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Boron–Pnictogen Multiple Bonds: Donor-Stabilized P═B and As═B Bonds and a Hindered Iminoborane with a B–N Triple Bond

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Reaction of the hindered phosphino- and arsinoboranes, Ar*Pn(H)–B(Br)Tmp (Ar* = $-\mathrm{C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}^{i}Pr_3)_2}$; Tmp = 2,2,6,6-tetramethylpiperidino; Pn = P and As, **1** and **3**, respectively) with 4-dimethylaminopyridine, DMAP, afforded the boranylidenephosphane and arsane, Ar*Pn═B(DMAP)Tmp (Pn = P and As, **2** and **4**) as deep red-purple solids. The analogous aminoboranes Ar′N(H)–B(X)Tmp (Ar′ = $-\mathrm{C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}Me_3)_2}$; X = Cl and Br; **5** and **6**) did not display any reactivity with DMAP, but in the presence of the amide base, $\mathrm{Na[N(SiMe_3)_2]}$, the clean formation of the uncomplexed iminoborane Ar′N≡BTmp (**7**) was observed. Attempts to generate an Sb═B bond were unsuccessful, as the required stibinoborane precursor, Ar*Sb(H)–B(Br)Tmp, could not be prepared; in place of clean Sb–B bond formation, the reduced product Ar*Sb═SbAr* was obtained. All compounds were characterized spectroscopically, and the X-ray crystal structures of **1**, **2**, **4**, **6**, and **7** were determined.

Introduction

Since the landmark preparation of a kinetically stabilized P═P double bond by Yoshifuji in 1981,[1] the synthesis of related species which exhibit multiple bonding to a heavy pnictogen (Group 15) atom has been an active field of study.[2] So far, the successful isolation of these systems was made possible mainly with the use of bulky ligands. One system which has resisted isolation using hindered ligands alone has been the boranylidenepnictane series RB═PnR′ (Pn = P, As, Sb, and Bi), as well as their heavier triel (Al−Tl) analogues.[3] The lightest member of the boranylidenepnictane series, iminoboranes RB≡NR′, display essentially B−N triple bonding and are readily accessible as monomeric species,[4] while the heavier Group 15 analogues are predicted to possess Pn═B double bonds with bent geometries at the pnictogen center in the gas phase.[5] Furthermore, the enthalpies of dimerization of the latter species are anticipated to be highly exothermic due to the presence of an active lone pair at the pnictogen and an accompanying empty p-orbital at boron; for example, the dimerization of the parent species HB═PH has been estimated to be exothermic by over 54 kcal/mol.[5a] The bent geometries and concomitant ease of dimerization calculated for heavy boranylidenepnictanes RB═PnR′ are a result of the increased inversion barrier at the pnictogen center upon descending the group. This effect makes it more difficult to achieve a linear RBPnR′ arrangement when heavy Group 15 elements are present.

To deal with the above-mentioned issues, we questioned if boron−pnictogen multiple bonding could be preserved by competitively binding a Lewis basic donor molecule to the empty p-orbital at boron within the RB═PnR′ unit. The reverse of this principle has been successfully used by Paine, Nöth, and co-workers to isolate the unique species, $\mathrm{(CO)_5Cr(Et_3C)P{=}BTmp}$ (Tmp = 2,2,6,6-tetramethylpiperidino). In this system, a Lewis acidic $\mathrm{Cr(CO)_5}$ unit was used to bind to the active lone pair at phosphorus in order to mitigate the dimerization tendency of the boranylidenephosphane moiety.[6] Recently we reported the implementation of a simple donor-stabilization protocol in the isolation of rare examples of P═B and As═B double bonds[7] and now describe in full detail this chemistry and our attempts to prepare the analogous B═N and B═Sb bonds.

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Table 1. Crystallographic Data for Compounds **1**, **2**, **4**, **6**, and **7**

	1	**2**	**4**	**6**	**7**
empirical formula	$C_{48}H_{74.5}BBrNP$	$C_{55}H_{84}BN_3P$	$C_{58}H_{91}AsBN_3$	$C_{33}H_{44}BBrN_2$	$C_{33}H_{43}BN_2$
fw	787.28	829.03	916.07	559.42	478.50
color	colorless	red	red	colorless	colorless
cryst dimens (mm^3)	0.57 × 0.17 × 0.16	0.68 × 0.57 × 0.26	0.18 × 0.08 × 0.07	0.25 × 0.19 × 0.09	0.23 × 0.15 × 0.12
cryst habit	needle	plate	plate	block	prism
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
unit cell dimensions					
a (Å)	16.0804(7)	12.8832(8)	12.7587(13)	10.9159(5)	14.2149(11)
b (Å)	16.9371(8)	19.9163(12)	21.142(2)	11.5290(6)	12.1924(9)
c (Å)	17.5600(8)	20.7647(13)	20.465(2)	11.7840(6)	16.3375(12)
α (deg)	79.3360(10)	90	90	89.2140(10)	90
β (deg)	84.3330(10)	95.8420(10)	96.813(2)	89.2680(10)	90.0310(10)
γ (deg)	83.0610(10)	90	90	83.5650(10)	90
V (Å^3)	4651.2(4)	5300.3(6)	5481.3(9)	1473.43(13)	2831.5(4)
Z	4	4	4	2	4
D (g cm^{-3})	1.124	1.039	1.110	1.261	1.122
abs coeff (mm^{-1})	0.949	0.088	0.657	1.419	0.064
F(000)	1698	1820	1992	592	1040
T (K)	90(2)	90(2)	90(2)	90(2)	90(2)
θ range (deg)	1.18−25.25	1.78−27.50	1.79−25.25	1.78−30.00	1.67−30.51
total data	44 092	46 847	37 429	16 728	39 179
observed data $I > 2\sigma I$	16 823	12 155	9934	8567	8520
R_{int}	0.0382	0.0325	0.0904	0.0273	0.0458
params	1002	560	588	388	326
R1/wR2 (all data)	0.0720/0.1136	0.0678/0.1658	0.1071/0.2001	0.0579/0.1411	0.0729/0.1744
R1/wR2 ($I > 2\sigma I$)	0.0409/0.1046	0.0556/0.1564	0.0775/0.1875	0.0461/0.1358	0.0576/0.1675
difference map (e·Å^{-3})	0.479/−0.438	1.040/−0.794	1.018/−0.684	0.638/−1.002	0.520/−0.471

Experimental Section

General. All reactions were performed with the use of modified Schlenk techniques under an atmosphere of nitrogen or in a Vacuum Atmospheres Nexus drybox. Solvents were dried using a Grubbs-type[8] solvent purification system manufactured by Glass Contour and degassed twice (freeze−pump−thaw method) prior to use. Ar*PnH$_2$ (Ar* = $-C_6H_3$-2,6-(C_6H_2-2,4,6-$^iPr_3)_2$; Pn = P, As, and Sb),[9] Ar′NH$_2$ (Ar′ = $-C_6H_3$-2,6-(C_6H_2-2,4,6-$Me_3)_2$),[10] TmpBCl$_2$,[11] and TmpBBr$_2$[12] were prepared according to literature procedures. ^{n}BuLi (2.5 M solution in hexanes), 4-dimethylaminopyridine (DMAP), and Na[N(SiMe$_3$)$_2$] were purchased from commercial sources and used as received. ^{1}H, ^{13}C{^{1}H}, and ^{31}P NMR spectra were obtained on a Varian Mercury 300 MHz spectrometer (300.1, 75.5, and 121.5 MHz, respectively) and referenced either internally to residual protio benzene in the C_6D_6 solvent or externally to 85% H_3PO_4. ^{11}B{^{1}H} NMR spectra were acquired with an INOVA 400 MHz spectrometer (96.6 MHz) and referenced externally to BF_3·OEt_2. Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer 1430 instrument, while UV−vis data were recorded on a Hitachi-1200 instrument. Melting points were obtained in sealed glass capillaries under nitrogen using a Mel-Temp II apparatus and are uncorrected.

X-ray Crystallography. Crystals of appropriate quality for X-ray diffraction studies were removed from a Schlenk tube under a stream of nitrogen and immediately covered with a thin layer of hydrocarbon oil (Paratone). A suitable crystal was selected, attached to a glass fiber, and quickly placed in a low-temperature stream of nitrogen.[13] Data for compound **1** were recorded on a Bruker SMART 1000 instrument using Mo Kα radiation (λ = 0.71073 Å) in conjunction with a CCD detector; data for compounds **2**, **4**, **6**, and **7** were similarly obtained except using a Bruker APEX II instrument. The collected reflections were corrected for Lorentz and polarization effects by using Blessing's method as incorporated into the program SADABS.[14,15] The structures were solved by direct methods and refined with the SHELXTL v.6.1 software package.[16] Refinement was by full-matrix least-squares procedures with all carbon-bound hydrogen atoms included in calculated positions and treated as riding atoms. Compound **1** crystallized with two molecules of hexane, of which one molecule of hexane was disordered over two positions and modeled with a 67:33 occupancy ratio. Compound **7** crystallized as a pseudomerohedral twin and was refined using the TWIN instruction in SHELXTL (twin matrix 1 0 0 0 −1 0 0 0 −1). Some details of the data collection and refinement are given in Table 1. Full crystallographic details for **2** and **4** are found in ref 7.

Preparation of Ar*P(H)−B(Br)Tmp (1). To a solution of Ar*PH$_2$ (0.964 g, 1.88 mmol) in 12 mL of Et$_2$O was added ^{n}BuLi (0.78 mL, 2.5 M solution in hexanes, 1.95 mmol), which resulted in the formation of a bright yellow solution containing Ar*PH(Li). After 1 h, this solution was added dropwise to a solution of TmpBBr$_2$ (0.588 g, 1.89 mmol) in 10 mL of Et$_2$O. The resulting pale yellow slurry was stirred for 24 h, and the solvent was removed to give a white solid. The product was extracted with 40 mL of hexanes and filtered through Celite to give a colorless solution. Concentration of the filtrate to ca. 6 mL, followed by cooling to ca. −20 °C for 24 h, resulted in the precipitation of a white

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microcrystalline solid that was separated from the mother liquor and dried under vacuum (0.950 g, 68%). Crystals of **1** suitable for X-ray diffraction were subsequently grown from a cold (−40 °C) solution in hexanes. ^{1}H NMR (C_6D_6): δ 0.88 (t, J = 6.6 Hz, 4H, CH_2 Tmp), 1.16 (s, 12H, CH_3, Tmp), 1.23 (br d, 12H, CH(CH_3)$_2$), 1.25 (d, J = 6.9 Hz, 12H CH(CH_3)$_2$), 1.36 (m, 2H, CH_2 Tmp), 1.54 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$, 2.84 (septet, J = 6.9 Hz, 2H, CH(CH$_3$)$_2$), 3.38 (very broad, 4H, CH(CH$_3$)$_2$), 4.04 (d, $^1J_{HP}$ = 214.2 Hz, 1H, PH), 7.18 (m, 1H, ArH), 7.20 (s, 4H, ArH), and 7.24−7.26 (m, 2H, ArH). ^{11}B NMR (C_6D_6): δ 46.3 (br, $\Delta\nu_{1/2}$ = 1140 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 14.3, 24.4, 26.2, 31.2, 32.4 (d, J = 9.1 Hz), 34.8, 35.3, 57.7, 138.5, 139.1 (d, J = 12.5 Hz), 145.1 (d, J = 10.3 Hz), 147.5, and 148.6. ^{31}P NMR (C_6D_6): δ −80.1 (d, $^1J_{PH}$ = 214 Hz). IR (Nujol mull, CsI plates): 2265 (m), ν(P−H). mp (°C): 214−216.

Preparation of Ar*P═B(DMAP)Tmp (2). Precooled toluene (−78 °C, 12 mL) was added to a Schlenk flask containing a mixture of **1** (0.269 g, 0.36 mmol) and DMAP (0.114 g, 0.90 mmol). Upon the addition of toluene, a pale yellow solution was observed along with undissolved DMAP. The reaction was slowly warmed to room temperature and stirred for 2 days to give a purple solution along with a white precipitate (DMAP·HBr). The reaction was filtered, the solvent was then removed from the filtrate, and the product was crystallized from hexanes (4 mL, ca. −20 °C, 2 weeks) to give large well-formed rods of **2** that were dark red in color (0.045 g, 16%). ^{1}H NMR (C_6D_6): δ 0.72 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$), 0.81 (br, 4H, CH_2 Tmp), 1.24 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.36 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.46 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.51 (s, 12H, CH_3 Tmp), 1.58 (m, 2H, CH_2 Tmp), 1.82 (s, 6H, N(CH_3)$_2$ DMAP), 1.90 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 2.93 (septet, 2H, CH(CH$_3$)$_2$), 3.18 (septet, 2H, CH(CH$_3$)$_2$), 3.36 (septet, 2H, CH(CH$_3$)$_2$), 5.55 (br d, 2H, CH DMAP), 7.13 (s, 2H, ArH), 7.24 (m, 1H, ArH), 7.35 (m, 1H, ArH), 7.36 (s, 2H, ArH), 7.48 (d, J = 7.5 Hz, 2H, ArH), and 8.95 (br d, 2H, CH DMAP). ^{11}B NMR (C_6D_6): δ 41.2 (br, $\Delta\nu_{1/2}$ = ca. 800 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 14.4, 19.4, 23.1, 23.70, 23.75, 24.6, 24.7, 26.1, 27.7, 31.4, 32.0, 35.0, 38.4, 42.7, 52.7, 120.2, 121.2, 124.0, 125.9, 129.6, 140.6, 145.0, 146.5 (d, J = 5.2 Hz), 147.0, 148.6, 150.6, and 154.5. ^{31}P NMR (C_6D_6): δ 57.3 (s). mp (°C): 169−172 (dec). UV−vis (hexane, nm [ϵ, cm^{-1} M^{-1}]): 370 (shoulder), 534 [2280].

Synthesis of Ar*As═B(DMAP)Tmp (4). To a solution of Ar*AsH_2 (0.602 g, 1.08 mmol) in 15 mL of Et_2O (0.570 g, 1.11 mmol) was added ^{n}BuLi (0.45 mL, 2.5 M solution in hexanes, 1.13 mmol), which resulted in the formation of an orange-yellow solution containing Ar*AsH(Li). After 45 min, this solution was added dropwise to a solution of TmpBBr_2 (0.393 g, 1.26 mmol) in 8 mL of Et_2O. The resulting pale yellow solution was stirred for 24 h, and the solvent was removed to give a white solid. The product was extracted with 25 mL of hexanes and filtered through Celite to give a colorless solution of Ar*As(H)-B(Br)Tmp (**3**).[17] The solution of in situ generated **3** was then added to excess DMAP (0.345 g, 2.76 mmol) to give a deep blue-violet solution over a white precipitate. This mixture was stirred for 24 h and filtered through a pad of Celite. Cooling of the filtrate to ca. −20 °C yielded **4** as red-purple dichroic crystals after 2 days (0.095 g, 16%; based upon the quantitative formation of **3**). ^{1}H NMR (C_6D_6): δ 0.77 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 0.87 (br, 4H, CH_2 Tmp), 1.22 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.35 (d, J = 6.9 Hz, 18H, CH(CH_3)$_2$), 1.48 (s, 12H, CH_3 Tmp), 1.55 (m, 2H, CH_2 Tmp), 1.81 (s, 6H, N(CH_3)$_2$ DMAP), 1.85 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.64 (septet, J = 6.9 Hz, 2H, CH(CH$_3$)$_2$), 2.92 (septet, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 3.05 (septet, J = 6.9 Hz, 2H, CH(CH$_3$)$_2$), 5.61 (br d, 2H, ArH DMAP), 7.14 (d, J = 1.8 Hz, 2H, ArH), 7.24 (t, 1H, ArH), 7.33 (br, 2H, ArH), 7.48 (d, J = 7.5 Hz, 2H, ArH), and 9.42 (br d, 2H, ArH DMAP). ^{11}B NMR (C_6D_6): δ 51.2 (br, $\Delta\nu_{1/2}$ = ca. 750 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 14.4, 19.3, 23.0, 23.8, 24.7, 26.1, 27.2, 27.6, 31.47, 31.53, 32.0, 33.3, 35.0, 38.5, 42.5, 52.1, 120.2, 121.2, 124.6, 129.6, 141.3, 145.0, 147.0, 148.0, 148.7, 154.3, and 154.6. mp (°C): 147 (chars); 169−173 (melts). UV−vis (hexane, nm [ϵ, cm^{-1} M^{-1}]): 328 (shoulder) and 584 [2530].

Attempted Preparation of Ar*Sb(H)−B(Br)Tmp. Following a literature procedure,[9] a solution of Ar*SbH(Li) in diethyl ether was prepared from Ar*SbH_2 and ^{n}BuLi. The red-orange solution of Ar*SbH(Li) was then added to either TmpBCl_2 or TmpBBr_2 in cold (−78 °C) diethyl ether. In both instances, deep orange solutions were obtained after warming the reaction mixture to room temperature. Filtration and cooling of the reaction mixtures to ca. −20 °C afforded clean samples of olive green Ar*Sb═SbAr* as judged by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (20−35% isolated yield).[18] The remaining mother liquors were analyzed by NMR and were shown to contain complicated mixtures from which pure stibinoborane Ar*Sb(H)−B(X)Tmp (X = Cl or Br) could not be isolated.

Preparation of Ar′N(H)−B(Cl)Tmp (5). To a solution of Ar′NH_2 (0.496 g, 1.66 mmol) in 12 mL of diethyl ether was added dropwise a solution of ^{n}BuLi (0.69 mL, 2.5 M solution in hexanes, 1.72 mmol). The resulting yellow solution was stirred for 45 min and added to a solution of TmpBCl_2 (0.373 g, 1.67 mmol) in 5 mL of Et_2O. The reaction mixture was then stirred for 16 h to give a yellow solution over a white precipitate. Removal of the solvent gave a pale yellow residue to which was added 20 mL of hexanes. The mixture was then filtered through Celite and concentration of the filtrate to ca. 15 mL resulted in the spontaneous crystallization of a colorless product. Crystallization was continued at ca. −20 °C (24 h) to give a crop of well-formed colorless crystals (365 mg, 45%). ^{1}H NMR (C_6D_6): δ 0.85 (s, 12H, CH_3 Tmp), 1.20 (t, J = 6.6 Hz, 4H, CH_2 Tmp), 1.41 (m, 2H, CH_2 Tmp), 2.19 (s, 6H, p-CH_3 Mes), 2.20 (s, 12H, o-CH_3 Mes), 4.99 (s, N-H, 1H), 6.85 (s, 4H, Ar-H Mes), and 7.0−7.1 (m, 3H, Ar-H). ^{11}B NMR (C_6D_6): δ 31.0 (br, $\Delta\nu_{1/2}$ = ca. 530 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 17.3, 20.98, 21.06, 30.7, 39.4, 51.6, 126.5, 128.9, 130.2, 136.3, 136.6, 137.5, 138.7, and 140.4. IR (Nujol mull, CsI plates): 3358 cm^{-1} (w, sharp), ν(N−H). mp (°C): 193−198 (dec).

Preparation of Ar′N(H)−B(Br)Tmp (6). To a solution of Ar′NH_2 (0.677 g, 2.27 mmol) in 15 mL of diethyl ether was added dropwise a solution of ^{n}BuLi (0.90 mL, 2.5 M solution in hexanes, 2.25 mmol). The resulting yellow solution was stirred for 45 min and added to a solution of TmpBBr_2 (0.698 g, 2.24 mmol) in 5 mL of benzene. The reaction mixture was then stirred for 16 h to give a yellow solution over a white precipitate. Removal of the solvent gave a pale yellow residue to which was added 30 mL of hexanes. The mixture was then filtered through Celite and concentration of the filtrate to ca. 20 mL and cooling to ca. −20 °C to give a crop of well-formed colorless crystals after 2 days (0.250 g, 21%). ^{1}H NMR (C_6D_6): δ 0.84 (s, 12H, CH_3 Tmp), 1.16 (t, J = 6.6 Hz, 4H,

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(17) Despite numerous attempts, we were not able to obtain a clean sample of the arsinoborane **3**. Analysis of crude product by ^{1}H and ^{13}C NMR revealed the presence of unreacted Ar*AsH_2 along with unknown Tmp-containing products. IR spectroscopy contained two identifiable As−H bands at 2105 and 2080 cm^{-1}, with the former band assignable to Ar*AsH_2.[9] We assume that **3** is generated by the reaction of Ar*AsH(Li) and TmpBBr_2 due the isolation of clean boranylidenearsane **4** in the subsequent reaction with DMAP (albeit in low yield). However, at the moment we cannot rule out the presence of a reaction surrogate to **3** in solution, which is also transformed to **4** upon reaction with DMAP.

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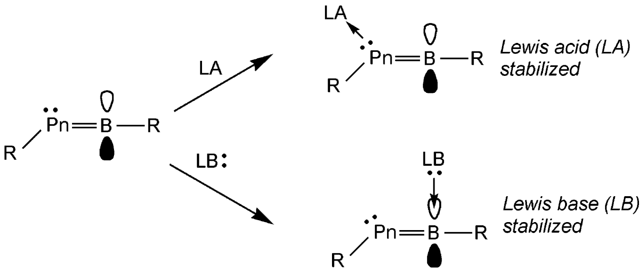
Scheme 1. Possible Routes to Stable Pnictogen−Boron Double Bonds



CH_2 Tmp), 1.42 (quintet, $J = 6.6$ Hz, 2H, CH_2 Tmp), 2.19 (s, 6H, p-CH_3 Mes), 2.22 (s, 12H, o-CH_3 Mes), 5.36 (s, N-*H*, 1H), 6.84 (s, 4H, Ar-*H* Mes), and 7.01−7.13 (m, 3H, Ar-*H*). ^{11}B NMR (C_6D_6): δ 30.2 (br, $\Delta\nu_{1/2}$ = ca. 630 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 17.8, 21.0, 21.2, 30.4, 40.3, 51.7, 126.7, 129.0, 130.5, 136.4, 136.7, 137.4, 138.8, and 140.7. IR (Nujol mull, CsI plates): 3362 cm^{-1} (w, sharp), ν(N−H). mp (°C): 201−204 (dec).

Attempted Preparation of Ar′N═B(DMAP)Tmp. Reaction of **5** and **6** with DMAP did not give any noticeable reaction (even upon prolonged heating of **5** in refluxing toluene, 5 days). Attempts to generate Ar′N═B(DMAP)Tmp by reacting either **5** or **6** with DMAP in the presence of the silylamide salt Na[N($SiMe_3$)$_2$] gave exclusively the iminoborane product Ar′N≡BTmp **7** as determined by NMR, IR, and X-ray diffraction studies; see below for an independent preparation of **7**.

Preparation of Ar′N≡BTmp (7). To a mixture of **6** (0.216 g, 0.41 mmol) and Na[N($SiMe_3$)$_2$] (81 mg, 0.44 mmol) was added 12 mL of THF. The initially clear, pale yellow mixture clouded upon stirring for 24 h. The volatiles were then removed, and the product was extracted with 20 mL of hexanes. After the mixture was filtered through Celite, the colorless filtrate was concentrated to 8 mL and cooling to ca. −20 °C for 3 days yielded **7** as small colorless prisms (0.080 g, 44%). ^{1}H NMR (C_6D_6): δ 0.71 (s, 12H, CH_3 Tmp), 0.96 (t, $J = 6.6$ Hz, 4H, CH_2 Tmp), 1.18 (quintet, $J = 6.6$ Hz, 2H, CH_2 Tmp), 2.24 (s, 6H, p-CH_3 Mes), 2.26 (s, 12H, o-CH_3 Mes), 6.90 (s, 4H, Ar-*H* Mes), and 6.98−7.09 (m, 3H, Ar-*H*). ^{11}B NMR (C_6D_6): δ 10.6 (br, $\Delta\nu_{1/2}$ = ca. 500 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 17.5, 20.6, 21.2, 31.1, 38.1, 51.6, 120.9, 128.3, 128.7, 135.7, 136.0, 136.7, and 139.4. IR (Nujol mull, CsI plates): 2037 [w, ν(^{10}B≡N)] and 1982 cm^{-1} [m, ν(^{11}B≡N)]. mp (°C): 193−196.

Results and Discussion

Preparation of the Phosphinoborane 1 and Its Conversion into the Boranylidenephosphane 2. As mentioned in the Introduction, we initially set out to prepare species with multiple bonding between boron and a heavy pnictogen atom, e.g., P and As, with the aid of donor molecules (illustrated conceptually in the lower portion of Scheme 1). In line with prior work in this field,[19] we viewed the unsaturated species Ar*P═B(L)Tmp (Ar* = $-C_6H_3$-2,6-(C_6H_2-2,4,6-^{i}Pr$_3$)$_2$; L = donor) as a suitable synthetic target. It was hoped that the steric bulk imposed by the terphenyl ligand at phosphorus, coupled with the facile introduction of the Tmp group at boron, would encourage the synthesis of a stable P═B double bond when a suitable donor molecule was present. Therefore, we constructed the requisite phosphinoborane precursor **1** from which HBr elimination could be induced to yield a P═B bond.

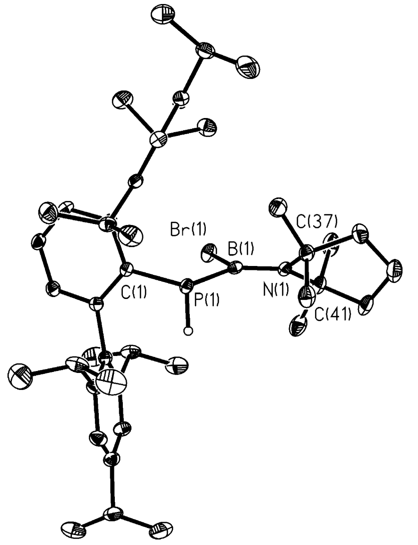


Figure 1. Molecular structure of **1** with thermal ellipsoids presented at the 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with bracketed values belonging to a second molecule of **1** in the asymmetric unit: P(1)−B(1) 1.958(3) [1.950(3)], P(1)−C(1) 1.839(2) [1.839(2)], P(1)−H(1) 1.29(2) [1.30(2)], B(1)−N(1) 1.390(3) [1.389(3)]; C(1)−P(1)−B(1) 106.93(11) [107.52(11)], C(1)−P(1)−H(1) 98.2(9) [98.6(11)], P(1)−B(1)−N(1) 122.31(18) [122.78(18)], P(1)−B(1)−Br(1) 115.17(14) [114.79(14)], Br(1)−B(1)−N(1) 122.23(18) [122.26(19)], B(1)−N(1)−C(37) 119.6(2) [119.80(19)], B(1)−N(1)−C(41) 122.8(2) [122.7(2)].

Compound **1** was prepared by the reaction of the dihaloborane, TmpBBr$_2$, with 1 equiv of Ar*P(H)Li in diethyl ether and isolated as a white microcrystalline solid in moderate yield (68%). The ^{31}P NMR spectrum of **1** consisted of a doublet resonance at −80.1 ppm ($^1J_{PH}$ = 214 Hz) attributable to a PH group, while a broad signal at +46.3 ppm was detected by ^{11}B NMR spectroscopy; the latter signal lies within the typical range observed for three coordinate boron environments.[20] Due to the broad nature of both the ^{31}P and ^{11}B resonances, no P−B coupling was observed. Crystals suitable for study by X-ray diffraction were subsequently grown from cold hexane, and the structure of **1** is shown in Figure 1.

Phosphinoborane **1** exists as a monomer in the solid state with two independent molecules in the asymmetric unit of the crystal lattice. The average P−B length in **1** is 1.954(4) Å, while the average B−N distance is 1.390(4) Å. The pyramidal phosphorus geometry, in conjunction with the long P−B bond length, strongly suggests a lack of any appreciable P→B dative π bonding. For comparison, the P−B bond lengths in the related Tmp-substituted phosphinoboranes MesP(H)−B(Cl)Tmp and [(^{i}Pr$_2$N)$_2$B]P(H)−B(Cl)Tmp are 1.948(3) and 1.925(5) Å, respectively.[19a,21] The average B−N distance in **1** was similar to that in the above-mentioned Tmp derivatives [1.380(3) and 1.397(5) Å] and considerably

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(19) (a) Arif, A. M.; Boggs, J. E.; Cowley, A. H.; Lee, J. G.; Pakulski, M.; Power, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 6083. (b) Kölle, P.; Linti, G.; Nöth, H.; Wood, G. L.; Narula, C. K.; Paine, R. T. *Chem. Ber.* **1988**, *121*, 871.

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(21) Dou, D.; Wood, G. L.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Inorg. Chem.* **1992**, *31*, 1695.

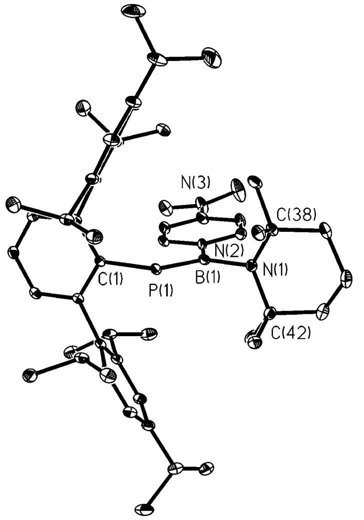

Figure 2. Molecular structure of **2** with thermal ellipsoids presented at the 30% probability level. The hydrogen atoms and disordered DMAP have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with values corresponding to the disordered DMAP in parentheses: P(1)−B(1) 1.8092(17), P(1)−C(1) 1.8509(14), B(1)−N(1) 1.4837(19), B(1)−N(2) 1.593(2) [1.548(2)]; C(1)−P(1)−B(1) 114.36(7), P(1)−B(1)−N(1) 119.48(11), P(1)−B(1)−N(2) 127.41(13) [132.7(4)], N(1)−B(1)−N(2) 113.09(14) [107.8(4)], B(1)−N(1)−C(38) 117.98(12), B(1)−N(3)−C(42) 117.84(12), C(38)−N(1)−C(42) 119.16(11).

shorter than the B−N(Tmp) bond length of 1.465(3) Å within the dimeric diphosphadiboretane [^{t}BuPBTmp]$_2$.[22] Furthermore, planar geometries exist at both the boron and nitrogen centers in **1**, suggesting that some multiple bonding exists between these two atoms.

Upon mixing **1** with an excess of DMAP in toluene,[23] a deep purple mixture was observed. After separation of the DMAP·HBr byproduct, deep-red crystals were obtained and identified as the novel base-stabilized boranylidenephosphane, **2**, with the help of X-ray crystallography (Figure 2, Scheme 2) in combination with NMR (^{1}H, ^{11}B, ^{13}C, and ^{31}P) and UV−vis spectroscopy. This product was exceedingly air and moisture sensitive but was found to be quite thermally robust (mp = 169−172 °C).

Consistent with the assigned structure, broad singlet resonances were detected in the ^{31}P (+57.3 ppm) and ^{11}B (+41.2 ppm) NMR spectra of **2**. The ^{31}P NMR resonance was considerably deshielded in comparison to that of the phosphinoborane precursor **1** (−80.1 ppm); the ^{11}B NMR signal for **2** is similar to that for **1**, indicating the retention of a 3-coordinate boron environment. The UV−vis spectrum of **2** was dominated by a broad absorption centered at 534 nm (ϵ = 2280 M^{-1} cm$^{-1)}$ which has been tentatively assigned to an allowed π-to-π* transition associated with the P═B chromophore.

As depicted in Figure 2, monomeric **2** displays bonding parameters fully consistent with the presence of a discrete P═B double bond. Most relevant is the short P−B bond distance of 1.8092(17) Å, which is considerably shorter than typical P−B single bonds (e.g., the average P−B single bond length in **1** is 1.954(4) Å). Furthermore, the phosphorus center in **2** is 2-coordinate with a C(ipso)−P−B bending angle of 114.36(7)°, consistent with approximate sp^2 hybridization at phosphorus. As anticipated, the neighboring boron center adopts a trigonal planar geometry [angle sum = 360.0(2)°] with a dative B−N interaction at 1.571(6) Å (av) involving DMAP,[24] along with a shorter B−N single bond distance [1.4837(19) Å] incorporating the Tmp ligand. The long B−N length to the Tmp group, coupled with the relative twisted orientation of the nitrogen (Tmp) and boron planes, suggests that minimal π-bonding exists between N and B; thus, the π-bonding is concentrated between phosphorus and boron.

Compound **2** represents the first example of a neutral base-stabilized boranylidenephosphane, though multiple bonding between phosphorus and boron has been observed previously. For example, comparably short P−B bond lengths exist in the anionic borylphosphides [RP═BR′$_2$]$^-$ [1.810(4)−1.833(6) Å],[25] and short distances were occasionally observed in a series of hindered monomeric phosphinoboranes R$_2$PBR′$_2$ [1.839(8)−1.871(3) Å].[26] In addition, a very short P−B interaction of 1.7453(5) Å was found in the unique acid-stabilized species [(CO)$_5$Cr(Et$_3$C)P═BTmp]; this compound also exhibited a nearly linear P−B−N(Tmp) angle of 176.1(3)° and a short B−N length of 1.339(5) Å, consistent with the allenic bonding form >P═B═N<.[6] The presence of an sp-hybrized boron center in [(CO)$_5$Cr(Et$_3$C)P═BTmp], coupled with an electron-withdrawing Cr(CO)$_5$ moiety at phosphorus, could help explain the ca. 0.06 Å contraction in the P−B bond length when compared to our base-stabilized analogue **2**. However, it is also plausible that the longer P−B distance in **2** could arise from the greater steric congestion at the P and B centers in this compound.

Preparation of the Boranylidenearsane 4. Given the successful preparation of **2**, we decided to investigate the preparation of heavier pnictogen congeners. Following the protocol described above, the lithiated arsenide Ar*AsH(Li) was reacted with 1 equiv of TmpBBr$_2$ to give the arsinoborane **3**.[17] Subsequent treatment of **3** with an excess of DMAP in hexanes rapidly afforded a dark blue-violet solution, which yielded dark purple-red dichroic crystals upon workup. These crystals were identified as the novel boranylidenearsane **4** by X-ray crystallography (Figure 3) and further analyzed by NMR and UV−vis spectroscopy. As in

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(22) Nöth, H.; Schwartz, M.; Weber, S. *Chem. Ber.* **1985**, *118*, 4716.

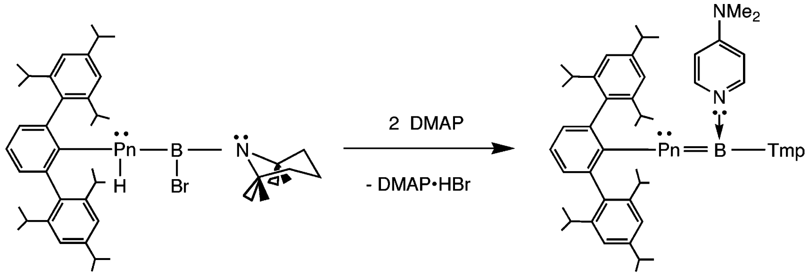
(23) For reports concerning the use of DMAP to stabilize reactive main group species, see: (a) Thomas, F.; Schulz, S.; Nieger, M. *Eur. J. Inorg. Chem.* **2001**, 161. (b). Schulz, S. *Struct. Bond.* **2002**, *103*, 117. (c) Rivard, E.; Huynh, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 2286. (d) Blättner, M.; Nieger, M.; Ruban, A.; Schoeller, W. W.; Niecke, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2768. (e) Schulz, S.; Thomas, F.; Priesmann, W. M.; Nieger, M. *Organometallics* **2006**, *25*, 1392. (f) An interesting DMAP-mediated route to labile Group 13−15 bonds has been reported: Thomas, F.; Schulz, S.; Mansikkamäki, H.; Nieger, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5641.

(24) For comparison, the B−N distances within the DMAP·BX$_3$ adducts (X = halogen or C$_6$F$_5$) range from 1.589(5) to 1.602(6) Å; Gerald Lesley, M. J.; Woodward, A.; Taylor, N. J.; Marder, T. B.; Cazenobe, I.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, D. W.; Kakkar, A. K.; *Chem. Mater.* **1998**, *10*, 1355.

(25) Bartlett, R. A.; Rasika Dias, H. V.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 1306.

(26) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426.

Scheme 2. Preparation of the P═B and As═B Double-Bonded Species **2** and **4**



Pn = P **1**
As **3**

Pn = P **2**
As **4**

the case of **2**, crystals of the arsenic derivative **4** were exceedingly air- and moisture-sensitive, yet possessed considerable thermal stability (decomposes at 147 °C).

The ^{11}B NMR spectrum of **4** consisted of a broad resonance at +51 ppm, while a transition at 584 nm (ϵ = 2530 M^{-1} cm^{-1}) was found in the UV−vis spectrum. This absorption is significantly red-shifted from that of **2** and is in line with the anticipated weaker As═B bond in **4** (i.e., smaller π-to-π^* energy gap).

The molecular structure of **4** closely resembles that of its phosphorus counterpart **2**. A short As−B bond [1.914(6) Å] was found which parallels the As═B distances observed [1.926(6) and 1.936(11) Å] within the borylarsenide anion $[PhAs{=}BMes_2]^-$, which is, to our knowledge, the only other example of a structurally authenticated As═B double bond in a molecular species.[27,28] For comparison, the As−B distances within the 3-coordinate arsinoboranes $R_2As{-}BR_2$ (which do not have appreciable As−B multiple bonding) range from 2.06 to 2.20 Å.[27b] The B−N distances in 4 were similar to those observed in **2** with distances of 1.567(7) and 1.469(7) Å to the DMAP and Tmp ligands, respectively. The C(ipso)−As−B bending angle of 113.5(2)° (i.e., sp^2-hydridized arsenic), in conjunction with the planar geometry at boron, reinforces the assignment of an As═B double bond in **4**.

Attempted Preparation of the Stibinoboranes of Ar*Sb(H)−B(X)Tmp (X = Cl and Br). Attempts to form a hitherto unknown Sb═B bond were not successful, as our efforts to prepare the required stibinoborane Ar*Sb(H)-B(X)-Tmp (X = Cl or Br) from $TmpBX_2$ and the known stibinide, Ar*SbH(Li), resulted in the formation of significant quantities of the olive green distibene Ar*Sb═SbAr*[18] in place of clean Sb−B bond formation. Analogous synthetic routes were not explored for bismuth, as the required bismuthane precursor, Ar^*BiH_2, is unstable and spontaneously eliminates H_2 at low temperatures to yield the dibismuthene, Ar*Bi═BiAr*.[9,29] It seems a possiblity that the increased stability of the lone pair in the heavier elements decreases the nucleophilic character of the pnictogen center, thus reducing the probability of Sb−B bond formation by nucleophilic attack on boron. This effect could also increase the possiblity of Li−X (X = halogen) exchange with $TmpBX_2$, and in the case above, subsequent HX elimination from an unstable Ar*Sb(H)X intermediate might have occurred to give the distibene Ar*Sb═SbAr*.[30]

Synthesis of the Aminoboranes 5 and 6 and Their Conversion into the Iminoborane 7. The chemistry of iminoboranes RB≡NR′ has been well explored, and a number of interesting reaction sequences including their cycloaddition and coordination chemistries have been discovered.[4,31,32] Interestingly, to our knowledge, there have not been any examples of iminoboranes acting as Lewis acids in the presence of neutral donors, while the role of iminoboranes as Lewis bases in the presence of electron-deficient substrates has been well documented.[33] Therefore, we were motivated to extend our donor-stabilization protocol to include the B═N double-bonded species ArN═B(DMAP)-Tmp, which would contain the hitherto unknown iminoborane ArN≡BTmp unit acting as a Lewis acid toward the strong donor DMAP (Ar = terphenyl ligand).

Recently we developed a high-yield, large-scale synthesis of the very bulky aniline $Ar'NH_2$ via the reduction of the readily available azido precursor $Ar'N_3$ with $Li[AlH_4]$ ($Ar' = -C_6H_3$-2,6-$(C_6H_2$-2,4,6-$Me_3)$).[10,34] Hence we decided to use $Ar'NH_2$ as a reaction synthon to access the aminoborane

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[27] (a) Petrie, M. A.; Shoner, S. C.; Rasika Dias, H. V.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1033. (b) Petrie, M. A.; Olmstead, M. M.; Hope, H.; Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 3221.

[28] Short P−B and As−B distances have been reported in the Zintl anions $[PBP]^{3-}$ and $[AsBAs]^{3-}$, see: (a) von Schnering, H. G.; Somer, M.; Hartweg, M.; Peters, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 65. (b) Somer, M.; Carrillo-Cabrera, W.; Peters, K.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **2000**, *626*, 897.

[29] Hardman, N. J.; Twamley, B.; Power, P. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2771.

[30] For, example halophosphines of the general form RPH(X) tend to eliminate HX to yield phosphinidene oligomers $(RP)_x$: Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4845.

[31] (a) Paetzold, P.; von Plotho, C.; Schmidt, G.; Boese, R.; Schrader, B.; Bougeard, D.; Pfeiffer, U.; Gleiter, R.; Schäfer, W. *Chem. Ber.* **1984**, *117*, 1089. (b) Paetzold, P.; von Plotho, C.; Niecke, E.; Rüger, R. *Chem. Ber.* **1983**, *116*, 1678. (c) Männig, D.; Narula, C. K.; Nöth, H.; Wietelmann, U. *Chem. Ber.* **1985**, *118*, 3748. (d) Klöfkorn, C.; Schmidt, M.; Spaniol, T.; Wagner, T.; Costisor, O.; Paetzold, P. *Chem. Ber.* **1995**, *128*, 1037.

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[33] (a) Nöth, H.; Weber, S. *Chem. Ber.* **1985**, *118*, 2554. (b) Böck, B.; Braun, U.; Habereder, T.; Mayer, P.; Nöth, H. *Z. Naturforsch.* **2004**, *59B*, 681.

[34] Gavenonis, J.; Tilley, T. D. *Organometallics* **2004**, *23*, 31.

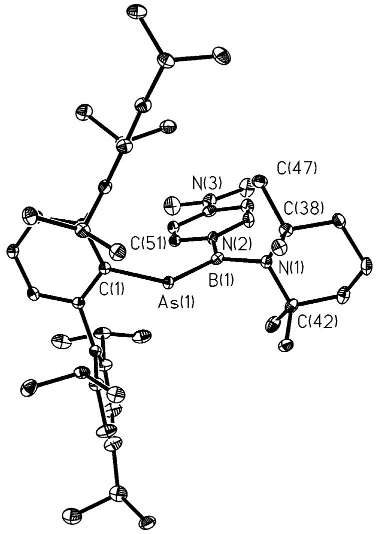

Figure 3. Molecular structure of **4** with thermal ellipsoids presented at the 30% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): As(1)−B(1) 1.914(6), As(1)−C(1) 1.987(5), B(1)−N(1) 1.469(7), B(1)−N(2) 1.567(7); C(1)−As(1)−B(1) 113.5(2), As(1)−B(1)−N(1) 119.3(4), As(1)−B(1)−N(2) 128.6(4), N(1)−B(1)−N(2) 112.1(4), B(1)−N(1)−C(38) 120.3(4), B(1)−N(1)−C(42) 118.1(4), C(38)−N(1)−C(42) 118.3(4).

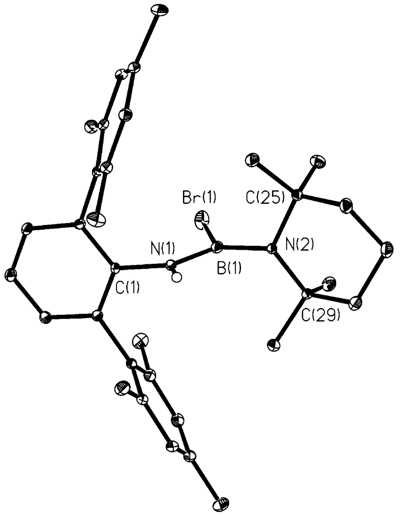

Figure 4. Molecular structure of **6** with thermal ellipsoids presented at the 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)−B(1) 1.390(3), C(1)−N(1) 1.432(2), B(1)−N(2) 1.446(3), C(1)−N(1)−B(1) 132.63(18), N(1)−B(1)−N(2) 124.4(2), N(1)−B(1)−Br(1) 113.39(16), Br(1)−B(1)−N(2) 122.25(17), B(1)−N(2)−C(25) 117.32(16), B(1)−N(2)−C(29) 117.83(16), C(25)−N(2)−C(29) 119.86(15).

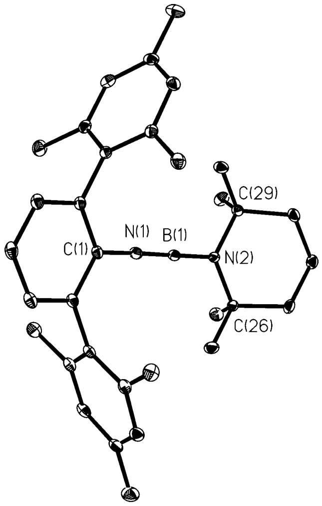

Figure 5. Molecular structure of **7** with thermal ellipsoids presented at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)−B(1) 1.254(3). C(1)−N(1) 1.366(2), B(1)−N(2) 1.374(3), N(2)−C(26) 1.491(2), N(2)−C(29) 1.496(2); C(1)−N(1)−B(1) 171.7(2), N(1)−B(1)−N(2) 179.4(2), B(1)−N(2)−C(26) 119.99(16), B(1)−N(2)−C(29) 119.42(17), C(26)−N(2)−C(29) 120.59(14).

precursors Ar′N(H)−B(X)Tmp (X = Cl and Br; **5** and **6**). The aminoboranes **5** and **6** were synthesized by the coupling of in situ generated Ar′NH(Li) (derived from Ar′NH$_2$ and ^{n}BuLi) with TmpBCl$_2$ and TmpBBr$_2$, respectively, in diethyl ether. Compounds **5** and **6** were isolated as colorless crystals in low to moderate yield and were characterized by ^{1}H, ^{11}B, and ^{13}C{^{1}H} NMR and IR spectroscopy and, in the case of **6**, X-ray diffraction (Figure 4).

The NMR spectra of **5** and **6** were consistent with the assigned monomeric structure, as broad resonances were observed in the ^{11}B NMR spectra at 31.0 and 30.2 ppm, respectively. These resonances were shielded relative the phosphinoborane derivative **1** (^{11}B, 46.3 ppm), yet still appear in the spectral region associated with 3-coordinate boron environments.[20] The N−H groups in **5** and **6** were identified by ^{1}H NMR spectroscopy and appeared as singlet resonances at 4.99 and 5.36 ppm, respectively, while weak N−H vibrations were located at 3358 and 3362 cm^{-1} in the IR spectra of **5** and **6**, respectively.

The molecular structure of **6** was determined by X-ray crystallography, and the resulting thermal ellipsoid plot is depicted in Figure 4. Of note, a considerably shorter B−N distance was found between the boron center and the aniline nitrogen N(1) [1.390(3) Å] when compared to the remaining B−N interaction involving the amino nitrogen of the Tmp ligand [B(1)−N(2) = 1.446(3) Å]. As in **1**, there appears to be some B−N π-bonding present (i.e., between B(1) and N(1)); however, in this case it does not involve the Tmp ligand. The slightly pyramidal nature of the amide nitrogen atom of the Tmp group in **6** [angle sum at N(2) = 355.0(5)°], coupled with the longer B−N distance than in phosphinoborane **1** support the lack of appreciable B−N(Tmp) π-bonding in **6**.[35] Furthermore, the Tmp group is rotated by ca. 90° from the N−B−N plane, which should dramatically reduce the chance of any π-bonding between the N atom in the Tmp group and boron.

In an attempt to generate the iminoborane adduct Ar′N=B(DMAP)Tmp, both **5** and **6** were treated with DMAP in either toluene or hexanes. No reaction was observed at room temperature in hexanes, and upon refluxing **5** with DMAP in toluene, no change was detected after 5 days (by ^{1}H NMR). From these results, we reasoned that a stronger base was needed in order to induce HX elimination from the aminoboranes **5** and **6**. Upon mixing either **5** or **6** with the silylamide salt, Na[N(SiMe$_3$)$_2$], and an excess of DMAP in THF, a new colorless crystalline product was

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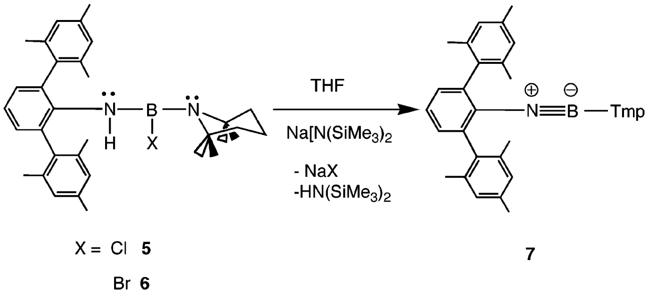
Scheme 3. Preparation of the Iminoborane **7**



obtained upon workup. This product no longer contained N−H functionality; however, the anticipated DMAP adduct was not formed, as resonances belonging to DMAP were not found in the NMR spectrum of the isolated product. Notably, a single ^{11}B NMR resonance was detected at 10.6 ppm which closely matched the ^{11}B NMR chemical shifts (11.8−12.2 ppm) reported for the N-substituted iminoboranes Mes*N≡B−N(SiMe$_3$)R (Mes* = C_6H_2-2,4,6-^{t}Bu$_3$; R = alkyl or silyl group).[36] More convincing evidence that the product was the hindered iminoborane Ar′N≡BTmp (**7**) was obtained from the infrared spectrum, as two closely spaced bands were found at 2037 and 1982 cm^{-1} in an approximate ratio of 1:4. Similar vibrations are found in various iminoboranes with the higher frequency band belonging to the $\nu(^{10}\text{B}\equiv\text{N})$ mode, while the more abundant ^{11}B isotope (ca. 80% abundance) has a $\nu(^{11}\text{B}\equiv\text{N})$ vibrational mode that is lower in frequency by 50−60 cm^{-1}.[37] Fortunately, crystals suitable for an X-ray diffraction study could be grown from hexanes that conclusively identified the product as the iminoborane **7** (Figure 5, Scheme 3).

Upon inspecting the structure of **7**, the most prominent feature of the molecule is the nearly linear geometry of the C(ipso)−N−B−N core [N(1)−B(1)−N(2) angle = 179.4(2)°; C(1)−B(1)−N(1) angle = 171.7(2)°]. Moreover, there is a very short B(1)−N(1) distance of 1.254(3) Å which signals the presence of a formal B−N triple bond in **7**; of note, typical B−N lengths in structurally characterized iminoboranes range from ca. 1.23 to 1.26 Å.[36,38] In addition, a relatively short B−N(Tmp) bond length of 1.374(3) Å [B(1)−N(2)] was also observed. This bond is considerably shorter than the B−N(Tmp) distance in the precursor **6** [1.446(3) Å], and the contraction of this bond in **7** can be attributed, in part, to the decrease in the covalent radius of boron (sp^2 to sp hydridization) from **6** to **7**, although a contribution to the structure of the canonical form Ar*N=B=Tmp cannot be ruled out.

The isolation of **7** highlights the ability of terphenyl ligands to stabilize low coordination environments, as the related species, (^{t}BuNBTmp)$_2$, is a dimer despite the presence of a bulky *tert*-butyl group at nitrogen.[22,39] Mixing **7** with an excess of DMAP did not result in any appreciable coordination; thus, the strong B−N intramolecular triple bonding interaction in **7** is preferred over a dative interaction with DMAP.

Conclusions

A new class of stable main group species featuring P=B and As=B bonds was prepared using a simple donor-stabilization strategy. Attempts to generate the Sb=B analogue have not been successful to date due to undesired redox chemistry, while the formation of a stable B−N triple bond occurred in preference to a donor-stablilized B=N double bond. Future work will involve the preparation of new unsaturated bonding environments using this method and exploring the reaction chemistry of the boranylidene-pnictanes **2** and **4**.

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Supporting Information Available: X-ray crystallographic structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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