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# Reactivity of B-Xanthyl N-Heterocyclic Carbene-Boranes

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Dedicated to Philippe Renaud on the occasion of his 60th birthday

The synthesis and reactivity of mono and bis-S-xanthyl NHC-boranes is reported. The new NHC-boranes are prepared via nucleophilic exchange at boron from either mono or bis-triflyl NHC-boranes, themselves obtained by protolysis of the NHC-BH<sub>3</sub> starting compounds. The B-H bond of the S-xanthyl NHC-boranes can be cleaved both homolytically and heterolytically, albeit the latter is more synthetically useful. The S-xanthyl NHC-boranes can reduce both aldehydes and imines. The B-S bond can also be cleaved homolytically. Under UV irradiation, the S-xanthyl NHC-boranes generate NHC-boryl radicals that can initiate radical polymerizations of acrylates.

**Keywords:** Boron • Radical reactions • Polymerization • NHC-Boranes • Xanthates

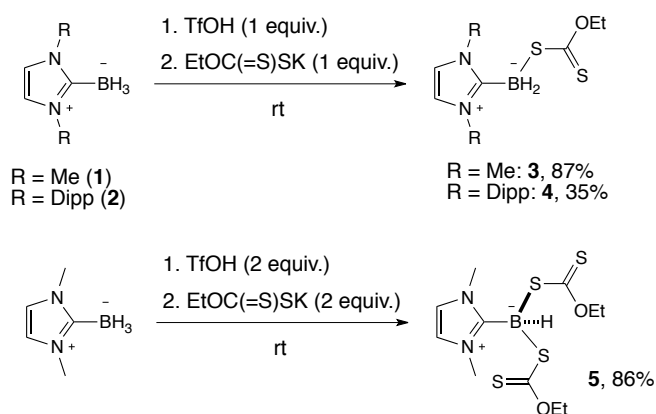
## Introduction

N-Heterocyclic carbene-boranes have emerged as a new family of reagent for inorganic<sup>[1–7]</sup> and polymer synthesis.<sup>[8–13]</sup> In organic synthesis, NHC-boranes have been shown to be excellent H-atom donors for radical reductions,<sup>[14–16]</sup> hydride sources for the reduction of carbonyl or imine compounds,<sup>[17–22]</sup> or partners for borylations.<sup>[23–32]</sup> Yet in almost all these cases, the boron atom was only substituted by hydrogen atoms. We became interested in how the established was affected by substitution at boron. Installing a sulfur (an arylsulfide)<sup>[33,34]</sup> proved rewarding since the corresponding B-S bond could be photolyzed to generate NHC-Boryl radicals, which initiated radical polymerizations.<sup>[35]</sup> Alternatively the Curran group demonstrated that the thiol substituent could become a nucleophile, leading to sulfides.<sup>[36]</sup> However the same NHC-Boryl sulfides could also undergo H-atom abstraction or hydride transfer, leading to bis-thiyl derivatives.<sup>[33]</sup> This means that not only their B-S bond, but also their B-H bonds could be activated. We wondered if that dual reactivity could be extended to other sulfur containing NHC-boranes. In the present communication we examine the reactivity of S-xanthyl NHC-boranes (NHCBX).

## Results and Discussion

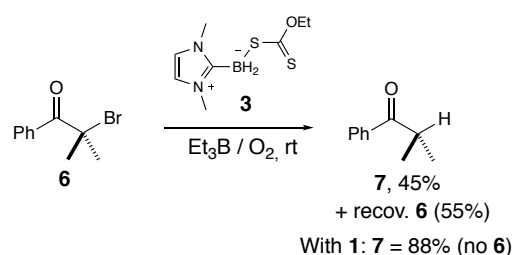
For the purpose of this study we prepared three different NHCBXs starting from the parents NHC-BH<sub>3</sub> derivatives (Scheme 1). Following our established route,<sup>[37]</sup> IMe-BH<sub>3</sub> derivative **1** was converted to mono-xanthyl compound **3** using one equivalent of triflic acid and potassium xanthate (87% yield), while its bis xanthyl analogue **5** was prepared in 86% yield adapting the published procedure by using two equivalents of triflic acid that generates an IMe-BH(OTf)<sub>2</sub> intermediate which is substituted twice at Boron with 2 equivalents of potassium xanthate. From the reactivity of **3** and **5** we expected to gather information on the influence of

substitution at Boron. To examine the role of the steric size of the carbene, we also prepared IPr-derived NHCBX **4** in 35% yield.



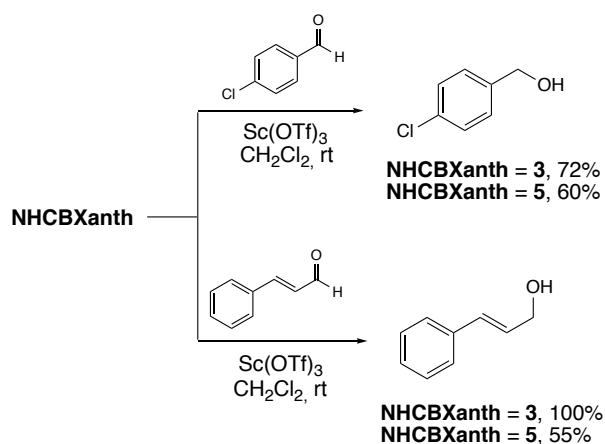
**Scheme 1.** Preparation of the target S-xanthyl NHC-boranes (NHCBXs).

We first looked at the behavior of **3** as H-atom donor.<sup>[16,38]</sup>  $\alpha$ -Bromo ketone **6** was mixed with one equivalent of **3** in the presence of Et<sub>3</sub>B (Scheme 2). Air was bubbled in the reaction medium via syringe addition. The reaction yielded 45% of dehalogenated ketone **7**, together with 55% of recovered starting material. In comparison, the same reaction with NHCB **1** delivered only **7** in 88% yield. This suggests that **3** could be a competent radical mediator, but the added substituent lowers its efficiency. We did not attempt to develop this aspect further.



**Scheme 2.** Radical dehalogenation with S-xanthyl NHC-borane **3**.

We next looked at the possibility of hydride transfer. Actually, the NHCBX's have two transferrable nucleophiles: the hydride or the xanthate. With a view to favor the hydride transfer, we targeted the reduction of aldehydes.<sup>[21]</sup>



**Scheme 3.** Hydride transfer from S-xanthyl NHC-Boranes to aldehydes.

In a typical experiment, *p*-chlorobenzaldehyde was treated with NHCBX **3** at room temperature in dichloromethane in the presence of one equivalent of scandium (III) triflate (Scheme 3). The reaction delivered 72% of the corresponding benzyl alcohol. Gratifyingly, bis-xanthate derivative **5** was also able to transfer its hydride, albeit in a slightly reduced yield (60%).

When cinnamaldehyde was reacted with **3**, only aldehyde reduction was observed, no 1,4 reduction, and the reaction was quantitative. Switching to bis-xanthyl borane **5** delivered cinnamyl alcohol, again in reduced yield (55%). Nonetheless, the combined results show that the xanthyl substitution at boron does not harm the hydridic reactivity of the NHC-Borane, but that steric hindrance lowers the yields.

**Table 1.** Reductive Amination with S-xanthyl NHC-Boranes.

Entry	NHCBX	R <sub>1</sub>	R <sub>2</sub>	Product, yield (%)
1 <sup>a</sup>	<b>3</b>	4-Cl	H	<b>8a</b> , 89
2 <sup>b</sup>	<b>4</b>	4-Cl	H	<b>8a</b> , 50
3	<b>3</b>	4-NO <sub>2</sub>	H	<b>8b</b> , 46
4	<b>3</b>	4-Cl	4-Br	<b>8c</b> , 70
5	<b>3</b>	- <sup>c</sup>	H	<b>8d</b> , 96
6	<b>5</b>	4-Cl	H	<b>8a</b> , 84

<sup>a</sup> Conditions: Aldehyde (1 equiv); aniline (1 equiv);  $\text{CH}_2\text{Cl}_2$  (2 mL); 4 Å molecular sieves; AcOH (1.3 equiv) and NHCBX (1.3 equiv) were stirred at rt. unless otherwise noted the reaction took 2h. <sup>b</sup> Reaction took 12h. <sup>c</sup> Cinnamaldehyde was used.

We next tried to extend the previous reaction to reductive aminations.

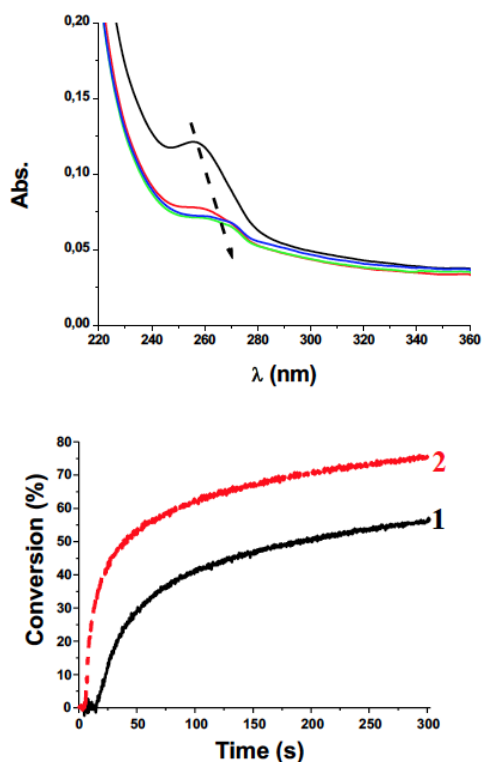
We used our previously reported methodology (Table 1).<sup>[19]</sup> It relies on the stability of the NHC-Boranes toward acetic acid, which was not guaranteed with the S-xanthyl group that could be intrinsically acid-sensitive, or make the hydride more basic and therefore able to react with the acetic acid to generate dihydrogen.

In a typical experiment (Table 1, Entry 1),<sup>[19]</sup> A solution of 4-chlorobenzaldehyde (1 equiv) and aniline (1 equiv) in 2 mL of dichloromethane at room temperature was stirred for 1h over 4 Å molecular sieves. Acetic acid (1.3 equiv) and S-xanthyl NHC-Borane **3** (1.3 equiv) were added to the reaction mixture. The resulting slurry was stirred for an additional hour, before work-up. This delivered 89% of amine **8a**. The reductive elimination worked well with 4-Bromo aniline (70% of **8c**, Entry 4), but less so when paranitrobenzaldehyde was used (**8b**, 46%, Entry 3). The reaction was not limited to arylaldehydes, since cinnamaldehyde led to the corresponding amine in 96% yield (Entry 5). Other NHCBX's were tested. With the more sterically hindered **4**, only 50% of **8a** was isolated (Entry 2), while the bis-xanthyl derivative **5** led to 84% of **8a** (Entry 6). Overall, the reductive amination results further support that the S-xanthyl derivatives retain the hydridic character of NHC-boranes, but that steric hindrance on the carbene is an issue. A second xanthate does not affect the reactivity.

The combined results presented thus far show that the B-H bond of the NHCBX's can be activated. The hydridic reactivity is better from a synthetic point of view, as it leads to better yields. While the homolytic scission is possible too, it is not efficient enough to be applied in synthesis. Given our previous experience with the photolysis of S-aryl NHC-boryl sulfides,<sup>[ref]</sup> we wondered if we could use a similar B-S bond cleavage in a synthetically useful way.

The UV spectrum of **4** exhibits a band at around 255 nm, that disappears after 30s irradiation with a Hg-Xe UV lamp (intensity approx. 60 mW/cm<sup>2</sup>, Figure 1, top). This band corresponds to the B-S bond of **4**. Its disappearance suggests that the bond gets photolyzed under UV irradiation. We therefore examined whether **4** could be a competent Type I photoinitiator for the polymerization of acrylates.<sup>[35]</sup>

When trimethylolpropane triacrylate (TMPTA) was irradiated under UV (with a filter to stop any wavelength below 300 nm), it led to a polymer. The self-initiated polymerization was monitored by the disappearance of the IR band corresponding to the olefin (Figure 1, bottom, curve 1). The polymerization only starts after a lagging time of several seconds. It however leads to the expected polymer with 50% conversion. Full conversion is not possible for two reasons. Since the monomer has three reactive functions it rapidly leads to cross-linked networks that make the remaining olefin unaccessible geometrically, all the more so because the formulation becomes very hard quickly.



**Figure 1.** Homolytic activation of the B–S bond in **4**. (top) Real-time UV-vis spectra of **4** under irradiation with a Hg-Xe lamp (intensity  $\sim 60 \text{ mW/cm}^2$ ). The dashed arrow shows the disappearance of the absorption of the B–S chromophore; (bottom) UV-triggered ( $\lambda > 300 \text{ nm}$ ) photopolymerization of TMPTA (Trimethylolpropane triacrylate) alone (curve 1) and in the presence of **4** (2 mol%, curve 2).

Gratifyingly, when 2 mol% of **4** were added, the lagging time disappeared, the polymerization rate increased (almost vertical initial conversion) and the conversion improved slightly to 60%. In other words, **4** acts as a Type I photoinitiator able to generate initiating radicals upon light (UV) irradiation. The lagging time is due to inhibition by dioxygen, which blocks the radical polymerization. Its disappearance strongly supports that the photopolymerization in the presence of **4** is indeed initiated by NHC-Boryl radicals, the latter being able to efficiently trap the dioxygen in a way that does not stop the polymerization.<sup>[9]</sup>

## Conclusions

To conclude, the installation of one or two S-xanthyl substituent(s) at boron is possible. The resulting new NHC-Boranes are both good hydrides and Type I photo-initiators. That is, both their B–H and B–S bonds can be cleaved for reactivity. Further work will focus on exploiting the specific properties of S-xanthates in radical chemistry. Radical thio-boration should be accessible via the degenerate radical processes extensively studied by Zard.<sup>[39]</sup> In polymer chemistry, this would open to RAFT polymerization and with that to boron-initiated controlled radical polymerization, or to the synthesis of block copolymers using light. Our first forays in that direction show that the B–H bonds still present in **3-5** are detrimental. More molecular engineering is required to reach that goal.

## Experimental Section

### General remarks

Reactions were performed using oven-dried glasswares under an atmosphere of argon. All separations were carried out under flash-chromatographic conditions on silica gel 5Redi Sep prepacked column, 230-400 mesh) at medium pressure (20 psi) with use of a CombiFlash Companion or under preparative high pressure liquid chromatography (Knauer, Smartline Autosampler 3900 and Wellchrom preparative pump K-1800). The reactions were monitored by thin-layer chromatography on Merck silica gel plates (60 F<sub>254</sub> aluminum sheets) which were revealed by ultraviolet and spraying with vanillin (15% + sulfuric acid [2.5%] in EtOH), followed by heating. Reagent-grade chemicals were obtained from diverse commercial suppliers (Sigma-Aldrich and Alfa Aesar) and were used as received. <sup>1</sup>H NMR (300, 400, 500 and 700 MHz), <sup>11</sup>B NMR (96, 128 and 160 MHz) and <sup>13</sup>C NMR (75, 100, 125 and 175 MHz) spectra were recorded on Bruker Advance spectrometers at 298 K. Spectra were recorded at room temperature in the indicated deuteriated solvents, and chemical shifts were reported in parts per million (ppm) downfield relative to TMS using the residual solvent proton resonance of CDCl<sub>3</sub> (<sup>1</sup>H = 7.27 ppm, <sup>13</sup>C = 77.0 ppm) or C<sub>6</sub>D<sub>6</sub> (<sup>1</sup>H = 7.16 ppm, <sup>13</sup>C = 128.0 ppm) as the internal standard. The <sup>11</sup>B chemical shift are given relative to BF<sub>3</sub>·OEt<sub>2</sub> (<sup>11</sup>B = 0 ppm). Multiplicities are declared as follow: *s* (singlet), *brs* (broad singlet), *d* (doublet), *t* (triplet), *q* (quadruplet), *dd* (doublet of doublet), *dt* (doublet of triplet), *m* (multiplet). Coupling constants *J* are given in Hz. The resonances of hydrogen and carbon atoms connected to the boron atom are not usually observed in <sup>1</sup>H and <sup>13</sup>C NMR spectra because of quadrupole broadening. Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR system using diamond window Dura SampliIR II and the data are reported in reciprocal centimeters (cm<sup>−1</sup>). Melting points were recorded in open capillary tubes on a Büchi B-450 apparatus and are uncorrected. High resolution mass spectra (HRMS) were recorded using a Micromass LCT Premier XE instrument (Waters) and are determined by electrospray ionization (ESI). Elemental analyses were carried out at the Institut de Chimie des Substances Naturelles (ICSN, Gif-sur-Yvette, France).

Trimethylol-propane triacrylate (TMPTA) was obtained from Allnex and used as received. The UV/vis spectra were taken on a JASCO V530 spectrometer. The polychromatic UV light delivered from a Xe-Hg lamp (Hamamatsu, L8252, 150 W, filtered for  $\lambda > 300 \text{ nm}$ ) was used. Upon irradiation, the polymerization kinetics were recorded by Real-Time FT-IR as reported previously.<sup>[8,11]</sup>

### Preparation of the S-xanthyl NHC-Boranes

NHCBX **4** was prepared as described previously.<sup>[37]</sup>

**3.** In a round-bottom flask, IMe–BH<sub>3</sub> (573 mg, 5.21 mmol) was dissolved in anhydrous dichloromethane (50 mL) at room temperature. Triflic acid (450  $\mu\text{L}$ , 5.21 mmol) was added dropwise. The colorless solution was left

at rt for one hour until the evolution of gas subsided. A solution of potassium ethyl xanthogenate (1.644 g, 10.2 mmol) in acetonitrile (50 mL) was then added via canula. The resulting yellow solution was left at rt for one hour after the end of the addition. The solvents were then removed in vacuo, after which the solid residue was redissolved (partly) in chloroform (100 mL). The slurry was filtered and the filtrate was concentrated and triturated with pentane. The slightly yellow solid was dried (1.04 g, 87% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 1.31 (t,  $J$  = 7.0 Hz, 3H,  $\text{CH}_2\text{Me}$ ), 2.20–2.86 (m [broad q.], 2H,  $\text{BH}_2$ ), 3.90 (s, 6H, NMe), 4.50 (q,  $J$  = 7.0 Hz, 2H,  $\text{CH}_2\text{Me}$ ), 6.86 (s, 2H,  $\text{HC}=\text{C}$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 160 MHz):  $\delta$  = –24.8 (t,  $J$  = 101 Hz).

**5.** In a round-bottom flask,  $\text{Ime-BH}_3$  (524 mg, 4.76 mmol) was dissolved in anhydrous dichloromethane (50 mL) at room temperature. Triflic acid (900  $\mu\text{L}$ , 10.4 mmol) was added dropwise. The colorless solution was left at rt for one hour until the evolution of gas subsided. A solution of potassium ethyl xanthogenate (2.688 g, 16.7 mmol) in acetonitrile (50 mL) was then added via canula. The resulting yellow solution was left at rt for one hour after the end of the addition. The solvents were then removed in vacuo, after which the solid residue was redissolved (partly) in chloroform (100 mL). The slurry was filtered and the filtrate was concentrated and triturated with pentane. The slightly yellow solid was dried (1.43 g, 86% yield). IR (neat, diamond):  $\nu$  = 3162, 3128, 3112, 2988, 2464, 1705, 1610, 1572  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 1.34 (t,  $J$  = 7.0 Hz, 6H,  $\text{CH}_2\text{Me}$ ), 4.00 (s, 6H, NMe), 4.49 (q,  $J$  = 7.0 Hz, 2H,  $\text{CH}_2\text{Me}$ ), 4.52 (q,  $J$  = 7.0 Hz, 2H,  $\text{CH}_2\text{Me}$ ), 6.89 (s, 2H,  $\text{HC}=\text{C}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 14.0 ( $\text{CH}_2\text{Me}$ ), 37.3 (NMe), 69.4 ( $\text{CH}_2\text{Me}$ ), 121.8 ( $=\text{CH}$ ), 191.1 ( $\text{C}=\text{S}$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 160 MHz):  $\delta$  = –14.4 (d,  $J$  = 111 Hz); HRMS calc. for  $\text{C}_{11}\text{H}_{19}\text{BN}_2\text{O}_2\text{S}_4\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ): 373.0320, found: 373.0327.

### General Procedures

**Aldehyde reductions.** In a Schlenk flask, the NHCX (1 equiv.) and the aldehyde (1 equiv.) were dissolved in dichloromethane (to reach 0.5 M concentration). The scandium triflate (1 equiv.) was added and the mixture was stirred overnight, filtered, concentrated in vacuo and purified by flash column chromatography.

**Reductive eliminations.** A solution of the aldehyde (1 equiv) and aniline (1 equiv) in dichloromethane (2 mL) was stirred at room temperature over 4 Å molecular sieves for 1 h. Acetic acid (1.3 equiv) and the NHCX (1.3 equiv) were then added and the resulting reaction mixture was stirred for one hour, and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography.

**Radical Photopolymerization.** TMPTA was used as the monomer in the film photopolymerization experiments. The experiments were carried out in laminate. The films (25  $\mu\text{m}$  thick) deposited on a  $\text{BaF}_2$  pellet were irradiated (see the irradiation sources). The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 1630  $\text{cm}^{-1}$ .

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## Author Contribution Statement

A.-L. V. designed and carried out the molecular experiments, and contributed to their analyses. E. L. and J. L. defined the general strategy; secured the funding, contributed to the analysis of the results, and wrote the drafts of the manuscript. J. L. carried out the polymer experiments.

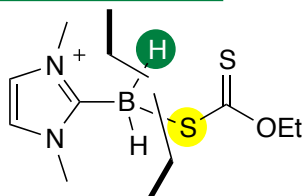
## References

- [1] Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, 'A Stable, Neutral Diborene Containing a B:B Double Bond.', *J. Am. Chem. Soc.* **2007**, 129, 12412–12413.
- [2] P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, Alfredo. Vargas, 'Base-Stabilized Diborenes: Selective Generation and  $\eta^2$  Side-on Coordination to Silver(I).', *Angew. Chem. Int. Ed.* **2012**, 51, 9931–9934, S9931/1–S9931/11.
- [3] P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, I. Krummenacher, Alfredo. Vargas, 'Boron Radical Cations from the Facile Oxidation of Electron-Rich Diborenes.', *Angew. Chem. Int. Ed.* **2014**, 53, 5689–5693.
- [4] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, Alfredo. Vargas, 'Ambient-Temperature Isolation of a Compound with a Boron-Boron Triple Bond.', *Science* **2012**, 336, 1420–1422.
- [5] D. Auerhammer, M. Arrowsmith, P. Bissinger, H. Braunschweig, T. Dellermann, T. Kupfer, C. Lenczyk, D. K. Roy, M. Schaefer, Christoph. Schneider, 'Increasing the Reactivity of Diborenes: Derivatization of NHC-Supported Dithienyldiborenes with Electron-Donor Groups.', *Chem. Eur. J.* **2018**, 24, 266–273.
- [6] N. Holzmann, M. Hermann, Gernot. Frenking, 'The boron-boron triple bond in  $\text{NHC} \rightarrow \text{B} \equiv \text{B} \leftarrow \text{NHC}$ .', *Chem. Sci.* **2015**, 6, 4089–4094.
- [7] J. Boehnke, T. Dellermann, M. A. Celik, I. Krummenacher, R. D. Dewhurst, S. Demeshko, W. C. Ewing, K. Hammond, M. Hess, E. Bill, E. Welz, M. I. S. Roehr, R. Mitric, B. Engels, F. Meyer, Holger. Braunschweig, 'Isolation of diborenes and their 90°-twisted diradical congeners.', *Nat. Commun.* **2018**, 9, 1–7.
- [8] M.-A. Tehfe, M. Makhlof Brahmi, J.-P. Fouassier, D. P. Curran, M. Malacria, L. Fensterbank, E. Lacôte, Jacques. Lalevée, 'N-Heterocyclic Carbenes-Borane Complexes: A New Class of Initiators for Radical Photopolymerization.', *Macromolecules* **2010**, 43, 2261–2267.
- [9] M.-A. Tehfe, J. Monot, M. Brahmi, H. Bonin-Dubarle, D. P. Curran, M. Malacria, L. Fensterbank, E. Lacôte, J. Lalevée, J.-Pierre. Fouassier, 'N-heterocyclic carbene-borane radicals as efficient initiating species of photopolymerization reactions under air.', *Polym. Chem.* **2011**, 2, 625–631.
- [10] E. Lacôte, D. P. Curran, J. Lalevée, 'NHC-boranes: air- and water-tolerant co-initiators for type II photopolymerizations', *Chimia* **2012**, 66, 382–5.
- [11] J. Lalevée, S. Telitel, M. A. Tehfe, J. P. Fouassier, D. P. Curran, Emmanuel. Lacôte, 'N-Heterocyclic Carbene Boranes Accelerate Type I Radical Photopolymerizations and Overcome Oxygen Inhibition.', *Angew. Chem. Int. Ed.* **2012**, 51, 5958–5961, S5958/1–S5958/9.
- [12] M.-A. Tehfe, J. Monot, M. Malacria, L. Fensterbank, J.-P. Fouassier, D. P. Curran, E. Lacôte, Jacques. Lalevée, 'A Water-Compatible NHC-Borane: Photopolymerizations in Water and Rate Constants for Elementary Radical Reactions.', *ACS Macro Lett.* **2012**, 1, 92–95.

- [13] F. Le Quémener, D. Subervie, F. Morlet-Savary, J. Lalevée, M. Lansalot, E. Bourgeat-Lami, E. Lacôte, 'Visible-Light Emulsion Photopolymerization of Styrene', *Angew. Chem. Int. Ed.* **2018**, *57*, 957–961.
- [14] X. Pan, E. Lacôte, J. Lalevée, D. P. Curran, 'Polarity Reversal Catalysis in Radical Reductions of Halides by N-Heterocyclic Carbene Boranes.', *J. Am. Chem. Soc.* **2012**, *134*, 5669–5674.
- [15] S.-H. Ueng, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, 'Radical Deoxygenation of Xanthates and Related Functional Groups with New Minimalist N-Heterocyclic Carbene Boranes.', *Org. Lett.* **2010**, *12*, 3002–3005.
- [16] S.-H. Ueng, M. Makhlof Brahmi, E. Derat, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, 'Complexes of Borane and N-Heterocyclic Carbenes: A New Class of Radical Hydrogen Atom Donor.', *J. Am. Chem. Soc.* **2008**, *130*, 10082–10083.
- [17] Q. Chu, M. Makhlof Brahmi, A. Solov'yev, S.-H. Ueng, D. P. Curran, M. Malacria, L. Fensterbank, Emmanuel. Lacôte, 'Ionic and Organometallic Reductions with N-Heterocyclic Carbene Boranes.', *Chem. Eur. J.* **2009**, *15*, 12937–12940, S12937/1–S12937/59.
- [18] L. B. de Oliveira Freitas, P. Eisenberger, C. M. Crudden, 'Mesoionic Carbene-Boranes.', *Organometallics* **2013**, *32*, 6635–6638.
- [19] M. Horn, H. Mayr, E. Lacôte, E. Merling, J. Deaner, S. Wells, T. McFadden, D. P. Curran, 'N-Heterocyclic Carbene Boranes are Good Hydride Donors.', *Org. Lett.* **2012**, *14*, 82–85.
- [20] B. S. N. Huchenski, M. R. Adams, R. McDonald, M. J. Ferguson, A. W. H. Speed, 'Synthesis and Catalytic Reactivity of Bis(amino)cyclopropenylidene Carbene–Borane Adducts', *Organometallics* **2016**, *35*, 3101–3104.
- [21] D. M. Lindsay, David. McArthur, 'The synthesis of chiral N-heterocyclic carbene-borane and -diorganoborane complexes and their use in the asymmetric reduction of ketones.', *Chem. Commun.* **2010**, *46*, 2474–2476.
- [22] T. Liu, L. Chen, Z. Sun, 'Asymmetric Reduction of tert-Butanesulfinyl Ketimines by N-Heterocyclic Carbene Boranes', *J. Org. Chem.* **2015**, *80*, 11441–11446.
- [23] A. Prokof'evs, A. Boussonniere, L. Li, H. Bonin, E. Lacôte, D. P. Curran, E. Vedejs, 'Borenium ion catalyzed hydroboration of alkenes with N-heterocyclic carbene-boranes', *J. Am. Chem. Soc.* **2012**, *134*, 12281–8.
- [24] M. Toure, O. Chuzel, J.-Luc. Parrain, 'Asymmetric Rhodium-Directed anti-Markovnikov Regioselective Boracyclopentannulation.', *J. Am. Chem. Soc.* **2012**, *134*, 17892–17895.
- [25] A. Boussonniere, X. Pan, S. J. Geib, D. P. Curran, 'Borenium-Catalyzed Hydroborations of Silyl-Substituted Alkenes and Alkynes with a Readily Available N-Heterocyclic Carbene-Borane.', *Organometallics* **2013**, *32*, 7445–7450.
- [26] S.-C. Ren, F.-L. Zhang, J. Qi, Y.-S. Huang, A.-Q. Xu, H.-Y. Yan, Y.-Feng. Wang, 'Radical borylation/cyclization cascade of 1,6-enynes for the synthesis of boron-handled hetero- and carbocycles.', *J. Am. Chem. Soc.* **2017**, *139*, 6050–6053.
- [27] T. Watanabe, D. Hirose, D. P. Curran, Tsuyoshi. Taniguchi, 'Borylative Radical Cyclizations of Benzo[3,4]cyclodec-3-ene-1,5-diyne and N-Heterocyclic Carbene-Boranes.', *Chem. Eur. J.* **2017**, *23*, 5404–5409.
- [28] J.-K. Jin, F.-L. Zhang, Q. Zhao, J.-A. Lu, Y.-Feng. Wang, 'Synthesis of Diverse Boron-Handled N-Heterocycles via Radical Borylative Cyclization of N-Allylcyanamides.', *Org. Lett.* **2018**, *20*, 7558–7562.
- [29] J. Qi, F.-L. Zhang, Y.-S. Huang, A.-Q. Xu, S.-C. Ren, Z.-Y. Yi, Y.-Feng. Wang, 'Radical Borylative Cyclization of 1,6-Dienes: Synthesis of Boron-Substituted Six-Membered Heterocycles and Carbocycles.', *Org. Lett.* **2018**, *20*, 2360–2364.
- [30] Y.-J. Yu, F.-L. Zhang, J. Cheng, J.-H. Hei, W.-T. Deng, Y.-Feng. Wang, 'Lewis Base-Boryl Radicals Enabled the Desulfurative Reduction and Annulation of Thioamides.', *Org. Lett.* **2018**, *20*, 24–27.
- [31] W. Dai, S. J. Geib, D. P. Curran, 'Facile Synthesis of  $\alpha$ -N-Heterocyclic Carbene-Boryl Ketones from N-Heterocyclic Carbene-Boranes and Alkenyl Triflates.', *J. Am. Chem. Soc.* **2019**, *141*, 12355–12361.
- [32] S.-C. Ren, F.-L. Zhang, A.-Q. Xu, Y. Yang, M. Zheng, X. Zhou, Y. Fu, Y.-Feng. Wang, 'Regioselective radical  $\alpha$ -borylation of  $\alpha,\beta$ -unsaturated carbonyl compounds for direct synthesis of  $\alpha$ -borylcarbonyl molecules.', *Nat. Commun.* **2019**, *10*, 1–10.
- [33] X. Pan, A.-L. Vallet, S. Schweizer, K. Dahbi, B. Delpéch, N. Blanchard, B. Graff, S. J. Geib, D. P. Curran, J. Lalevée, Emmanuel. Lacôte, 'Mechanistic and Preparative Studies of Radical Chain Homolytic Substitution Reactions of N-Heterocyclic Carbene Boranes and Disulfides.', *J. Am. Chem. Soc.* **2013**, *135*, 10484–10491.
- [34] A.-L. Vallet, E. Lacôte, 'Thiolation of NHC-boranes: influence of the substitution at boron', *Org. Biomol. Chem.* **2019**, *17*, 4234–4237.
- [35] S. Telitel, A.-L. Vallet, S. Schweizer, B. Delpéch, N. Blanchard, F. Morlet-Savary, B. Graff, D. P. Curran, M. Robert, E. Lacôte, Jacques. Lalevée, 'Formation of N Heterocyclic Carbene-Boryl Radicals through Electrochemical and Photochemical Cleavage of the B-S bond in N Heterocyclic Carbene-Boryl Sulfides.', *J. Am. Chem. Soc.* **2013**, *135*, 16938–16947.
- [36] X. Pan, D. P. Curran, 'Neutral Sulfur Nucleophiles: Synthesis of Thioethers and Thioesters by Substitution Reactions of N-Heterocyclic Carbene Boryl Sulfides and Thioamides.', *Org. Lett.* **2014**, *16*, 2728–2731.
- [37] A. Solov'yev, Q. Chu, S. J. Geib, L. Fensterbank, M. Malacria, E. Lacôte, D. P. Curran, 'Substitution reactions at tetracoordinate boron: synthesis of N-heterocyclic carbene boranes with boron-heteroatom bonds.', *J. Am. Chem. Soc.* **2010**, *132*, 15072–15080.
- [38] S.-H. Ueng, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, 'Radical reductions of alkyl halides bearing electron withdrawing groups with N-heterocyclic carbene boranes.', *Org. Biomol. Chem.* **2011**, *9*, 3415–3420.
- [39] For a recent example, see: S. Z. Zard, 'The Xanthate Route to Ketones: When the Radical Is Better than the Enolate.' *Acc. Chem. Res.* **2018**, *51*, 1722–1733.

Entry for the Table of Contents

B–H scission releases  $\text{H}^\bullet$  or  $\text{H}^-$



B–S homolytic scission leads to radical polymerization initiation

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Installation of S-xanthates on NHC-Boranes make them both hydrides and Type I photopolymerization photoinitiators. #Boron chameleons