NHC-Boranes

Influence of Electronic Effects on the Reactivity of Triazolylidene-Boryl Radicals: Consequences for the use of N-Heterocyclic Carbene Boranes in Organic and Polymer Synthesis

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Abstract: A small library of triazolylidene-boranes that differ only in the nature of the aryl group on the external nitrogen atom was prepared. Their reactivity as hydrogen-atom donors, as well as that of the corresponding N-heterocyclic carbene (NHC)-boryl radicals toward methyl acrylate and oxygen, was investigated by laser flash photolysis, molecular orbital calculations, and ESR spin-trapping experiments, and benchmarked relative to the already known dimethyltriazolylidene-borane. The new NHC-boranes were also used as co-

Introduction

N-Heterocyclic carbene-boranes (NHC-boranes) have emerged as valid surrogates for the toxic tin hydrides in synthetic freeradical chemistry^[1] and 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⁻¹ 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 initiating the polymerization of acrylates. However the NHC-boranes are also hydrides,^[4] which actually

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initiators for the Type I photopolymerization of acrylates. This allowed a structure-reactivity relationship with regard to the substitution pattern of the NHC to be established and the role of electronic effects in the reactivity of NHC-boryl radicals to be probed. Although their rate of addition to methyl acrylate depends on their electronegativity, the radicals are all nucleophilic and good initiators for photopolymerization reactions.

makes them poor H-atom donors to nucleophilic alkyl and aryl radicals. This is why 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 Rovis et al. was an attractive target for investigation, as one can easily prepare NHCs with strongly electron withdrawing to strongly electron 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 electron withdrawing groups such as $C_6F_{5,}^{[6e]}$ whereas others proceed optimally when electron-rich groups^[6f] or largely neutral substituents^[6g] are located at that position.

In the present work, we prepared a small library of triazolylidene-boranes that differ only in the nature of the aryl group on the external nitrogen atom (**2–8**, Figure 1). Their reactivity as 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**. The new NHC-boranes were also used as co-initiators for the Type II photopolymerization of acrylates.

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

Results and Discussion

All NHC-boranes were prepared by our standard method, that is, from the NHC, generated in situ, and $BH_3 \cdot SMe_2$.^[7] The ¹¹B chemical shifts of NHC-boranes **2–8** vary from –34.1 ppm for **6** to –36.7 ppm for **3** and **4**. They lie 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 of the aryl substituent.

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

The NHC-boryl radicals **1–8** were generated by hydrogen abstraction from the corresponding NHC-boranes^[2f] in two different ways: 1) by a *tert*-butoxyl radical [Eq. (1b)] generated by UV photocleavage of di-*tert*-butyl peroxide [Eq. (1a)]; 2) by hydrogen-atom transfer to the triplet state of benzophenone [³BP, Eq. (2b)], obtained on photoexcitation of benzophenone [Eq. (2a)].

$$tBuOOtBu + h\nu \rightarrow 2 tBuO$$
 (1a)

 $tBuO' + NHC-BH_3 \rightarrow tBuOH + NHC-BH_2'$ (k_{H1}) (1b)

$$\mathsf{BP} + h\nu \to {}^3\mathsf{BP} \tag{2a}$$

$${}^{3}\text{BP} + \text{NHC-BH}_{3} \rightarrow \text{BPH}^{\bullet} + \text{NHC-BH}_{2}^{\bullet} \quad (k_{\text{H2}})$$
 (2b)

The decay of the UV/Vis signal of the NHC-boryl radicals was monitored by nanosecond LFP with a Q-switched nanosecond Nd/YAG laser (λ_{exc} =355 nm, 9 ns pulses, energy reduced to 10 mJ). The hydrogen-abstraction rate constants k_{H1} and k_{H2} for reactions (1 b) and (2b), respectively, were determined accord-

Table 1. Hydrogen-abstraction rate constants for reactions (1 b) and (2 b)			
and quantum yields of NHC-boryl radicals for reaction (2b). The BDEs			
were evaluated at the UB3LYP/6-31G* level of theory.			

NHC-BH ₃	k _{H2} (³ BP) [10 ⁸ M ⁻¹ s ⁻¹]	$\Phi_{ m boryl}$ 3 BP/NHC-BH $_3$	k _{н1} (tBuO⁺) [10 ⁸ м ^{−1} s ^{−1}]	BDE (BH) [kcal mol ⁻¹]
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].				

ing to our previously introduced procedure.^[2e,f] They are listed in Table 1.

For reaction (1b), the $k_{\rm H1}$ values were derived from the rise time of NHC-BH₂[•] (time needed for the signal to rise after the pulse). tBuO[•] is silent in LFP for $\lambda > 300$ nm, and thus only the NHC-boryl radicals can be observed (see also Figure 2, inset). A typical spectrum (that of NHC-boryl radical **4**[•]) is shown in Figure 2 A.



Figure 2. A) Time-resolved UV/Vis spectrum of 4[•] in di-*tert*-butylperoxide/ace-tonitrile for t = 200 ns; [4] = 0.05 M. Inset: the kinetics at 360 nm. B) Kinetics at 525 nm of ³BP in acetonitrile for different [4].

The $k_{\rm H2}$ values for reaction (2b) were determined from the quenching of ³BP, the signal of which is easily observed at 525 nm (Figure 2B). In the absence of any NHC-BH₃, the observed signal disappearance corresponds to the regular decay of ³BP (Figure 2B). When an 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 by 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 confirmed that the observed species are the desired NHC-boryl radicals (Figure 3). In the presence of phenyl *N-tert*-butyl nitrone (PBN), NHC-boranes **3**, **4**, and **8** led to the respective nitroxyl radical adducts, which

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Figure 3. Experimental (a) and simulated (b) ESR spectra in spin-trapping experiments for the PBN adducts of the NHC-boryl radicals derived from A) 3 in ditert-butyl peroxide, B) 4 in di-tert-butyl peroxide/tert-butylbenzene, and C) 8 in di-tert-butyl peroxide/tert-butylbenzene (the ESR spectral simulation includes ¹⁰B).

were characterized. The signals exhibit the following hyperfine coupling constants (HFCs): $a_N = 15.1$ G, $a_B = 4.0$ 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 HFCs for boryl radicals.

All rate constants measured for hydrogen abstraction were very high (> $10^8 \text{ M}^{-1} \text{ s}^{-1}$) for both the *tert*-butoxyl radical and ³BP (Table 1, entries 1–8). However, whereas the k_{H1} values were almost constant, some slight variations were observed in k_{H2} [(1.7-8)× $10^8 \text{ M}^{-1} \text{ s}^{-1}$], and the NHC-boranes featuring electron-donating groups were the slowest electron donors (with one exception; compare Table 1, entries 7 and 8 to entries 2–6). The quantum yields for H exchange are higher for the electron-rich NHC-boranes **7** and **8** and slightly lower for the electron-poor **3–6**.

The two reactions differ in the nature of the H-abstracting partner. Unlike tBuO', 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 tBuO' induces an alignment between the three atoms (O, H, and B). Hence, the influence of the *tert*-butyl substituent is minimal. In contrast, ³BP is a conjugated biradical that requires a different geometry for H transfer, which might generate more steric strain. It is interesting to consider the structurally different imidazolydinene-borane $\mathsf{DiMe-Imd-BH}_{3},^{[2e]}$ which transfers its hydrogen atom faster to ³BP (9.6×10⁸ μ^{-1} s⁻¹) than to *t*BuO[•] (2.7×10⁸ μ^{-1} s⁻¹). DiMe-Imd- BH_3 is a faster hydrogen donor than 1, likely because of the electronic differences of the carbenes: imidazolydinene-carbenes are more electron rich than triazolydinenes,^[8] so that the B-H bonds have greater hydridic character and are 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 of theory. Compared to 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⁻¹, Table 1).

Although 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 ($\pm 2.6 \text{ kcal mol}^{-1}$), it appears that electron-withdrawing groups tend to diminish the



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

B–H BDE. We thus calculated the SOMOs of **2**[•] (*N*-phenyl) and **3**[•] (*N*-pentafluorophenyl). The two orbitals are highly similar (Figure 4). The spin density on boron is slightly lower for **3**[•] (0.511 versus 0.502 for **2**[•] at the UB3LYP/6-31G* level of theory). This trend is in agreement with the Rablen model, in which 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 nitrogen atoms already contribute to the overlap with the boryl radical, and the additional donation from the substituents is negligible.

Reactivity of NHC-boryl radicals towards methyl acrylate and O_2

Because of their relevance to the photopolymerization of acrylates in the presence of air, the rate constants for the addition of NHC-boryl radicals to methyl acrylate (Scheme 1 a) and coupling with dioxygen (Scheme 1 b) were measured (Figure 5). For that purpose, we selected **3'** and **4'** as representative electron-poor NHC-boryl radicals and **8'** as representative electronrich NHC-boryl radical. The known values for **1'** and **2'** were also added for comparison. The rates of decay of the signals of the NHC-boryl radicals were measured for different quencher



Scheme 1. Reactions of NHC-boryl radicals: addition to methyl acrylate (a) and coupling with dioxygen (b).



Figure 5. Kinetics at 380 nm for **8'** in di-*tert*-butylperoxide/acetonitrile (75/ 25%); [**8**] = 0.032 μ for different [methyl acrylate] from 0 to 0.11 μ ; Inset: zoom of the rise time of **8'** in the absence of methyl acrylate.

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]	$k_{\rm add}$ (methylacrylate) [10 ⁶ m ⁻¹ s ⁻¹]	k _{add} (O ₂) [10 ⁸ м ⁻¹ s ⁻¹]
1		2 70	a =[2d]	[a]

1	1'	2.70	17 ^[2d]	>6 ^[a]
2	2'	2.85 ^[a]	6 ^[2f]	>2 ^[b]
3	3.	3.13	0.8	>5
4	4'	2.98	2.5	>5
5	8'	2.81	3.8	> 5

concentrations (see Figure 5 for the addition of **8** to methyl acrylate), and these data were processed in the usual way to give the elementary rate constants listed in Table 2.^[2e,f]

All radicals react extremely fast with oxygen, and the reactions are 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°; Table 2, entries 1 and 3). The more electron withdrawing the substituents on the NHC-borane, the less rapid the addition to methyl acrylate (compare 3° and 4°; Table 2, entries 3 and 4). Radical 8° adds faster than both 3° and 4°, but significantly slower than 1° and 2° (Table 2, entry 5). On the whole, though, all the NHC-boryl radicals considered add rapidly to the electron-poor acrylate, and are thus nucleophilic species. For comparison, the fastest imidazolydinene-boryl radical adds to methyl acrylate with a rate of $3.8 \times 10^7 \,\text{m}^{-1} \,\text{s}^{-1}$, 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 ($\chi_M = \frac{1}{2}$ (IP + EA), Table 2, column 2). Both the ionization potential (IP) and electron affinity (EA) were calculated at the UB3LYP/6-31 + G* level of theory by optimization of the relevant radicals and ions.

Radical 1' had the lowest χ value (2.70). Introduction of a phenyl substituent led to an increase in 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 addition of three methoxyl substituents to 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] Interestingly, the Mulliken electronegativity appears to be strongly related to the rate constant for addition to methyl acrylate: the lower the electronegativity, the faster the addition to methyl acrylate (Figure 6).



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

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 group has three strongly electron donating substituents. However, 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 methoxyl groups is



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Figure 7. SOMO for 8' (UB3LYP/6-31G*).

thus largely canceled, because the aryl ring is not fully conjugated, and **8**^{\cdot} behaves as a less electron rich version of **1**^{\cdot} owing to the -l effects of the oxygen atoms.

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 triazolydinene family for the polymerization part of this article.

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

We 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 under in laminated conditions, in which the formulations (monomer and photoinitiating 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 poly-



Scheme 2. NHC-borane as co-initiator in the photopolymerization of TMPTA.

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Figure 8. Radical photopolymerization profiles for different BP/co-initiator couples (1/1 wt % w/w in TMPTA as laminate). a) Without co-initiator, b) BP/ **3**, c) BP/**4**, d) BP/**7**, e) BP/**1**, f) BP/**6**, and g) BP/**8**.

chromatic light source, and the evolution of the double-bond content was followed by real-time FTIR spectroscopy ($\approx 1630 \text{ cm}^{-1}$) at room temperature.^[2f] The benchmark photopolymerization was run in the presence of BP alone (Figure 8a). It led 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, Figure 8b–g). The differences between the different NHC-boranes were not large, and the polymerizations were fast in all cases. However, the initial rates of the systems vary in the order Figure 8 c $\approx d < g < b \approx f < e$. After a short lag time, the rate for Figure 8 f was similar to that of Figure 8 b.

The inhibition observed in Figure 8 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 1) the highly efficient formation of NHC-boryl radicals by H transfer to ³BP (Table 1); 2) their high reactivity towards electron-deficient acrylates (Table 2); 3) fast quenching of oxygen by NHC-boryl radicals; and 4) fast reaction of the electrophilic NHC-boraperoxyl adduct radicals with a hydrogen atom from another, nucleophilic B–H bond, which converts NHC-boraperoxyl 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 on the reactivity of NHC-boryl radicals derived from triazolylidene-carbenes. For the compounds studied, polar effects have a weak effect on the BH 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 ³BP/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.

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