DOI: 10.1002/hlca.201900198

COMMUNICATION

HELVETICA chimica acta

Reactivity of B-Xanthyl N-Heterocyclic Carbene-Boranes

Anne-Laure Vallet,[a] Sofia Telitel,[b] Jacques Lalevée,*[b] and Emmanuel Lacôte*[c]

[a] ICSN-CNRS, Bâtiment 27, 1 avenue de la Terrasse, FR-91198 Gif-sur-Yvette Cedex, France
[b] Université de Haute-Alsace, CNRS, IS2M UMR 7361, FR-68100 Mulhouse, France, e-mail: jacques.lalevee@uha.fr
[c] Univ. Lyon, Université Claude Bernard Lyon 1, CNRS, CNES, ArianeGroup, LHCEP, Bât. Raulin, 2 rue Victor Grignard, FR-69622 Villeurbanne, France, e-mail: emmanuel.lacote@univ-lyon1.fr

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 through nucleophilic exchange at boron from either mono- or bis-triflyl NHC-boranes, themselves obtained by protolysis of the NHC-BH_3 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

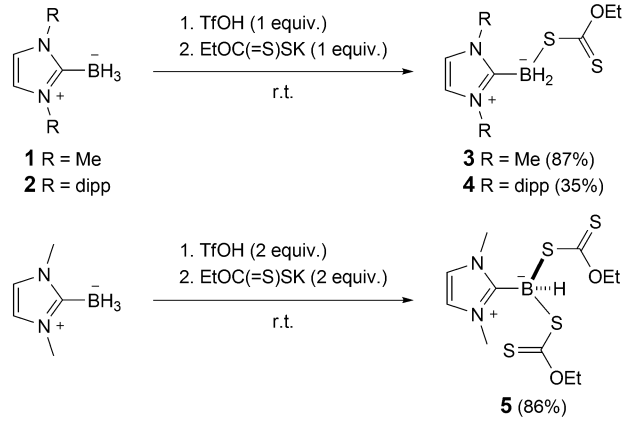
N-Heterocyclic carbene-boranes (NHC-boranes) have emerged as a new family of reagent for inorganic[1–7] and polymer synthesis.[8–13] In organic synthesis, NHC-boranes have been shown to be excellent H-atom donors for radical reductions,[14–16] hydride sources for the reduction of carbonyl or imine compounds,[17–22] or partners for borylations.[23–32] Yet in almost all these cases, the B-atom was only substituted by H-atoms. We became interested in how the established reactivity was affected by substitution at boron. Installing a sulfur (an arylsulfide)[33,34] proved rewarding since the corresponding B–S bond could be photolyzed to generate NHC-boryl radicals, which initiated radical polymerizations.[35] Alternatively, the *Curran* group demonstrated that the thiyl substituent could become a nucleophile, leading to sulfides.[36] However the same NHC-boryl sulfides could also undergo H-atom abstraction or hydride transfer, leading to bis-thiyl derivatives.[33] 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[1] NHC-borane (NHCBX) compounds.

Results and Discussion

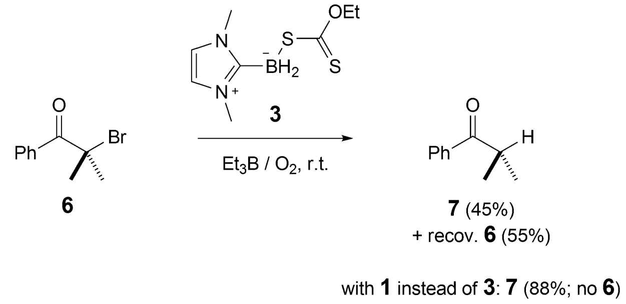
For the purpose of this study, we prepared three different NHCBXs starting from the parent NHC-BH_3 derivatives (*Scheme 1*). Following our established route,[37] IMe-BH_3 derivative **1** was converted to mono-xanthyl compound **3** using one equivalent of triflic acid and potassium xanthate (87 % yield), 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$(OTf)_2$ intermediate which is substituted twice at boron with two equivalents of potassium xanthate. From the reactivity of **3** and **5**, we expected to gather information on the influence of substitution at boron.

---

[1] In this context, 'xanthyl' derives from xanthate, not xanthene.



Scheme 1. Preparation of the target S-Xanthyl NHC-boranes (NHCBXs). dipp = 2,6-diisopropylphenyl.



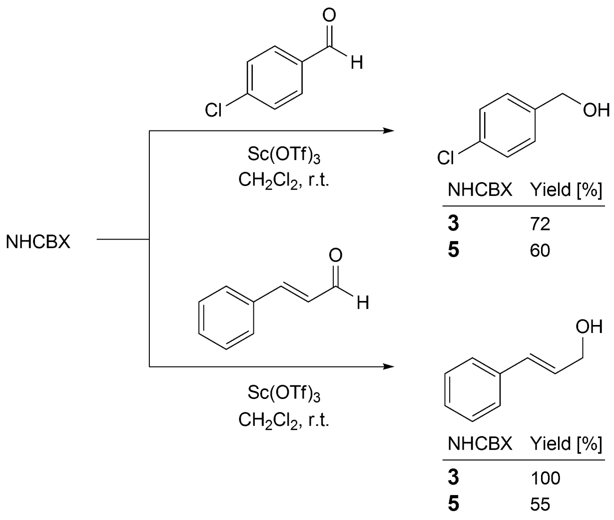
Scheme 2. Radical dehalogenation with S-Xanthyl NHC-borane **3**.

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

We first looked at the behavior of **3** as H-atom donor.[16,38] α-Bromo ketone **6** was mixed with one equivalent of **3** in the presence of Et_3B (*Scheme 2*). Air was bubbled in the reaction medium through 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 ketone **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.

We next looked at the possibility of hydride transfer. Actually, the NHCBXs have two transferrable nucleophiles: the hydride or the xanthate. With a view to favor the hydride transfer, we targeted the reduction of aldehydes.[21]

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%).



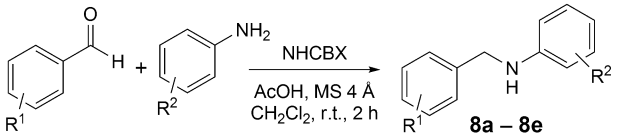
Scheme 3. Hydride transfer from S-Xanthyl NHC-boranes (NHCBXs) to aldehydes.

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 is likely an issue.

We next tried to extend the previous reaction to reductive aminations. We used our previously reported methodology (*Table 1*).[19] 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*),[19] A solution of 4-chlorobenzaldehyde (1 equiv.) and aniline (1 equiv.) in 2 mL of dichloromethane at room temperature was stirred for 1 h over 4 Å molecular sieves. Acetic acid (1.3 equiv.) and S-xanthyl NHC-borane **3** (1.3 equiv.) were added to the mixture. The resulting slurry was stirred for an additional hour, before work-up. This delivered 89% of amine **8a**. The reductive amination worked well with 4-bromoaniline (70% of **8c**, *Entry 4*), but less so when *para*-nitro benzaldehyde was used (**8b**, 46%, *Entry 3*). The

Table 1. Reductive Amination with S-Xanthyl NHC-boranes.



Entry	NHCBX	R^1	R^2	Product, yield [%]
1[a]	**3**	4-Cl	H	**8a**, 89
2[b]	**4**	4-Cl	H	**8a**, 50
3	**3**	4-NO_2	H	**8b**, 46
4	**3**	4-Cl	4-Br	**8c**, 70
5	**3**	–[c]	H	**8d**, 96
6	**5**	4-Cl	H	**8a**, 84

[a] Conditions: Aldehyde (1 equiv.); aniline (1 equiv.); CH_2Cl_2 (2 mL); 4 Å molecular sieves; AcOH (1.3 equiv.) and NHCBX (1.3 equiv.) were stirred at r.t. Unless otherwise noted, the reaction took 2 h. [b] Reaction took 12 h. [c] Cinnamaldehyde was used.

reaction was not limited to arylaldehydes, since cinnamaldehyde led to the corresponding amine in 96% yield (*Entry 5*). Other NHCBXs 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 NHCBXs 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,[35] 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^2, *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.[35]

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 functionalities, it rapidly leads to cross-linked networks that make the remaining olefin inaccessible geometrically, all the more so because the polymer quickly crosslinks, resulting in the reaction mixture freezing up.

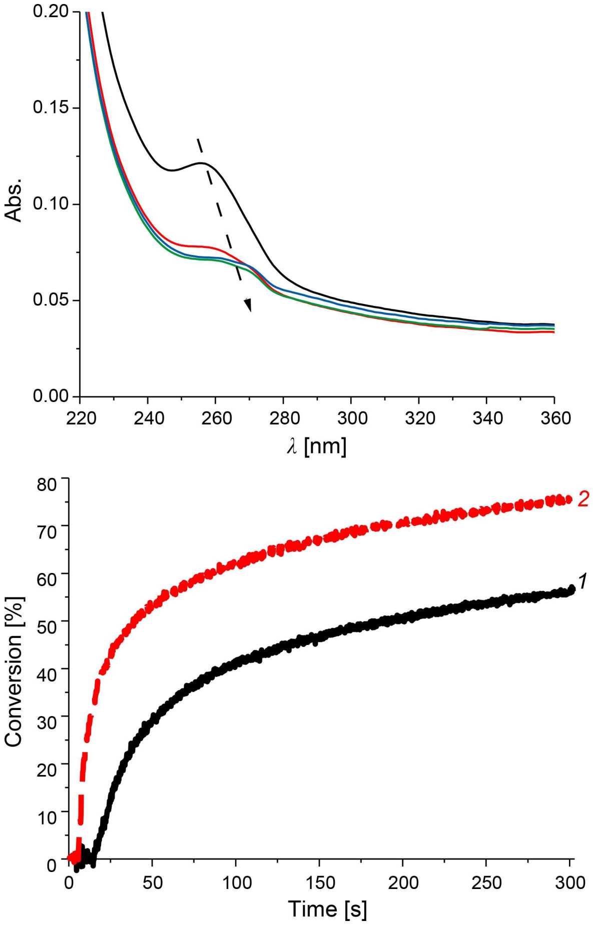
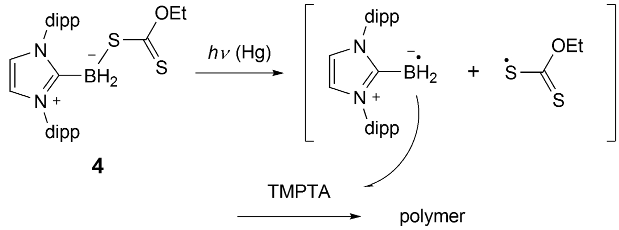


Figure 1. Homolytic activation of the B–S bond in **4**. (top) Real-time UV/Vis spectra of **4** under irradiation with a Hg–Xe lamp (intensity *ca.* 60 mW/cm^2). The dashed arrow shows the disappearance of the absorption of the B–S chromophore; (bottom) UV-triggered ($\lambda > 300$ nm) photopolymerization 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



Scheme 4. Suggested mechanism of the photopolymerization. dipp = 2,6-diisopropylphenyl; TMPTA = trimethylolpropane triacrylate (= 2,2-bis[(acryloyloxy)methyl]butyl acrylate).

(*Scheme 4*). 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.[9] Given that the radicals obtained are the same as these obtained from the corresponding S-Aryl NHC-boranes, we deduced that the polymerization reactivities would be very similar for the all family and did not examine the other S-xanthyl NHC-boranes.

Conclusions

To conclude, the installation of one or two S-xanthyl substituent(s) at boron is possible. The resulting new NHC-boranes are good hydrides and one representative of the family is a good Type I photoinitiator. 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 through the degenerate radical processes extensively studied by *Zard*.[39] 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 glassware 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_{254}* 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. ^{1}H-NMR (300, 400, 500, and 700 MHz), ^{11}B-NMR (96, 128, and 160 MHz) and ^{13}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 $CDCl_3$ (^{1}H = 7.27 ppm, ^{13}C = 77.0 ppm) or C_6D_6 (^{1}H = 7.16 ppm, ^{13}C = 128.0 ppm) as the internal standard. The ^{11}B chemical shift are given relative to $BF_3 \cdot OEt_2$ (^{11}B = 0 ppm). Multiplicities are declared as follow: *s* (*singlet*), br. *s* (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 ^{1}H- and ^{13}C-NMR spectra because of quadrupole broadening. Infrared spectra (IR) were recorded on a *PerkinElmer* FT-IR system using diamond window *Dura SamplIR II* and the data are reported in reciprocal centimeters [cm^{-1}]. Melting points were recorded in open capillary tubes on a *Büchi B-450* apparatus and are uncorrected. High resolution mass spectra (HR-MS) 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).

Trimethylolpropane 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 $\lambda > 300$ nm) was used. Upon irradiation, the polymerization kinetics were recorded by Real-Time FT-IR as reported previously.[8,11]

Preparation of the S-Xanthyl NHC-Boranes

NHCBX **4** was prepared as described previously.[37]

Compound **3**. In a round-bottom flask, IMe-BH_3 (573 mg, 5.21 mmol) was dissolved in anhydrous dichloromethane (50 mL) at room temperature. Triflic acid (450 μL, 5.21 mmol) was added dropwise. The colorless solution was left at r.t. 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 through canula. The resulting yellow solution was left at r.t. 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}H-NMR ($CDCl_3$, 500 MHz): 1.31 (*t*, $J=7.0$, CH_2Me); 2.20–2.86 (*m* [broad *q*], BH_2); 3.90 (*s*, 2 MeN); 4.50 (*q*, $J=7.0$, CH_2Me); 6.86 (*s*, 2 HC=). ^{11}B-NMR ($CDCl_3$, 160 MHz): −24.8 (*t*, $J=101$).

Compound **5**. In a round-bottom flask, IMe-BH_3 (524 mg, 4.76 mmol) was dissolved in anhydrous dichloromethane (50 mL) at room temperature. Triflic acid (900 μL, 10.4 mmol) was added dropwise. The colorless solution was left at r.t. 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 through canula. The resulting yellow solution was left at r.t. 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): 3162, 3128, 3112, 2988, 2464, 1705, 1610, 1572. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.34 (*t*, $J=7.0$, 2 CH_2Me); 4.00 (*s*, 2 MeN); 4.49 (*q*, $J=7.0$, CH_2Me); 4.52 (*q*, $J=7.0$, CH_2Me); 6.89 (*s*, 2 HC=). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.0 (CH_2Me); 37.3 (MeN); 69.4 (CH_2Me); 121.8 (=CH); 191.1 (C=S). ^{11}B-NMR ($CDCl_3$, 160 MHz): −14.4 (*d*, $J=111$). HR-ESI-MS: 373.0327 ($C_{11}H_{19}BN_2NaO_2S_4^+$, $[M+Na]^+$; calc. 373.0320).

General Procedures

Aldehyde Reductions. In a *Schlenk* flask, the NHCBX (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 NHCBX (1.3 equiv.) were then added and the resulting mixture was stirred for 1 h 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 μm thick) deposited on a BaF_2 pellet were irradiated (see the irradiation sources). The evolution of the double bond content was continuously followed by real time FT-IR spectroscopy (*JASCO FTIR 4100*) at about 1630 cm^{-1}.

Acknowledgements

This work was supported by CNRS, UHA, and ANR (grant NHCX). *A.-L. V.* thanks ICSN for a doctoral stipend. We thank *Frédéric LeQuéméner* (Université Claude Bernard Lyon 1) for sharing his know-how on the preparation of **3** and **4**.

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.* and *S. T.* 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, A. Vargas, 'Base-Stabilized Diborenes: Selective Generation and η^2 Side-on Coordination to Silver(I)', *Angew. Chem. Int. Ed.* **2012**, *51*, 9931–9934; *Angew. Chem.* **2012**, *124*, 10069–10073.

[3] P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, I. Krummenacher, A. Vargas, 'Boron Radical Cations from the Facile Oxidation of Electron-Rich Diborenes', *Angew. Chem. Int. Ed.* **2014**, *53*, 5689–5693; *Angew. Chem.* **2014**, *126*, 5797–5801.

[4] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. 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, C. 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, G. Frenking, 'The boron–boron triple bond in NHC→B≡B←NHC', *Chem. Sci.* **2015**, *6*, 4089–4094.

[7] J. Böhnke, 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. Röhr, R. Mitrić, B. Engels, F. Meyer, H. Braunschweig, 'Isolation of diborenes and their 90°-twisted diradical congeners', *Nat. Commun.* **2018**, *9*, 1197.

[8] M.-A. Tehfe, M. Makhlouf Brahmi, J.-P. Fouassier, D. P. Curran, M. Malacria, L. Fensterbank, E. Lacôte, J. 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.-P. 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*, 382–385.

[11] J. Lalevée, S. Telitel, M. A. Tehfe, J. P. Fouassier, D. P. Curran, E. Lacôte, 'N-Heterocyclic Carbene Boranes Accelerate Type I Radical Photopolymerizations and Overcome Oxygen Inhibition', *Angew. Chem. Int. Ed.* **2012**, *51*, 5958–5961; *Angew. Chem.* **2012**, *124*, 6060–6063.

[12] M.-A. Tehfe, J. Monot, M. Malacria, L. Fensterbank, J.-P. Fouassier, D. P. Curran, E. Lacôte, J. 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 Quéméner, 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; *Angew. Chem.* **2018**, *130*, 969–973.

[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. Makhlouf 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. Makhlouf Brahmi, A. Solovyev, S.-H. Ueng, D. P. Curran, M. Malacria, L. Fensterbank, E. Lacôte, 'Ionic and Organometallic Reductions with N-Heterocyclic Carbene Boranes', *Chem. Eur. J.* **2009**, *15*, 12937–12940.

[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, D. 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.-Y. Chen, Z. Sun, 'Asymmetric Reduction of *tert*-Butanesulfinyl Ketimines by N-Heterocyclic Carbene Boranes', *J. Org. Chem.* **2015**, *80*, 11441–11446.

[23] A. Prokofjevs, A. Boussonnière, 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*, 12281–12288.

[24] M. Toure, O. Chuzel, J.-L. Parrain, 'Asymmetric Rhodium-Directed anti-Markovnikov Regioselective Boracyclopentannulation', *J. Am. Chem. Soc.* **2012**, *134*, 17892–17895.

[25] A. Boussonnière, 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.-F. 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, T. Taniguchi, 'Borylative Radical Cyclizations of Benzo[3,4]cyclodec-3-ene-1,5-diynes 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.-F. 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.-F. 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.-F. Wang, 'Lewis Base–Boryl Radicals Enabled the Desulfuriza-

tive Reduction and Annulation of Thioamides', *Org. Lett.* **2018**, *20*, 24–27.

[31] W. Dai, S. J. Geib, D. P. Curran, 'Facile Synthesis of α-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.-F. Wang, 'Regioselective radical α-borylation of α,β-unsaturated carbonyl compounds for direct synthesis of α-borylcarbonyl molecules', *Nat. Commun.* **2019**, *10*, 1934.

[33] X. Pan, A.-L. Vallet, S. Schweizer, K. Dahbi, B. Delpech, N. Blanchard, B. Graff, S. J. Geib, D. P. Curran, J. Lalevée, E. 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. Delpech, N. Blanchard, F. Morlet-Savary, B. Graff, D. P. Curran, M. Robert, E. Lacôte, J. 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. Solovyev, 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] S. Z. Zard, 'The Xanthate Route to Ketones: When the Radical Is Better than the Enolate', *Acc. Chem. Res.* **2018**, *51*, 1722–1733.

Received August 8, 2019
Accepted September 3, 2019