

Oxy-Borylenes as Photoreductants: Synthesis and Application in Dehalogenation and Detosylation Reactions

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Dedicated to Professor Mukund P. Sibi on the occasion of his 70th birthday.

Abstract: While the range of accessible borylenes has significantly broadened over the last decade, applications remain limited. Herein, we present tricoordinate oxy-borylenes as potent photoreductants that can be readily activated by visible light. Facile oxidation of CAAC stabilized oxy-borylenes (CAAC)(IPr₂Me₂)BOR (R = TMS, CH₂CH₂C₆H₅, CH₂CH₂(4-F)C₆H₄) to their corresponding radical cations is achieved with mildly oxidizing ferrocenium ion. Cyclovoltammetric studies reveal ground-state redox potentials of up to -1.90 V vs. Fc^{+/0} for such oxy-borylenes placing them among the strongest organic super electron donors. Their ability as photoreductants is further supported by theoretical studies and showcased by the application as stoichiometric reagents for the photochemical hydrodehalogenation of aryl chlorides, aryl bromides and unactivated alkyl bromides as well as the detosylation of anilines.

traced by trapping experiments.^[2,3] In two seminal studies, Braunschweig showed that borylenes may be stabilized and isolated, either in a terminal or bridged position, by coordination to an electron rich transition metal.^[4] Inspired by a report from Robinson, who showed that the reduction of (NHC)BBR₃ (NHC = *N*-heterocyclic carbene) led to a stable diborene,^[5] a formal dimer of the dicoordinate borylene, in 2011 Bertrand and co-workers were able to isolate the first metal-free borylene (CAAC)₂BH (**1**) via stabilization with two cyclic (alkyl)(amino)carbenes (CAACs), thus delocalizing the free lone pair at boron (Scheme 1a).^[6] CAACs were shown to be more nucleophilic than NHCs therefore acting as stronger σ donors to the empty p orbitals at boron while simultaneously being better π acceptors to decrease the Lewis basicity of the boron atom.^[7] Subsequently, the application of CAAC as ligand in combination with an amino-substituent on boron, resulting in a push-pull effect, allowed for the isolation of dicoordinate borylene (CAAC)BN(TMS)₂, whose electrophilicity under one atmosphere of CO gave rise to the corresponding mixed base stabilized tricoordinate borylene (CAAC)(L)BR with L = CO and R = N(TMS)₂.^[8] Moreover, the reduction of (CAAC)BBR₂CN in the presence of an excess of PEt₃, enabled the synthesis of the first phosphine ligated borylene (CAAC)(PEt₃)BCN.^[9] This strategy was further applied for the synthesis of several mixed Lewis-base tricoordinate halo- and pseudohalo-borylenes.^[10,11]

Their meanwhile good availability allowed to better explore the general reactivity of such tricoordinate bory-

Introduction

The chemistry of borylenes, in which boron adopts the +1 oxidation state, has attracted increasing attention over the last decades.^[1] Free monocoordinate borylenes, bearing a lone pair and only one substituent at boron, are highly electron rich, transient species, which have not yet been isolated, but could be studied spectroscopically and be

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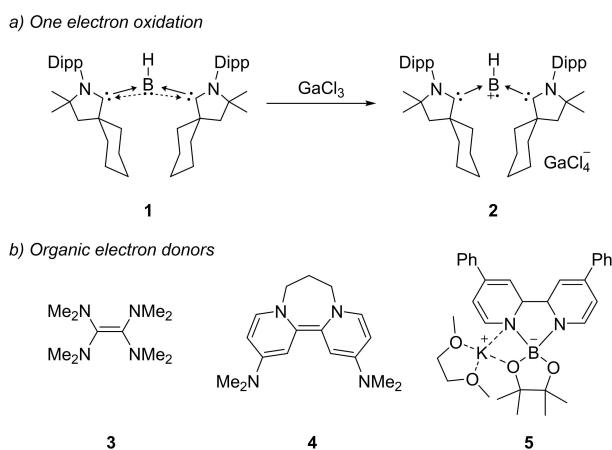
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Scheme 1. a) One electron oxidation of borylene **1** to radical cation **2**.
b) Organic electron donors **3–5**. Dipp = 2,6-diisopropylphenyl.

lenes. The nucleophilic nature of boron in borylene **1** was documented by protonation using triflic acid.^[6] Moreover, Kinjo and co-workers demonstrated that bis(oxazol-2-ylidene)-stabilized borylenes can act as σ donors which coordinate to Lewis acids and transition metals like gold and chromium. As an application, Au-borylene complexes were successfully used as catalysts for the hydroamination of alkynes in the presence of KBAr^{F}_4 .^[12] For tricoordinate (CAAC)(CO)BDur (Dur = 2,3,5,6-tetramethylphenyl) it was shown that under UV light irradiation, CO is readily cleaved off and the free dicoordinate borylene can either be trapped intermolecularly by a Lewis base or undergo intramolecular C–H insertion.^[13] Furthermore, the one electron oxidation of borylene **1** to the corresponding boryl radical cation **2** was realized by adding mildly oxidizing GaCl_3 (Scheme 1a). Cyclic voltammetric studies revealed a reversible oxidation at -0.940 V vs. $\text{Fc}^{+/0}$.^[6] Reversible chemical redox operation was achieved for pseudohalo-borylenes (CAAC)(IⁱPr)BCN (IⁱPr = 1,3-diisopropylimidazol-2-ylidene) and (CAAC)-(IⁱPr)BSCN by one electron oxidation using AgOTf and subsequent reduction with strongly reducing KC_8 .^[11b] Braunschweig and co-workers showed that the absorption maxima (350 nm–530 nm) and also the ground state redox potential for chloro-borylenes (CAAC)(L)BCl, ranging from -0.95 V (L = PET_3) to -1.26 V (L = IME_4) vs. $\text{Fc}^{+/0}$ depend on the ligand L.^[10a]

These potentials are comparable to those of organic electron donors like tetrakis(dimethylamino)ethene (**3**, TDAE), that was successfully used for the reduction of electron-poor perfluoro alkenes.^[14] Along with **3**, a wide range of organic electron donors based on electron-rich alkenes were developed since, which enable the reduction of alkyl halides and arenesulfonamides among other substrates.^[15]

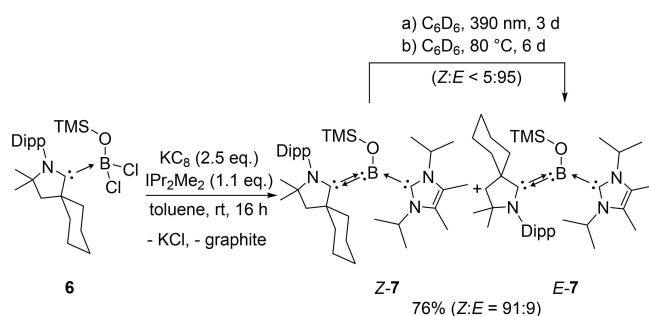
Importantly, upon UV light irradiation of electron donor **4**, the reduction of even more challenging substrates such as aryl chlorides could be achieved.^[16] Converting the energy of light, especially visible light, into chemical redox potential, i.e. photoinduced electron transfer (PET), has attracted great attention over the last decades.^[17] Especially the design

of new concepts and photosystems for difficult reductions, e.g. of aryl/alkyl halides, is of major interest.^[18] In this regard the activation of a “super electron donor” by visible light irradiation was demonstrated for boronate **5**. With a ground-state redox potential of -1.11 V vs. $\text{Fc}^{+/0}$, irradiation at 400 nm resulted in an excited state potential of -3.87 V vs. $\text{Fc}^{+/0}$ enabling the challenging reduction of electron-rich aryl chlorides.^[19]

Based on the reported ground-state redox potentials and absorption properties of tricoordinate borylenes, we assumed that such borylenes should be very strong reductants in their excited states. Moreover, we reasoned that installing an electron-donating substituent on boron could further increase the borylene redox potential. We therefore initiated a program towards the synthesis of oxy-borylenes (CAAC)-(IPr₂Me₂)BOR. In addition, their physical properties and first applications as photoreductants in synthesis were studied.

Results and Discussion

Room temperature reduction of (CAAC^{Cy})Cl₂BOTMS (**6**, CAAC^{Cy} = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene, for its preparation see the Supporting Information) with 2.5 equivalents KC_8 in the presence of IPr₂Me₂ (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) in toluene provided the tricoordinate siloxy-borylenes **Z-7** and **E-7** as a 91:9 diastereoisomeric mixture in 76% yield (Scheme 2). NMR analysis revealed characteristic ¹¹B NMR resonances at 13.8 ppm (major isomer) and 17.6 ppm (minor isomer) for these two compounds. Of note, depending on the batch the isomer ratio slightly varied (see Supporting Information). Slow evaporation of the dark red toluene solution yielded single crystals of **Z-7** suitable for X-ray crystallographic analysis, which allowed the unambiguous assignment of the relative configuration of the major isomer with respect to the C=B double bond (Figure 1a).^[20] Interestingly, irradiation of a **Z/E**-isomeric mixture of **7** in C₆D₆ at room temperature using a 390 nm LED resulted in full isomerization to the **E**-isomer.^[11a] Full isomerization to the **E**-borylene could also be achieved by heating of a C₆D₆ solution of **Z-7/E-7** at 80 °C for six days, showing that **E-7** is the thermodynamic product whereas reduction of **6** leads



Scheme 2. Synthesis and isomerization of tricoordinate siloxyborylenes **Z-7** and **E-7**.

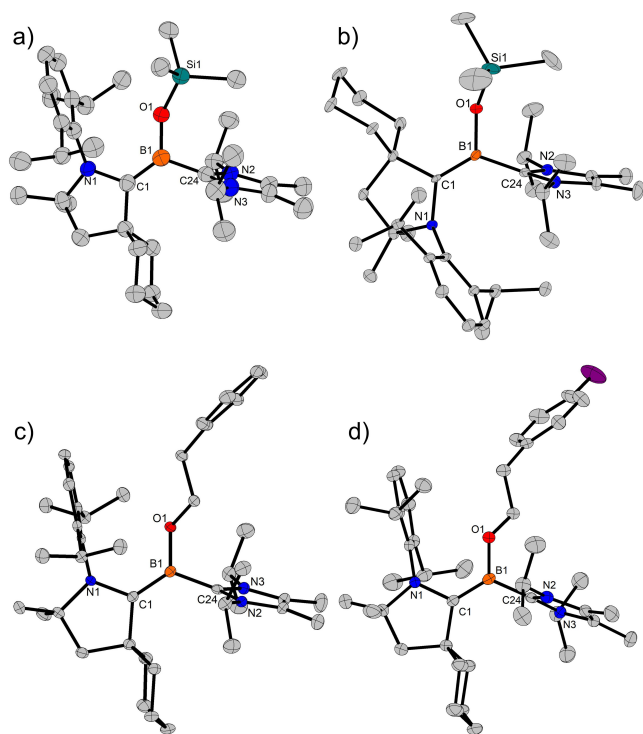
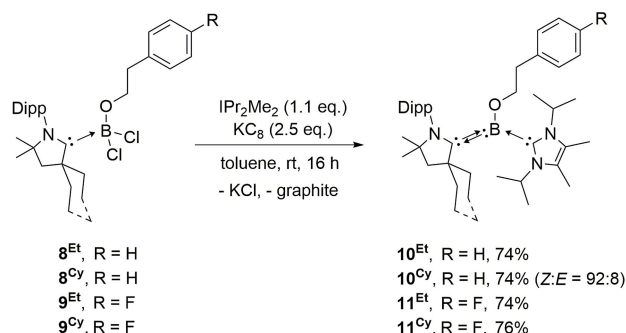


Figure 1. Molecular structures of a) *Z*-7 (only the independent molecule A is depicted), b) *E*-7, c) *Z*-10^{Cy}, d) *Z*-11^{Cy}. Hydrogen atoms are omitted for clarity and thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles for *Z*-7 (molecule A): B1–O1 1.457(5), B1–C1 1.444(6), B1–C24 1.601(6), O1–B1–C24–N3 ca. –71°. For *E*-7: B1–O1 1.440(3), B1–C1 1.446(4), B1–C24 1.614(3), O1–B1–C24–N3 ca. –80°. For *Z*-10^{Cy}: B1–O1 1.448(2), B1–C1 1.453(3), B1–C24 1.615(3), O1–B1–C24–N3 ca. –65°. For *Z*-11^{Cy}: B1–O1 1.445(2), B1–C1 1.451(2), B1–C24 1.609(2), O1–B1–C24–N2 ca. 62°.

mainly to the kinetic product *Z*-7. This is confirmed by DFT calculations which indicate that *E*-7 is more stable ($\Delta G_{298}(\text{Z-7} \rightarrow \text{E-7}) = -2.3 \text{ kcal mol}^{-1}$, see Supporting Information). The structure of *E*-7 was also confirmed by X-ray analysis (Figure 1b).

To evaluate the influence of the nature of the O-substituent on the properties and structure of the oxy-borylenes, the reduction of phenethyl- and 4-fluorophenethyl-dichloro precursors **8** and **9** was performed, aiming at evaluating their steric as well as electronic effect as compared to the parent trimethylsilyl-substituent (Scheme 3). Reduction of **8–9** yielded the corresponding borylenes **10–11** in all cases as dark purple powders in good yields (74–76%). While borylenes **10^{Et}**, **11^{Et}** and **11^{Cy}** were obtained with complete *Z*-selectivity, **10^{Cy}** was formed as a 92:8 *Z/E*-mixture of isomers favoring the *Z*-isomer. In contrast to *Z*-7, photoisomerization of the *Z/E*-mixture of **10^{Cy}** at 390 nm for 24 h could not be achieved.

Comparison of the solid-state structures shows, that there are only slight differences between the oxy-borylenes *Z*-7, *E*-7, *Z*-10^{Cy} and *Z*-11^{Cy}. They all show a trigonal planar boron center, connected to CAAC, that is only slightly tilted away from the borylene plane (torsion angle O1–B1–C1–N1 = ca. 2°–9°). The B–C^{CAAC} bond (1.44–



Scheme 3. Synthesis of phenethyl- and 4-fluorophenethyl-substituted borylenes **10** and **11**.

1.46 Å) is shortened, typical for a B=C double bond,^[21] indicating a strong π backdonation from the boron center to the CAAC ligand. In contrast, the IPr₂Me₂ ligand is turned almost perpendicular to the borylene plane (torsion angle O1–B1–C24–N2(3) = ca. 61°–80°), therefore only acting as σ donor to boron with negligible π overlap. This is further supported by the B–C^{IPr₂Me₂} bond length of 1.60–1.62 Å in line with a B–C single bond.^[21] The B–O bond length of 1.44–1.46 Å, typical for a B–O single bond,^[21] also indicates, that there is no significant π character involved. Comparison of these X-ray data shows, that neither the substituent on oxygen nor the relative orientation (*Z* or *E*) or choice of CAAC (CAAC^{Et} or CAAC^{Cy}) have a major influence on the core-solid-state structure of such borylenes.

To further explore their properties, cyclic voltammetry experiments of all oxy-borylenes were performed. For the TMS-O-substituted borylene *Z*-7, a fully reversible oxidation at $E_{1/2} = -1.88 \text{ V vs. Fc}^{+/0}$ and a second partially reversible oxidation at $E_{1/2} = -0.65 \text{ V vs. Fc}^{+/0}$ could be observed. This corresponds to an increased redox potential of –0.6 V as compared to the most strongly reducing chloroborylenes reported,^[10a] which shows that the donating ability of the oxygen-substituent on boron indeed has a major impact on the borylene redox potential. For the *E*-isomer of **7** the reversible oxidation was found at $E_{1/2} = -1.66 \text{ V vs. Fc}^{+/0}$. For the phenethyl-O-substituted borylenes **10** and **11**, a first reversible oxidation at $E_{1/2} = -1.84 \text{ V to } -1.90 \text{ V vs. Fc}^{+/0}$ and a second oxidation event at $E_{1/2} = -0.61 \text{ V to } -0.68 \text{ V vs. Fc}^{+/0}$ was measured, which depending on the substrate could be rendered reversible by an increase of the scan rate. This indicates, that the nature of the oxygen-bound substituent does not have a significant impact on the borylenes redox potential.

In contrast, the oxy-borylenes exhibited rather different absorption spectra depending on the oxygen-bound substituent as well as the *E/Z* geometrical structure of the CAAC (Figure 2a). In THF, while both *E*-7 and *Z*-7 exhibited broad absorption bands with a maximum wavelength (λ_{abs}) of around 430 nm, the molar absorption coefficient (ϵ) of *E*-7 ($2.28 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) is more than twice as large as that of *Z*-7 ($0.928 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). Furthermore, a significant red-shift relative to oxy-borylene **7** could be observed for the phenethyl-substituted **10^{Et}** and **11^{Et}** ($\lambda_{\text{abs}} = 505 \text{ nm}$, for both

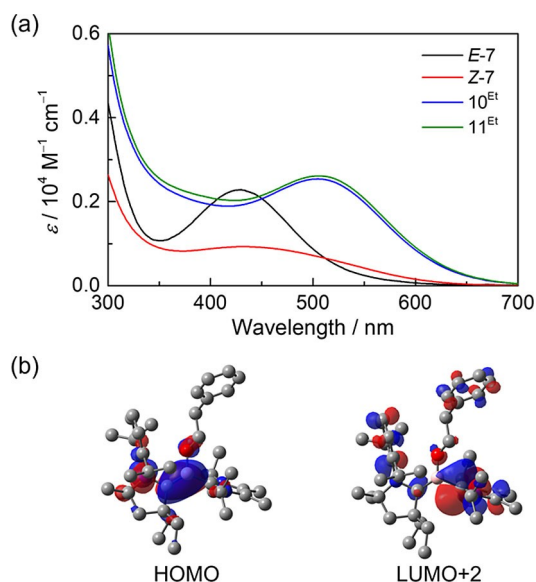


Figure 2. a) UV/Vis absorption spectra of *E*-7, *Z*-7, **10^{Et}** and **11^{Et}** in THF and b) pictorial drawings of HOMO and LUMO + 2 for **10^{Et}** calculated at the CAM-B3LYP/6-31G(d) level of theory.

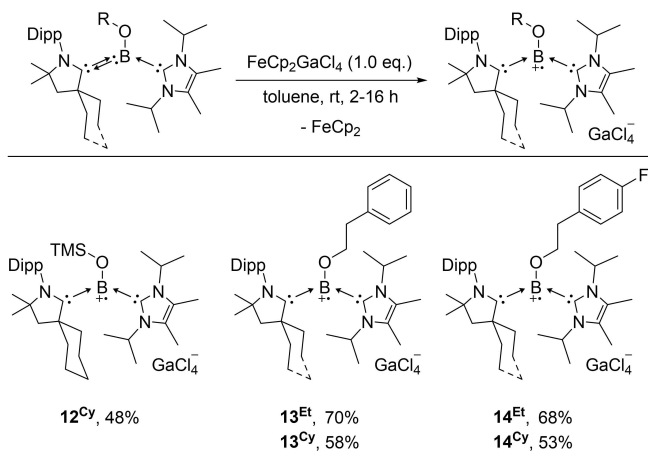
compounds), whereas the substituent on the phenyl group does neither affect the absorption maximum nor the ϵ value. The λ_{abs} values of **10^{Et}** and **11^{Et}** are even larger relative to that of a CAAC-substituted chloro-borylene bearing an orthogonally-oriented IMe₄ group reported by Braunschweig and co-workers.^[10a]

To gain in-depth insights into these differences, we conducted time-dependent (TD) DFT calculations on the four compounds *E*-7, *Z*-7, **10^{Et}** and **11^{Et}** at the CAM-B3LYP/6-31G(d) level of theory including THF as a solvent using the polarizable continuum model (PCM). The calculated absorption spectra well reproduced the experimental results in terms of the spectral shape (Figure S27). Notably, the absorption bands around 430 nm observed for *E*-7 and *Z*-7 are not assigned to the S₀→S₁ electronic transition, but the S₀→S₂ and S₀→S₃ transition, respectively. The TD-DFT calculations indicate that their S₀→S₁ transitions, corresponding to the HOMO→LUMO transitions, for both *E*-7 and *Z*-7 have forbidden character with small oscillator strengths, while the transition energies are comparable or even smaller relative to those of **10^{Et}** and **11^{Et}**. In contrast, the S₀→S₁ transitions for **10^{Et}** and **11^{Et}**, mainly attributed to the HOMO→LUMO+2 and HOMO→LUMO+1 transitions, respectively, have larger oscillator strengths than those of **7**, which should be responsible for their larger molar absorption coefficients. For all four compounds, the HOMO is predominantly localized on the borylene B–C double bond, while the unoccupied MOs relevant to the electronic transitions are mainly localized on the orthogonally-oriented NHC moiety (Figure 2b). In a comparison between *E*-7 and *Z*-7, the HOMO of *Z*-7 is higher by 0.23 eV than that of *E*-7 (Figure S27), consistent with the cyclic voltammetry results, demonstrating the impact of the *E/Z* geometrical structures on the redox properties.

In accordance with the CV measurements the preparative one-electron oxidation of oxy-borylenes proved to be feasible upon treatment with FeCp₂GaCl₄^[22] in toluene at room temperature (Scheme 4). The reaction could be readily monitored by the naked eye by a color change from dark red/purple solutions to yellow suspensions. Since the resulting boryl radical cations did not show any solubility in toluene, filtration, subsequent extraction of the greyish residue with acetonitrile and removal of solvent afforded the clean persistent boryl radical cations **12^{Cy}**, **13^{Et}**, **13^{Cy}**, **14^{Et}** and **14^{Cy}** as orange crystals in moderate to good yields (48–70%). X-ray crystal structure analysis of **12^{Cy}** and **14^{Cy}** showed that the boron center remains trigonal planar, but the reduced electron density at boron leads to a lengthening of the B–C^{CAAC} bond (1.51–1.52 Å), now only showing partial double bond character (Figure 3). Consequently, a slightly shortened B–O-bond (1.39–1.52 Å) can be observed, as a result of π donation from the OR-substituent to the boron center.

The liquid-state CW EPR spectra for **12^{Cy}** and **14^{Cy}** in Figure 3 show g-factors around 2.0035 (Table S2) and magnetic hyperfine coupling to one ¹⁴N nucleus ($I=1$, $A_N \approx 6.7$ G) and one ¹¹B nucleus ($I=3/2$, $A_B \approx 1.4$ to 1.7G), which is in a good agreement with the spin density calculations (Figure 3b), which indicate a spin delocalization over all four atoms (N–C–B–O). The spin distribution of **13^{Et}** shows the same form (see Supporting Information). Consequently, a quartet of triplets is theoretically expected, however, the individual components are only partially resolved due to relatively strong line broadening effects as shown by the simulations displayed in Figure S10. The A_N values are similar to, whereas the A_B values are significantly lower than those published on similar boryl radicals.^[10a]

To evaluate the applicability of the novel borylenes as photoreductants, the reductive dehalogenation of aryl halides was studied. We were pleased to find, that all three tested borylenes **7**, **10^{Et}** and **11^{Et}** (1.2 equivalents) were able to hydrodehalogenate 4-chloroanisole (**15a**) upon 405 nm LED light irradiation in dimethylacetamide (DMA) as solvent at room temperature. The TMS-O-substituted bor-



Scheme 4. Synthesis of boryl radical cations **12–14** by one electron oxidation.

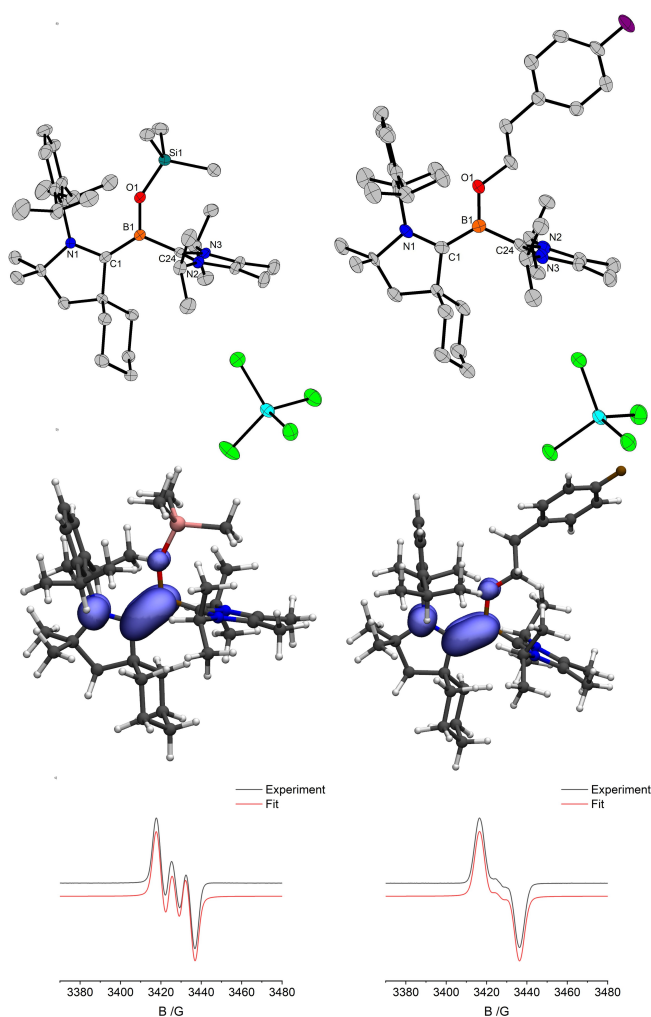
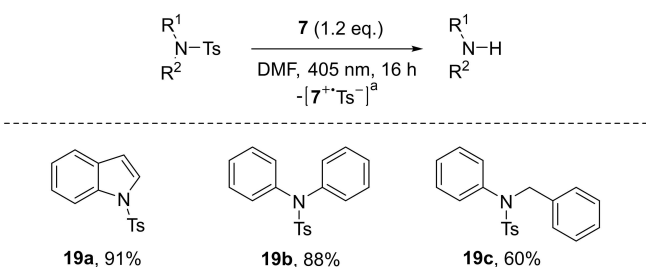
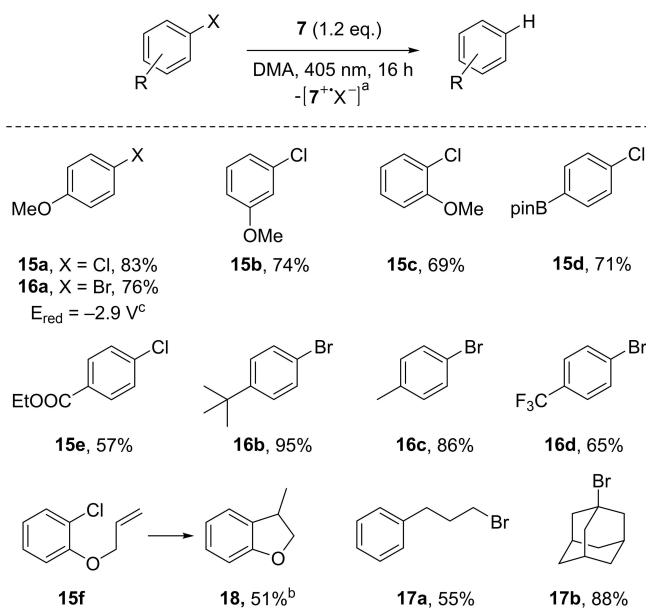


Figure 3. a) Molecular structures of 12^{Gy} (left) and 14^{Gy} (right). Hydrogen atoms are omitted for clarity and thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles for 12^{Gy} : B1–O1 1.385(3), B1–C1 1.518(4), B1–C24 1.612(4), O1–B1–C24–N3 ca. -80° . For 14^{Gy} : B1–O1 1.383(7), B1–C1 1.515(8), B1–C24 1.603(8), O1–B1–C24–N2 ca. -77° . b) Spin density isosurface plots ($(\rho_\alpha - \rho_\beta)$, 5×10^{-3} a.u.), obtained with PW6B95/def2-TZVP c) Liquid-state CW EPR spectra of the radical 12^{Gy} (left) and 14^{Gy} (right) recorded in ACN at X-band and at rt. The black curve represents the experimental spectrum and the red curve is the best-fit simulation.

ylene **7** (used as a mixture of isomers) afforded anisole in 83% yield, whereas a lower efficiency was noted for the reduction with 10^{Et} and 11^{Et} (49%, 57%). Control experiments revealed the necessity of light as well as the borylene for the reduction.

Based on these initial results, all following experiments were conducted with the most efficient reductant **7**. A number of electron-rich and electron-poor aryl bromides and aryl chlorides **15–16** were subjected to the photochemical reduction and the corresponding hydrodehalogenated products were obtained in moderate to excellent yields (57–95%, Scheme 5). Of note, ester substituents and boronic ester moieties are tolerated (see **15e** and **15d**). The dehalogenation of aryl halide **15f** afforded dihydrobenzofur-



Scheme 5. Photoreduction of various aryl and alkyl halides and tosylated amines with borylene **7**. Reactions were performed at a 0.1 mmol scale. Yields were determined by GC-FID measurements using mesitylene as internal standard. ^a Byproduct which partially decomposed during the reaction. ^b Yield determined by ¹H NMR measurements using CH₂Br₂ as internal standard. ^c vs. SCE.^[23]

ane **18** (51%) resulting from a 5-*exo*-cyclization of the intermediate aryl radical with subsequent reduction. This result supports the radical nature of the dehalogenation. Next the reduction of alkyl bromides was attempted and we were pleased to find that the tertiary alkyl bromide **17b** was smoothly reduced in 88% yield to adamantane. It was further shown that the reaction of the unactivated primary alkyl bromide **17a** to propyl benzene worked, albeit a lower yield was obtained in this case (55%).

Finally, the reductive *N*-deprotection of tosylated anilines was studied. Pleasingly, applying the same reaction conditions, detosylation of the Ts-indole **19a** was achieved in 85% yield. An even better yield of 91% was obtained upon switching to dimethylformamide (DMF) as solvent. Under these optimized conditions, tosylated anilines **19b** and **19c** could be converted to the free anilines in 88% and 60% yield, respectively.

To get insights into the mechanism of the photo-mediated reduction we first performed the dehalogenation of the aryl bromide **16b** in fully deuterated DMF in place of DMA. Analysis by GC-MS (see Supporting Information)

revealed that the desired *tert*-butylbenzene was partially deuterated, suggesting that the solvent as well as the oxidized boron species act as H-atom donors in the reduction of the intermediate aryl radical, which is generated upon single electron reduction and mesolysis of the C–Br bond of the starting halide. In addition, we analyzed the fate of the boron species by using EPR and GC measurements. In the crude reaction mixture of the reduction of chloroanisole **15a** with borylene **7**, we could identify the boryl radical cation, as expected byproduct (see Supporting Information for experimental and simulated data). However, this boryl radical cation was found not to be stable under the reaction conditions (see Supporting Information for GC-trace), which is in accordance with its likely role as H-atom donor and the fact, that none of our attempts to render the reaction catalytic was successful.

Conclusion

In summary, we have shown that oxy-borylenes under visible light irradiation are efficient single electron transfer reductants. Structures of the oxy-borylenes and also their oxidized persistent radical cations were characterized by X-ray diffraction. For the latter, EPR studies were conducted. All compounds were additionally analyzed by cyclovoltammetry revealing a reversible first oxidation of the oxy-borylenes. We have found that the installation of an electron-donating siloxy or alkoxy substituent on the boron atom leads to a significant increase of the ground state redox potential to up to -1.90 vs. $\text{Fc}^{+/0}$ as compared to literature known tricoordinate borylenes. Their absorption properties were examined and further investigated by theoretical studies. The ability of oxy-borylenes to compete with the most efficient organic SET-reductants has been documented by the application of oxy-borylene **7** as efficient photo-reductant for the hydrodehalogenation of aryl and alkyl halides as well as for the deprotection of *N*-tosylated anilines.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Boron Compounds · EPR Spectroscopy · Photochemistry · Radical Reactions · SET Reduction

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