A donor-stabilization strategy for the preparation of compounds featuring P=B and As=B double bonds

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A new class of heavier group 15 compounds demonstrating multiple bonding with boron has been synthesized using a simple donor-stabilization protocol.

The preparation of stable compounds with multiple bonds between heavier main group elements is an extremely active field of study.[1] In many instances the presence of suitably bulky ligands enables the isolation of kinetically stable monomeric species with unusual bonding. In this context, our group has profited by the use of hindered terphenyl ligands (Ar) in order to prepare a series of main group species of formula ArEEAr (E = group 13–15 element).[2] These compounds display novel reactivity and, in the case of the digermyne derivative, ArGeGeAr, clean activation of H_2 was observed under ambient conditions.[3] As part of efforts to obtain new unsaturated inorganic systems, we are now exploring the use of donor molecules to isolate bonding motifs previously unattainable with bulky ligands alone. We now report our preliminary investigations, which involve the successful preparation of rare species featuring well-defined P=B and As=B bonds.

Stable compounds with triple bonds between boron and nitrogen were first reported in the 1980s through the seminal preparation of monomeric iminoboranes RN≡BR by Paetzold and coworkers.[4] These species are characterized by their extremely short B–N linkages (1.23 to 1.26 Å) and linear geometry, both consistent with the presence of B–N triple bonds. However, the phosphorus congeners of iminoboranes have not been isolated to date.[5] Calculations performed on the simplest boranylidenephosphane, HPBH, highlight some possible reasons behind the previously observed synthetic difficulties. Unlike linear iminoboranes, HPBH has been predicted to be a bent molecule (H–P–B = 94.5°) with a B–P bond length of 1.756 Å, indicative of a P=B double bond rather than a triple bond. Furthermore, due to the presence of an unoccupied p-orbital at boron and an active lone pair at phosphorus, the dimerization energy of HPBH has been calculated to be exothermic by over 54 kcal/mol.[6] Therefore in order to suppress dimerization of RP=BR′ units and thus preserve P=B multiple bonding: (a) large substituents need to be present at P and B, (b) the lone pair at P has to be sequestered by a Lewis acceptor, and/or (c) the empty p-orbital at B has to be occupied by either an intra- or intermolecular donor (Scheme 1).

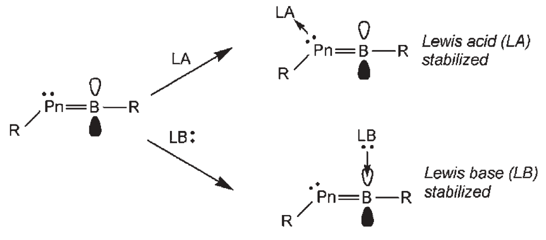
Currently, only one example of a stable boranylidenephosphane analogue is known, [$(CO)_5Cr(Et_3C)P$=BTmp] (**1**), and its synthesis requires the binding of a Lewis acidic $Cr(CO)_5$ unit to phosphorus in order to suppress dimerization of the P=B core (Tmp = 2,2,6,6-tetramethylpiperidino).[7] Against the backdrop of this work, we speculated that suitable donor molecules could be used to facilitate access to a boron–pnictogen multiple bond.

In line with prior work in this field,[8] 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 boranylidenephosphane derivative when a suitable donor molecule was present. Therefore, we constructed the requisite phosphinoborane precursor Ar*P(H)–B(Br)Tmp (**2**) from which HBr elimination could be induced to yield a P=B bond. Compound **2** was prepared from the reaction of the known dihaloborane[9] $TmpBBr_2$ with one equiv. of Ar*P(H)Li[10] in diethyl ether.[11]

Upon mixing **2** with an excess of the strong donor DMAP (4-dimethylaminopyridine) in toluene,[12] a deep purple mixture was observed immediately.† After separation of the DMAP·HBr byproduct, deep-red crystals were obtained and identified as the novel base-stabilized boranylidenephosphane, Ar*P=B(DMAP)Tmp **3**, with the help of X-ray crystallography‡ (Fig. 1, Scheme 2) in combination with NMR (^{1}H, ^{11}B, ^{13}C and ^{31}P) and UV-vis spectroscopy. This product was found to be exceedingly air- and moisture-sensitive, though 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 **3**. The ^{31}P NMR resonance was considerably downfield of that of the phosphinoborane precursor **2** (−80.1 ppm; $^1J_{PH}$ = 211 Hz); the ^{11}B NMR signal for **3** lies within the range typically observed for three-coordinate boron environments.[13] The UV-vis spectrum of **3** consists of 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 Fig. 1, monomeric **3** displays bonding parameters fully consistent with the presence of a discrete P=B double bond. Most relevant is the presence of a very short P–B bond distance of



Scheme 1 Possible routes to stable pnictogen–boron double bonds.

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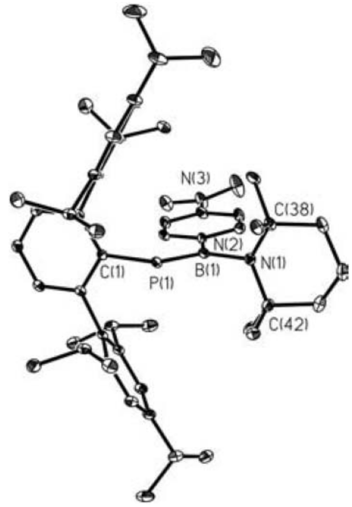
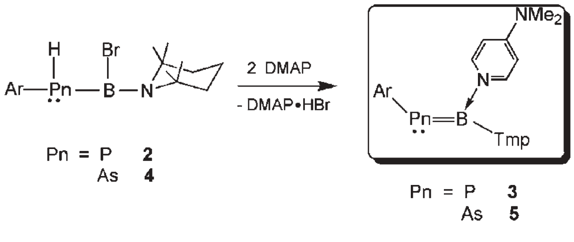


Fig. 1 Molecular structure of **3** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms and disordered DMAP have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with values involving the disordered DMAP in parentheses: P(1)–B(1) 1.8092(17), P(1)–C(1) 1.8509(14), B(1)–N(1) 1.4837(19), B(1)–N(2) 1.593(2) [1.548(5)]; 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(1)–C(42) 117.84(12), C(38)–N(1)–C(42) 119.16(11).

1.8092(17) Å, which is considerably shorter than typical P–B single bonds (*e.g.* P–B single bond length in **2** is 1.954(4) Å). Furthermore, the phosphorus center in **3** is 2-coordinate with a C(ipso)–P–B bending angle of 114.36(7)°, consistent with 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 (avg.) involving DMAP,[14] along with a B–N single bond of 1.4837(19) Å with the Tmp ligand. The observed B–N bond length to the Tmp group, coupled with the almost perpendicular orientation of Tmp, suggests that minimal π-bonding exists between N and B; thus the π-bonding is concentrated between the P and B centers.

Although compound **3** represents the first example of a neutral base-stabilized boranylidenephosphane, 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) to 1.833(6) Å],[15] and longer distances were observed in a series of hindered monomeric phosphinoboranes R$_2$PBR'$_2$ [1.839(8) to 1.871(3) Å].[16] In addition, a very short P–B interaction of 1.7453(5) Å was observed in the novel acid-stabilized species [(CO)$_5$Cr(Et$_3$C)P=BTmp] **1**;[7a] 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<. The presence of an sp-hybrized boron center in **1**, coupled with an electron withdrawing Cr(CO)$_5$ moiety at phosphorus, helps explain the *ca.* 0.06 Å contraction in the P–B bond length in **1** when compared to our base-stabilized analogue **3**.



Scheme 2 Preparation of the P=B and As=B bonded species **3** and **5**.

Given the successful preparation of **3**, we decided to investigate the preparation of heavier congeners. Following the protocol described above, the lithium arsinide Ar*AsH(Li)[10] was reacted with one equiv. of TmpBBr$_2$ to give the arsinoborane Ar*As(H)–B(Br)Tmp **4**.[11] Subsequent treatment of **4** with an excess of DMAP in hexanes rapidly afforded an intense dark-blue solution which yielded dark-purple/red dichroic crystals upon work-up. These crystals were identified as the novel boranylidenearsane Ar*As=B(DMAP)Tmp **5** by X-ray crystallography (Fig. 2) and further analyzed by NMR and UV-vis spectroscopy. As in the case of **3**, crystals of the arsenic derivative **5** were exceedingly air- and moisture-sensitive, yet had considerable thermal stability (decomposition at 147 °C). Furthermore, samples of **5** remained unchanged in benzene solution for *ca.* one month.

The ^{11}B NMR spectrum of **5** consisted of a broad resonance at +51 ppm, while a transition at 584 nm (ε = 2530 M^{-1} cm^{-1}) was the dominant feature of the UV-vis spectrum. This absorption is significantly red-shifted from that of **3**, consistent with the weaker As=B bond in **5** [*i.e.* smaller HOMO(π) to LUMO(π*) gap].

The molecular structure of **5** closely matches that of its phosphorus counterpart **3**. 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 borylarsinide anion [PhAs=BMes$_2$]$^-$, which is, to our knowledge, the only other example of a structurally authenticated As=B double bond.[17] For comparison, the As–B distances within the 3-coordinate arsinoboranes R$_2$As–BR$_2$ (which do not have appreciable As–B multiple bonding) range from 2.06 to 2.20 Å.[17b] The B–N distances in **5** were similar

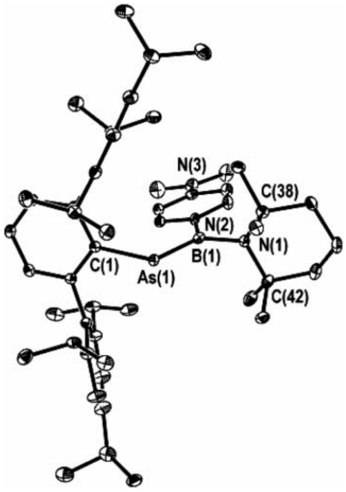


Fig. 2 Molecular structure of **5** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): As(1)–B(1) 1.914(6), As(1)–C(1) 1.987(5), B(1)–N(1) 1.469(7), B(1)–N(2) 1.567(7); C(1)–As(1)–B(1) 113.5(2), As(1)–B(1)–N(1) 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).

to those observed in **3** 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 **5**.

Attempts to form a hitherto unknown Sb=B bond were not successful, because our efforts to prepare the required stibinoborane Ar*Sb(H)–B(Br or Cl)Tmp from $TmpBBr_2$ (or $TmpBCl_2$)[18] and the known antimonide, Ar*SbH(Li)[10] resulted in the formation of significant quantities of the olive green distibene[11] Ar*Sb=SbAr* in place of clean Sb–B bond formation.

In conclusion, a new class of stable main group species featuring P=B and As=B bonds was prepared by using a simple donor-stabilization strategy. Future work will involve the preparation of new unsaturated bonding environments using this method, as well as exploring the reaction chemistry of the boranylidene pnictanes **3** and **5**.

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Notes and references

† All manipulations were carried out under strictly anhydrous and anaerobic conditions. **3**: Pre-cooled toluene (−78 °C, 12 mL) was added to a Schlenk flask containing a mixture of **2** (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 mixture was slowly warmed to room temperature and stirred for 2 d to give a purple solution along with a white precipitate (DMAP·HBr). The reaction mixture was filtered and the solvent was then removed and the product was crystallized from hexane (4 mL, *ca.* −20 °C, 2 weeks) to give large well-formed rods of **3** that were dark-red in color (0.045 g, 16%). ^1H 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, Ar*H*), 7.24 (m, 1H, Ar*H*), 7.35 (m, 1H, Ar*H*), 7.36 (s, 2H, Ar*H*), 7.48 (d, J = 7.5 Hz, Ar*H*), 8.95 (br d, 2H, *CH* DMAP). ^{11}B NMR (C_6D_6): δ 41.2 (br, $\Delta\nu_{1/2}$ = *ca.* 800 Hz). $^{13}C\{^1H\}$ 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].

Compound **5** was prepared in a similar manner to **3** except that hexane was used as the reaction solvent. *Data for* **5**: Red-purple dichroic crystals; 15% yield. ^1H 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, Ar*H* DMAP), 7.14 (d, J = 1.8 Hz, 2H, Ar*H*), 7.24 (m, 1H, Ar*H*), 7.33 (br, 2H, Ar*H*), 7.48 (d, J = 7.5 Hz, 2H, Ar*H*), 9.42 (br d, 2H, Ar*H* DMAP). ^{11}B NMR (C_6D_6): δ 51.2 (br, $\Delta\nu_{1/2}$ = *ca.* 750 Hz). $^{13}C\{^1H\}$ 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), 584 [2530].

‡ Details of the X-ray diffraction studies: **3·(hexane)$_{0.5}$**, $C_{55}H_{84}BN_3P$: monoclinic, space group $P2_1/n$, a = 12.8832(8) Å, b = 19.9163(12) Å, c = 20.7647(13) Å, $\alpha = \gamma = 90°$, β = 95.8420(10)°, V = 5300.3(6) Å^3, Z = 4, μ(Mo-Kα) = 0.088 mm^{-1}. 46847 total reflections, 12155 independent (R_{int} = 3.25%). Goodness-of-fit on F^2 = 1.102, final R indices [$I > 2\sigma(I)$], R_1 = 5.35%, wR_2 = 15.75% (all data), DMAP was disordered over two positions (76/24 ratio); **5·(hexane)**, $C_{58}H_{91}AsBN_3$: monoclinic, space group $P2_1/n$, a = 12.7587(13) Å, b = 21.142(2) Å, c = 20.465(2) Å, $\alpha = \gamma = 90°$, β = 96.813(2)°, V = 5481.3(9) Å^3, Z = 4, μ(Mo-Kα) = 0.657 mm^{-1}. 37429 total reflections, 9934 independent (R_{int} = 9.04%). Goodness-of-fit on F^2 = 1.089, final R indices [$I > 2\sigma(I)$], R_1 = 7.75%, wR_2 = 16.58% (all data). CCDC 614372–614373. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609748k

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