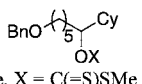
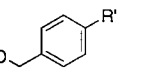
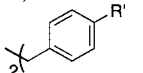
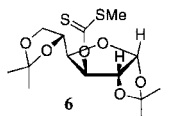
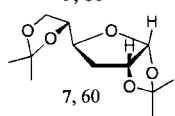


Table 2. NHC Borane Reduction of Xanthates initiated with Et₃B/O₂

$\text{R-O-C(=S)SMe} \xrightarrow[\text{PhH, rt, 2 h}]{\text{NHC-BH}_3 \text{ (1 equiv) / Et}_3\text{B (n equiv) / O}_2} \text{R-H}$				
Entry	Substrate	NHC borane	n	Product, yield (%)
1	4a	3	2	5a , 84 ^a
2	4b	3	1	5b , 80
3	4b	3	0.2	5b , 79
4	4b	3	0.5	5b , 71 ^{b,c}
5	4b	2	1	5b , 75
6	4c	3	2	BnO-C(S)=CH-Et 5c , 58 ^d
7	 4e , X = C(=S)SMe	3	2	5e , 75 ^a
8	4e	2	1	5e , 80
9	 8 , R' = CH ₂ On-Pent	3	1	 9 , 80
10	 6	2	1	 7 , 60

^a Run using 2 equiv of NHC/borane complex. ^b Recovered SM, 21%^c Run using 0.5 equiv of NHC/borane complex. ^d 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 Et₃B/O₂ conditions⁹ 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 Et₃B (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 Et₃B and Et₃B–OH₂ are known to be modest radical hydrogen atom donors,¹⁰ we conducted control experiments with **4b** to assess whether either was intervening, in other words, whether the NHC borane was superfluous. The amount of Et₃B 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 Et₃B and Et₃B–OH₂ are usually conducted with large excesses of reagents.¹⁰ The results of these control experiments support the proposition that the NHC borane is the primary hydrogen donor under these conditions.

Finally, the BD₃ 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 ¹H 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.¹¹

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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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