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Formation of Boron–Main Group Element Bonds by Reactions with A Tricoordinate Organoboron L_2PhB: (L = oxazol-2-ylidene)

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Supporting Information Placeholder

ABSTRACT: Reactivity of L_2PhB: **1** (L = oxazol-2-ylidene) as well as its transition metal (Cr, Fe) complexes towards main group substrates have been systematically examined, which led construction of B–E (E = C, Ga, Cl, H, F, N) bonds. The combination of **1** and triethylborane (Et_3B) smoothly captured carbon dioxide (CO_2) concomitant with the formation of B–C and B–O bonds. The soft basic boron center in **1** readily reacted with soft acidic gallium trichloride ($GaCl_3$) to afford extremely stable adduct **4** involving a B–Ga bond. Alkylation of neutral tricoordinate organoboron was firstly achieved by treatment of **1** with dichloromethane (DCM) and methyl trifluoromethanesulfonate (MeOTf), both of which afforded ionic species featuring an additional B–C bond. Comparatively, redox reactions took place when halides of heavier elements such as germanium dichloride ($GeCl_2$), dichlorophenylphosphine ($PhPCl_2$) and chlorodiphenylbismuth (Ph_2BiCl) were employed as substrates, from which cationic species **7** bearing a B–Cl bond was obtained. In addition, reactions of metal complexes [**2**: $Cr(\mathbf{1})(CO)_5$, **8**: $Fe(\mathbf{1})(CO)_4$] with cationic electrophiles were investigated. With HOTf and $FN(SO_2Ph)_2$, the corresponding ionic species featuring a B–H bond **9**, a B–F bond **10** were formed via a formal electrophilic substitution reaction whereas the reaction of **1** with F•Py-BF_4 resulted in the formation of a dicationic boron species **11** with a B–N bond.

INTRODUCTION

Since the first report of a bottleable boryllithium by Nozaki and Yamashita et al.,[1,2] isolable nucleophilic boron species have been attracting significant attention because of not only the fundamental curiosity in diverse structures but their feasible applications in synthesis of novel boron derivatives.[3] Indeed, boron-metal derivatives including transition metal boryl and borylene complexes have been widely utilized to construct boron compounds involving unprecedented B–E bonds.[4-6] Meanwhile, metal-free tricoordinate boron species isoelectronic with amines, namely borylenes, have been developed in recent years.[7-9] Among them, Bertrand and co-workers reported that compounds **I**, **IIa**-**b** (Figure 1) can be protonated by the reaction with a Brønsted acid, confirming the basic property of the boron centers.[7] Significantly, Braunschweig et al. demonstrated that borylene bis(isonitrile) compound **III** formed a complex with gallium halides revealing the Lewis basic nature of the boron center.[8a]

Despite the great progress on the synthesis of metal-free borylenes, investigation on their reactivity has been less reported which is in sharp contrast to the extensive studies on the boryl metals.[4-6] Recently, we reported the isolation of a mono-valent organoboron species **1** supported by two oxazol-2-ylidenes (Figure 1).[9a] Analogous to compounds **I-III**, the tricoordinate boron in **1** is formally surrounded by eight electrons indicating the electron-richness. Indeed, **1** readily underwent protonation with Brønsted acid to afford the corresponding ion. Additionally, direct complexation between **1** and transition metals, for instance $Cr(CO)_5(thf)$, rendered borylene-metal complexes such as $Cr(\mathbf{1})(CO)_5$ **2**. We have also shown that azaborabutadiene derivatives can be formed by the reaction of **1** with arylnitriles.[9b] These preliminary studies indicate the versatile utility of **1** as a building block for the synthesis of novel boron-containing molecules, which promoted us to continually investigate its hitherto unknown reactivity towards main group substrates. Herein, we report the reactivity of **1** towards group 13, 14, 15 elements. Moreover, the reactions of chromium and iron complexes of **1** with cationic electrophiles are also discussed.

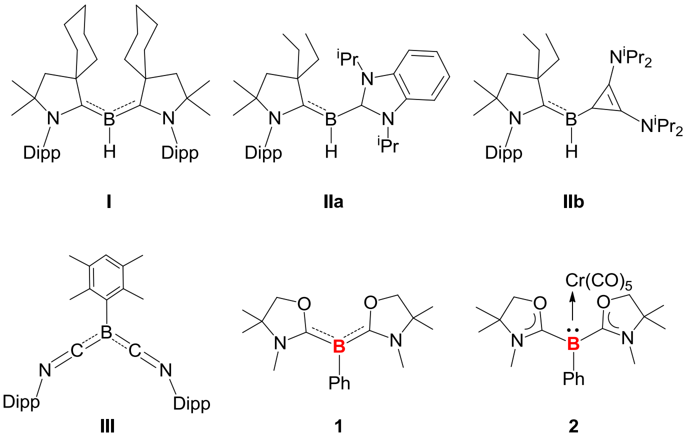


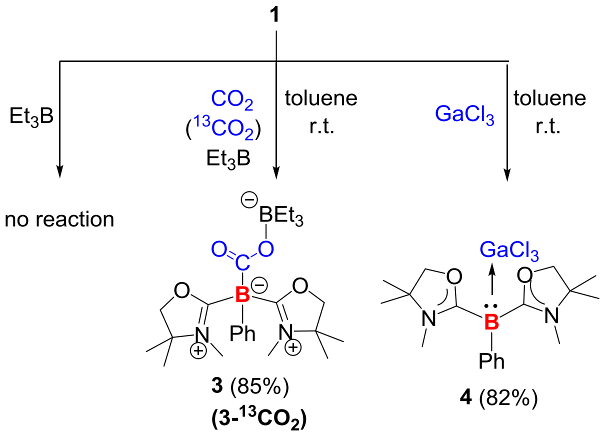
Figure 1. Examples of neutral tricoordinate boron compounds featuring basic and/or nucleophilic nature (**I-III**, **1**) and **1**-chromium adduct (**2**) (Dipp = 2,6-diisopropylphenyl).

■ RESULTS AND DISCUSSION

Reactivity of 1 towards group 13 elements

The previous study confirmed that compound **1** does not react with triethylborane (Et_3B),[9b] probably due to the mismatch of the softness/hardness of the respective boron centers in **1** and Et_3B, in terms of the hard-soft acid-base (HSAB) theory, in addition to steric hindrance. We postulated that combination of the unquenched Lewis basicity of **1** and the Lewis acidity of Et_3B would serve as an all boron frustrated Lewis pair and undergo small molecule capture and activation.[10] To examine this hypothesis, we carried out the reaction of **1** with CO_2 in the presence of Et_3B. One equivalent of CO_2 was injected using gas-tight syringe into a toluene solution of **1** and Et_3B at ambient temperature. The color of the solution turned from red to colorless, and a white solid precipitated immediately. After work-up, **3** was obtained in 85% yield (Scheme 1). The ^{11}B NMR spectrum of **3** in a CD_2Cl_2 solution displays a broad peak and a sharp peak at 4.7 ppm and –15.1 ppm, corresponding to the boron atoms in Et_3B and **1** units of **3**, respectively. Both of signals significantly shifted upfield with respect to those of Et_3B (86.1 ppm) and **1** (1.1 ppm),[9b] indicating the presence of two tetra-coordinate boron centers in **3**. By employing $^{13}CO_2$ under the same reaction condition, we prepared **3-^{13}C**. Comparatively, an additional broad peak was observed at 186.7 ppm in the ^{13}C NMR spectrum of **3-^{13}C**, and ^{11}B NMR spectrum displays a doublet at –14.8 ppm ($^1J_{CB}$ = 64.5 Hz). These data indicate that the ^{13}C atom of $^{13}CO_2$ moiety is coordinated by the B atom of **1**.

Scheme 1. Reactions of 1 with CO_2 and $GaCl_3$.



The solid-state structure of **3** was determined by single crystal X-ray diffraction studies (Figure 2), which revealed the zwitterionic character of **3** formed via a cleavage of one of the C=O bonds in CO_2. One of the oxygen atoms of CO_2 coordinates to Et_3B whereas the carbon atom is bound to boron atom of **1**. Both boron atoms display tetrahedral arrangement with the B1–C19 bond length of 1.647(2) Å and B2–O3 bond length of 1.592(2) Å, which correlate well with those for CO_2 activated products by 1,3,2,5-diazadiborinine[10i] (1.673(7) Å, 1.509(6) Å) and 1,4,2,5-diazadiborinine[10h] (1.72(2) Å, 1.475(15) Å). The crystal structure is well reproduced by its computationally optimized structure (B–C 1.672 Å; B–O 1.639 Å, respectively).

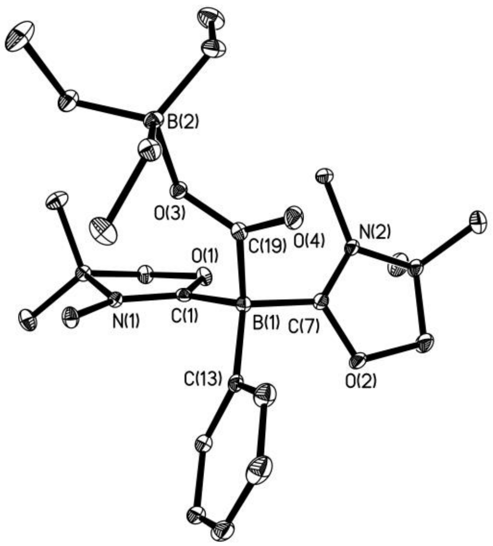


Figure 2. Solid-state structure of **3**. (Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms are omitted for clarity).

Different from the inertness of **1** towards Et_3B, treatment of a toluene solution of **1** with one equivalent of gallium trichloride ($GaCl_3$) at ambient temperature led to a rapid fading of the red colour, and a white solid of **4** was gained in 82% yield (Scheme 1). Braunshweig et al. reported that $GaCl_3$ and $GaBr_3$ adducts of **III** partially and slowly decomposed during the crystallization, and therefore their solid state structures remain unrevealed.[8a] By contrast, compound **4** is thermally stable, and it decomposes only at 269 °C. In the ^{11}B NMR spectrum of **4**, a sharp signal was observed at –17.2 ppm which is shifted upfield compared with that of **1**, indicating the presence of a tetracoordinate boron in **4**. Single crystals of **4** suitable for X-ray diffractometry were obtained by recrystallization from an acetonitrile and toluene mixed solvent at room temperature, and X-ray diffraction analysis revealed that the tetracoordinate boron is bound to the gallium center in an η^1–fashion (Figure 3a). Note that the GaCl$_3$ organoboron complex has never been structurally characterized thus far. The B1–Ga1 distance of 2.169(17) Å is nearly identical to that of **III**-GaI$_3$ adduct (2.179(9) Å).[8a] To further investigate the electronic property of the B–Ga bond in **4**, we performed quantum chemical calculations. The HOMO of **4** displays the dative bonding from boron to gallium atom, which is formed by the sp$^{4.54}$ hybrid orbital of the boron and the sp$^{0.50}$ hybrid orbital of the gallium atom, respectively (Figure 3b). Natural Bond orbital (NBO) analysis gave Wiberg bond index (WBI) value of the B–Ga bond (0.599), which is larger than those of **III**-GaCl$_3$ (0.496) and **III**-GaI$_3$ (0.467). Natural Population Analysis (NPA) indicates an overall charge transfer of 0.51 *e* from **1** to gallium trichloride, and the calculated bond dissociation energy (BDE) for the B:→Ga bond in **4** is 62.5 kcal·mol^{-1}. Much smaller bonding interaction (BDE: 11.5 kcal·mol^{-1}) was estimated for the B:→B dative bond in **1**-Et$_3$B adduct. Indeed, the optimized structure of **1**-Et$_3$B displays a significantly long B–B bond distance (4.00 Å), which may account for the instability of **1**-Et$_3$B, in line with the complete dissociation in the solution.

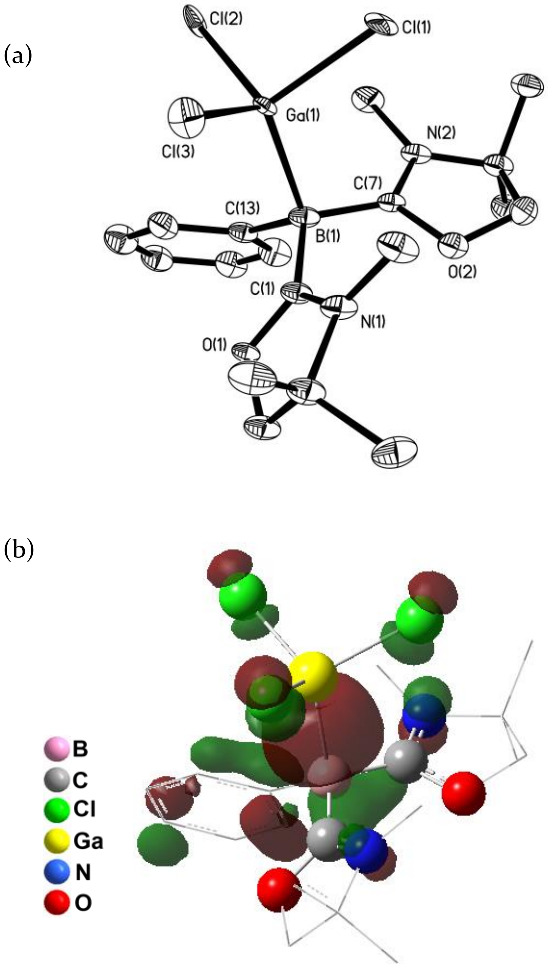
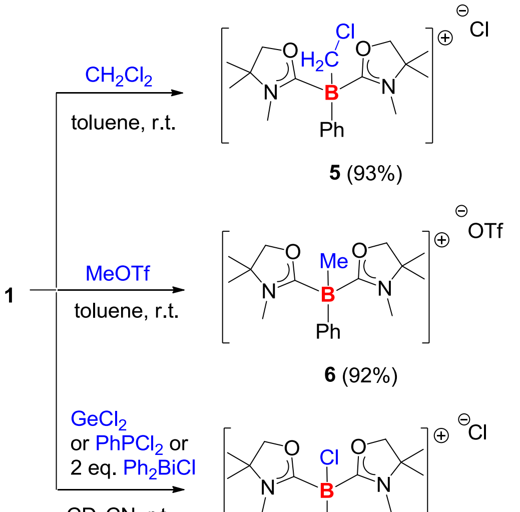


Figure 3. (a) Solid-state structure of **4** (Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms are omitted for clarity). (b) Plot of the HOMO (–7.20 eV) of **4**. (hydrogen atoms are omitted for clarity. The isovalue of 0.05 was utilized for generating the images).

Reactivity of 1 towards group 14 and 15 elements

Next, we turned our attention to the reaction of **1** with group 14 and 15 substrates. First, we examined the reaction of **1** with dichloromethane (DCM). Treatment of **1** with one equivalent of DCM in toluene occurred instantaneously as indicated by the fast decoloration of the reaction mixture. After work-up, a white solid of **5** was obtained in 93% yield (Scheme 2). In the ^{1}H NMR spectrum of **5**, a new singlet appears at 3.41 ppm (2H) while the ^{11}B NMR spectrum displays a sharp singlet at –14.1 ppm, which is significantly shifted upfield compared with that of **1**. The data indicate that a tetracoordinate boron is generated via formation of a B–C bond. Recrystallization of **5** from a DCM solution at –20 °C afforded colorless single crystals, which were subjected to X-ray diffraction study (Figure 4a). Compound **5** is an ionic species with a chloromethyl group on the boron atom. The boron center is tetra-coordinated by four carbon atoms with a distorted tetrahedral geometry. All the B–C (1.622(4)–1.638(4) Å) bond distances are in accordance with the reported data for typical B–C single bonds.[11] Under the similar reaction condition, treatment of **1** with methyl trifluoromethansulfonate (MeOTf) smoothly afforded the corresponding methylated cation **6** (Scheme 2). The ^{1}H NMR spectrum displays a sharp singlet for the Me groups on the boron atom at 0.34 ppm, while ^{11}B NMR spectrum shows a resonance at –16.6 ppm corresponding to the tetracoordinate boron. The solid-state structure of **6** was decisively confirmed by X-ray diffraction analysis (Figure 4b). It is salient to mention that although protonation of neutral organoborons was reported by Betrand et al. and our group,[7a,9a] the electrophilic alkylation has never been achieved before.

Scheme 2. Reactions of 1 with DCM, MeOTf, GeCl$_2$, PhPCl$_2$ and Ph$_2$BiCl.



The nucleophilic property of **1** is accompanied with its electron-rich nature of the boron center. Concomitantly, **1** exhibits a peculiar redox property based the low oxidation state of the boron. Thus, compound **1** features a strong reducing ability as confirmed by the negative oxidation potential (−1.108 V).[9c] Indeed, **1** readily undergoes one or two electron oxidations to furnish corresponding diboron di- and mono-cationic species respectively.[9c,9e] We were curious to check if either the redox reaction or complexation would proceed between **1** and heavier group 14-15 elements. We began our investigation with germanium dichloride (GeCl$_2$). A mixture of **1** and one equivalent of GeCl$_2$ was prepared in a J. Young NMR tube using CD$_3$CN as a solvent. The black precipitate was observed immediately, and both the ^{1}H and ^{11}B NMR spectra showed the quantitative formation of **7** (Scheme 2).[9e] Meanwhile, no reaction was confirmed between **1** and a germylene :Ge(NSiMe$_3$)$_2$ even at 50 °C. We also confirmed that both dichlorophenylphosphine (PhPCl$_2$) and chlorodiphenylbismuth (Ph$_2$BiCl) oxidized **1** to afford **7** quantitatively (Scheme 2). Previously, we observed that the reaction of **1** with CuCl initially afforded the corresponding acid/base adduct **1-CuCl** which gradually decomposed to **7** through self-redox reaction.[9e] Similar process could be one of the plausible mechanisms for the formal oxidation of **1** to **7** by chloride containing substrates (GeCl$_2$, PhPCl$_2$, Ph$_2$BiCl). However, during these reactions, no formation of germanium, phosphorus and bismuth derivatives supported by **1** were detected.

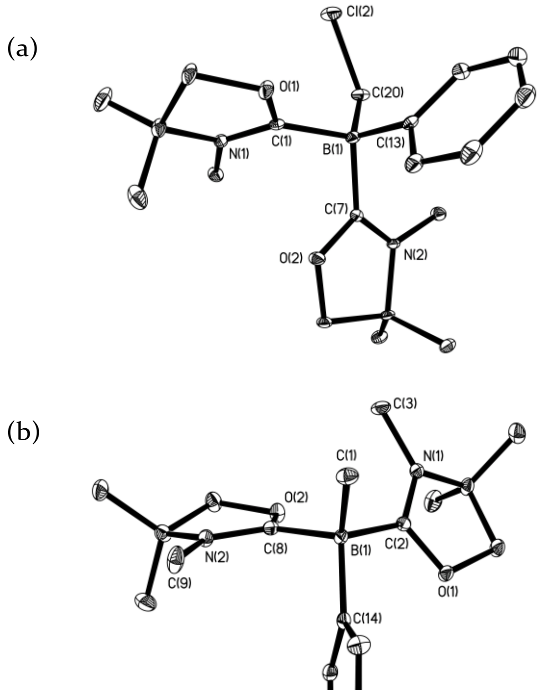


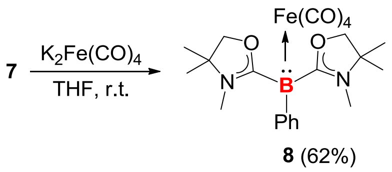
Figure 4. Solid-state structures of **5** (a) and **6** (b). (Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms and counterions are omitted for clarity).

Synthesis of 1-Fe complex (8) and reactivity of 2 and 8 towards cationic electrophiles

Transition metal borylene complexes have been widely investigated since Braunschweig et al. and Cowley et al. independently reported the seminal works.[12] Early studies have shown the versatile applications of metal borylene complexes in constructing novel boron-containing compounds through borylene transfer from metal to metal[12] and main group[13] substrates. Previously, we reported that direct complexation between **1** and transition metals may provide a reliable way for the synthesis of metal borylene complexes involving B:→M dative bonds.[9a,9e] Meanwhile, it has been reported that salt elimination between boron halides and transition metal alkali salts is one of the most useful routes for the preparation of transition metal boryl and borylene complexes,[14] which prompted us to examine the reaction of **7** and K$_2$Fe(CO)$_4$.

A mixture of **7** and one equivalent of K$_2$Fe(CO)$_4$ in THF was stirred at ambient temperature for two days. After work-up, product **8** was obtained as a red solid in 62% yield (Scheme 3). The ^{11}B NMR spectrum of **8** display a sharp singlet at −18.0 ppm, while all the ^{1}H NMR resonances shift downfield compared with these of **1**. An X-ray diffraction study identified product **8** as an iron organoboron complex in which the boron center coordinates to the Fe atom in an η^1-fashion (Figure 5a). The B1–Fe1 bond distance 2.343(5) Å in **8** is much longer than the B=Fe bonds (1.792(8)–1.907(5) Å) in terminal and cationic iron borylene complexes,[15] indicating its single bond character. We performed quantum chemical calculations to investigate intrinsic electronic property of **8**. The HOMO is mainly the σ-bonding between boron and iron atoms with a WBI of 0.3493 and a BDE of 54.15 kcal mol^{-1}, suggesting the B:→Fe dative bond character (Figure 5b). Note that this is the rare structural authentication of the B:→Fe dative bonded compound.[12a,b]

Scheme 3. Synthesis of iron organoboron complex 8.



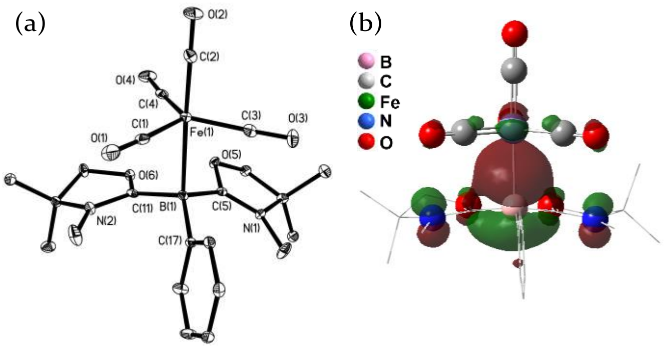
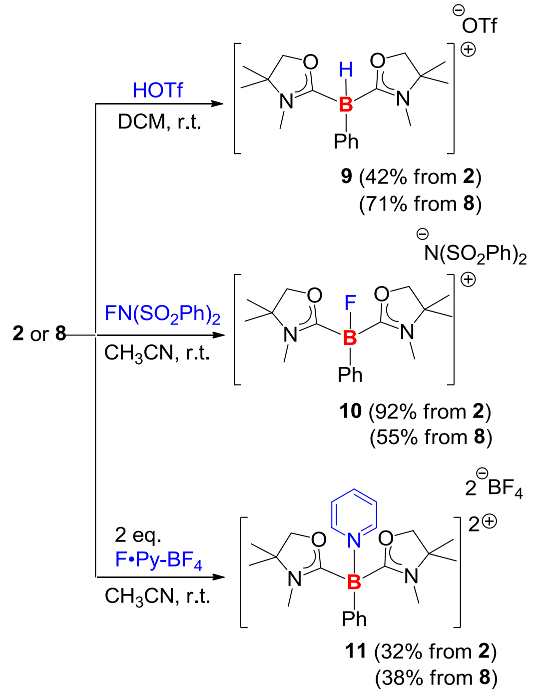


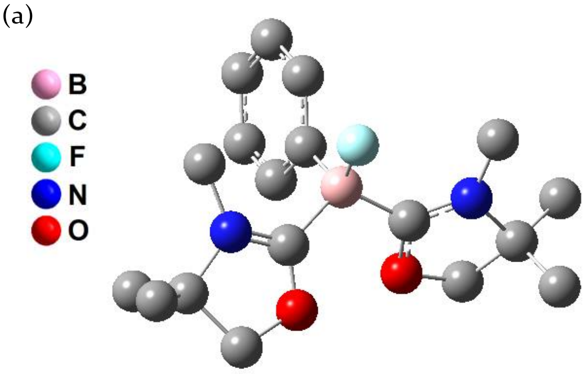
Figure 5. (a) Solid-state structure of **8** (Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms are omitted for clarity). (b) Plot of the HOMO (–6.17 eV) of **8.** (hydrogen atoms are omitted for clarity. The isovalue of 0.05 was utilized for generating the images).

Since the reactivity of **1**-metal complexes still remains unexplored,[9c] with compound **8** in hand, we investigated the reactivity of **2** and **8** towards cationic electrophiles. Reaction of **2** with HOTf was first testified. Addition of one equivalent of HOTf to a DCM solution of **2** gave a dark solution immediately. After removal of all volatiles, the residue was washed with toluene and recrystallized from an acetonitrile and toluene mixed solvent to give colorless crystals of **9** in 42% yield (Scheme 4). All the NMR date of **9** fit with those of the reported protonated product of **1**. Next, we attempted the reaction of **2** with $FN(SO_2Ph)_2$ which is widely used as a fluorinating reagent.[16] A mixture of **2** with one equivalent of $FN(SO_2Ph)_2$ in acetonitrile was stirred at room temperature for 10 minutes. After work-up, **10** was obtained as a yellow solid in 92% yield (Scheme 4). The ^{19}F NMR spectrum of **10** in a CD_3CN solution displays a broad peak at –214.7 ppm, while the ^{11}B NMR spectrum shows a doublet peak at –1.8 ppm ($^1J_{BF}$ = 61.3 Hz) indicating the formation of the B–F bond. Unfortunately, all attempts to obtain single crystals of **10** were unsuccessful, which hampered the structural characterization. The computationally optimized structure of the cationic fragment of **10** revealed the boron atom displays a tetrahedral arrangement with a short B–F bond distance of 1.419 Å (Figure 6a).[11]

Scheme 4. Reactions of 2 and 8 with HOTF, $FN(SO_2Ph)_2$ and F•Py-BF_4.



Comparatively, **2** reacted with another fluorinating reagent F•Py-BF_4, which afforded a different product **11**. The ^{11}B NMR spectrum displayed two sharp peaks at –1.2 ppm and –4.9 ppm corresponding to the central boron and $^-BF_4$ counterion respectively, while only one sharp peak at –151.6 ppm for $^-BF_4$ was observed in the ^{19}F NMR spectrum. Additionally, one set of peaks for pyridine unit was observed in the ^{1}H NMR spectrum, indicating the coordination of pyridine to the boron center. The colorless crystals of **11** suitable for the X-ray studies were grown from a toluene and THF mixed solvent and the structure was confirmed to be a pyridine coordinated dicationic boron species (Figure 6b). Note that dicationic boron species are still rare, and most of them are accessible through coordination of Lewis-bases towards boron halide precursors.[17] The C-N bond distances (1.605(4) Å) of the pyridine ring in 11 are comparable to those (1.575(5)-1.605(10) Å) of pyridines-stabilized dicationic boron compounds reported by the groups of Cowley and Braunschweig.[17g,17h,17j] Following the similar procedures with employment of iron complex **8** as the starting material, these three products **9**, **10** and **11** were gained in 71%, 55% and 38% yields, respectively. The former two reactions can be viewed as formal electrophilic substitution of the transition metal organoboron complexes although the electron transfer process is the most plausible reaction pathway.



(b)

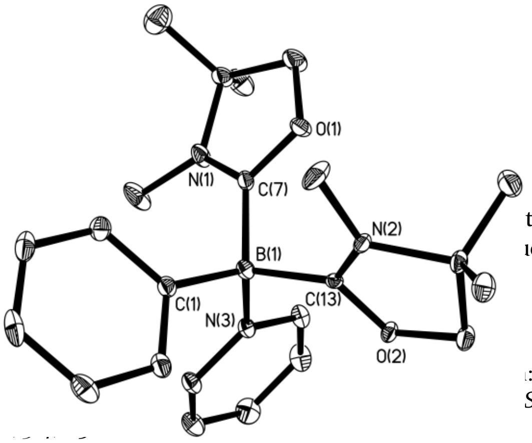


Figure 6. (a) Optimized structure of the cationic fragment of **10** (hydrogen atoms are omitted for clarity. (b) Solid-state structure of **11** (Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms and counterions are omitted for clarity).

■ CONCLUSION

The reactivity of **1** towards main group substrates was investigated. While the soft basic boron in compound **1** did not interact with hard acidic Et_3B, this Lewis pair readily activated CO_2.[18] Comparatively, soft acidic $GaCl_3$ formed the adduct with **1** which was fully characterized by standard spectroscopic means and an X-ray diffraction analysis. Nucleophilic attack of **1** towards DCM and MeOTf produced alkyl-substituted compounds **5** and **6**, in excellent yields, whereas the chlorides of heavier group 14 and 15 element oxidized **1** to afford ionic species **7**. In addition, we demonstrated that reaction of **7** with $K_2Fe(CO)_4$ afforded complex **8** bearing a B:→Fe dative bond. Treatment of **2** and **8** with HOTf and $FN(SO_2Ph)_2$ furnished the corresponding ion pairs **9** and **10**, respectively. In contrast, the reactions of **2** and **8** with F•Py-BF_4 gave boron dication **11**. Such apparent substitution reactions have never described before for the transition metal organoboron complexes. Collectively, formation of boron–main group element bonds involving B–H, B–C, B–N, B–F, B–Cl, and B–Ga bondings has been achieved by the reactions with **1**, **2** and **8**, demonstrating their potential applications in building novel boron-containing molecules.

■ ASSOCIATED CONTENT

Supporting Information.

Complete experimental data, and crystallographic data (CIF) of **3**-**6**, **8** and **11** and computational details including Cartesian coordinates for stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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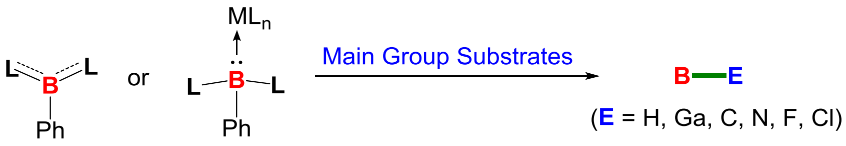
(18) The reactivity of **1**/BEt_3 towards other small molecules has also been examined. No reactions were observed between **1**/BEt_3 and H_2 as well as CO, even at a high temperature. Meanwhile, the reactions with O_2, N_2O or PhC≡CH resulted in the fast decomposition of **1** at ambient temperature.

SYNOPSIS TOC



Formation of boron–main group element bonds involving B–H, B–C, B–N, B–F, B–Cl, and B–Ga bondings has been achieved by the reactions with L_2PhB: **1** (L = oxazol-2-ylidene) or its Cr and Fe complexes, demonstrating their potential applications for construction of novel boron-containing molecules.