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Cationic 1,2-Azaborine Adducts of Trimethylphosphine, Triphenylphosphine oxide, and Pyridine-*N*-oxide

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Summary

The first cationic 1,2-azaborine adducts of neutral phosphorous- and oxygen-based nucleophiles have been synthesized and characterized via spectroscopic and single crystal X-ray diffraction analysis.

A primary feature of boron-containing compounds is their Lewis acidity. Indeed, the chemistry of boron is dominated by reactions that fill its valence shell. For example, neutral, three-coordinate boranes have been utilized as catalysts or co-catalysts in olefin polymerization¹ and in numerous organic transformations.² In regard to Lewis acidity, boron cations, especially 2- and 3-coordinate borinium and borenium cations, respectively, have been of significant interest as even more powerful electrophiles than their neutral counterparts (Scheme 1).³ Despite the potential of borinium and borenium cations serving as Lewis acids, relatively few examples are known, which is likely due to the lack of a general synthesis of this family of compounds. Recently we reported the synthesis of pyridine-substituted borenium cations based on the aromatic boron heterocycle, 1,2-dihydro-1,2-azaborine (Scheme 1).⁴ Herein we describe the first examples of phosphorous- and oxygen-substituted 1,2-dihydro-1,2-azaborine (hereafter referred to as 1,2-azaborine) cations from a common precursor **1** (Scheme 2). We also demonstrate that **1** possesses Lewis acidity on par with other highly electrophilic boron-based Lewis acids.

1,2-Azaborine **1**⁴ reacts cleanly with PMe_3 to provide borenium cation **2** in 99% yield as a crystalline, white solid (Scheme 2). The ^{11}B NMR chemical shift of compound **2** (δ 28.7 ppm in CD_2Cl_2) is characteristic of a 3-coordinate boron atom, suggesting that the triflate group is fully dissociated in solution. In the ^{31}P NMR spectrum, a broad signal is observed at -25.0 ppm, which is similar to the phosphorous chemical shift reported for borabenzene• PMe_3 adduct.⁵

The solid-state structure of phosphine-substituted **2** is illustrated in Figure 1.⁶ The structural parameters of **2** are similar to the observed structure of the trimethylphenylphosphonium cation,⁷ with which **2** is isoelectronic. The B-P bond in **2** is long ($\text{B}(1)\text{--P}(1) = 1.947(3)$ Å) relative to the $\text{C}_{\text{aryl}}\text{--P}$ bond in trimethylphosphonium iodide ($\text{C}_{\text{aryl}}\text{--P} = 1.797(6)$ Å) which is likely due to the increased van der Waals radius of boron (1.92 Å) relative to carbon (1.70 Å).⁸ The 1,2-azaborine ring is planar and the intra-ring bond distances are virtually identical to those of pyridine-substituted 1,2-azaborine cations.⁴ The phosphorous atom in **2** is pyramidal, with the sum of the three Me--P--Me angles equal to 320° . The sum of Me--P--Me

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Supporting Information Available: Experimental procedures, compound characterization data, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

angles in the corresponding $\text{PhPMe}_3^+\text{I}^-$ was 327° .⁷ Additional crystallographic information for **2** can be found in the Supporting Information.

Having demonstrated that phosphines and pyridines readily substitute at the boron atom of **1**, we were interested in determining whether the corresponding oxides could serve as nucleophiles to generate oxygen-substituted azaborine cations. The reaction of **1** with triphenylphosphine oxide produced borenium triflate **3** in 89% isolated yield, while the addition of pyridine N-oxide to a solution of **1** provided compound **4** in 99% yield (Scheme 3).

The crystal structures of **3** and **4** are presented in Figures 2 and 3, respectively. In **3**, the phosphine oxide is bound to boron through oxygen. The B(1)–O(1) bond is long (1.433(2) Å) relative to typical covalent B(sp²)–OR bonds (1.35–1.38 Å),⁹ but consistent with dative B(sp²)–O bonding.¹⁰ The C(4)–B(1)–O(1)–P(1) dihedral angle of 18° indicates partial π -overlap between oxygen's lone-pair and boron's p-orbital. Furthermore, the long P(1)–O(1) bond in **3** (1.556(1) Å) relative to typical phosphine oxides (1.48–1.50 Å)⁹ indicates a significant reduction of the double-bond character in the P–O bond upon coordination to boron. The structural parameters of the pyridine oxide adduct **4** are virtually identical to **3** with regard to the 1,2-azaborine ring. An examination of the relevant bond lengths in the exocyclic pyridine N-oxide substituent again indicates partial π -overlap between oxygen and boron (C(4)–B(1)–O(1)–N(2) dihedral angle in **4** is approximately 3°). Interestingly, the pyridine ring is twisted completely perpendicular to the 1,2-azaborine ring.

Burford¹¹ and Britovsek¹² have used the ³¹P NMR chemical shifts of triphenylphosphine oxide-borane adducts as a measure of the relative Lewis acidity of several strongly acidic boranes. For example, the ³¹P chemical shift of free Ph₃PO at δ 25.5 ppm was shifted downfield significantly to δ 45.8 ppm ($\Delta\delta = 20.3$ ppm) upon coordination to B(C₆F₅)₃.¹¹ By comparison, the ³¹P chemical shift of **3** in CD₂Cl₂ appears at δ 57.3 ppm,¹³ a downfield shift of 28.5 ppm from free Ph₃PO in CD₂Cl₂.¹⁴ The Lewis acidity of compound **1** is therefore likely on par with some of the strongest Lewis acids reported, though it must be noted that the previously reported adducts contain dative B–O bonds and 4-coordinate boron atoms while the formation of **3** involves the dissociation of triflate wherein a trigonal planar boron atom is maintained. By comparison, the ³¹P chemical shift of protonated Ph₃PO–H⁺ has been reported at δ 57.2 ppm.¹⁵

In summary, we have synthesized the first examples of 1,2-azaborine cation adducts of oxygen- and phosphorous-based nucleophiles. In solution and the solid state, these new compounds **2–4** contain 3-coordinate boron atoms and are members of the relatively unexplored class of borenium cations. The boron atom in 1,2-azaborine cations is strongly Lewis acidic, which may provide opportunities in organic synthesis and catalysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

ORTEP illustration of **2**, with thermal ellipsoids drawn at the 35% probability level (hydrogen atoms and triflate counterion have been omitted for clarity). Bond distances (in Å): B(1)–N(1) 1.419(3); B(1)–P(1) 1.947(3); B(1)–C(4) 1.492(3); C(4)–C(3) 1.368(3); C(3)–C(2) 1.402(3); C(2)–C(1) 1.358(3); C(1)–N(1) 1.365(3).

Figure 2.

ORTEP illustration of **3**, with thermal ellipsoids drawn at the 35% probability level (hydrogen atoms and triflate counterion have been omitted for clarity). Bond distances (in Å): B(1)–N(1) 1.420(3); B(1)–O(1) 1.433(2); B(1)–C(4) 1.496(3); C(4)–C(3) 1.369(3); C(3)–C(2) 1.403(3); C(2)–C(1) 1.357(3); C(1)–N(1) 1.368(2); P(1)–O(1) 1.5563(13); Torsion angles: C(4)–B(1)–O(1)–P(1) 18.0°.

Figure 3. ORTEP illustration of **4**, with thermal ellipsoids drawn at the 35% probability level (hydrogen atoms and triflate counterion have been omitted for clarity). Bond distances (in Å): B(1)–N(1) 1.414(3); B(1)–O(1) 1.429(3); B(1)–C(4) 1.492(3); C(4)–C(3) 1.363(3); C(3)–C(2) 1.408(4); C(2)–C(1) 1.349(4); C(1)–N(1) 1.371(3); N(2)–O(1) 1.383(2); Torsion angles: C(4)–B(1)–O(1)–N(2) 2.7°; 1,2-azaborine plane-pyridine plane 85.5°.

Scheme 1.
Boron cations, L = neutral nucleophile.

Scheme 2.
Synthesis of **2**. Tf = trifluoromethanesulfonyl.

Scheme 3.

Synthesis of 1,2-azaborine cations **3** and **4**. Tf = trifluoromethanesulfonyl.