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Influence of Electronic Effects over the Reactivity of Triazolylidene-Boryl Radicals. Consequences for the use of NHC-Boranes in Organic and Polymer Synthesis

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Abstract

A small library of triazolylidene-boranes which differ only by the nature of the aryl group on the external nitrogen has been prepared. Their associated reactivity as B–H hydrogen atom donors, as well as that of the corresponding NHC-boryl radicals toward methyl acrylate and oxygen were investigated by laser flash photolysis (LFP), molecular orbital calculations and ESR-spin trapping experiments, and benchmarked relative to the already known dimethyl-triazolylidene-borane.

The new NHC-boranes were also used as co-initiators for the Type II photopolymerization of acrylates. This allowed us to establish a structure/reactivity relationship with regard to the substitution pattern of the NHC and to probe the role of electronic effects in the reactivity of NHC-boryl radicals. Although their rate of addition to methyl acrylate depends on their electronegativity the radicals are all nucleophilic and good initiators for the photopolymerization reactions.

Graphical Abstract

The influence of electronic effects over the reactivity of NHC-boryl radicals was studied using various methods. The addition rate of the radicals to methyl acrylate depends on their electronegativity. All NHC-boranes studied were however good co-initiators for the Type II photopolymerization of acrylates, suggesting the addition rate is not the determining factor of the polymerization.

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Keywords

B; Carbenes; Radicals; Polymerization; Photochem. react

Introduction

N-Heterocyclic carbene-boranes (NHC-boranes) have emerged as valid surrogates for the toxic tin hydrides in synthetic free radical chemistry,[1] as well as efficient co-initiators for the radical photopolymerization of acrylates.[2] This is principally due to their relatively low B–H bond dissociation energies (BDEs, in the 80–88 kcal/mol range), a consequence of the stabilization of the boryl radicals by complexation with the NHC.[3] The NHC-boryl radicals are highly nucleophilic, and thus add rapidly to electron-poor olefins, which is one factor explaining their high efficiency for polymerization initiation of acrylates. However the NHC-boranes are also hydrides,[4], which actually makes them poor H-atom donors to nucleophilic alkyl and aryl radicals. This is why the radical reactions using them as mediators require polarity reversal catalysis conditions.[1c]

We have extensively studied the influence of sterics on the reactivity of NHC-boranes and NHC-boryl radicals.[5] We now report how polar effects on the NHC affect the radical reactivity of NHC-boranes, and what this means for their structural optimization as radical mediators and Type II photopolymerization co-initiators. For that purpose, the library of triazolylidene NHCs developed by the Rovis group was an attractive target for investigation, as one can easily prepare NHCs with strongly electron-withdrawing to strongly donating substituents.[6] The impact of the N-aryl substituent on NHC catalyzed reactions has been extensively documented [6d] with some reactions benefiting from strongly withdrawing groups such as the C₆F₅ [6e] while others are optimal when electron-rich groups [6f] or largely neutral substituents [6g] are found at that position.

In the present article, we have prepared a small library of triazolylidene-boranes which differ only by the nature of the aryl group on the external nitrogen (**2–8**, Figure 1). Their associated reactivity as B–H hydrogen atom donors, as well as that of the corresponding NHC-boryl radicals toward methyl acrylate and oxygen were investigated by laser flash photolysis (LFP), molecular orbital calculations and ESR-spin trapping experiments, and benchmarked relative to the already known **1**. Finally, the new NHC-boranes were also used as co-initiators for the Type II photopolymerization of acrylates.

Results and Discussion

All NHC-boranes were prepared using our standard method, that is from the in situ generated NHC with the BH₃•SMe₂ complex.[7] The ¹¹B chemical shifts for the NHC-boranes **2–8** vary from –34.1 ppm for **6** to –36.7 ppm for **3** and **4**. They fall in the usual chemical range observed for other NHC-boranes (e. g. –37.6 ppm for **1**) and there is no apparent correlation between chemical shifts and electronic effects on the arene.

Hydrogen atom abstraction from NHC-boranes: access to NHC-boryl radicals

The NHC-boryl radicals **1•–8•** were generated by hydrogen abstraction reaction from the corresponding NHC-boranes[2f] in two different ways, i) from a *tert*-butoxyl radical (1b; *t*-BuO•) generated by photocleavage of the di-*tert*-butyl peroxide upon UV light (1a); ii) by hydrogen atom transfer to the benzophenone triplet state (³BP, 2b). ³BP was obtained upon light excitation of benzophenone (2a).

The decay of the UV-vis signal of the NHC-boryl radicals was followed by nanosecond laser flash photolysis (LFP) using a Q-switched nanosecond Nd/YAG laser ($\lambda_{\text{exc}} = 355 \text{ nm}$, 9 ns pulses; energy reduced down to 10 mJ). The hydrogen abstraction rate constants for reactions 1b (k_{H1}) and 2b (k_{H2}) were determined according to our previously introduced procedure.[2e,f] They are gathered in Table 1.

For the former (1b), the k_{H1} s were derived from the rising time of NHC-BH₂• (time needed for the signal to rise after the pulse). *t*-BuO• is silent in LFP for $\lambda > 300 \text{ nm}$, thus only the NHC-boryls can be observed (see also Figure 2 in inset). A typical spectrum (that of NHC-boryl radical **4•**) is given (Figure 2A).

The k_{H2} s for the latter (2b) were determined from the quenching of ³BP, whose signal is easily observed at 525 nm (Figure 2B). In the absence of any NHC-BH₃, the signal disappearance observed corresponds to the regular decay of ³BP (Figure 2B). When a NHC-borane is present, ³BP undergoes a fast H-atom exchange to deliver ketyl radical BPH•. The signal for ³BP is thus rapidly quenched and BPH• shows a residual absorption (Figure 2B). Because BPH• is formed together with the NHC-boryl radical via the H-atom transfer, the quantum yield for the formation of BPH• is equal to that of the NHC-boryl radical in all cases. It can be extracted from the optical density of BPH•.[2e,f]

ESR-spin trapping experiments confirm that the observed species are the desired NHC-boryl radicals (Figure 3). In the presence of the nitron phenyl *N-tert*-butyl nitron (PBN), NHC-boranes **3**, **4** and **8** lead to the respective nitroxyl radical adducts which were characterized. The signals exhibit the following hyperfine coupling constants: $a_{\text{N}} = 15.1 \text{ G}$, $a_{\text{B}} = 4.0 \text{ G}$, a_{H}

= 2.5 G for **3**[•]; $a_N = 15.1$ G, $a_B = 4.1$ G, $a_H = 2.7$ G for **4**[•]; $a_N = 15.1$ G, $a_B = 3.8$ G, $a_H = 2.6$ G for **8**[•]. These values are in the range of the known *hfc*s for boryl radicals.

All rate constants measured for the B–H hydrogen abstraction were very high (above 10^8 M⁻¹.s⁻¹) for both the *t*-butoxyl radical and ³BP (Table 1, entries 1–8). However, while the k_{H1} values were almost constant, some slight variations were observed in k_{H2} (1.7 to 8×10^8 M⁻¹.s⁻¹), and the NHC-boranes featuring electron-donating groups were the least rapid electron-donors (with one exception, compare entries 7–8 to entry 2–6). The quantum yields for the H-exchange are higher for the “rich” NHC-boranes **7–8** and slightly lower for the “poor” **3–6**.

The two reactions differ by the nature of the H-abstracting partner. Unlike *t*-BuO[•], ³BP is a more conjugated species that can develop stacking interactions with the NHC-boranes, which affect the exchange for reaction 2b. Steric hindrance is another factor that could explain the different behaviors of the initiators. The H-transfer to *t*-BuO[•] induces an alignment between the three atoms (O, H and B). Hence, the influence of the *t*-butyl substituent is minimal. In contrast, ³BP is a conjugated biradical that requires a different geometry for the H-transfer, which might generate more steric strain. It is interesting to consider the structurally different *imidazolydinene*-borane DiMe-Imd-BH₃.^[2e] The latter transfers its hydrogen atom faster to ³BP (9.6×10^8 M⁻¹.s⁻¹) than to *t*-BuO[•] (2.7×10^8 M⁻¹.s⁻¹). DiMe-Imd-BH₃ is a faster hydrogen donor than **1**, likely a consequence of the electronic differences of the carbenes: imidazolydinene carbenes are more electron-rich than triazolydinenes,^[8] giving greater hydridic character to the B–H bonds and making them more suitable to react with electrophilic radicals.

We next calculated the B–H BDEs using the hybrid functional B3LYP.^[9] They were determined from reactants and products fully optimized at the B3LYP/6-31G* level. Compared to the reference compounds **1** and **2**, the BDEs were similar for NHC-boranes **7–8** and slightly lower for NHC-boranes **3–6** (78–79 kcal/mol, Table 1).

While caution must be exercised because of the difficult modeling of the B–H BDEs of NHC-boranes,^[3a,10] and the small differences within the range of error (± 2.6 kcal/mol), it appears however that electron-withdrawing groups tend to diminish the B–H BDE. We thus calculated the SOMOs of **2**[•] (N-phenyl) and **3**[•] (N-pentafluorophenyl). Both orbitals are highly similar (Figure 4). The spin density on boron is slightly lower for **3**[•] (0.511 vs. 0.502 for **2**[•] at the UB3LYP/6-31G* level). This trend is in agreement with the Rablen model, where spin delocalization influences the B–H BDE.^[3b] The more spin is delocalized on the Lewis base (owing to the electron-withdrawing substituents on the NHC), the lower the BDE. On the contrary, the system is not modified by the presence of the donating groups: the two nitrogens are already contributing to the overlap with the boryl radical, and the additional donation from the substituents is negligible.

Reactivity of NHC-boryls towards methyl acrylate and O₂

Because of their relevance to the photopolymerization of acrylates in the presence of air, the rate constants for NHC-boryl radical addition to methyl acrylate (Scheme 1a) and coupling with dioxygen (Scheme 1b) were measured (Figure 5).

For that purpose, we selected **3•** and **4•** as representatives of the “electron-poor” NHC-boranes, and **8•** as representative “electron-rich” NHC-boranes. The known values for **1•** and **2•** were also added for comparison. The rates of decay of the NHC-boryl radicals signals were measured for different quencher concentrations (see Figure 5 for the addition of **8•** to methyl acrylate), and this data was processed in the usual way to give the elementary rate constants shown in Table 2.[2e,f]

All radicals react extremely fast with oxygen. This reaction is not affected by the substitution pattern of the NHCs. This property of NHC-boryl radicals is at the root of the high oxygen tolerance of radical photopolymerizations initiated by NHC-boranes. In contrast, the addition rate to methyl acrylate ranged from 0.8×10^6 to $17 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (compare the rates for **1•** and **3•**, Entries 1 and 3). The more electron-withdrawing elements on the NHC-borane, the less rapid the addition to methyl acrylate (compare **3•** and **4•**, Entries 3 and 4). Radical **8•** adds faster than both **3•** and **4•**, but significantly slower than **1•** and **2•** (Entry 5). On the whole, though, all the NHC-boryl radicals considered add fast to the electron-poor acrylate, and are thus nucleophilic species. For comparison, the fastest imidazolydinene-boryl radical adds to methylacrylate with a $3.8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ rate, close to that of **1•**. [2e]

To help with the interpretation of the results we also calculated the Mulliken electronegativity (χ) of the five NHC-boryl radicals [$\chi_M = \frac{1}{2}(\text{IP} + \text{EA})$, Table 2, column 2]. Both the ionization potential (IP) and electron affinity (EA) were calculated at the UB3LYP/6-31+G* level by optimization of the relevant radicals and ions.

Radical **1•** had the lower χ value (2.70). The introduction of a phenyl substituent led to an increase of the electronegativity (to 2.85). The addition of halogen substituents further increased the χ value (to 2.98 for **4•** and 3.13 for **3•**). In contrast, the adjunction of three methoxy substituents onto the phenyl ring did not affect the χ value of the radical (2.81 for **8•**). DiMe-Imd-BH₂• has a calculated χ value of 2.72.[1c] Most interestingly, the Mulliken electronegativity appears strongly related to the addition rate constant onto methyl acrylate: the lower the electronegativity, the faster the addition onto methyl acrylate (Figure 6).

We believe that the pattern observed in the triazolydinene family is a direct result of electronic effects. Increasingly less donating substituents at nitrogen lead to more electron back-donation from the boron atom to the NHC in the NHC-boryl radicals. The latter are thus less prone to cede an electron, which is reflected by a higher χ value. Accordingly, they are also less prone to add to an electron-poor olefin. The case of **8•** is more problematic at first sight since the aryl has three strongly donating substituents. But, as for the other NHC-boryl radicals, in fact the trimethoxyphenyl group in **8•** adopts an out of plane conformation (Figure 7). The strongly donating character of the methoxy groups is thus largely canceled because the arene is not fully conjugated and **8•** behaves as a less electron-rich version of **1•** because of the –I effects of the oxygens.

The fact that **1•** and DiMe-Imd-BH₂• have roughly the same electronegativity despite the electronic difference of the NHC shows that one must remain highly cautious in building a

structure/electronegativity correlation over structurally different radicals. We will thus only consider the triazolidinene family for the polymerization part of this article.

NHC-boranes as co-initiators for the Type II photopolymerization of acrylates

We next carried out the radical photopolymerization of Trimethylolpropane triacrylate (TMPTA) using a two-component photoinitiating system (benzophenone-BP/NHC-BH₃, Scheme 2 and Figure 8).

The film polymerizations were carried out in laminated conditions, in which the formulations (monomer and photo-initiating system) were sandwiched between two polypropylene films. The 20 μm thick laminated films were deposited on a BaF₂ pellet and irradiated with a 150 W Xe-Hg polychromatic light source and the evolution of the double bond content was followed by real-time FTIR spectroscopy ($\sim 1630\text{ cm}^{-1}$) at room temperature.[2f] The benchmark photopolymerization was run in the presence of BP alone (Figure 8, curve a). It leads to a final conversion of about 45% with an inhibition time of 24 s. In contrast, when the NHC-boranes were present, no such inhibition was observed and the conversion was generally better (in the 50–55% range, curves b–g). The differences between the different NHC-boranes were not strong, and the polymerizations were fast in all cases. However one can see that the initial speed of the systems vary in the order $c \sim d < g < b \sim f < e$. After a short lagging time, the speed for curve f was similar to that of b.

The inhibition observed in curve a is due to the residual oxygen in the sandwiched formulation. Dioxygen is an inhibitor, and the polymerization only starts when it has been consumed.[11] This inhibition is suppressed in the presence of the NHC-borane co-initiators, and better polymerization profiles were obtained (higher polymerization rates and final conversions). We have shown that the suppression of the inhibition period is due to (i) the highly efficient formation of NHC-boryl radicals by H-transfer to ³BP (Table 1); (ii) their high reactivity towards electron-deficient acrylates (Table 2); (iii) a fast quenching of oxygen by NHC-boryl radicals; (iv) and the fast reaction of the electrophilic NHC-boraperoxy adduct-radicals with a hydrogen atom from another nucleophilic B–H bond formed, which converts NHC-boraperoxy radicals back to polymerization initiating “boryl” radicals.[2e]

Interestingly, the efficiency of the NHC-borane co-initiators is not correlated to their addition rate to the monomer, since **3** performs very well despite being the slowest to add to methyl acrylate. On the other hand, the better co-initiators seem to be those with the higher H-transfer rates to ³BP (see **1**, **3**, **6** and **8**). It thus appears that the rate-limiting event for the co-initiator efficiency is not the addition to the monomer, which is rapid even for the slower NHC-boranes, but the H-transfer to ³BP. The latter reaction is bimolecular and its rate depends on the stacking/steric interactions that develop between the two reacting partners.

Conclusion

We have studied the influence of polar effects over the reactivity of NHC-boryl radicals derived from triazolidinene carbenes. For the compounds studied, polar effects have a weak effect on the B–H BDE and the direct H-atom transfer rate to oxygen-centered radicals. In

contrast, we observed a correlation between the addition rate of the NHC-boryl radicals to methyl acrylate and their calculated electronegativity. The bimolecular interaction $^3\text{BP}/\text{NHC-borane}$ was also influenced by the NHC-borane structure, presumably because of steric/stacking interactions. Overall, the present work shows that NHC-boranes featuring an improved interaction with the excited state of the initiator should be better Type II photopolymerization co-initiators.

Supplementary Material

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Figure 1.
Structure of the NHC-boranes used in the study.

Figure 2.

(A) Time resolved spectrum for $4^\bullet$ in di-*tert*-butylperoxide/acetonitrile for $t = 200$ ns; $[4] = 0.05$ M. Inset: the kinetic at 360 nm. (B) Kinetics at 525 nm for 3BP in acetonitrile for different $[4]$.

Figure 3.

ESR spectra observed in spin trapping experiments for the PBN adduct of the NHC-boryl radical derived from (A) **3** in di-*tert*-butylperoxide; (B) **4** in di-*tert*-butylperoxide/*tert*-butylbenzene and (C) **8** in di-*tert*-butylperoxide/*tert*-butylbenzene (the ESR spectrum simulation includes ^{10}B): experimental (a) and simulated (b) spectra.

Figure 4. Calculated SOMOs for **2*** (left) and **3*** (right) at UB3LYP/6-31G* level for two different views (B is indicated by an arrow).

Figure 5.

Kinetics at 380 nm for $8^\bullet$ in di-*tert*-butylperoxide/acetonitrile (75%/25%); $[8] = 0.032\text{M}$ for different [methylacrylate] from 0 to 0.11 M; Inset: zoom for the rising time of $8^\bullet$ in absence of methylacrylate.

Figure 6. Relationship between the addition rate constants onto acrylate (k_{add}) and the calculated electronegativities of the NHC-boryl radicals (see values and compounds structures in Table 2 and Figure 1).

Figure 7.
Singly Occupied Molecular Orbital (SOMO) for **8•** (UB3LYP/6-31G* level).

Figure 8. Radical photopolymerization profiles for different BP/co-initiator couples (1%/1% w/w; in TMPTA, in laminate): (a) without co-initiator; (b) BP/3 (C₆F₅); (c) BP/4 (Cl₃); (d) BP/7 (OMe); (e) BP/1 (DiMe-Triaz); (f) BP/6 (bis-CF₃); (g) BP/8 (Tri-OMe).

Scheme 1.

Reactions of NHC-boryl radicals: addition to methyl acrylate (a) and coupling with dioxygen (b).

Scheme 2.
NHC-borane co-initiated photopolymerization of TMPTA.

Table 1

Rate constants for hydrogen abstraction for reactions (1b) and (2b) and NHC–boryl radical quantum yields for (2b). The bond dissociation energies (BDEs) were evaluated at UB3LYP/6-31G* level.

NHC–BH ₃	k _{H2} (³ BP) 10 ⁸ M ⁻¹ s ⁻¹	Φ (boryl) ³ BP/NHC–BH ₃	k _{H1} (tBuO [•]) 10 ⁸ M ⁻¹ s ⁻¹	BDE (B–H) kcal/mol
1	3	0.9	1.4 ^[a]	80.4 ^[a]
2	5.5 ^[b]	0.9 ^[b]	1.5 ^[b]	80.2
3	6	0.8	1.8	78.1
4	1.7	0.7	1.5	79
5	7	0.5	-	78.6
6	8	0.7	1.9	78.1
7	1.7	0.9	1.4	80.2
8	2.2	0.9	1.4	80.5

^[a] see Ref. [2d];

^[b] see Ref. [2f].

Table 2

Rate constants characterizing the reactivity of NHC-boryls towards methylacrylate and oxygen. See text for the calculation of the Mulliken electronegativity (χ).

Entry	Radical	χ (eV)	k_{add} (methylacrylate) $10^6 \text{ M}^{-1}\text{s}^{-1}$	k_{add} (O_2) $10^8 \text{ M}^{-1}\text{s}^{-1}$
1	1$\cdot$	2.70	17 ^[a]	>6 ^[a]
2	2$\cdot$	2.85 ^a	6 ^[b]	>2 ^[b]
3	3$\cdot$	3.13	0.8	>5
4	4$\cdot$	2.98	2.5	>5
5	8$\cdot$	2.81	3.8	>5

^[a] see Ref. [2d];

^[b] see Ref. [2f].