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Published on Web 07/16/2009

N-Heterocyclic Carbene Boryl Radicals: A New Class of Boron-Centered Radical

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Abstract: Reduction of xanthates by *N*-heterocyclic carbene boranes (NHC-boranes) has been suggested to occur by a radical chain mechanism involving heretofore unknown NHC-boryl radicals. In support of this suggestion, both the expected borane dithiocarbonate product and an unexpected borane xanthate product have now been isolated. These are the first NHC-boranes with boron−sulfur bonds, and their structures have been secured by spectroscopic and crystallographic means. The first rate constants for H-atom transfer from an NHC borane complex were determined by using the ring opening of a substituted cyclobutylcarbinyl radical as a clock reaction. The rate constant for reaction of the NHC-borane with a secondary alkyl radical at ambient temperature is 4×10^4 M^{-1} s^{-1}, and the Arrhenius function displayed an entropic term (log *A* term) that was typical for a bimolecular reaction. The B−H bond dissociation energy of an NHC-borane complex has been estimated at 88 kcal/mol. The putative NHC-boryl radical in these transformations has been detected by EPR spectroscopy. Spectral analysis suggests that it is a π-radical, analogous to the benzyl radical.

Introduction

Carbon-radical chain reaction methodology has become an essential component of organic syntheses.[1] In the simplest version of a chain reaction, a carbon radical is generated from a precursor and reduced by H-atom transfer from a donor. In turn, the radical formed from the H-atom donor reacts with another precursor to produce a second carbon radical, and the cycle repeats. Group 14 metal hydrides, especially tin hydrides such as tributyltin hydride, are well suited for reductive chain reactions based on the kinetics of their reactions with carbon radicals,[2] but concerns about toxicity of tin and an emphasis on green chemistry have led to an increasing interest in alternative hydrogen atom donors for carbon radical reductions.[3]

Useful alternatives to metal hydrides must react rapidly enough with carbon radicals to maintain chain reactions, and fast H-atom transfer reactions require weak hydrogen-element bonds in the H-atom donor. Inherently strong hydrogen-element bonds can sometimes be considerably weakened by Lewis acid−base complexation, and recent work has shown that the O−H bonds of trialkylborane−water (alcohol) and titanium(III)−water complexes can serve as H-atom donors to carbon radicals.[4]

Free boranes have strong boron−hydrogen bonds so they do not behave as hydrogen atom donors.[5] In contrast, complexes of boranes such as amine boranes ($R_3N{-}BH_3$)[6,7] and phosphine boranes ($R_3P{-}BH_3$)[8] can serve as radical hydrogen atom donors in some settings. However, the B−H bonds of such complexes

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[‖] University of St. Andrews.

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(4) (a) Spiegel, D. A.; Wiberg, K. B.; Schacherer, L. N.; Medeiros, M. R.; Wood, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 12513–12515. (b) Pozzi, D.; Scanlan, E. M.; Renaud, P. *J. Am. Chem. Soc.* **2005**, *127*, 14204–14205. (c) Cuerva, J. M.; Campaña, A. G.; Justicia, J.; Rosales, A.; Oller-López, J. L.; Robles, R.; Cárdenas, D. J.; Buñuel, E.; Oltra, J. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 5522–5526. (d) Medeiros, M. R.; Schacherer, L. N.; Spiegel, D. A.; Wood, J. L. *Org. Lett.* **2007**, *9*, 4427–4429. (e) Allais, F.; Boivin, J.; Nguyen, V. T. *Beilstein J. Org. Chem.* **2007**, *3*, No. 46. (f) Jin, J.; Newcomb, M. *J. Org. Chem.* **2008**, *73*, 7901–7905.

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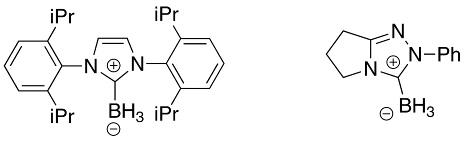


imidazol-2-ylidene borane, **1a**

1,2,4-triazol-3-ylidene borane, **1b**

Figure 1. Structures of *N*-heterocyclic carbene boranes used in xanthate reductions.

are still rather strong,[9] so the derived boryl radicals (for example, $R_3N-BH_2•$) can also abstract hydrogen atoms from suitable substrates. Such complexes are useful in applications of "polarity reversal catalysis" of radical reactions.[10]

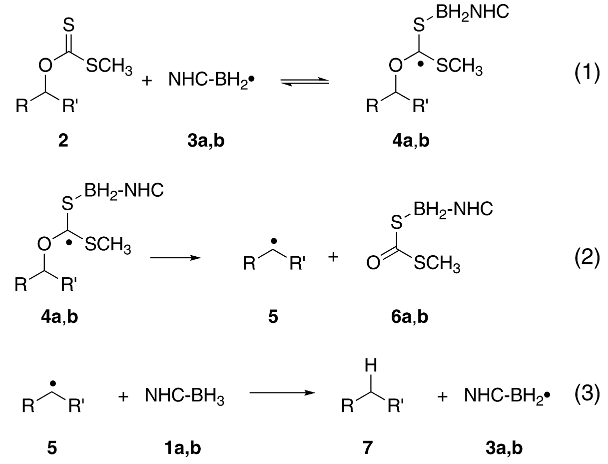
Based on a structural analysis and calculations of B−H bond dissociation energies (BDEs), we recently suggested the *N*-heterocyclic carbene boranes would serve as radical hydrogen atom donors.[11] This suggestion was supported experimentally by reductive deoxygenation of a collection of secondary xanthates (Barton-McCombie reaction[12]) with stable NHC-boranes 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene borane **1a** and 2-phenyl-1,2,4-triazol-3-ylidene borane **1b** (Figure 1).

We suggested[11a] that this transformation occurs by a radical chain reaction that is analogous to the reduction of xanthates by other radical hydrogen atom donors such as tin and silicon hydrides.[12] This implies the intermediacy of heretofore unknown NHC-boryl radicals. Here we describe the isolation and characterization of the expected boron-derived product from reaction of a secondary xanthate with an NHC-boryl radical.[13] We also describe an unexpected boron product isolated from the reaction of a primary xanthate with the NHC-boryl radical. We provide the first rate constant measurements for hydrogen abstraction from an NHC-borane by an alkyl radical, and this in turn allows an estimate of the BDE of the boron−hydrogen bond. Finally, we observe the postulated NHC-boryl radical in these transformations directly by EPR spectroscopy. Taken together, the results confirm the existence of NHC-boryl radicals and secure the radical chain mechanism for xanthate reduction.

Results and Discussion

Mechanistic Framework. The postulated propagation steps for the reduction of xanthates by NHC-boranes are shown in Scheme 1.[12] NHC-boryl radical **3a**,**b** adds to the C═S bond of the xanthate **2** (possibly reversibly) to provide adduct **4a**,**b** (step 1). Fragmentation of **4a**,**b** provides alkyl radical **5** (step 2), which in turn abstracts hydrogen from the starting NHC-borane **1a**,**b** to complete the chain cycle (step 3). If this mechanism is correct, then it should be possible to characterize the borane product **6a**,**b** (step 2) and to measure a rate constant (k_H) for the radical hydrogen transfer reaction (step 3).

Scheme 1. Postulated Chain Mechanism for Reduction of Xanthates by *N*-Heterocyclic Carbene Boranes



NHC = *N*-heterocyclic carbene,
a series, imidazol-2-ylidene
b series, triazol-3-ylidene

We expected from the preliminary studies[11a] that the radical hydrogen transfer reaction would have a rate constant $\leq 10^5$ M^{-1} s^{-1} because a hexenyl radical probe substrate gave only the cyclized product and because deuterium labeling with an NHC-BD_3 reagent was only moderately efficient (70%). Accordingly, we selected the opening of a cyclobutylcarbinyl radical[14] as an appropriate clock reaction[15] to time the radical hydrogen transfer. We started by using the clock substrate to investigate the boron-derived products.

Boron-Derived Reaction Products. A flask containing a benzene solution of undecylcyclobutyl carbinyl xanthate **2a**, NHC-borane **1a**, and triethylborane (1 equiv each, Scheme 2) was exposed to air by piercing its stopper with a needle. After 24 h, the starting xanthate was consumed. The mixture was charged to silica gel, and initial elution with dichloromethane provided a nonpolar fraction consisting of directly reduced and ring opened products[16] (see below for the discussion of the reduced products). Subsequent elution with dichloromethane/methanol (8/1) provided pure boron-derived product, (methylthiocarbonylthio)borane **6a**, as a white solid, mp 201−202 °C.

With **6a** in hand, we repeated the previously reported[11a] reduction of secondary xanthate **2b** but now with an eye toward isolating the boron product rather than the deoxygenation product. Indeed, **6a** was produced in 66% yield after flash chromatography. Likewise, reduction of the xanthate derivative of 2-octanol **2c** by a similar preparative procedure provided the same product **6a** in 70% isolated yield (see Supporting Information). Evidently, **6a** is the boron product formed in the reductions of secondary xanthates by **1a**.

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(14) Jin, J.; Newcomb, M. *J. Org. Chem.* **2007**, *72*, 5098–5103.

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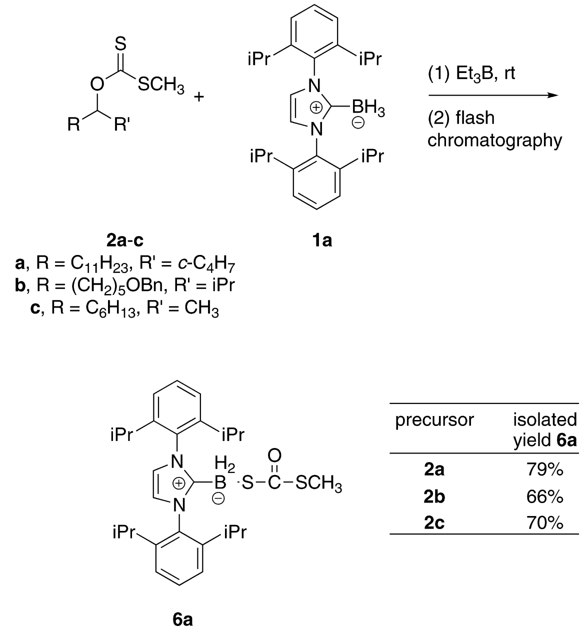
(16) GC analysis of this experiment showed a 76% yield of **18** along with 5% of **20.**

Scheme 2. Isolation of Boron-Derived Product **6a**



precursor	isolated yield **6a**
2a	79%
2b	66%
2c	70%

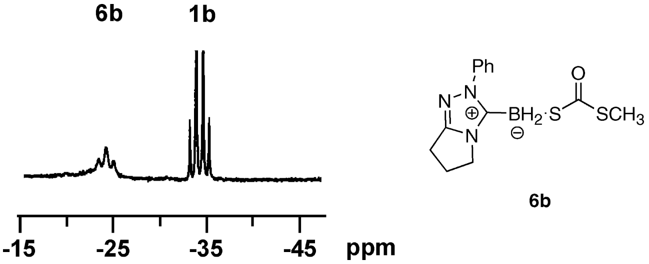
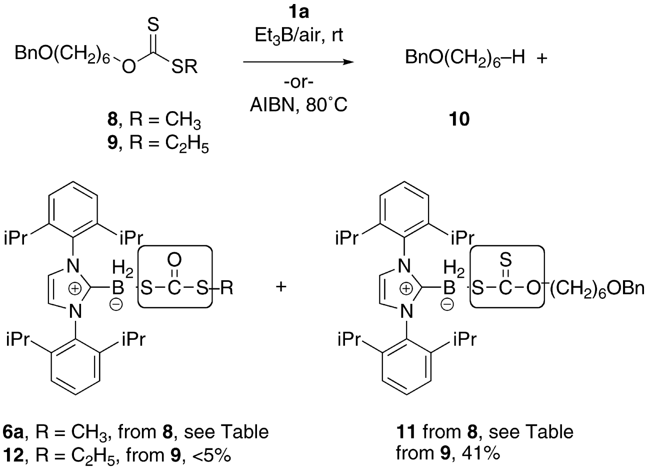


Figure 2. Structure of **6b** and 128.4 MHz ^{11}B NMR spectrum showing evidence for its formation in the reaction of **1b** with **2b** after 40 min at 70 °C.

Scheme 3. Isolation of a Second Type of Boron-Derived Product **11**



Products from reduction of **8**

	8	1a	10	6a	11
Et_3B	–	59%	55%	19%	9%
AIBN	12%	54%	36%	33%	33%

(Methylthiocarbonylthio)borane **6a** was characterized by the usual battery of spectroscopic methods (^{1}H and ^{13}C NMR, IR, MS), and full data are contained in the Supporting Information. The ^{11}B NMR spectrum of **6a** at 298 K exhibited a broad singlet at −25.6 ppm in $CDCl_3$ and at −25.2 ppm in C_6D_6 and $C_6D_5CD_3$. Upon heating a sample in toluene-d_8 to 80 °C,[17] the resonance sharpened to a triplet, $J_{B-H} = 105$ Hz. Contrast these data to the ^{11}B NMR spectrum of the precursor **1a**, which exhibits a quartet at −34.5 ppm, $J_{B-H} = 90$ Hz (C_6D_6).

In addition to surviving flash chromatography unscathed, (methylthiocarbonylthio)borane **6a** was recovered unchanged after heating at 150 °C in mesitylene-d_{12} for 17 h. The compound was also stable to heating with AIBN but slowly degraded on exposure to Et_3B and air. For example, the yield of **6a** in the reaction with the xanthate derivative of undecylcyclobutylcarbinol decreased to 28% when the mixture was exposed to air for 3 days prior to isolation. This degradation may explain our early difficulties in isolating the boron-derived products from reductions with **1a**.

Attempts to characterize the boron-derived product from the reduction of a secondary xanthate with **1b** were only partially successful. In a reaction between **1b** and **2b** conducted in an NMR tube (C_6D_6/CD_3CN, 9/1, 70 °C), we observed a new triplet in the ^{11}B NMR spectrum whose chemical shift was in the region expected for **6b** (−24.2 ppm). However, after a brief increase in intensity over 40 min, this peak began to fade. Figure 2 shows the appearance of the spectrum at the 40 min point, while the complete time course is in the Supporting Information. After 90 min, the intensity of the new peak had decreased considerably, and several other overlapping resonances began to appear.[18]

Apparently, the boron-derived product from **1b** is much less stable than that derived from **1a**. Because of that, we focused the following rate constant and experiments on the radical **3a** derived from **1a**.

A second class of boron product was obtained from the reduction of primary xanthate **8** as shown in Scheme 3. Standard reaction of **1a** (2 equiv) and **8** (1 equiv) initiated by Et_3B and air provided the reduced product **10** (55%), the starting borane **1a** (59%), the (methylthiocarbonylthio)borane **6a** formed together with **10** (19%), and a new oxycarbonothioylthioborane **11** (9%).[19]

The oxycarbonothioylthioborane **11**, hereafter called a borane xanthate, was also a stable white solid, mp 117−119 °C, exhibiting a broad resonance in the ^{11}B NMR spectrum at −24.4 ppm in $CDCl_3$. Other spectral data of **11** are summarized in the Supporting Information.

Borane **6a**, a dithiocarbonate with B−S and C−S single bonds and a C=O double bond, is the expected product of a Barton/McCombie reaction resulting from cleavage of the C−O single bond of the precursor. In contrast, **11** is an *O*-alkyl xanthate with B−S and C−O single bonds and a C=S double bond that results from cleavage of the C−S single bond of the

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[17] Beall, H.; Bushweller, C. H. *Chem. Rev.* **1973**, *73*, 465–486.

[18] An attempt to isolate C−O cleavage product **6b** from this mixture by chromatography did not succeed. However, we did isolate a small amount (∼5%) of an impure sample whose major component was tentatively assigned by NMR analysis to be the C−S cleavage product, NHC−$BH_2SC(=S)OCH$(*i*Pr)$(CH_2)_5OBn$, where NHC is 1,2,4-triazol-3-ylidene.

[19] The yield of recovered **1a** is based on the starting amount of **1a**, while all other yields are based on the starting amount of **8**.

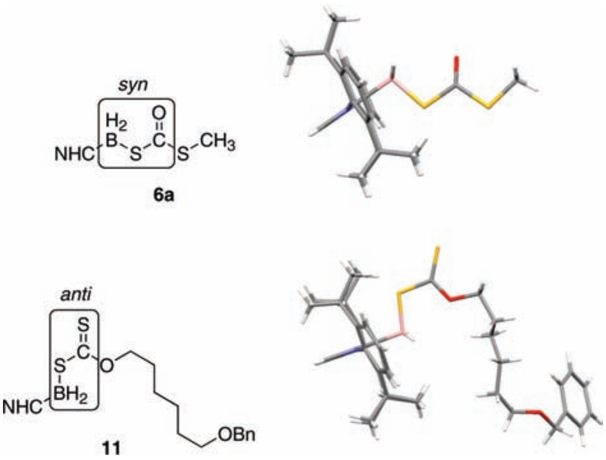

Figure 3. X-ray crystal structures of **6a** and **11**.

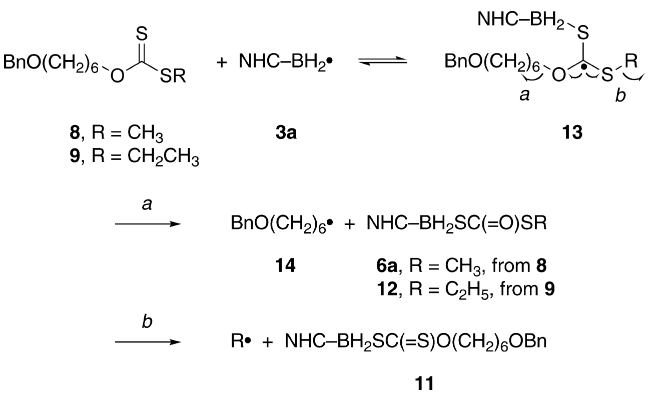

Figure 4. C−O (a) and C−S (b) fragmentation pathways provide the two boron products **6a** and **11**.

precursor. This latter class of product has also been observed in tin hydride xanthate cleavages.[20]

Knowing that the yields of boron-derived products might be decreased by prolonged exposure to Et_3B and air, we conducted a similar experiment at 80 °C between **8** and **1a** with initiation by AIBN. After 2 h, the mixture was cooled and the products were separated by flash chromatography to provide boron products **6a** (33%) and **11** (33%), reduced product **10** (36%), and starting materials, xanthate **8** (12%) and NHC-borane **1a** (54%).

To further favor the formation of the C−S cleavage product over the C−O cleavage one, we conducted a reduction of *S*-ethyl xanthate derivative **9** initiated by AIBN as above. This produced **11** in 41% isolated yield. In contrast, only traces of **12** were formed (<5%).

The structures of both **6a** and **11** were confirmed by X-ray crystallography, and diagrams of the two structures oriented to feature the sulfur substituent on boron are shown in Figure 3. (Other diagrams that better show the *N*-heterocyclic carbene substituent are presented in the Supporting Information.) Interestingly, the $BH_2S-C(O)$ bond of **6a** is *syn*, while the corresponding $BH_2S-C(S)$ bond of **11** is *anti*.

The different boron products arise from two different modes of fragmentation of adduct radical **13**, as shown in Figure 4.[20] Path "a" is a C−O cleavage that provides radical **14** (precursor to **10**) and **6a**, while path "b" is a C−S cleavage that provides a methyl (or ethyl) radical and boron xanthate **11**. Pathway "b" is favored relative to "a" because a weaker single bond is cleaved (C−S versus C−O), but it is disfavored because it provides both a less stable radical (Me• versus 1°-alkyl **14**) and a less stable molecule (**6a** has a C═O bond while **11** has a C═S bond). The approximately equal yields of **6a**/**10** and **11** in the AIBN-initiated reaction of *S*-methyl xanthate **8** suggest that radical **13** partitions to **6a** and **11** with a ratio of ∼1/1 at 80 °C. The C−S path "b" becomes favored when radicals of comparable stability are produced, as shown by the predominance of **11** over **12** in the reduction of *S*-ethyl analogue **9**.

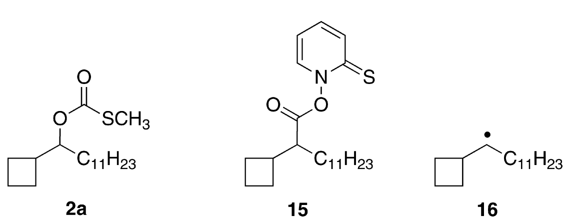

Figure 5. Xanthate **2a** and PTOC **15** precursors of substituted cyclobutylcarbinyl radical probe **16**.

The C−S cleavage pathway "b" has precedent in Barton−McCombie reactions[20] and is also reminiscent of group transfer reactions of carbon-substituted xanthates.[21] But in such cases the radical resulting from fragmentation of the C−S bond is usually more stable than that resulting from fragmentation of the C−O bond.

Rate Constant Measurements. Having isolated the boron-derived product from cyclobutylcarbinyl xanthate **2a**, we initially tried using the same substrate for rate constant measurements on radical **16** (Figure 5). Reductions progressed well at high concentrations (0.2−0.4 M) and temperatures (rt and above) typically used for preparative experiments.[11a] However, as the concentrations and temperatures were reduced to generate standard kinetic plots, the chains did not propagate well and the starting xanthate was not consumed efficiently. Although using xanthate **2a** for a full kinetic study was not successful, we did still learn from preliminary analyses of reduced products that radical **16** was a suitable clock.

Accordingly, we turned to an alternative precursor to radical **16**, the PTOC ester **15**.[22a] PTOC esters are photolabile when irradiated with visible light, and they react to completion even when chain propagation steps are inefficient. In principle, they are better precursors for an indirect kinetic study, but the use of a PTOC ester radical precursor in a kinetic study introduces another complication in that PTOC esters can react with carbon-centered radicals to give alkyl pyridyl sulfide products.[22b]

In the case of an indirect kinetic study using radical **16** derived from **15**, the reactions shown in Scheme 4 are possible. Radical **16** ring opens to acyclic radical **17** with a known rate constant k_r (path 1),[22a] is trapped by the NHC-borane **1a** to give cyclobutane **18** (path 2), or reacts in a "self-trapping" reaction with precursor **15** to give the cyclobutylcarbinyl pyridyl sulfide **19** (path 3). The acyclic radical **17** formed by ring opening of **16** is trapped by the NHC-borane **1a** to give **20** (path 4) or reacts with the PTOC precursor **15** to give sulfide **21** (path 5). Small amounts of cisoid ring opened products (*cis*-isomers of **20** and **21**) are expected, but the amount of *cis*-4-hexadecene

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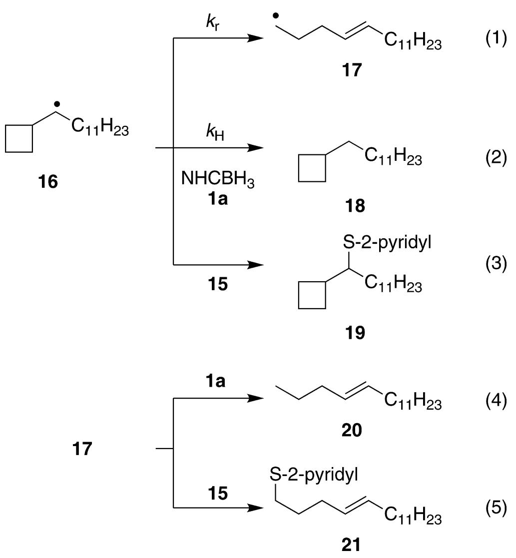
[20] Barton, D. H. R.; Crich, D.; Löbberding, A.; Zard, S. Z. *Tetrahedron* **1986**, *42*, 2329–2338.

[21] Quiclet-Sire, B.; Zard, S. Z. *Top. Curr. Chem.* **2006**, *264*, 200–236.

[22] (a) Jin, J.; Newcomb, M. *J. Org. Chem.* **2008**, *73*, 4740–4742. (b) Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1987**, *28*, 1615–1618.

[23] Newcomb, M. *Tetrahedron* **1993**, *49*, 1151–1176.

Scheme 4. Evolution of Radical Probe **16** to Directly Trapped (**18**, **19**) and Ring Opened (**20**, **21**) Products



found in the reaction of **16** with tin hydride was previously shown to be inconsequential.[22a]

The rate constant k_H for reaction of the NHC-borane with radical **16** can be determined from the concentration of the H-atom donor, the product mixture ratio, and the rate constant for ring opening of radical **16** (k_r) via eq 1, where $[X-H]_{aver}$ is the average concentration of the trapping reagent over the course of the reaction.[23] Because reactions were conducted with excess trapping agent, using the average concentration of X−H in a pseudo-first-order kinetic expression introduces an insignificant error in comparison to using a second-order kinetic expression.[23]

The reaction of the PTOC ester **15** with radical **16** reduces the amount of probe radical from the reaction mixture, but the yield of product **19** is not of consequence for the kinetic determination. The amount of pyridyl sulfide **21** obtained is important for the kinetic determination, however, because it is produced from the ring-opened radical **17**. Rate constants for ring opening of **16** (k_r) were previously determined at various temperatures, and an Arrhenius function for the ring-opening reaction is available.[22a]

$$k_H = (k_r/[X-H]_{aver}) \times ([\mathbf{18}]/([\mathbf{20}] + [\mathbf{21}])) \qquad (1)$$

Kinetic studies were conducted in deoxygenated benzene or toluene by adding NHC-borane **1a** to a temperature-equilibrated solution containing PTOC ester **15** and irradiating the stirred solution with a tungsten-filament bulb. The reaction mixtures were checked periodically by TLC, and samples were analyzed when PTOC ester **15** was no longer detected. Yields of products **18**−**21** were determined by GC, and the total yields of these products for reactions with 0.01 to 0.02 M **1a** were in the range 65−98%. Because the amounts of alkyl pyridyl sulfides **19** and **21** formed were significant, we isolated these products from bulk reactions and identified them by ^{1}H and ^{13}C NMR spectroscopy and high resolution mass spectrometry as described in the Supporting Information.

Detailed kinetic results are in the Supporting Information. From the ratios of products as determined by GC, the rate constant for trapping by NHC-borane **1a** was determined via eq 1. We conducted multiple reactions at 28 °C and a set of variable temperature studies to generate a relative Arrhenius function (see below). For a set of seven trapping reactions conducted at 28 °C with 0.01 or 0.02 M **1a**, the rate constant for trapping was $k_H = (3.4 \pm 1.0) \times 10^4$ M^{-1} s^{-1} where the error is at 1σ.

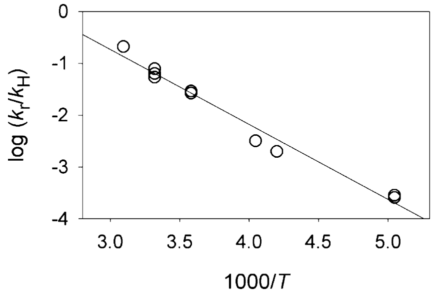


Figure 6. Relative Arrhenius plot for rearrangement of radical **16** and its trapping by NHC-borane **1a**.

The temperature-dependent function for the H-atom transfer reaction of donor **1a** was obtained from a series of reactions conducted over the temperature range −75 to 50 °C. From 10 reactions run with 0.01 M **1a**, we obtained the relative Arrhenius function in eq 2, which is shown graphically in Figure 6. This relative Arrhenius function was subtracted from the Arrhenius function for ring opening of radical **16**, given in eq 3,[22a] to give the Arrhenius function for radical trapping by NHC-borane **1a** in eq 4. In these equations, all errors are listed at 1σ, and the activation energies are in kcal/mol. Solving the Arrhenius function in eq 4 for 28 °C gives $k_H = 3.8 \times 10^4$ M^{-1} s^{-1}, in excellent agreement with the average value determined from studies at this temperature.

$$\log(k_r/k_H) = (3.61 \pm 0.29) - (6.62 \pm 0.34)/2.3RT \qquad (2)$$

$$\log(k_r) = (13.2 \pm 0.4) - (13.5 \pm 0.6)/2.3RT \qquad (3)$$

$$\log(k_H) = (9.6 \pm 0.5) - (6.9 \pm 0.7)/2.3RT \qquad (4)$$

From the Arrhenius function in eq 4, the H-atom transfer reaction of NHC-borane **1a** displays a "normal" log A term for a second-order H-atom transfer. That is, the entropic demand for the reaction is typical for a simple bimolecular reaction and similar to the entropic demand in, for example, H-atom transfer from a group 14 metal hydride.[2] In contrast, H-atom transfer from methanol in the Lewis acid complex Et$_3$B•CH$_3$OH had an unusually small log A term (high entropy demand) indicating a highly organized transition state or an unfavorable equilibrium prior to the rate-determining step.[14,22a] Thus, NHC-borane **1a** reacts with the characteristics of a covalent molecule that donates the H-atom in a single elementary process, which is consistent with the postulated mechanism of reaction.

Because the H-atom transfer from NHC-borane **1a** competes with "self-trapping" by the PTOC ester for both the cyclic radical **16** and the acyclic radical **17**, it is possible in principle to use those competitions to estimate the rate constant for the reaction of **1a**. From the results at 28 °C listed in the Supporting Information, this approach leads to a conclusion that the rate constant for H-atom transfer from **1a** is 2−3 times greater than that found from the clock reaction approach. This difference might result because the estimated rate constant for the PTOC self-trapping reaction is too large.[22b] But irrespective of the origin of the difference, the latter result is not consistent with the original attempted kinetic studies. If the rate constant for reaction of **1a** was on the order of 10^5 M^{-1} s^{-1}, then the

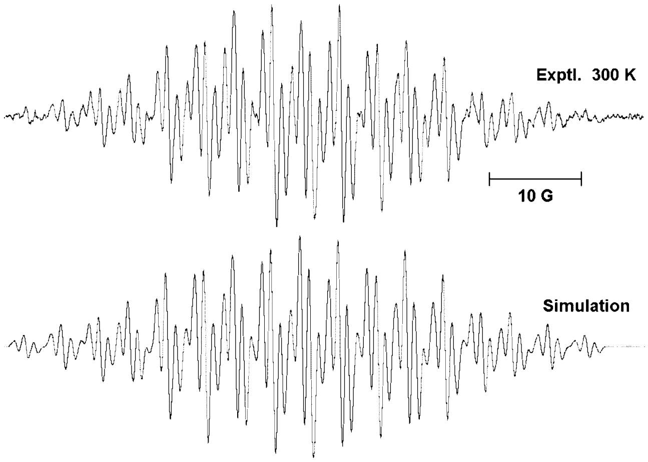


Figure 7. Solution EPR spectrum of NHC-BH_2• radical **3a**. Top: First derivative experimental spectrum at 300 K in *t*-BuPh. Bottom: Computer simulation with parameters noted in Table 1.

5-hexenyl radical should not have cyclized completely in the presence of **1a**.[11a]

In an effort to benchmark the rate constant measurement for **1a**, we also briefly investigated reactions of alkyl radicals with two amine boranes (Me_3N•BH_3 and pyridine•BH_3) and phosphine boranes (*n*-Bu_3P•BH_3 and Ph_3P•BH_3). These reagents proved to be poor hydrogen donors and did not provide enough of the directly reduced products to allow determination of a rate constant. With $k_H < 10^4$ M^{-1} s^{-1}, they are clearly less reactive than **1a** toward alkyl radicals.

The availability of the rate constant k_H allows a preliminary estimate of the bond dissociation energy (BDE) by applying an Evans−Polanyi relationship;[24] the estimated boron−hydrogen BDE of **1a** is ~88 kcal/mol. Though this estimate could be in error by several kcal/mol, it is considerably higher than the calculated BDE for **1a** of 80 kcal/mol.[11a] Nonetheless, the BDE of **1a** is still very much lower than experimental or high-level computed values of B−H BDEs for borane (BH_3, ~105 kcal/mol) and its ammonia and water complexes (102−104 kcal/mol).[5,9] The estimated BDE of **1a** is also below the computed BDE of phosphine borane (92−93 kcal/mol),[9] and indeed the competition experiments clearly show that **1a** is a better H-donor than Bu_3P•BH_3 toward a secondary alkyl radical.

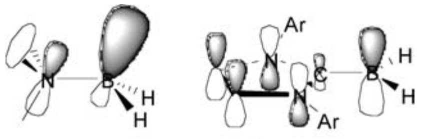
EPR Experiments. Having provided strong circumstantial evidence for the existence of NHC-boryl radicals by product studies and rate constant measurements, we next examined the possibility of directly detecting **3a** in solution by EPR spectroscopy. We selected di-*tert*-butyl peroxide (DTBP) to generate the NHC-boryl radical because of the convenience of generating *t*-BuO• by UV irradiation. The *t*-BuO• radical is EPR “silent”, so we expected that clean spectra would be obtained provided that *t*-BuO• promptly abstracted a hydrogen atom from NHC-borane **1a**.

When a deaerated solution of **1a** and DTBP in *tert*-butylbenzene was UV irradiated in the resonant cavity of a 9 GHz EPR spectrometer, the spectrum shown in Figure 7 was obtained. The spectrum was very well simulated with the hyperfine splittings shown in Table 1. The simulated spectrum is also shown in Figure 7.

Table 1. Comparison of NHC-Boryl EPR Parameters with Those of Model Radicals

Radical	T/K or DFT basis set	*g*-factor	*a*(^{11}B) G	*a*(2N) G	*a*($2H_\alpha$) G	*a*(other) G
3a	300	2.0028	7.3	4.0	11.4	1.0 (2H)
model NHC[a]	EPR-iii[b]		5.3	3.1	−10.0	−1.2 (2H)
Me_3N-BH_2[c]	280	2.0022	51.3	1.4 (1N)	9.6	1.4 (9H)
Et_3P-BH_2[c]	183	2.0020	17.6		16.8	43.6 (^{31}P)

[a] *N*,*N′*-Diphenylimidazol-2-ylidene-BH_2•. [b] B3LYP/EPR-iii//B3LYP/6-31G(d). [c] See ref 26.



3a

Figure 8. Sketches of the SOMOs of an amine-boryl radical (left) and radical **3a**.

The hyperfine splittings (hfs) are entirely appropriate for radical **3a**, and comparison of these with the DFT computed values for a model NHC-BH_2• radical (Table 1) provide further support.[25] Thus, the photochemically generated *t*-BuO• radicals efficiently abstract H-atoms from **1a** to generate **3a**. The EPR spectroscopic observation of **3a** provides strong support for the mechanism of Scheme 1.

Amine-boryl radicals such as Me_3N-BH_2• and phosphine-boryl radicals have been extensively studied by Roberts and others.[7,8,10] EPR spectra show them to be σ-type radicals, pyramidal at boron.[26] The much smaller *a*(^{11}B) and larger *a*(N) hfs of **3a** show that this radical is planar at boron and that the unpaired electron is delocalized into the NHC ring. In essence, the NHC-boryl radical is not a σ-type radical but is instead a π-type radical quite like benzyl.[27] The sketches of the SOMOs of amine-boryl radical Me_3N-BH_2• and the NHC-boryl radical **3a** are compared in Figure 8 to illustrate this difference.

The DFT computation for the model *N*,*N′*-diphenylimidazol-2-ylidene-BH_2• radical was in full agreement with this conclusion. Formation of such a resonance-stabilized radical is likely an important factor in lowering the BDE of the B−H bond and the transition state energy of H-atom transfer reactions of NHC-boranes. This agrees with Rablen’s original conclusion,[9] based on a theoretical study of Lewis base complexed boranes, that the extent of lowering of B−H BDEs is greater when the spin density is delocalized away from boron and onto the associated Lewis base. Further, because of the substantial structural differences, the chemistry of NHC-boryl radicals may differ from the known chemistry of amine- and phosphine-boryl radicals, and new reactivity patterns are foreseen.

Conclusions

In summary, we have isolated and characterized both the boron dithiocarbonate product resulting from standard C−O cleavage of primary and secondary xanthates and a boron xanthate product resulting from C−S cleavage during the reduction of primary xanthates. These compounds are the first NHC-boranes with boron−sulfur bonds. The first rate constants

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(24) Roberts, B. P.; Steel, A. J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2155–2162.

(25) For the B3LYP/EPR-iii//B3LYP/6-31G(d) basis set, see: Barone, V. In *Recent Advances in Density Functional Theory*; Chong, D. P., Ed.; World Scientific Publishing Co.: Singapore, 1996.

(26) (a) Paul, V.; Roberts, B. P.; Robinson, C. A. S. *J. Chem. Res. (S)* **1988**, 264–265. (b) Kirwan, J. N.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1989**, 539–550.

(27) Tumanskii, B.; Sheberla, D.; Molev, G.; Apeloig, Y. *Angew. Chem. Int. Ed.* **2007**, *46*, 7408–7411.

for H-atom transfer reactions of the NHC-borane **1a** with a secondary alkyl radical clock have been determined. At ambient temperature, the reaction has a rate constant of 4×10^4 M^{-1} s^{-1}, and the Arrhenius function for the reaction demonstrates a typical entropic term indicating a simple H-atom transfer in the rate-limiting step. Finally, we observed the NHC-boryl radical by EPR spectroscopy, and spectral analysis suggests that it is a π-radical, perhaps more analogous to the benzyl radical than to apparently similar amine- and phosphine-boryl σ-radicals. These results support the intermediacy of the NHC-boryl radical and secure the radical mechanism for the reduction of xanthates with NHC-boranes.

The NHC-borane **1a** reacts nearly 2 orders of magnitude less rapidly than the prototypical tin hydride reagent Bu_3SnH and 1 order of magnitude less rapidly than $(TMS)_3SiH$.[2] However, NHC-borane **1a** reacts 2 orders of magnitude *faster* than the prototypical silane Et_3SiH,[2] which cannot be used in conventional carbon radical chain reactions. Accordingly, it occupies a valuable position on the scale of hydrogen atom donors, capable of allowing relatively slow radical cyclizations or additions to occur at high reagent concentrations.

The analysis of BDEs presents a similar picture. At 88 kcal/mol, NHC-borane **1a** has a considerably weaker bond to H than $Et_3Si{-}H$ (95.1 kcal/mol). Its bond is stronger than $(TMS)_3SiH$ (84 kcal/mol) and Bu_3SnH (78.6 kcal/mol) and comparable to Bu_3GeH (88.6 kcal/mol).

Finally, with the existence NHC-boryl radicals firmly established, the door is open for their further study. The ready availability and good stability of NHC-boranes provides a convenient source of NHC-boryl radical precursors that will facilitate this study.

Experimental Section

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]-(methylthiocarbonylthio)borane (IPr-IMD-BH_2-S-C(=O)-SCH_3) (6a), from Reaction of Undecylcyclobutylcarbinyl Xanthate 2a. Triethylborane (1 M solution in hexane, 0.15 mL, 0.15 mmol) was added to the solution of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane (**1a**) (IPr-IMD-BH_3)[11a] (58.4 mg, 0.15 mmol) and undecylcyclobutylcarbinyl xanthate **2a** (48.0 mg, 0.15 mmol)[14] in benzene (0.85 mL). The solution was exposed to air by piercing the septum stopper with a needle. The mixture was stirred at room temperature for 20 h. The reaction mixture was loaded onto a silica gel column (h = 20 cm, d = 4 cm) for flash chromatography (elution with CH_2Cl_2, CH_2Cl_2/MeOH = 8:1) to give compound **6a** (58.0 mg, 79%) as a white solid. A lower yield (28%) was obtained with a longer reaction time (3 days).

Crystals of **6a** for X-ray analysis were grown from methanol at 20 °C, and the complete data are contained in the accompanying cif file. Mp 201−202 °C; IR (thin film, cm^{-1}): ν_{max} 3165, 3132, 2963, 2927, 2870, 2458 (B−H), 2390 (B−H), 1631 (C=O), 1471, 1036, 855; ^1H NMR (300 MHz, $CDCl_3$): δ 7.49 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 4H), 7.08 (s, 2H), 2.55 (septet, J = 6.9 Hz, 4H), 2.07 (s, 3H), 1.34 (d, J = 6.9 Hz, 12H), 1.15 (d, J = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 145.4, 133.3, 130.4, 124.0, 123.0, 28.9, 25.5, 22.6, 13.6; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −25.6 (br s); ^{11}B NMR (96.3 MHz, C_7D_8): δ −25.2 (br s, $w_{1/2}$ = 288 Hz); ^{11}B NMR (96.3 MHz, C_7D_8, 353 K): δ −25.1 (t, J = 105 Hz); LRMS (EI) m/z: 508 ($[M]^+$, 0.4), 493 ($[M - CH_3]^+$, 2.4), 447 (11), 433 (97), 399 (100), 389 (20), 357 (26), 186 (15), 75 (35); HRMS (EI) calcd. for $C_{28}H_{38}{}^{11}BN_2OS_2$ ($[M - CH_3]^+$): 493.2519, found 493.2517.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]-[6-(benzyloxy)hexyloxycarbonothioylthio]borane (IPr-IMD-BH_2-S-C(=S)-O$(CH_2)_6$OBn) (11). AIBN-initiated free radical reaction: A solution of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane (**1a**) (IPr-IMD-BH_3)[11a] (161.0 mg, 0.4 mmol), *O*-6-(benzyloxy)hexyl *S*-methyl xanthate (**8**) (59.7 mg, 0.2 mmol), and AIBN (16.4 mg, 0.1 mmol) in deoxygenated benzene (2 mL) was refluxed for 2 h. After cooling to room temperature, the solvent was removed in vacuo, and the residue was purified by flash column chromatography (elution with hexane/ethyl acetate = 98:2, hexane/ethyl acetate = 9:1, hexane/ethyl acetate = 8:2) to give **11** (45 mg, 33%) as a white solid and **6a** (34 mg, 33%). A mixture of (hexyloxymethyl)benzene (**10**) and starting xanthate (**8**) (3/1) (21 mg, 48%) and recovered starting IPr-IMD-BH_3 (**1a**) (87 mg, 54%) were also isolated. Crystals of **11** suitable for X-ray analysis were grown from CH_2Cl_2/hexane, and the complete data are contained in the accompanying cif file. Mp 117−119 °C; IR (ATR, cm^{-1}): ν_{max} 2963, 2930, 2868, 2399, 1468, 1178, 1072, 1023; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 7.6 Hz, 4H), 7.33−7.26 (m, 5H), 7.08 (s, 2H), 4.49 (s, 2H), 4.19 (t, J = 6.7 Hz, 2H), 3.43 (t, J = 6.7 Hz, 2H), 2.56 (septet, J = 6.8 Hz, 4H), 1.65−1.50 (m, 4H), 1.34 (d, J = 6.8 Hz, 12H), 1.33−1.19 (m, 4H), 1.14 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.4, 145.4, 138.7, 133.3, 130.4, 128.3, 127.6, 127.4, 124.0, 123.0, 72.8, 72.6, 70.4, 29.6, 28.9, 28.1, 25.8, 25.7, 25.5, 22.7; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ −24.4 (br s); HRMS (EI) calcd. for $C_{41}H_{58}{}^{11}BN_2O_2S_2$ ($[M + H]^+$): 685.4033, found: 685.4034.

Acknowledgment. This work was supported by grants from the U.S. National Science Foundation (CHE-0601857 to M.N. and CHE-0645998 to D.P.C.) and the French Agence Nationale de la Recherche (ANR, BLAN0309 Radicaux Verts, and 08-CEXC-011-01 Borane). We thank Dr. Lise-Marie Chamoreau (IPCM, Paris) for solving a crystal structure. D.P.C. thanks l’état et la région Ile-de-France for a Chaire Blaise Pascal and ANR for a “chaire d’excellence”. A.S. thanks the University of Pittsburgh for a Graduate Excellence Fellowship. We dedicate this paper to Professor Keith U. Ingold on the occasion of his 80th birthday.

Supporting Information Available: Procedures and characterization of all new compounds not in the experimental section, details of kinetic experiments, copies of spectra of products, and cif files of the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA904103X