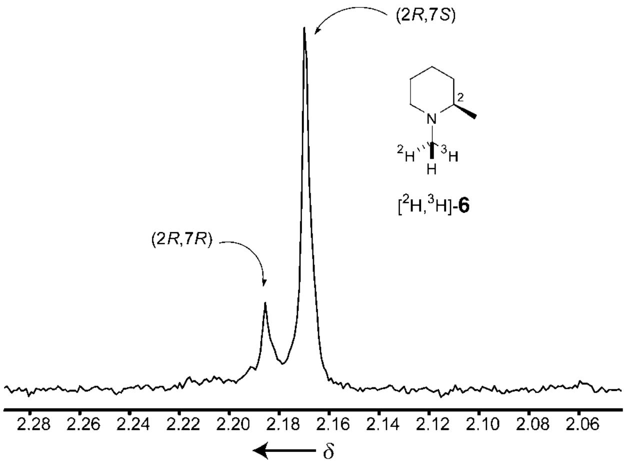

Figure 1. ^{3}H NMR spectrum of crude **6** (slow addition of $TiCl_4$) dissolved in CD_2Cl_2 acquired with simultaneous ^{1}H- and ^{2}H-decoupling (288 K, 640 MHz, 5-kHz spectral width, 2.8-s repetition time).

strategy for the synthesis of chiral *N*,*N*-ditosylmethylamine is an improvement on the Floss approach:[7b] 5 steps compared to 7 in previous reports, and an overall yield of 30 %, compared to < 5 % in the Floss synthesis. Our strategy affords chiral ditosylmethylamine with 66 % *ee* (62 % for the Schmidt degradation) and can also be used to synthesize the opposite enantiomer starting from commercially available (1*R*,2*S*)-2-amino-1,2-diphenylethanol.

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[12] Keeping in mind that upon standing with $TiCl_4$ for a few hours, enantiopure [^{2}H]-**2** is prone to epimerization at C2 through an open transition state (*N*-tosyliminium), a slow addition of $TiCl_4$ to the mixture of [^{2}H]-**2** and Et_3Si^3H and careful control of the temperature is mandatory to avoid scrambling of the stereochemistry at the stereogenic methyl center.

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The Extended Borinium Cation: $[(tBu_3PN)_2B]^+$[**]

Silke Courtenay, Joshua Y. Mutus, Robert W. Schurko, and Douglas W. Stephan[*]

Much of the recent interest in main group metallocenes has arisen from applications as materials precursors for chemical vapor deposition and as activators or catalysts in olefin polymerization. Nonetheless, structure and bonding considerations continue to motivate researchers, as less is known about these main group systems than the transition metal analogues. In this regard, recent studies by Cowley and coworkers, who have described the first examples of decamethylgallocenium[1] and decamethylborocenium cations,[2] and by Schnöckel et al, who have reported the decamethylalumocenium cation,[3] have begun to redress the balance. Only the Al species displays the symmetric bis-η^5-bonded structure analogous to ferrocene. The Ga species exhibits only marginal stability, while the boron compound is described as "tightly squeezed" presumably because of the high effective charge of the boron cation. It is noteworthy that the unsubstituted cyclopentadienyl (Cp) analogues of these cations are not known. In recent work, we employed bulky phosphinimide ligands as steric equivalents to cyclopentadienyl in the development of new active olefin polymerization catalysts.[4, 5] Herein, we employ this concept in the formation of a steric

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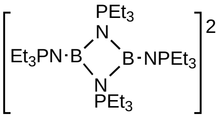
analogue of borocenium, that is the cation $[(t\mathrm{Bu_3PN})_2\mathrm{B}]^+$. In contrast to previously reported borinium ions,[6] this cation has a unique extended structure that contains a linear arrangement of the five atoms of the P=N–B–N=P linkage. This stands in marked contrast to boron derivatives of sterically less demanding phosphinimides for which the dimeric species $[(\mathrm{Et_3PN})_2\mathrm{B})_2]^{2+}$ (**I**),[7] the cyclic trications $[(\mathrm{Et_3PNBH})_3]^{3+}$[8] and $[(\mathrm{Et_3PNBH})_4\mathrm{NPEt_3}]^{3+}$ (**II**),[9] or the neutral borane $(\mathrm{Ph_3PN})_3\mathrm{B}$ (**III**) have been observed.[10]



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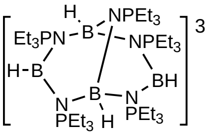

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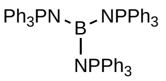


III

The lithium salt of tris-*tert*-butylphosphinimide, $[t\mathrm{Bu_3PN}]$-Li, reacts with $\mathrm{BCl_3}$ in refluxing toluene to give a white solid **1** in 72% yield. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **1** showed a single resonance signal, while a broad resonance signal was observed in the $^{11}\mathrm{B}\{^1\mathrm{H}\}$ NMR spectrum. While these data together with the ^{1}H and $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra confirmed the formation of a new species **1**, its identity was only established to be $[(t\mathrm{Bu_3PN})_2\mathrm{B}]\mathrm{Cl}$ by an X-ray crystallographic study (Figure 1). $[(t\mathrm{Bu_3PN})_2\mathrm{B}]\mathrm{Cl}$ (**1**) crystallized in a cubic space group in which the $[(t\mathrm{Bu_3PN})_2\mathrm{B}]^+$ ion possesses crystallographically imposed –3 symmetry.[11] This symmetry requires the B, N, and P atoms sit on the threefold axis of symmetry with the B atom at the center of inversion for the cation. This geometry dictates that both the N-B-N and P-N-B angles are linear. The N–B distance in **1** is 1.258(5) Å, which is thus substantially shorter than the B–N distance of 1.446(8) Å in $\mathrm{B(NPPh_3)_3}$[10] or that in the amidoboron cation $[(\mathrm{Me_2N})\mathrm{B}(\mathrm{NC_5H_6Me_4})]^+$ (1.30(4), 1.42(4) Å).[12] This observation is consistent with both the cationic nature of the B center and B–N multiple-bond character suggested by resonance structures in which the positive charge is distributed onto the N atoms (Scheme 1). The P–N bond length in **1** is 1.531(5) Å, typical of main group phosphinimide derivatives.[13] The chloride anion sits on a threefold symmetry axis and resides 7.30 Å away from the B center. It is noteworthy that **1** does not react with excess $[t\mathrm{Bu_3PN}]\mathrm{Li}$, consistent with the steric demands of these ligands and suggesting an inherent stability of the linear geometry of the five P=N–B–N=P atoms. In contrast, Dehnicke et al. have recently reported that the reaction of excess $[\mathrm{Ph_3PN}]\mathrm{Li}$ with $\mathrm{BF_3}$ affords the species $\mathrm{B(NPPh_3)_3}$.[10] Furthermore, in contrast to amidoborinium salts which are formed by abstraction of halide from $(\mathrm{R_2N})_2\mathrm{BX}$ by Lewis acids,[6, 12, 14] **1** represents the first example in which formation of a borinium cation is spontaneous for a chloride salt. This too reflects the steric demands of the bulky phosphinimide ligands.

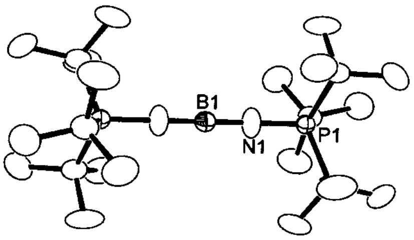
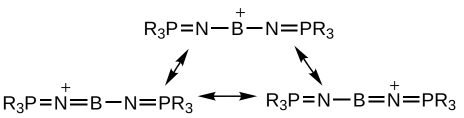
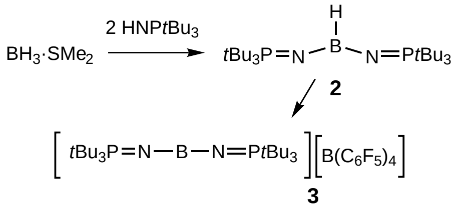


Figure 1. Structure of the cation of **1** (ORTEP drawing, 30% thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-N1 1.531(5), B1-N1 1.258(5); N1-B1-N1′ 180.0(4), B1-N1-P1 180.0(2).



Scheme 1. Resonance structures that are consistent with the cationic nature of the B center and the B–N multiple-bond character.

The related reaction of two equivalents of $\mathrm{HNP}t\mathrm{Bu_3}$ with $\mathrm{BH_3\cdot SMe_2}$ proceeds upon refluxing for 1 h to yield, after subsequent work-up, a white powder **2** in 75% yield (Scheme 2). While NMR data confirmed the formation of a new species, the data did not define the formulation unambiguously. Recrystallization from toluene/hexanes resulted in isolation of X-ray quality crystals, the subsequent structural determination of which revealed compound **2** to be isomorphorous with **1**. However, in the case of **2**, the structural refinement shows a sixfold disorder of a boron atom about the center of the –3 symmetry, thus confirming **2** as $(t\mathrm{Bu_3PN})_2\mathrm{BH}$ (Figure 2).[11] The N-B-N angle is approximately 117(2)°, while the P-N-B angle is 148.2(2)°.



Scheme 2. Synthesis of **2** and its conversion to **3**.

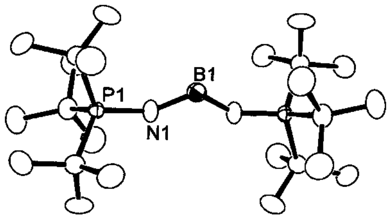


Figure 2. Structure of **2** (ORTEP drawing, 30% thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-N1 1.535(7), B1-N1 1.41(5); N1-B1-N1′ 117(2), B1-N1-P1 148.2(16).

Compound **2** reacts with $[Ph_3C][B(C_6F_5)_4]$ resulting in the abstraction of the B-bound hydride affording Ph_3CH and the borinium salt $[(t\mathrm{Bu}_3PN)_2B][B(C_6F_5)_4]$ (**3**; Scheme 2). The species **3** was isolated in 65 % yield. This species was also characterized by X-ray crystallography (Figure 3).[11] In this case, only a crystallographic center of symmetry is imposed on the molecule. The geometry at the boron center is linear, while that at the nitrogen centers approaches linearity with a P-N-B angle of 162.1(3)°. The remaining metric parameters of the cation are indistinguishable from those seen in **1** and the geometry of the $[B(C_6F_5)_4]^-$ ion is typical. The cation–anion separation is indicated by the B···B distance of 10.43 Å.

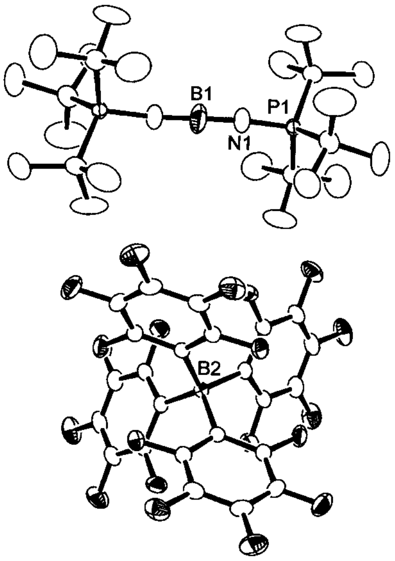


Figure 3. Structure of the cation (top) and anion (bottom) of **3** (ORTEP drawing, 30 % thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-N1 1.567(3), B1-N1 1.236(3); N1-B1-N1′ 180.0(3), B1-N1-P1 162.1(3).

$^{31}P\{^1H\}$ NMR data for **1** show an interesting solvent dependence. In CD_2Cl_2 the ^{31}P NMR resonance signal for **1** was observed at $\delta = 55.7$, whereas in C_6D_6 the signal appears at $\delta = 28.5$. This latter shift is in the range of that seen for **2** ($\delta = 31.2$). In contrast, the ^{31}P NMR resonance signal for **3** was observed at $\delta = 55.8$ in either CH_2Cl_2 or benzene. It is also noteworthy that addition of $AlCl_3$ to a solution of **1** in benzene results in a change in the ^{31}P NMR chemical shift to $\delta = 55.8$ consistent with the sequestering of the chloride ion in the $[AlCl_4]^-$ ion. These data suggest a tight ion pair of **1** forms in nonpolar solvents, while the ionic form is favored in polar solvents and in the solid state.

Ab initio calculations[15] carried out on the model system $[(H_3PN)_2B]^+$ support this view. Full geometry optimization calculations using Gaussian[16] B3LYP/6-311G** SCF basis sets[17, 18] predict that the boron atom in the $[(H_3PN)_2B]^+$ ion adopts a linear geometry, while in the proximity of chloride ion, the boron becomes trigonal planar with a B–Cl distance of 1.92 Å as expected. This suggests that the linear cationic species **1** is not electronically preferred but is induced by the steric bulk of the phosphinimide ligands. Additional calculations in which the cation of the model $[(H_3PN)_2B]Cl$ was constrained to a linear geometry reveal that a tight ion pair with a B···Cl distance of 2.90 Å is 312 kJ mol^{-1} more stable than infinitely separated ions. The corresponding NMR shielding calculations (B3LYP/6-311G** GIAO)[19, 20] predict that the phosphorus nuclei in the free cation are deshielded by $\delta = 37.3$ compared to those of the corresponding tight ion pair. These predictions compare with the experimentally observed $\Delta\delta$ value of 27.2 ppm, which infers that tight-ion pairing occurs for **2** in nonpolar solvents.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free N_2 by employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glove box. Solvents were purified by employing a Grubb's type column system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^1H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker Avance-300 and/or -500 spectrometers. ^1H and ^{13}C NMR spectra were referenced to $SiMe_4$. ^{31}P NMR, ^{11}B NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance-300 and were referenced to 85 % H_3PO_4, $NaBH_4$ (aq), and $CFCl_3$, respectively. Combustion analyses were performed at Guelph Chemical Laboratories, Guelph, Ontario.

1: BCl_3 (0.224 mmol, 224 μL, 1 M in heptane) was added to a suspension of $[t\mathrm{Bu}_3PN]Li$ (100 mg, 0.448 mmol) in toluene (10 mL). The resulting white suspension was refluxed overnight, the solvent evaporated, the product dissolved in toluene, and the solution filtered. Compound **1** crystallized in 72 % yield. ^1H NMR (CD_2Cl_2): $\delta = 1.46$ (d, $^3J(P,H) = 14.1$ Hz, 54 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 40.7$ (d, $^1J(P,C) = 48$ Hz), 29.3 (s); $^{31}P\{^1H\}$ NMR(CD_2Cl_2): $\delta = 55.7$; $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = 11.9$ (br); ^1H NMR (C_6D_6): $\delta = 1.35$ (d, $^3J(P,H) = 13$ Hz, 54 H); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta =$ 41.0(d, $^1J(P,C) = 53$ Hz), 30.2 (s); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 28.5$; $^{11}B\{^1H\}$ NMR (C_6D_6): $\delta = -6.1$ (br); elemental analysis calcd (%) for $C_{24}H_{54}BClN_2P_2$: C 60.19, H 11.37, N5.85; found: C 59.66, H 11.80, N 5.47.

2: $BH_3 \cdot SMe_2$ (173 μL, 2 M in diethyl ether) was added to a solution of $HNPt\mathrm{Bu}_3$ (150 mg, 0.690 mmol) in toluene (10 mL). The resulting suspension was refluxed for 1 h, cooled to 25 °C, and the solvent removed in vacuo. The product was isolated as a white powder in 75 % yield. Uptake of the powder in a minimum amount of toluene followed by addition of a couple of drops of hexanes resulted in the isolation of X-ray quality crystals. ^1H NMR (C_6D_6): $\delta = 1.37$ (d, $^3J(P,H) = 12.3$ Hz, 54 H); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 40.8$ (d, $^1J(P,C) = 50$ Hz), 30.5 (s); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta =$ 31.2; $^{11}B\{^1H\}$ NMR (C_6D_6): $\delta = 24.6$ (br); elemental analysis calcd (%) for $C_{24}H_{55}BN_2P_2$: C 64.86, H 12.47, N 6.30; found: C 64.20, H 12.82, N 5.96.

3: $[Ph_3C][B(C_6F_5)_4]$ (664 mg, 0.720 mmol) was added to a solution of **2** (320 mg, 0.720 mmol)in CH_2Cl_2 (5 mL). The solution was stirred overnight, the solvent removed in vacuo, and the resulting white powder washed once with hexanes (1 mL), toluene (1 mL), and hexanes (1 mL). This afforded **3** as a white powder in 65 % yield. Uptake of the powder in a minimum amount of toluene followed by addition of a couple of drops of hexanes resulted in the isolation of X-ray quality crystals. ^1H NMR (C_6D_6): $\delta = 1.46$ (d, $^3J(P,H) = 14.1$ Hz, 54 H); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 150.4-135.2$ (br), 40.8 (d, $^1J(P,C) = 48$ Hz), 29.3 (s); $^{31}P\{^1H\}$ NMR(CD_2Cl_2): $\delta = 55.8$ (s); $^{11}B\{^1H\}$ NMR(C_6D_6): $\delta = 11.1$ (br), -20.8 (s); $^{19}F\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ -133.4 (s), -164.1 (pseudo-t, $^3J(F,F) = 18$ Hz), -167.9 (s); elemental analysis calcd (%) for $C_{48}H_{54}B_2F_{20}N_2P_2$: C 51.36, H 4.84, N 2.50; found: C 51.62, H 4.94, N 2.33.

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[11] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-173106 (**1**), CCDC-173107 (**2**), and CCDC-173108 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Diffraction experiments were performed on a Siemens SMART System CCD diffractometer and solved by employing the SHELX-TL software package. **1**: Space group: $Pa\bar{3}$; $a = 14.6083(10)$ Å, $V = 3117.4(4)$ Å^3, $Z = 4$, $R = 0.0424$, $R_w = 0.1156$, GOF = 0.901. **2**: Space group: $Pa\bar{3}$; $a = 14.324(6)$ Å, $V = 2939(2)$ Å^3, $Z = 4$, $R = 0.0764$, $R_w = 0.1683$, GOF = 0.890. **3**: Space group: $P2/n$; $a = 11.727(3)$, $b = 8.370(2)$, $c = 27.150(8)$ Å, $\beta = 97.414(5)°$, $V = 2642.5(13)$ Å^3, $Z = 2$, $R = 0.0502$, $R_w = 0.1390$, GOF = 1.048.

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A Nanoscale Hybrid System Based on Gold Nanoparticles and Heteropolyanions**

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The preparation of hybrid organic–inorganic systems has witnessed major growth in the last few years.[1] Increasingly sophisticated nanocomposites with greater added value have been obtained. The interest in such systems lies in the synergy that arises through association of organic and inorganic moieties. An especially interesting class of materials are hybrids based on nanoparticles.[2] These are expected to find many applications as sensors or in the fields of magnetism, electronics, and optics. Gold nanoparticles are often involved in the synthesis of nanoscale hybrid systems. An interesting example is the formation of dimer and trimer nanocrystals by exploiting the recognition between oligonucleotide-functionalized Au nanoparticles.[3] The stability of such hybrids is strongly related to the irreversibility of the functionalization of the nanoparticles. In the case of Au, Ag, and CdS, alkylthiol groups provide a strong link to the particles.[3]

Smaller than gold nanoparticles and intermediate between the colloidal and molecular ranges, the polyoxometalates (POMs) have recently received increasing attention.[4–8] Polyoxometalates based on Mo or W constitute a full class of nanobuilding blocks. These metal oxo clusters play a role in many areas.[4] Their applications are due to a combination of several valuable properties,[5] and to their ability to behave as fully oxidized/(photo)reducible compounds.[4c] Their involvement in hybrid organic–inorganic materials is of great interest, and attention was recently paid to the development of ordered assemblies of POMs in such hybrid systems.[6] Although numerous studies deal with hybrids including POMs, only a few describe the preparation of hybrids with strong interactions between the organic and inorganic entities. One of these is a hybrid polymer in which organoimido polyoxomolybdates are pendant groups on polystyrene chains.[7] Some of us recently described the synthesis of new hybrid networks based on hydrosoluble polymer chains (polyacrylamide) cross-linked by hydrosoluble tetrafunctionalized polyanions.[8]

Here we report the synthesis of a new nanoscale hybrid system in which gold nanoparticles (4–12 nm) are associated with the prefunctionalized polyoxometalate γ-$[SiW_{10}O_{36}(RSi)_2O]^{4-}$ ($R = HSC_3H_6$), designated here as $[POM(SH)_2]^{4-}$. The organic part R plays two main roles: it forms a covalent link to gold particles through the thiol group

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