

## Complexes of Borane and N-Heterocyclic Carbenes: A New Class of Radical Hydrogen Atom Donor

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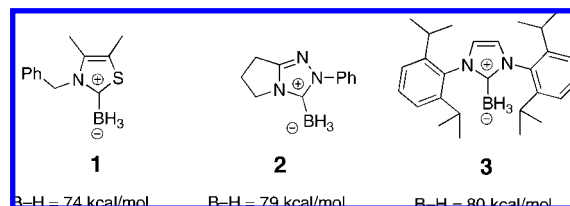
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Trialkyltin hydrides are often used as radical hydrogen donors, but the toxicity of such tin reagents detracts from their use in chemical processes that respect the principles of safe, sustainable synthesis. Many alternatives have been introduced to break the “tyranny of tin”,<sup>1</sup> yet its reign continues even if with weakened dominance.<sup>2</sup> Borane (BH<sub>3</sub>) is an attractive source of hydrogen because of its high hydrogen content, but the B–H bond dissociation energy (BDE) of borane is much too high (106.6 kcal/mol<sup>3a,b</sup>) for radical hydrogen transfer reactions. Lewis bases reduce the B–H BDE of the resulting complexes,<sup>4</sup> and radical reactions of amine boranes and phosphine boranes have been studied by Roberts and others.<sup>5,6</sup>

Calculations by Rablen show only a modest reduction in BDE for borane complexes of amines and phosphines (BDEs, 94–104 kcal/mol).<sup>4</sup> These bonds are much stronger than the X–H bonds of popular radical hydrogen donors like Bu<sub>3</sub>Sn–H (74 kcal/mol) and (Me<sub>3</sub>Si)<sub>3</sub>Si–H (79 kcal/mol).<sup>7</sup> These calculations also suggest that borane complexes of Lewis bases with the potential for  $\pi$ -conjugation have considerably lower BDEs because of delocalization of spin density in the resulting ligated boryl radicals (L–BH<sub>2</sub>•). However, many of the complexes that were calculated (with HCN or formaldehyde, for example) are transitory in solution. Further, such ligands are reduced by BH<sub>3</sub>.

We hypothesized that complexes of N-heterocyclic carbenes and borane (NHC boranes) would have weakened B–H bonds due to  $\pi$ -conjugation and perhaps be better hydrogen donors than amine and phosphine boranes. However, only a few NHC boranes are known, and their chemistry is little explored.<sup>9</sup> Thus, we first tested the hypothesis with BDE calculations at the UB3LYP/LACVP\* level. For reference, the BDE of BH<sub>3</sub> at this level is 111.7 kcal/mol, and complexation of BH<sub>3</sub> with THF lowers the BDE by less than 2 kcal/mol (109.9 kcal/mol). The structures and BDEs of three representative NHC boranes are shown in Figure 1. The NHC ligands dramatically reduce the BDEs, and the calculated values (74–80 kcal/mol) are squarely within the range of popular tin and silicon hydrides.<sup>7</sup>

New NHC borane complex **2** and known complex **3**<sup>9c</sup> were easily assembled from reaction of BH<sub>3</sub>–THF with the corresponding carbenes. The compounds were air-stable, white crystalline solids. The data from an initial series of Barton-McCombie deoxygenations with **2** and **3** are summarized in Table 1. In a typical experiment, xanthate **6**, NHC borane **2** (2 equiv), and AIBN (0.5 equiv) were heated in refluxing benzene for 2 h. After standard workup and flash chromatography, deoxy sugar **7** was isolated in 61% yield (entry 8). A range of secondary xanthates were deoxygenated in comparable yields (entries 1–7).



**Figure 1.** Calculated B–H BDEs of selected NHC–BH<sub>3</sub> complexes (UB3LYP/LACVP\* level).

**Table 1.** NHC Borane Reduction of Xanthates Initiated with AIBN

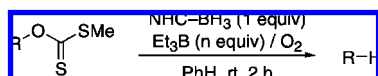
Entry	Substrate	NHC borane	AIBN (equiv)	Product, yield (%)
1	 <b>4a</b> , X = C(=S)SMc	<b>3</b>	2	<b>5a</b> , 65 <sup>a,b</sup>
2	 <b>4b</b> , X = C(=S)SMc	<b>3</b>	2	<b>5b</b> , 64 <sup>b,c</sup>
3	<b>4a</b>	<b>2</b>	0.5	<b>5a</b> , 70 <sup>d</sup>
4	<b>4b</b>	<b>2</b>	0.5	<b>5b</b> , 63 <sup>d</sup>
5	<b>4b</b>	<b>2</b>	0.2	<b>5b</b> , 67 <sup>d,e</sup>
6	 <b>4c</b> , X = C(=S)SMc	<b>2</b>	0.5	 <b>5c</b> , 57 <sup>f</sup>
7	 <b>4d</b> , X = C(=S)SMc	<b>2</b>	0.5	 <b>5d</b> , 67 <sup>d,g</sup>
8	 <b>6</b>	<b>2</b>	0.5	 <b>7</b> , 61 <sup>a</sup>

<sup>a</sup> Run using 2 equiv of NHC borane complex. <sup>b</sup> Reaction took 10 h. <sup>c</sup> Run using 2.5 equiv of NHC/borane complex. <sup>d</sup> SM recovered, 20%. <sup>e</sup> Reaction took 4 h. <sup>f</sup> E/Z ratio was ~3:1. <sup>g</sup> Diastereomeric ratio was 2.6:1.

Reduction of simple xanthates **4a,b** with complex **3** and 2 equiv AIBN gave **5a,b** in about 65% yield (entries 1,2). Similar yields were obtained with complex **2** (entries 3–5) even though less AIBN was used (20–50%). Little reaction occurred when the AIBN level was reduced to 10% or below, and no reaction occurred when the NHC borane was omitted. The cyclopropyl carbonyl radical precursor **4c** provided the open product **5c** (entry 6), while the

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**Table 2.** NHC Borane Reduction of Xanthates initiated with Et<sub>3</sub>B/O<sub>2</sub>

Entry	Substrate	NHC borane	n	Product, yield (%)
1	<b>4a</b>	<b>3</b>	2	<b>5a</b> , 84 <sup>a</sup>
2	<b>4b</b>	<b>3</b>	1	<b>5b</b> , 80
3	<b>4b</b>	<b>3</b>	0.2	<b>5b</b> , 79
4	<b>4b</b>	<b>3</b>	0.5	<b>5b</b> , 71 <sup>b,c</sup>
5	<b>4b</b>	<b>2</b>	1	<b>5b</b> , 75
6	<b>4c</b>	<b>3</b>	2	BnO-C(SMe)=CH-Et <b>5c</b> , 58 <sup>d</sup>
7	<b>4e</b> , X = C(=S)SMe	<b>3</b>	2	<b>5e</b> , 75 <sup>a</sup>
8	<b>4e</b>	<b>2</b>	1	<b>5e</b> , 80
9	<b>8</b> , R' = CH <sub>2</sub> On-Pent	<b>3</b>	1	<b>9</b> , 80
10	<b>6</b>	<b>2</b>	1	<b>7</b> , 60

<sup>a</sup> Run using 2 equiv of NHC/borane complex. <sup>b</sup> Recovered SM, 21%<sup>c</sup> Run using 0.5 equiv of NHC/borane complex. <sup>d</sup> E/Z ratio was ~3:1.

hexenyl radical precursor **4d** provided the closed product **5d** (entry 7). In aggregate, these results support the intermediacy of radicals.

The data from a second set of reactions under popular Et<sub>3</sub>B/O<sub>2</sub> conditions<sup>9</sup> are summarized in Table 2. These reactions were conducted in benzene at room temperature. Septa were pierced with a needle to admit ambient air. The isolated yields of products from these experiments were generally higher than those with AIBN initiation, ranging from 71–84% (except for entry 10, 60%). Again, the cyclopropyl radical precursor **4c** gave an opened product (entry 6). In contrast, the benzyl radical precursor **8** gave not a reduced but a dimerized product **9** (80%, entry 9). We also reduced **4b** with 50% (0.5 equiv) of both **3** and Et<sub>3</sub>B (entry 4). Interestingly, while 21% starting **4d** was recovered, the yield of **5b** was 71%. This raises the possibility that the complexes can donate more than one H atom.

Because both Et<sub>3</sub>B and Et<sub>3</sub>B–OH<sub>2</sub> are known to be modest radical hydrogen atom donors,<sup>10</sup> we conducted control experiments with **4b** to assess whether either was intervening, in other words, whether the NHC borane was superfluous. The amount of Et<sub>3</sub>B was reduced to 20% without detriment (entry 3). The use of rigorously dry solvents and dry oxygen instead of air did not decrease the yield either. No reaction occurred when the oxygen was omitted, and only traces of product (13%) were formed when the NHC borane was omitted. This low yield is not surprising since reductions with Et<sub>3</sub>B and Et<sub>3</sub>B–OH<sub>2</sub> are usually conducted with large excesses of reagents.<sup>10</sup> The results of these control experiments support the proposition that the NHC borane is the primary hydrogen donor under these conditions.

Finally, the BD<sub>3</sub> analogue of **2** was prepared and used to reduce **6** under the conditions of Table 2, entry 10. The isolated yield of **7** was only 27%, but it contained 70% deuterium at the deoxy position as assessed by integration of its <sup>1</sup>H NMR spectrum. This result (reduced yield, substantial but incomplete labeling) presages a substantial isotope effect.

These early results show that NHC boranes are competent radical hydrogen atom donors. By changing the NHC ligand and the borane substituents, there is promise to modulate both the BDE of the B–H bond (see Figure 1) and the steric environment about the B–H bond. In the immediate future, an increased understanding of these preliminary results will expedite development of the class. For example, what is the rate constant for hydrogen transfer from NHC boranes? And what is the fate of the NHC boryl radical that is presumably produced? Open questions aside, the promise is clear. To fashion a new tin or silicon hydride, especially a chiral one, can be an arduous process. In contrast, NHCs can be ligated to boranes to make new complexes in one step. Many achiral and chiral NHCs are already available, and the class is growing rapidly thanks to applications in metal and organocatalysis.<sup>11</sup>

**Acknowledgment.** We thank UPMC, CNRS, IUF, and ANR (grant BLAN0309 “Radicaux verts”) for funding. DPC thanks l’état et la région Ile-de-France for a Chaire Blaise Pascal and NSF for funding. We thank Drs. Julien Coulomb and Jason Clyburne for helpful discussions. We thank Dr. Lise-Marie Chamoreau for solving the X-ray structure.

**Supporting Information Available:** Experimental procedures and characterization of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA804150K