_2PBpin with antiaromatic pentaphenyl-1*H*-borole and 9-phenyl-9-borafluorene, providing the first example of the synthesis of P-donor adducts that do not have a donor bound to boron.[53] The products are obtained in high yields and are stable up to 70 °C. In addition, the unique coordination chemistry of Ph_2PBpin provides insight into a potential new reactivity mode.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-2158-9726.

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(53) **Adducts 1 and 2: General Procedure**
A solution of PPh_2Bpin (0.50 mmol, 156 mg) in benzene (4 mL) was added dropwise to a solution of pentaphenyl-1*H*-borole or 9-phenyl-9-borafluorene (0.5 mmol) in benzene (4 mL) at rt. The solution instantly became colorless, and the mixture was stirred for 10 min at rt. The solvent was then removed in vacuo and the residue was washed with cold pentane (2 × 5 mL) and dried in vacuo.

1

Pale-yellow powder; yield: 319 mg (84%,); mp 216–219 °C. FTIR (neat): (ranked intensity) 1593 (11), 1483 (8), 1438 (9), 1340 (12), 1245 (5), 1129 (2), 1028 (13), 958 (14), 841 (4), 792 (6), 741 (7), 693 (1), 542 (10), 505 (3), 460 (15) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 6.9 Hz, 2 H), 7.43–7.38 (m, 6 H), 7.33–7.27 (m, 3 H), 7.24–7.22 (m, 4 H), 6.90–6.85 (m, 6 H), 6.82–6.78 (m, 6 H), 6.75–6.74 (m, 4 H), 6.59 (d, *J* = 7.0 Hz, 4 H), 1.01 (s, 12 H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 154.5, 153.5, 153.4, 143.5, 140.5, 135.4 (d, *J* = 8.5 Hz), 135.2 (d, *J* = 12.8 Hz), 130.4 (d, *J* = 2.6 Hz), 130.3 (d, *J* = 2.6 Hz), 129.7, 127.7, 127.6, 127.3, 126.9, 126.8, 125.9, 125.4, 125.2, 125.0, 124.3, 86.5, 86.5, 24.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –34.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.8, –5.2. HRMS (ESI): the adduct peak was not observed in the HRMS. Anal. Calcd for $C_{52}H_{47}B_2O_2P$: C, 82.56; H, 6.26. Found: C 82.36, H 6.32.

Single crystals of **1** for X-ray diffraction studies were grown from a CH_2Cl_2 solution by vapor diffusion into toluene.

2

White powder; yield: 256 mg (93%,); mp 189–191 °C. FTIR (neat): (ranked intensity) 1483 (14), 1435 (8), 1373 (12), 1348 (10), 1244 (6), 1128 (4), 1103 (13), 961 (11), 836 (5), 734 (1), 696 (3), 647 (9), 616 (15), 506 (2), 427 (7) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.7 Hz, 4 H), 7.55 (d, *J* = 7.2 Hz, 2 H), 7.41 (td, *J* = 7.2, 1.6 Hz, 2 H), 7.30–7.15 (m, 13 H), 7.12 (t, *J* = 7.2 Hz, 2 H), 1.15 (s, 12 H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 153.0, 149.4, 134.6 (d, *J* = 7.5 Hz), 134.2, 132.9, 130.5 (d, *J* = 2.6 Hz), 128.3 (d, *J* = 9.5 Hz), 127.5, 126.5, 126.2, 125.8, 125.6, 125.6, 86.6, 86.6, 24.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –35.2. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.9, –9.3. HRMS (ESI): *m/z* [M + H] calcd for $C_{36}H_{36}B_2O_2P$: 553.2634; found: 553.2610. Anal. Calcd for $C_{36}H_{35}B_2O_2P$: C, 78.29; H, 6.39. Found: C, 78.54; H, 6.55.

Single crystals for X-ray diffraction studies were grown from a CH_2Cl_2 solution of **2** by vapor diffusion into toluene.