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Substitution Reactions at Tetracoordinate Boron: Synthesis of N-Heterocyclic Carbene Boranes with Boron−Heteroatom Bonds

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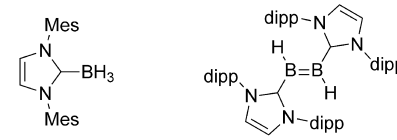
Abstract: Boryl halide, carboxylate and sulfonate complexes of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (dipp-Imd-BH_2X, X = halide or sulfonate) have been prepared from the parent borane dipp-Imd-BH_3 by (1) substitution reactions with R−X (X = halide or sulfonate), (2) reactions with electrophiles (like I_2 or NIS), or (3) acid/base reactions with HX (provided that HX has a pK_a of about 2 or less). Dipp-Imd-BH_2I is most conveniently prepared by reaction with diiodine while dipp-Imd-BH_2OTf is best prepared by reaction with triflic acid. These and other less reactive complexes behave as electrophiles and can be substituted by a wide range of heteroatom nucleophiles including halides, thiolates and other sulfur-based nucleophiles, isocyanate, azide, nitrite, and cyanide. The resulting products are remarkably stable, and many have been characterized by X-ray crystallography. Several are members of very rare classes of functionalized boron compounds (boron azide, nitro compound, nitrous ester, etc.).

Introduction

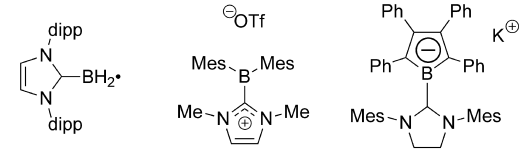
Most classes of complexes between neutral Lewis bases and borane ($LB•BH_3$) are transient.[1] For example, complexes with ethers, sulfides, alkenes, carbonyl groups, etc. readily equilibrate in solution. Such exchanges often precede the hydroboration reaction of a functional group by borane. In other words, complexes of most Lewis bases with borane express free borane chemistry. Amine-boranes ($R_3N•BH_3$) are more stable and have a considerable chemistry of their own,[2] but most still release borane under suitable thermal conditions. Phosphine-boranes ($R_3P•BH_3$) are even more stable.[3]

Perhaps the most stable class of borane−Lewis base complexes are those with stable carbenes.[4] A number of N-heterocyclic carbene boranes (NHC-boranes) have been recently described (Figure 1), and most are robust complexes that are stable to ambient conditions and chromatography. None has yet shown any tendency to express borane chemistry. Unlike boranes and borohydrides, most NHC-boranes are resistant to oxidation as well as to acid and base hydrolysis.

Stable NHC-borane complexes



NHC-borane reactive intermediates



dipp = 2,6-diisopropylphenyl
Mes = mesityl (2,4,6-trimethylphenyl)

Figure 1. Selected examples of stable NHC-borane complexes and derived reactive intermediates.

Early work on NHC-boranes focused on structure, and interesting complexes of BH_3,[5] BF_3,[6] and other simple boranes[7,8] were characterized by crystallography and other means. More recently, the chemistry of such complexes has garnered attention. The NHC ligand has been used to stabilize boron−boron double bonds[8] and to generate unusual reactive intermediates like boryl radicals,[9] borenium cations,[10] and, most recently, boryl anions

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10.1021/ja107025y

(Figure 1).[11] NHC-boranes are also starting to be used as synthetic reagents in radical,[12] ionic,[13] and organometallic reactions.[14] The structures and therefore reactions of these species appear to be unique in boron chemistry. For example, NHC-boryl radicals have a very different structure from amine-boryl and phosphine-boryl radicals.[9b]

With few exceptions, NHC-borane complexes have been prepared by direct complexation of the NHC with a suitable borane (BH_3, BF_3, etc.). The BH_3 complexes were initially prepared from BH_3•THF or BH_3•SMe_2, but they can now be prepared from inexpensive, easy to handle amine-boranes as well.[15] While apparently very general, the scope of this direct complexation method is limited by the availability of boranes. Compounds such as acyl boranes that are not readily available by direct complexation can now be made from boryl anions.[11b]

We became interested in developing methods to synthesize new NHC-boranes directly from existing NHC-boranes for two reasons. First, we wanted to better understand the existing chemistry of NHC-boranes. For example, recent work with NHC-boranes as synthetic reagents has focused on the transformation of the organic component of the reaction. But each transformation must also have a parallel new NHC-borane product. In radical reactions of xanthates, the NHC-borane products have been isolated and characterized,[9a] and we set out to do likewise for representative ionic transformations. Second, we wanted to expand the available classes of NHC-boranes in order to study their structures and reaction chemistry. For example, common functional groups in carbon chemistry like azides and nitro groups are rarely found bound to boron atoms. These and many other functionalized NHC-borane complexes could not be produced by direct complexation because the needed borane is not available.

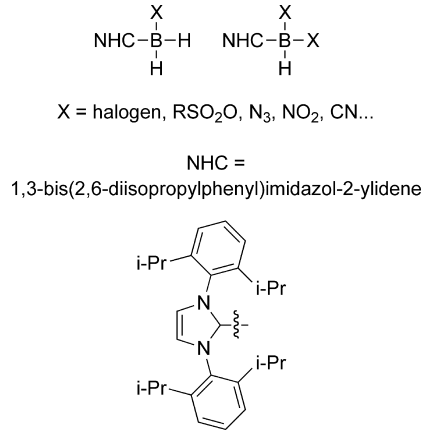

Figure 2. Generic structures of new substituted 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene carbene boranes.

Here we describe a detailed study of substitution reactions of the prototypical 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene class of carbene borane complexes (hereafter abbreviated dipp-Imd-BH_3, dipp-Imd-BH_2OTf, etc.). Borane complexes of the dipp ligand were introduced by Robinson,[8] and we chose this ligand because it is featured in many other recent applications of NHC-boranes. We describe the synthesis of over two dozen new complexes with one (NHC-BH_2X) or two (NHC-BHX_2) heteroatoms or heteroatom-based functional groups (Figure 2). These are made by ionic substitutions, reactions with electrophiles, acid/base reactions, and, perhaps most generally, direct displacement of leaving groups on tetracoordinate boron with nucleophiles. Many of the complexes are new types of NHC-boranes, and indeed several, including azide, nitro, and nitrous ester, are rare examples of stable compounds of boron bonded to such functional groups.

Results and Discussion

Substitution Reactions with Halides and Sulfonates. We have recently described thermal reductions of halides and sulfonates with various NHC-boranes.[13a] Reaction temperatures vary from rt for 1°-alkyl triflates up to 150 °C or more for less reactive substrates or leaving groups. The reactions are thought to occur by ionic mechanisms for primary halides and sulfonates. However, compounds like carbon tetrachloride and carbon tetrabromide are also reduced, possibly by a radical chain pathway as suggested for the reaction between amine-boranes and CCl_4 or CCl_3Br.[16]

The focus of that preliminary work was on optimizing the reaction conditions and on isolating the products formed from transformation of the halide or sulfonate. To learn about the

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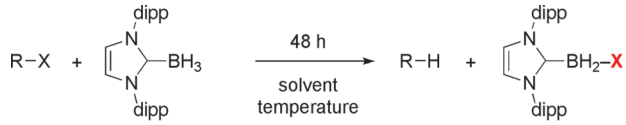
Table 1. Formation of dipp-Imd-BH_2X from Reduction of Alkyl Halides and Sulfonates



dipp-Imd-BH_3, **1** dipp-Imd-BH_2X, **2–7**
X = Cl, Br, I, OTs, OMs, OTf

Entry	R–X	equiv	solvent	temp (°C)	prod, X =	yield[a,b]	^{11}B NMR ($CDCl_3$), δ
1	$C_{12}H_{25}Cl$	1	BTF	140	**2**, Cl	N.D.	−18.7
2	CCl_4	64	$CCl_4/CDCl_3$[c]	80	**2**, Cl	84%[a]	−18.7
3	$C_{12}H_{25}Br$	1.5	toluene	140	**3**, Br	70%[b]	−23.0
4	$C_{12}H_{25}Br$	1.5	toluene	140	**3**, Br	19%[a]	−23.0
5	CBr_4	1	C_6D_6[c]	80	**3**, Br	56%[b]	−23.0
6	$C_{12}H_{25}I$	1	C_6D_6	180	**4**, I	90%[b]	−33.0[d]
7	C_4H_9I	1	PhH	180	**4**, I	100%[b]	−33.0[d]
8	$C_{12}H_{25}OTs$	1.5	toluene	140	**5**, OTs	70%[b]	−11.4
9	$C_{12}H_{25}OMs$	1.5	toluene	140	**6**, OMs	60%[a]	−11.0
10	$C_{12}H_{25}OTf$	1.5	1,4-dioxane	25	**7**, OTf	N.D.	−8.8

[a] Isolated yield after flash chromatography. [b] Isolated yield after filtration. [c] 72 h. [d] C_6D_6.

products formed from the NHC-borane component, we conducted a series of reactions that were followed by ^{11}B NMR spectroscopy. In most cases, the boron products of these reactions were subsequently isolated. Table 1 summarizes selected results from this series of experiments.

In a typical reaction, dipp-Imd-borane **1** (1 equiv) and dodecyl chloride (1 equiv) were heated in benzotrifluoride[17] (BTF, $C_6H_5CF_3$) at 140 °C for a fixed time period of 48 h. At that time, about 50% of borane **1** was converted to chloroborane **2** as indicated by ^{11}B NMR spectroscopy (entry 1). An easier route to make **2** involved heating of **1** in carbon tetrachloride at reflux for 72 h (entry 2). Full conversion to **2** was observed. Chloride **2** was a robust compound that was isolated in 84% yield after flash chromatography. A second sample of **2** was prepared by direct complexation of the carbene with $BH_2Cl{\bullet}SMe_2$, though in much lower yield (27%, see Supporting Information).

The bromoborane **3** was cleanly formed by reduction of dodecyl bromide (1.5 equiv) with **1** in toluene at 140 °C. It precipitated directly upon cooling and was isolated in 70% yield by simple filtration (entry 3). However, the sample isolated in this way contained about 10% of the corresponding imidazolium bromide (dipp-Imd•HBr). We repeated the experiment, this time conducting flash chromatography after filtration. However, bromoborane **3** proved to be sensitive to silica gel; it was isolated in good purity but in only 19% yield (entry 4). Reaction of **1** with carbon tetrabromide (1 equiv) at 80 °C in benzene-d_6 for 72 h provided a better route to **3**. The bromoborane again precipitated on cooling and was isolated by filtration (hexane wash) in 56% yield in pure form (entry 5). Experiments conducted with more than 1 equiv of carbon tetrabromide showed partial conversion to the dibromoborane **8**, which was also produced by reaction with dibromine as described below. Again, another sample of **3** was made by direct complexation with $Me_2S{\bullet}BH_2Br$ (see Supporting Information).

Iodoborane **4** was cleanly produced by the reduction of either dodecyl iodide (entry 6, 90%) or butyl iodide (entry 7, 100%).

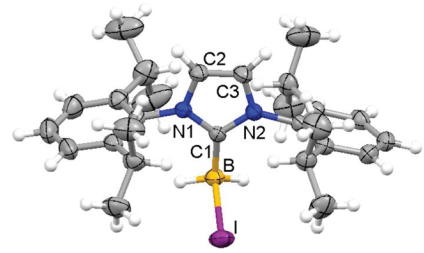


Figure 3. ORTEP diagram of the X-ray crystal structure of **4**•C_6H_6. The benzene molecule is omitted. Selected bond lengths (Å), angles (deg), and torsion angles (deg): B−I 2.313(2), B−C(1) 1.593(3), I−B−C(1) 108.5(1), I−B−C(1)−N(1) −98.6(2), I−B−C(1)−N(2) 86.4(2).

The latter procedure was more convenient because **4** could be isolated by simple evaporation of the solvent. This compound is hydrolytically sensitive (see below) and cannot be purified by flash chromatography.

The structure of **4** as a benzene solvate was confirmed by X-ray crystallographic analysis (Figure 3). The B−C(1) bond (1.593(3) Å) is slightly longer than the B−$C_{carbene}$ bond in **1** (1.585(4) Å).[8] The boron atom lies in the plane of an imidazolium ring (torsion angles (deg): C(2)−N(1)−C(1)−B −175.7(2), C(3)−N(2)−C(1)−B 175.5(2)), and the B−I bond is almost orthogonal to that plane (torsion angles (deg): I−B−C(1)−N(1) −98.6(2), I−B−C(1)−N(2) 86.4(2)). The B−I bond (2.313(2) Å) in **4** is longer than the bonds of the same type in *c*-Hex_3P-BI_3 (2.236(3), 2.237(3), 2.249(3) Å).[18]

NHC-boryl sulfonate esters dipp-Imd-BH_2OSO_2R **5**−**7** were prepared by reduction of corresponding alkyl sulfonates (entries 8−10). Pure tosylate dipp-Imd-BH_2OTs **5** was isolated in 70% yield by cooling and filtration of the reaction mixture (entry 8). The crude mesylate dipp-Imd-BH_2OMs **6** was contaminated with a small amount of corresponding imidazolium mesylate salt (dipp-Imd•HOMs). However, **6** was stable to flash chromatography and was obtained in pure form in 60% yield (entry 9). The reaction with dodecyl triflate is so fast that it can be performed at room temperature (entry 10). The formation of dipp-Imd-BH_2OTf **7** was confirmed by ^{11}B NMR of the crude reaction mixture, but the triflate could not be isolated in a pure form because of its susceptibility toward hydrolysis to the imidazolium triflate salt (dipp-Imd•HOTf).

The structure of a representative sulfonate, dipp-Imd-BH_2OTs **5**, was solved by X-ray crystallographic analysis.[19] Tosylate **5** exists as two similar but crystallographically independent molecules, only one of which is shown in Figure 4. In contrast to **4**, the tosyloxy substituent at the boron atom in **5** is not orthogonal to the plane of the imidazolylidene ring. Instead, it is closer to coplanar; the N−C−B−OSO_2Ar angle is 9.4° in the molecule shown in Figure 4 and −35.2° in the other molecule (see Supporting Information).

The ^{11}B NMR spectrum of precursor dipp-Imd-BH_3 **1** exhibits a clear quartet, with $^1J_{B-H}$ = 88 Hz. In contrast, substituted derivatives dipp-Imd-BH_2X **2**−**7** (Table 1) each showed a broad signal due to the quadrupole moment of the boron atom.[20]

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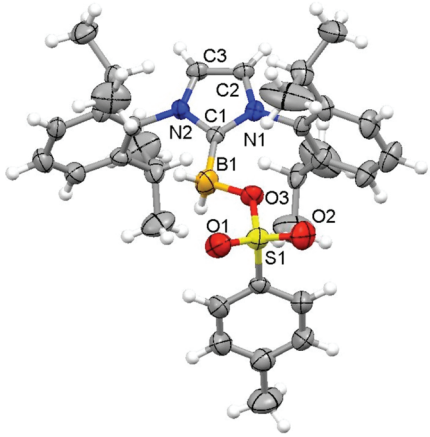


Figure 4. One of the two similar crystallograhic molecules of dipp-Imd-BH_2OTs **5**. Selected bond lengths (Å), angles (deg), and torsion angles (deg): S(1)−O(3) 1.500(3), B(1)−O(3) 1.522(7), B(1)−C(1) 1.606(7), S(2)−O(6) 1.518(3), B(2)−O(6) 1.557(8), B(2)−C(35) 1.597(7), S(1)−O(3)−B(1) 123.9(3), O(3)−B(1)−C(1) 108.8(5), S(2)−O(6)−B(2) 122.8(3), O(6)−B(2)−C(35) 105.9(4), N(1)−C(1)−B(1)−O(3) 9.4(8), N(2)−C(1)−B(1)−O(3) −169.1(4), N(3)−C(35)−B(2)−O(6) 147.4(4), N(4)−C(35)−B(2)−O(6) −35.2(7).

Heating of $CDCl_3$ solutions of **2** or **6** to 50 °C resulted in sharp triplets with $^1J_{B-H} = 107$ and 104 Hz respectively. The larger $^1J_{B-H}$ of these complexes compared to dipp-Imd-BH_3 **1** is due to the increased *s*-character of B−H bonds in **2**−**7**.[20c]

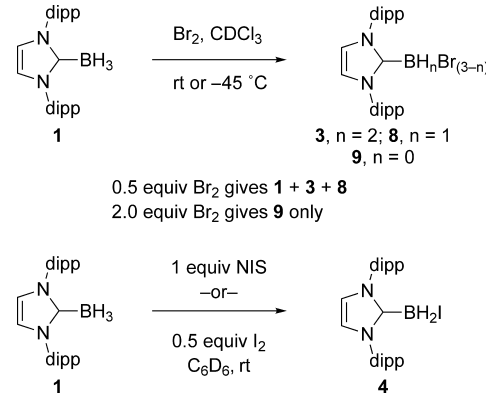
Stability of dipp-Imd-BH_2X Complexes (2−7) toward Hydrolysis. The six boron halides (**2**−**4**) and boryl sulfonates (**5**−**7**) are white solids that vary greatly in their stability toward moisture and column chromatography. At one extreme, dipp-Imd-BH_2Cl **2** survives column chromatography and can be exposed to water or dissolved in MeOH without decomposition. At the other extreme, the triflate **7** could only be generated in situ, and the iodide **4** could be isolated by filtration but suffered fast hydrolysis or methanolysis. In the middle are the mesylate **6**, tosylate **5**, and bromide **3**. The mesylate **6** may be the most stable of the three, since it survived flash chromatography reasonably well. Clearly there is a qualitative correlation between the leaving group ability of the group X and the hydrolytic sensitivity of the corresponding borane.

Addition of water or methanol to dipp-Imd-BH_2I was accompanied by vigorous evolution of a gas (presumably H_2) with formation of a corresponding imidazolium iodide (dipp-Imd•HI). This salt was isolated from one experiment, and its structure was confirmed by X-ray analysis (see Supporting Information). A ^{11}B NMR spectrum of the reaction with methanol showed a broad signal at +18.7 ppm that can be attributed to $B(OMe)_3$.[20b] Accordingly, we formulate the hydrolysis (R = H) or methanolysis (R = Me) reaction as shown below:

$$\text{dipp-Imd-BH}_2\text{X} + 3\text{ROH} \rightarrow \text{dipp-Imd•HX} + \text{B(OR)}_3 + 2\text{H}_2$$

This sensitivity to hydrolysis is unique to NHC-boranes containing good leaving groups. For example, precursor **1** is very stable to water, and indeed a related water-soluble carbene borane is known that is stable for weeks.[12b] Likewise, many of the usual new functionalized compounds presented below are not especially sensitive to hydrolysis. Additional information on the hydrolysis of the iodide **4**, including a possible sequence of steps, is provided in the Supporting Information. This hydrolysis is one of the few reactions discovered so far in which the boron atom can be disassociated from it NHC ligand. Such transformations could well be useful in some settings.

Scheme 1. Reactions of **1** with Halogen-Based Electrophiles



Electrophilic Halogenations. Seeking even simpler ways to make bromide **3** and iodide **4** for downstream applications, we tried several direct electrophilic halogenation reactions of carbene borane **1** (Scheme 1). These were patterned after classical halogenation reactions of amine-boranes.[21] Bromination reactions were not selective. For example, treatment of **1** with 0.5 equiv of Br_2 resulted in a rapid consummation of the Br_2 with formation of a mixture of monobromide **3**, dibromide **8**, and unreacted **1**, as assessed by ^{11}B NMR spectroscopy. In contrast, when 2 equiv of Br_2 were used, the known boron tribromide complex **9**[8] was the only product detected by ^{11}B NMR. The complete formation of **9** with only 2 equiv of Br_2 means that acid/base reactions must occur with the HBr that is generated. Reactions with *N*-bromosuccinimide (NBS) were also not selective.

In contrast, the addition of 1 equiv of *N*-iodosuccinimide (NIS) to **1** at rt quickly and cleanly provided boron iodide **4** as the only boron-containing product according to ^{11}B NMR analysis. However, the separation of iodide **4** from succinimide is not convenient. Addition of 0.5 equiv of I_2 to **1** also cleanly and quickly provided a solution of **4**. Presumably, I_2 consumes half of **1** to produce **4** and HI. The so formed HI consumes the other half of **1** in an acid/base reaction to produce **4** and H_2. The reaction of **1** with I_2 is the most convenient way to make **4**, which can then be used directly for displacement reactions (see below) or for reductive lithiations to make boryl anions.[11b]

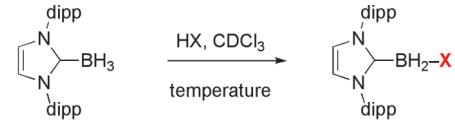
Brønsted Acid/Base Reactions. Touchstones for NHC-boranes include neutral amine- and phosphine-boranes and anionic borohydrides with electron-withdrawing groups like $NaBH_3CN$. All of these compounds react with Brønsted acids to some degree.[22] The reactions of **1** with Br_2 and I_2 indicate that it also reacts with strong acids. During the course of this work, a thesis of D. McArthur described reactions of Mes-Imd-BH_3 with HCl, TsOH, and TfOH, and his results are consistent with ours.[13c]

To learn more about the acid/base chemistry of **1**, we reacted it with a series of acids whose pK_a's ranged widely from about −14 to +14. Selected results are compiled in Table 2 in order of decreasing acidity of the acid. In a typical experiment (entry 1), 1 equiv of triflic acid was added to a solution of **1** in $CDCl_3$

(21) (a) Nöth, H.; Beyer, H. *Chem. Ber.* **1960**, *93*, 2251–2263. (b) Douglass, J. E. *J. Org. Chem.* **1966**, *31*, 962–963.

(22) (a) Drake, J. E.; Simpson, J. *J. Chem. Soc. A* **1968**, 974–979. (b) Ryschkewitsch, G. E. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 99–101. (c) Imamoto, T.; Oshiki, T. *Tetrahedron Lett.* **1989**, *30*, 383–384. (d) Oshiki, T.; Imamoto, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2846–2849.

Table 2. Brønsted Acid/Base Reactions of **1**



dipp-Imd-BH_3, **1** dipp-Imd-BH_2X, **2–3**, **5–7**, **10–12**

Entry	H−X	pK_a	temp (°C)	prod, X =	yield	^{11}B NMR ($CDCl_3$), δ
1	TfOH	−14	0	**7**, OTf	NMR[a]	−8.8
2	HBr[b]	−9	0	**3**, Br	NMR[a]	−23.0
3	HCl[c,d]	−8	0	**2**, Cl	81%	−18.7
4	TsOH[e]	−2.6	60	**5**, OTs	NMR[a]	−11.2
5	MsOH[d]	−2.6	0	**6**, OMs	88%	−11.0
6	CF_3COOH	−0.3	25	**10**, $OCOCF_3$	85%	−11.4
7	$Cl_2CHCOOH$	1.3	60	**11**, $OCOCHCl_2$	67%	−11.1
8	$NCCH_2COOH$[e]	2.5	60	**12**, $OCOCH_2CN$	24%	−11.9

[a] The product was observed by NMR spectroscopy but was not isolated in a pure form. [b] 33% solution of HBr in AcOH. [c] 4 M solution in 1,4-dioxane. [d] 2 equiv of acid. [e] Solid acids that required heating to dissolve.

at 0 °C. A rapid reaction ensued with essentially immediate evolution of hydrogen gas. After 5 min, analysis of the reaction mixture by ^{11}B NMR spectroscopy showed complete conversion to the boron triflate **7**. As mentioned above, triflate **7** is not easily isolated, so this is a very convenient way to generate it for use in situ.

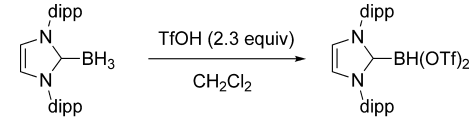
Similar reactions of **1** with strong acids HBr, HCl, MsOH, CF_3COOH (entries 2, 3, 5, 6) at 0 °C were also accompanied by intense bubbling, and ^{11}B NMR spectroscopy at the 5 min time point showed complete conversion to the corresponding products. The chloride **2**, mesylate **6**, and trifluoroacetate **10** are stable compounds that were isolated by flash chromatography in good yields (81−88%). However, in practice this is not needed since the solutions produced on mixing contain only the product and can be used directly in onward reactions.

TsOH is poorly soluble in $CDCl_3$ at room temperature; however, warming the mixture to 60 °C resulted in dissolution and clean conversion to **5** (entry 4). The reaction with $Cl_2CHCOOH$ was slow at room temperature (30% conversion after 3 h according to ^{11}B NMR spectroscopy) even though the acid is soluble in $CDCl_3$. But the complete conversion to **11** was observed after heating at 50 °C for 18 h (entry 7). Heating of $NCCH_2CO_2H$ at 60 °C to effect dissolution resulted in a slow reaction (20 h) to provide **12**, which was isolated in 24% yield.

The complex **1** did not react with weak acids such as $Ph_2P(=O)OH$ (pK_a = 2.3), *p*-$CH_3C_6H_4COOH$ (pK_a = 4.4), CH_3COOH (pK_a = 4.9), or phenol (pK_a = 10) even after a lengthy heating of the solutions in $CDCl_3$ at 60 °C. It is already well established that **1** does not react with water or alcohols either. To summarize, **1** reacts rapidly at room temperature or below with Brønsted acids of pK_a's of 0 or below (provided that the acids are dissolved). A transition occurs in the range of pK_a 1−2, where reactions become slower. Less acidic acids do not react with **1**, even on heating at 60 °C. These results suggest that acid catalyzed reductions or other reactions with NHC-boranes might be possible.

We also briefly studied the further acid/base reactions of several of the heterosubstituted NHC-boranes, but these proved to be considerably less reactive than **1**. Dipp-Imd-$BH_2OC(=O)CF_3$ **10** was the only product detected by ^{11}B NMR spectroscopy when 5 equiv of CF_3COOH were added to dipp-Imd-BH_3 **1**. Similarly, adding 2 equiv of either HCl or MsOH produced only monosubstituted complex **2** or **6**. In contrast, the reaction of **1** with 2.3 equiv of triflic acid in CH_2Cl_2 quickly produced a solution of dipp-Imd-$BH(OTf)_2$ **13** (Scheme 2). This ditriflate was not isolated, but its formation was indicated by ^{11}B NMR spectroscopy by a new, broad signal at −2.5 ppm. Subsequent double nucleophilic substitution reactions (see below) also confirmed that **13** was formed. Addition of 5 equiv of triflic acid to **1** produced only ditriflate **13**; no tritriflate was detected.

Scheme 2. Reaction of **1** with 2.3 equiv of TfOH Produces Ditriflate **13**



1 **13**

^{11}B NMR, −2.5 ppm

Nucleophilic Substitution Reactions. One of the characteristic reactions of boranes ligated to amines or phosphines and bearing leaving groups is nucleophilic substitution.[19,23] In addition, amine-ligated boryl iodides and triflates have also been used in hydroboration reactions.[24] In these reactions, the alkene is proposed to displace the iodide or triflate to start the reaction. We already observed that the NHC-BH_2X compounds with the best leaving groups react more or less readily with water and alcohols. Accordingly, we posited that NHC-boranes bearing leaving groups would react as electrophiles in nucleophilic substitution reactions. Having ready access to the needed boryl halides and sulfonates, we undertook a detailed study of such reactions. Many of the most interesting results are summarized in Table 3.

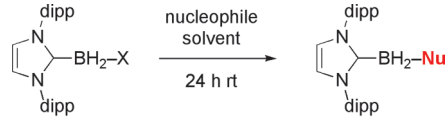
In a typical experiment, boryl triflate **7** was generated in situ by addition of TfOH to **1** in $CDCl_3$. Tetrabutylammonium fluoride (Bu_4NF, 2 equiv) was then added, and the mixture was stirred at room temperature for 20 h. Evaporation of the solvent and flash chromatography provided pure fluoroborane **14** as a white solid in 40% yield. Complete characterization data of **14**, including analysis of its characteristic ^{11}B and ^{19}F NMR spectra, are presented in the Supporting Information.

Iodide **4** was also used in several substitution reactions, and this was generated in situ by the reaction of **1** with 0.5 equiv of I_2. In one case, mesylate **6** was used, and this was generated in situ by the reaction of **1** with MsOH. A very diverse range of substitution products were formed, as shown in Table 3. Remarkably, all of these products are stable white solids that were isolated by flash chromatography. Because many of the compounds in Table 3 have functional groups that are rarely found bound to boron, the following discussion of the results in the table focuses on structure. However, complete details of the preparation and isolation are provided in the Supporting Information. Solvent choices were usually based on the solubility of the nucleophile. Results with additional nucleophiles beyond

(23) (a) Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1967**, *89*, 3145–3148. (b) Bratt, P. J.; Brown, M. P.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2161–2163. (c) Denniston, M. L.; Chiusano, M. A.; Martin, D. R. *J. Inorg. Nucl. Chem.* **1976**, *38*, 979–981.

(24) (a) Scheideman, M.; Shapland, P.; Vedejs, E. *J. Am. Chem. Soc.* **2003**, *125*, 10502–10503. (b) Clay, J. M.; Vedejs, E. *J. Am. Chem. Soc.* **2005**, *127*, 5766–5767. (c) Karatjas, A. G.; Vedejs, E. *J. Org. Chem.* **2008**, *73*, 9508–9510. (d) In contrast to the above hydroboration reactions with pyridine borane derivatives, no reaction was observed between dipp-Imd-BH_2OTf or dipp-Imd-BH_2I and $C_{12}H_{25}CH=CH_2$ in CH_2Cl_2/THF at rt.

Table 3. Nucleophilic Substitution of dipp-Imd-BH_2X **4**, **6**, or **7**



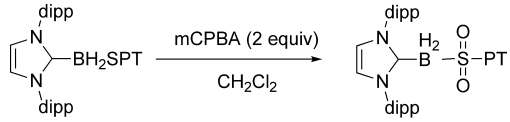
4, X = I
6, X = OMs
7, X = OTf

2, **3**, **14**–**25**

Entry	X	nucleophile	solvent	prod, Nu	yield	^{11}B NMR ($CDCl_3$), δ
1	OTf	Bu_4NF	$CDCl_3$/THF	**14**, F	40%	−6.1 (app q)
2	I	$BnEt_3NCl$	$CDCl_3$/THF	**2**, Cl	38%	−18.7 (br s)
3	OTf	PhMgBr	THF	**3**, Br	31%	−22.6 (br s)
4	OTf	PhSLi[a]	$CDCl_3$/THF	**15**, SPh	58%	−24.9 (br s)
5	I	PTSLi[a,b]	THF	**16**, SPT	42%	−23.5 (br s)
6	OTf	EtOC(=S)SK	$CDCl_3$/THF	**17**, SC(=S)OEt	35%	−24.4 (br s)
7	OTf	PhSC(=S)SLi[c]	$CDCl_3$/THF	**18**, SC(=S)SPh	65%	−22.9 (br s)
8	I	NaSCN	DMSO	**19**, NCS	24%	−23.2 (br s)
9	OTf	KOCN	DMSO	**20**, NCO	35%	−22.8 (t)
10	OTf	NaN_3	DMSO	**21**, N_3	42%	−17.2 (t)
11	I	NaN_3	DMSO	**21**, N_3	74%	−17.2 (t)
12[d]	OMs	NaN_3	DMSO	**21**, N_3	83%	−17.2 (t)
13	OTf	$NaNO_2$	DMSO	**22**, ONO	12%	−10.1 (t)
				23, NO_2	7%	−13.5 (br s)
14	I	$AgNO_2$	DMSO	**22**, ONO	27%	−10.1 (t)
				23, NO_2	10%	−13.5 (br s)
15	OTf	Bu_4NCN	$CDCl_3$/THF	**24**, CN	81%[e]	−36.7 (t)
16	I	NaCN	DMSO	**24**, CN	21%	−36.7 (t)
17[f]	I	AgCN	DMSO	**25**, NC	55%	−24.0 (br s)

[a] Prepared in situ by the reaction between thiol and *n*-BuLi. [b] PT = 1-phenyltetrazol-5-yl. [c] Prepared in situ from PhSLi and CS_2. [d] At 80 °C. [e] An inseparable 10:1 mixture of **24** and **25**. [f] 100 °C.

Scheme 3. Oxidation of Sulfide **16** to Sulfone **26**



16 **26** (71%)

those in Table 3 are also briefly summarized in the Supporting Information. For example, reduction of triflate **7** by $LiAlD_4$ is a convenient method to make dipp-Imd-BH_2D (**1**-d_1).

Substitution of iodide **4** by chloride ($BnEt_3NCl$) (entry 2) provided the chloride **2** (38% yield), while the reaction of triflate **7** with PhMgBr (entry 3) provided none of the phenyl substitution product (dipp-Imd-BH_2Ph) but instead returned the now familiar bromide **3** (31% yield after column chromatography).

The reaction of **7** with PhSLi (generated separately in situ from PhSH and BuLi) produced dipp-Imd-BH_2SPh **15** in 58% yield as a stable white solid (entry 4). Lithium 1-phenyl-1*H*-tetrazole-5-thiolate (LiSPT) reacted with **4** to give dipp-Imd-BH_2SPT **16** in 42% yield (entry 5). This compound was subsequently oxidized with *m*-chloroperoxybenzoic acid (mCPBA) to dipp-Imd-BH_2SO_2PT **26**, a stable, readily isolated compound (Scheme 3). The transformation is remarkable because the B−H bonds of the complex are inert to such a strong oxidant.

The structure of borane sulfone **26** was confirmed by X-ray analysis (Figure 5). The B−S bond is almost orthogonal to the plane of the imidazolylidene ring (torsion angle S−B−C(1)−N(1) is 89°). The only other boron-substituted sulfone characterized by X-ray analysis is (*P*−*B*)-(2-(borylsulfonyl)phenyl)dicyclohexylphosphine.[25] In that compound, the B−S bond is a part of a five-membered cycle yet has similar geometry parameters: B−S 1.899(4), S−C 1.793(3), B−S−C 100.7(1).

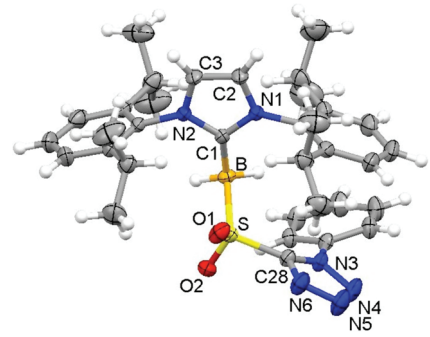


Figure 5. X-ray crystallographic structure of dipp-Imd-BH_2SO_2PT **26**. Selected bond lengths (Å), angles (deg), and torsion angles: B−S 1.908(1), S−C(28) 1.821(1), B−C(1) 1.586(2), B−S−C(28) 113.16(6), S−B−C(1) 112.59(9), B−S−C(28)−N(3) −46.9(1), B−S−C(28)−N(6) 146.6(1), S−B−C(1)−N(1) 88.6(1), S−B−C(1)−N(2) −100.9(1).

Reactions of triflate **7** with commercially available potassium ethyl xanthogenate KSC(=S)OEt (entry 6) and lithium carbontrithiolate LiSC(=S)SPh (prepared in situ from PhSH, BuLi, and CS_2, entry 7) gave corresponding products **17** and **18** with a general formula dipp-Imd-$BH_2SC(=S)R$. Dipp-Imd-$BH_2SC(=S)OEt$ **17** resembles one of the products of the radical reduction of primary xanthate with **1**, and it has the same chemical shift in the ^{11}B NMR spectrum as that reported for dipp-Imd-$BH_2SC(=S)O(CH_2)_6OBn$.[9a]

The chemistry of carbon compounds is replete with molecules containing both C−H bonds and functional groups multiply bonded to heteroatoms. The list is almost endless: carbonyl groups, nitro groups, nitriles, azides, isocyanates, and so on. In contrast, compounds containing B−H bonds and such functional groups are quite rare, especially so when the functional group is directly bonded to the boron. This is because most types of B−H bonds reduce multiple bonds with heteroatoms.

As a class, NHC-boranes present an interesting opportunity to explore such unusual functionalized compounds because they do not dissociate easily (no free borane reactions), because they are only very weak hydride donors, and because substitution reactions are readily effected. In practice, the scope of displacement reactions of NHC-BH_2X compounds with nucleophiles bearing heteroatomic multiple bonds and the stability of the resulting products extended well beyond our initial imagination (Table 3, entries 8−17).

The major product isolated from the substitution reaction between iodide **4** and NaSCN was isothiocyanate dipp-Imd-BH_2NCS **19** (entry 8). The related ambident nucleophile, potassium cyanate KOCN, also was borylated on the nitrogen atom to produce isocyanate dipp-Imd-BH_2NCO **20** in 35% yield (entry 9). The regioselectivities of both reactions were initially assigned based on the chemical shifts in the ^{11}B NMR spectra and on analyses of the IR spectra, as discussed in the Supporting Information.

Later, both structures were confirmed by X-ray crystallographic analysis, as shown in Figure 6. The bond lengths in the B−X−C−Y of moiety are similar to those in H_3N-BH_2NCS:[26a] B−N 1.534(8),

(25) Imamoto, T.; Hirakawa, E.; Yamanoi, Y.; Inoue, T.; Yamaguchi, K.; Seki, H. *J. Org. Chem.* **1995**, *60*, 7697–7700.
(26) (a) Kendall, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1973**, *12*, 2920–2922. (b) Shelly, K.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1992**, *31*, 2889–2892.

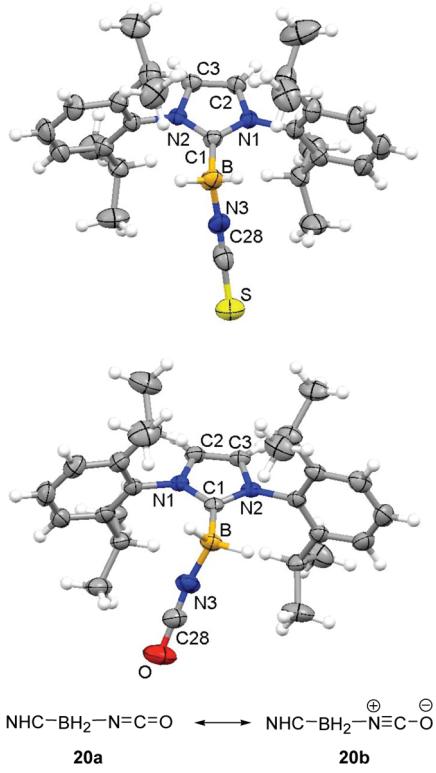


Figure 6. X-ray crystallographic structures of dipp-Imd-BH_2NCS **19** (top) and dipp-Imd-BH_2NCO **20** (bottom). Selected bond lengths (Å), angles (deg), and torsion angles for **19**: S−C(28) 1.648(3), C(28)−N(3) 1.089(4), B−N(3) 1.533(4), B−C(1) 1.608(4), N(3)−C(28)−S 178.2(3), B−N(3)−C(28) 169.2(3), N(3)−B−C(1) 109.8(2), N(3)−B−C(1)−N(1) −79.1(3), N(3)−B−C(1)−N(2) 102.2(3), B−N(3)−C(28)−S −31(10). Selected bond lengths (Å), angles (deg), and torsion angles for **20**: O−C(28) 1.207(3), C(28)−N(3) 1.129(3), B−N(3) 1.543(3), B−C(1) 1.613(3), N(3)−C(28)−O 178.7(3), B−N(3)−C(28) 166.6(2), N(3)−B−C(1) 107.7(2), N(3)−B−C(1)−N(1) 65.6(3), N(3)−B−C(1)−N(2) −112.5(2), B−N(3)−C(28)−O 150(11).

N−C 1.137(8), C−S 1.627(6), B−N−C 177.5(6), N−C−S 179.2(5) and in a polyborane derivative $[Et_3NH]_2$[*closo*-2-$B_{10}H_9NCO$]:[26b] B−N 1.498(7), N−C 1.128(7), C−O 1.187(7), B−N−C 172.3(3), N−C−O 177.8(4). The bond lengths suggest that the C−N bond may have some triple bond character as illustrated in the resonance forms **20a**, **20b**. The resonance form **20b** is stabilized because the positive nitrogen atom is adjacent to the negative boron atom. This resonance may also explain the high value of the B−N(3)−C(28) angle of 167°, which is closer to that expected for *sp*-hybridization of the nitrogen atom (180° angle) than that for sp^2-hybridization (120° angle).

Synthesis of borane azide dipp-Imd-BH_2N_3 **21** has been achieved from three different precursors: triflate **7**, iodide **4**, and mesylate **6** (entries 10−12) in 42%, 74%, and 83% yields, respectively. Heating of the reaction mixture at 80 °C was required for mesylate **6** because no reaction was observed at room temperature. Azide **21** is a stable white solid with a distinct melting point. It is much more stable toward hydrolysis than Me_3N-BH_2N_3, which has been prepared by pyrolysis of $[H_2B(NMe_3)_2]N_3$ or from Me_3N-BH_2I by exchange on Amberlite IRA-400 resin in the azide form.[27] The incorporation of an azide group was evident from the IR spectrum (strong band at 2096 cm^{-1}) and the high resolution mass spectrum.

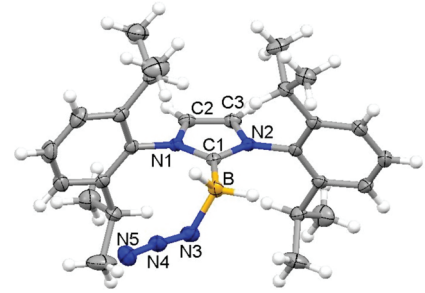


Figure 7. X-ray crystallographic structure of dipp-Imd-BH_2N_3 **21**. Selected bond lengths (Å), angles (deg), and torsion angles: N(5)−N(4) 1.137(2), N(4)−N(3) 1.212(2), B−N(3) 1.573(2), B−C(1) 1.614(2), N(5)−N(4)−N(3) 174.5(2), B−N(3)−N(4) 119.2(1), N(3)−B−C(1) 106.7(1), N(3)−B−C(1)−N(1) 59.0(2), N(3)−B−C(1)−N(2) −119.9(2), B−N(3)−N(4)−N(5) −178(2).

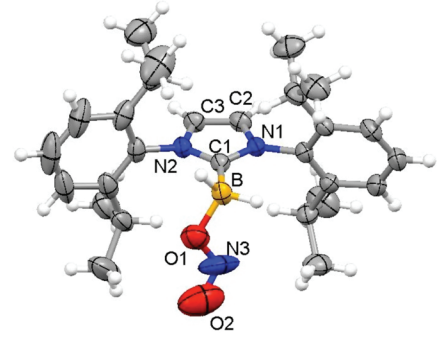


Figure 8. X-ray crystallographic structure of dipp-Imd-BH_2ONO **22**. Selected bond lengths (Å), angles (deg), and torsion angles: O(2)−N(3) 1.150(4), N(3)−O(1) 1.388(4), B−O(1) 1.512(3), B−C(1) 1.616(3), O(2)−N(3)−O(1) 110.3(3), B−O(1)−N(3) 108.2(2), O(1)−B−C(1) 110.5(2), O(1)−B−C(1)−N(1) −124.5(2), O(1)−B−C(1)−N(2) 57.1(3), B−O(1)−N(3)−O(2) 175.1(3).

X-ray crystallographic analysis confirmed the structure of **21** (Figure 7). The geometrical parameters are similar to those of another four-coordinate boron azide Py-9-BBN-N_3: B−N^{α} 1.588(3), N^{α}−N^{β} 1.196(3), N^{β}−N^{γ} 1.140(3), B−N^{α}−N^{β} 119.5(2), N^{α}−N^{β}−N^{γ} 176.3(3).[28] In contrast to dipp-Imd-BH_2NCO **20**, the B−N(3)−N(4) angle of 119° was consistent with sp^2-hybridization of N^{α}. Like azides bonded to carbon, the N^{α}−N^{β} bond (1.212(2) Å) is longer than the N^{β}−N^{γ} bond (1.137(2) Å).

The reaction of triflate **7** with $NaNO_2$ (entry 13) gave two products: the less polar boryl nitrite dipp-Imd-BH_2ONO **22** (12%) and more polar nitroborane dipp-Imd-BH_2NO_2 **23** (7%). These were stable toward aqueous workup and were easily separated by column chromatography. Reaction of iodide **4** with $AgNO_2$ (entry 14) gave the same products in better yields: **22** (27%) and **23** (10%). Reversing the pairings by reacting **7** with $AgNO_2$ and **4** with $NaNO_2$ also gave the same products according to ^{11}B NMR analysis of crude mixtures, but in lower yields.

Infrared spectroscopy was used for a preliminary assignment of the structures, and confirmation again came from the X-ray analyses of both samples (Figures 8, 9). For dipp-Imd-BH_2−O−N=O **22**, the N(3)−O(1) bond (1.388(4) Å) is longer than the N(3)−O(2) bond (1.150(4) Å) and these values are

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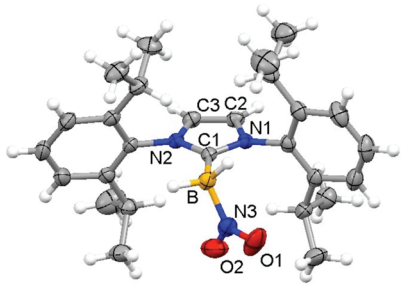


Figure 9. X-ray crystallographic structure of dipp-Imd-BH_2NO_2 **23**. Selected bond lengths (Å), angles (deg), and torsion angles: O(2)−N(3) 1.235(2), N(3)−O(1) 1.230(2), B−N(3) 1.591(2), B−C(1) 1.604(2), C(1)−N(1) 1.354(2), O(1)−N(3)−O(2) 120.6(1), B−N(3)−O(1) 120.9(1), B−N(3)−O(2) 118.5(1), N(3)−B−C(1) 107.4(1), N(3)−B−C(1)−N(1) −66.4(2), N(3)−B−C(1)−N(2) 114.6(1), C(1)−B−N(3)−O(1) 131.7(1), C(1)−B−N(3)−O(2) −50.4(2).

close to single N−O and double N═O bond lengths, respectively. The O(1)−N(3)−O(2) angle of 110° shows that the nitrite nitrogen atom has an accessible lone electron pair. In contrast, B−N(3)−O(1), B−N(3)−O(2), and O(1)−N(3)−O(2) angles in **23** are 121°, 119°, and 121° confirming a planar sp^2-hybridized nitrogen atom of a nitro group. The distances N(3)−O(1) and N(3)−O(2) are essentially equal (1.230(2) and 1.235(2) Å). A nitroborane salt $Cs[(CF_3)_3BNO_2]$ has similar structural parameters: B−N 1.613(9), N−O 1.218(7) and 1.230(8), B−N−O 119.3(6) and 121.5(6), O−N−O 119.1(6).[29]

To the best of our knowledge, **22** is the first boryl nitrite to be isolated and characterized. Previously only IR observation of transient CatBONO in a mixture with other compounds was reported.[30] Monosubstituted nitroboranes are also extremely rare.

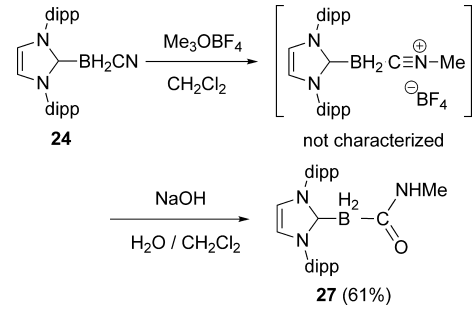
The substituents at the boron atom in **20**−**23** are not orthogonal to the plane of the imidazolylidene ring but form torsion angles between 50° and 70° (Figures 6−9).

The reaction between **7** and Bu_4NCN (2 equiv) provided boron nitrile dipp-Imd-BH_2CN **24** in 81% yield mixed with an inseparable impurity (∼10%) (entry 15). To show that this product was the nitrile **24**, it was converted to a boryl amide as described for ligated cyanoboranes Me_3N-BH_2CN and Ph_3P-BH_2CN.[31] First, **24** was methylated with $Me_3O^+BF_4^-$, and the (supposed) intermediate tetrafluoroborate was treated with 1 M NaOH (Scheme 4). After workup and column chromatography, amide **27** was isolated in 61% yield as a white solid. Once again, the robust nature of the NHC-borane component under rather vigorous conditions is remarkable.

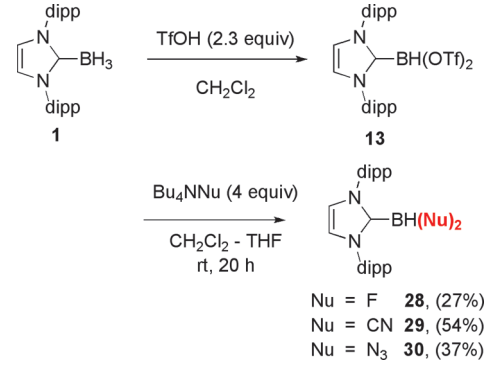
A pure sample of nitrile **24** was prepared by substitution of iodide **4** with NaCN in DMSO (entry 16). In contrast, reaction of **4** with AgCN in DMSO (entry 17) gave a different compound, tentatively assigned as the isonitrile **25** based on HRMS and ^{11}B NMR data. These complexes showed characteristic bands in the IR spectra corresponding to nitrile and isonitrile groups: **24** at 2187; **25** at 2192 cm^{-1}.[32]

Complexes **2**−**7** exhibit broad peaks in rt ^{11}B NMR spectra that resolved to triplets on heating. In contrast, the signals of

Scheme 4. Methylation and Basic Hydrolysis of Cyanoborane **24**



Scheme 5. One-Pot Double Substitution Reactions



21−**22**, and **24** were sharp triplets even at room temperature. This can be explained by the lower polarity of the B−X bonds in these compounds compared with complexes **2**−**7** and thus a more symmetrical distribution of charge around the boron atom. For example, in the ^{11}B NMR spectrum of dipp-Imd-BH_2(thexyl) a triplet was also observed at room temperature.[9b]

We closed this study by demonstrating that double substitutions at boron can occur by generation of a *bis*-electrophile and reaction with nucleophiles. Examples of such substitutions are shown in Scheme 5.

In situ generation of the bis-triflate **13** followed by addition of an excess of Bu_4NF gave difluoride dipp-Imd-BHF_2 **28** in 27% isolated yield. The substitution pattern at the boron atom was supported by *J*-couplings in the ^{11}B NMR and ^{19}F NMR spectra as well as by the high resolution mass spectrum. The BF_3 analog of **1** is already known[33] and the BH_2F complex is reported in Table 3, so this completes the series of fluoroborane analogs of **1**. All three compounds are stable under ambient lab conditions. An analogous series of trimethylamine-fluoroboranes has been made by reaction of Me_3N-BH_3 with HF.[34] However, reaction of Me_3N-BH_2I does not produce Me_3N-BH_2F but instead gives a mixture of Me_3N-BF_3 and Me_3N-BH_3.[23b]

Likewise, dicyanide **29** was prepared from ditriflate **13** and an excess of Bu_4NCN in 54% yield. As in the case of monocyanide **24** (Table 3, entry 15), this product also contained about 15% of an inseparable and unidentified impurity that exhibited a broad multiplet at −26.5 ppm in the ^{11}B NMR spectrum. Dipp-Imd-$BH(CN)_2$ exhibited a sharp doublet at −35.7 ppm. Just as monocyanide **24** can be considered as a boron nuclear analog of acetonitrile, dicyanide **29** is an analog of malononitrile. Finally, diazide **30** was obtained in 37% yield when ditriflate **13** was treated with Bu_4NN_3. This is a white

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crystalline solid stable below the melting point (220−222 °C). Slow evolution of gas (N_2) was observed when the melted compound was heated above 240 °C.

Elucidating the mechanism(s) of these substitution reactions will require further study. A nucleophilic substitution of chiral *c*-Hex_3P-BH(CO_2Me)Br with LiCN in DMF-THF and of chiral Me_3N-B(CH_2Ph)(CN)H with pyridine proceeded with inversion of the configuration at the boron atom, indicating that S_N2-B mechanisms should be considered.[35] Both S_N1-B and S_N2-B mechanisms were suggested for phosphine substitution in chiral Ph_3P-BH(Ipc)CN with PMe_2Ph (Ipc = isopinocampheyl) depending on the solvent.[36]

The intermediacy of borenium cation [dipp-Imd-BH_2]$^+$ or a solvent complex thereof is also possible. To investigate the latter possibility, we dissolved iodide dipp-Imd-BH_2I **4** in several solvents and recorded the ^{11}B NMR spectra of the samples. The following chemical shifts (δ) were observed: C_6D_6, −33.0; THF, −32.8; $CDCl_3$, −32.4; $(CH_3)_2CO$, −31.6; CH_3CN, −23.0; DMF, −5.2; DMSO-d_6, −8.8. The large changes in chemical shift observed upon dissolution in DMF and DMSO suggest that the iodide is ionized in these coordinating solvents to give the complex [dipp-Imd-BH_2•solvent]$^+$ I^-. Likewise, triflate **7** is presumably ionized in these solvents as well.

Conclusions

N-Heterocyclic carbene boranes bearing leaving groups (halogen, sulfonate) have been prepared by several means, and their substitution reactions have been studied. The NHC-borane halide and sulfonate complexes of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (dipp-Imd-BH_2X, X = halide or sulfonate) can be prepared from the parent borane dipp-Imd-BH_3 by three complementary routes: (1) substitution reactions with R−X, (2) reactions with electrophiles (like I_2 or NIS), or (3) acid/base reactions with HX (provided that HX has a pK_a of about 2 or less).

The stabilities of the resulting products to protic media and chromatography vary widely depending on the leaving group ability of the boron substituent. Like dipp-Imd-BH_3, dipp-Imd-BH_2Cl is a robust compound. At the other extreme, dipp-Imd-BH_2I is most conveniently prepared by reaction of dipp-Imd-BH_3 with diiodine and used directly in situ, while dipp-Imd-BH_2OTf is best prepared for in situ use by reaction with triflic acid.

Iodide **4**, triflate **7**, and other less reactive complexes behave as electrophiles and can be substituted by a wide range of heteroatom nucleophiles including halides, thiolates and other sulfur-based nucleophiles, isocyanate, azide, nitrite, and cyanide. The resulting products are remarkably stable and have been characterized by X-ray crystallography. Several are members of very rare classes of boron complexes (boron azides, nitro compounds, nitrous ester, etc.).

These results pave the way for future studies in several directions. For example, many other types of functionalized NHC-borane complexes should be accessible by the types of electrophilic, acid/base, and substitution reactions described herein. And because many of the compounds are robust and readily isolated, they could have interesting applications in organic synthesis, inorganic synthesis, or other areas.

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Supporting Information Available: Procedures and characterization data for all of the new complexes and cif files of the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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