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New Boryl Radicals Derived from N-Heteroaryl Boranes: Generation and Reactivity

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Abstract: Recently, boryl radicals have been the subject of revived interest. These structures were generated by hydrogen-abstraction reactions from the corresponding boranes (i.e., from amine or phosphine boranes). However, the classical issue remains their high B—H bond-dissociation energy (BDE), thereby preventing a very efficient hydrogen-abstraction process. In the present paper, new N-heteroaryl boranes that exhibiting low B—H BDE are presented; excellent hydrogen-transfer properties have been found. Both the generation and the reactivity of the associated boryl radicals have been investigated through their direct observation in laser flash photolysis. The boryl radical interactions with double bonds, oxygen, oxidizing agent, and alkyl halides have been studied. Some selected applications of N-heteroaryl boryl radicals as new polymerization-initiating structures are proposed to evidence their high intrinsic reactivity.

Keywords: bond energy · boranes · hydrogen transfer · polymerization · radical chemistry

Introduction

Boryl radicals ($B^{\cdot}$) are usually generated from borane complexes (BoC) by means of a hydrogen-abstraction reaction (mainly with an $\mathbf{L}\rightarrow BH_3$ structure, with **L** representing a selected ligand). Much work has been carried out with **L**= amines or phosphines, and the reactivity of the associated boryls has mainly been investigated by steady-state experiments.[1] The derived amine boryl radicals are bent σ radicals with a high boron spin density.[2–3] They are relatively nucleophilic and can be used as polarity-reversal catalysts.[4–5] However, the high B—H bond-dissociation energy (BDE) of amines or phosphine boranes usually prevents their use in initiating radical chain reactions; the corresponding hydrogen-abstraction process is not efficient enough.

Recently, Rablen et al. have evidenced through a theoretical approach that the radical stability (and hence the B—H BDE) is closely related to the degree of the spin delocalization from the boron atom ($B^{\cdot}$) to the associated Lewis base,[6a–b] that is, small ligands with N, O, S, or P atoms linked to BH_3 were investigated. This seminal work has been extended recently to a larger range of borane complexes.[6c]

To overcome the B—H BDE limitation for the hydrogen-abstraction process, different experimental approaches have been very recently proposed with the design of N-heterocyclic carbene boranes (NHC-boranes).[7–9] The synthesis of N-heteroaryl boranes was also proposed.[10] Through carefully selected new substituent effects on the borane moiety, the B—H BDE were brought down to about 70–90 kcal mol^{-1} compared to 92–105 kcal mol^{-1} for amine or phosphine boranes.[7–11]

The recent revival of interest in the use of boryl radicals in organic synthesis is strongly associated to the elegant development of NHC-borane complexes.[7–9] This new family of ligated boranes has been recently used in radical reductions of xanthates and related derivatives. NHC-boranes serve as radical hydrogen-atom donors in Barton–McCombie reactions.[2,7] They are characterized by planar π-type boryl radicals.[9,11b] Indeed, due to the empty π orbital on the central carbene carbon atom, a significant spin delocali-

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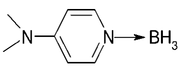
zation from the boron radical center into the NHC ligand was found.

N-Heteroaryl boranes were also proposed as compounds with low B−H BDE. Very high rate constants for the hydrogen abstraction from B−H were found.[10a] The aim of the present paper is to examine the effects of the Lewis base coordination on the boryl radical formation as well as the reactivity of the generated boryl radicals using a new set of N-heteroaryl boranes. Because the kinetic data associated with the boryl radicals is rather scarce,[11] this work will also give the opportunity to collect kinetic information that has been unknown up to now.



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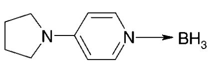

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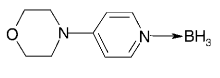

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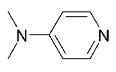

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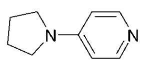

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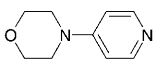

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The generation of the boryl radicals, their transient absorption spectra, their interaction with double bonds, oxygen, oxidizing agent, and alkyl halides will be examined by laser flash photolysis (LFP) experiments. Molecular orbital (MO) calculations and electron spin resonance (ESR) spin-trapping experiments will bring complementary insights to the involved mechanisms. The polymerization-initiating ability of N-heteroaryl boranes in thermal or photochemical processes will also be checked as a proof of their high hydrogen lability and the high reactivity of the associated boryl radicals.

Results and Discussion

Formation of the N-heteroaryl-borane radicals

Laser flash photolysis (LFP): For the generation of the boryl radicals, an approach based on a hydrogen-abstraction reaction by the *tert*-butoxyl radical *t*Bu-O˙ was selected [Eq. (1)]. According to Equation (1), the interaction of the *tert*-butoxyl radical with different BoCs yields transients, the intense absorption of which can be directly followed at $\lambda >$ 300 nm (Figure 1). The corresponding rise time allows for easy access to the *t*Bu-O˙/BoC interaction rate constants k_H. For **1**–**3**, the hydrogen-abstraction reaction can occur from B−H or α(C−H), thus leading to boryl or aminoalkyl radicals, respectively. The calculated absorption spectra for the transients are in agreement with that of boryl radicals (Figure 1, Table 1). For aminoalkyl radicals derived from **1**–**3** by α(C−H) abstraction, the maximum absorption is expected at about 450 nm, which would be in agreement with the spectra obtained for the aminoalkyl derived from **1'**–**3'** (Table 1, Figure 2). Independently, the radicals formed by Equation (1) were also characterized by the ESR spin-trapping technique (ESR-ST) using phenyl *N-tert*-butyl nitrone (PBN). A third hyperfine splitting (HFS) constant a_B due to the boron nuclei must be included to reproduce the experimental spectra (Figure 3A). The a_B found here are in good agreement with previous results on other boryls: $3.5 < a_B <$ 4.7 G[1c,g] ($a_B = 3.7$ and $a_B = 3.8$ G for the boryl radicals derived from **1** and **2**, respectively). In agreement with LFP data, this demonstrates that the hydrogen abstraction preferentially occurs on the borane moiety because aminoalkyl radicals are not observed in ESR-ST. A comparison of the

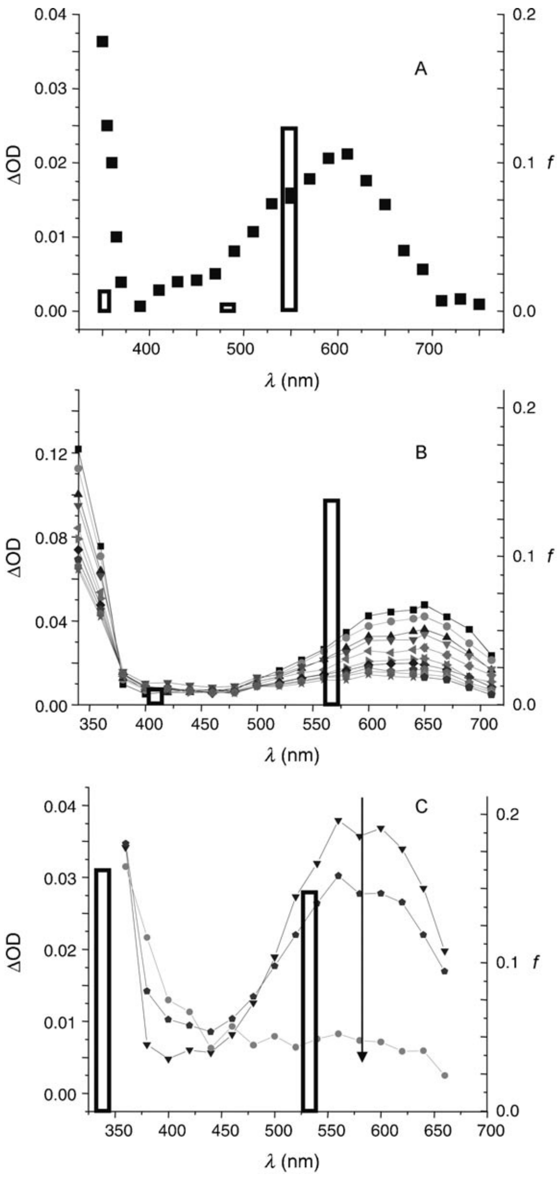


Figure 1. Transient absorption spectra of the boryl radicals derived from A) **1**; B) **2**, and C) **3** in acetonitrile/di-*tert*-butylperoxide. The rise of the boryl radical occurs within 500 ns: A) $t = 0.5$ µs; B) recorded at different times after the laser excitation from 0.5 to 7 µs by steps of 0.77 µs; C) recorded at different times after laser excitation: 0.5, 1.5, and 16 µs, respectively. The calculated absorption spectra are also given (vertical bars) together with the oscillator strength (λ).

Table 1. Rate constants (k_H) that characterize the formation of the boryl radicals at RT; oxidation potential E_{ox} and bond-dissociation energy (BDE) of the N-heteroaryl-boranes. An isodesmic reaction was used in [10a]. Experimental and calculated absorption properties of the N-heteroaryl-boranes radicals.

	E_{ox} [V]	BDE (B–H) [kcal mol^{-1}]	k_H (tBu–O$^\bullet$) [10^7 M^{-1} s^{-1}]	λ_{max} [nm]	
				Exptl	Calcd
1	0.55	81.3 (96.8[a])	28	620	545 (432[b])
2	0.44	82.2 (94.8[a])	31	650	565 (442[b])
3	0.57	81.9 (95.4[a])	22	575	535 (445[b])
1′		(95.4[a])	4.7	460	412[b]
2′		(94.5[a])	6.7	480	404[b]
3′		(95.2[a])	2.1	460	398[b]

[a] α(C–H) bond-dissociation energy for the formation of the aminoalkyl radicals. For the hydrogen abstraction from other amines, quite similar rate constants were found in ref. [14b]. [b] λ_{max} for the aminoalkyl radicals derived from **1**–**3** or **1′**–**3′**.

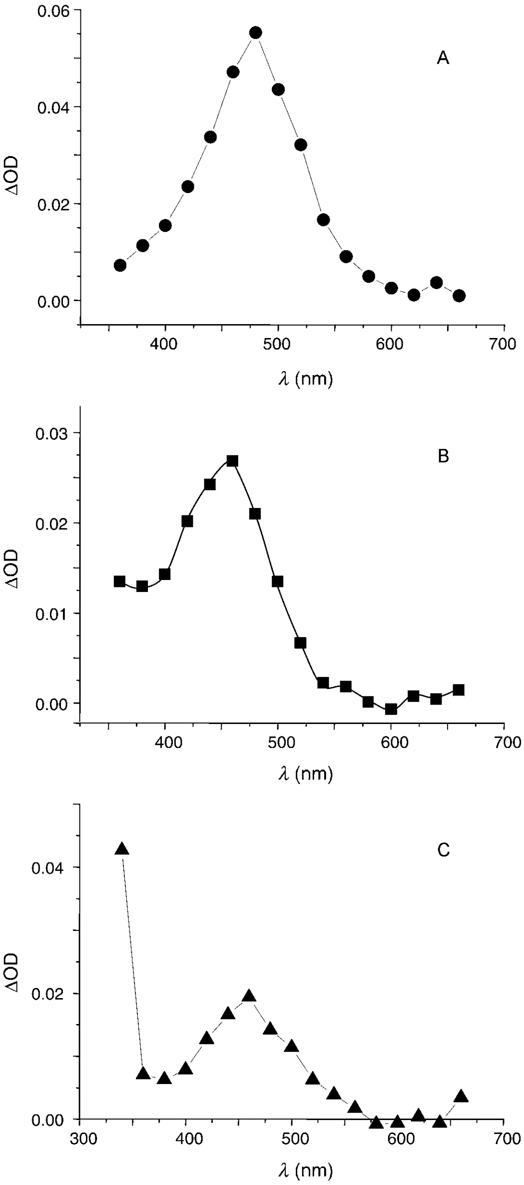


Figure 2. Transient absorption spectra of the aminoalkyl radicals derived from A) **1′**, B) **2′**, and C) **3′** in acetonitrile/di-*tert*-butylperoxide (at t = 0.5 μs; the rise of the aminoalkyl radical occurs within 500 ns).

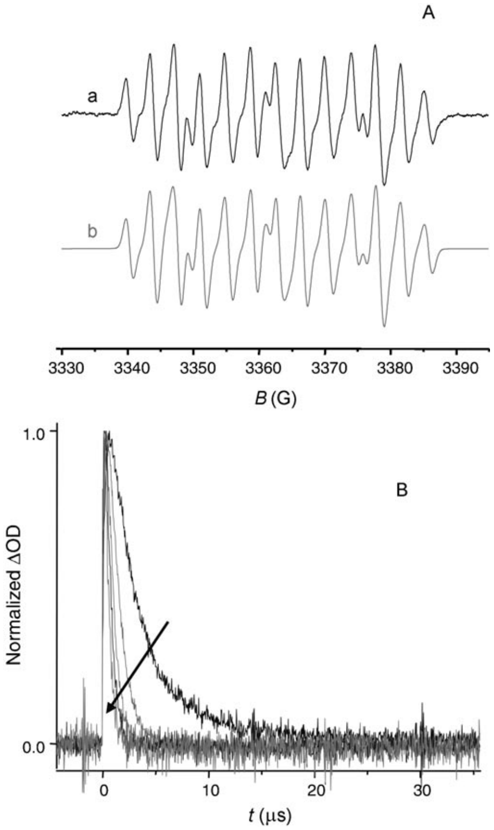


Figure 3. A) ESR spectrum observed in spin trapping experiments for the adduct of the N-heteroaryl-borane radical derived from **2** using PBN in acetonitrile/di-*tert*-butylperoxide (a minor product ascribed to a carbon-centered radical is also observed; signal < 10%). B) Decay traces (recorded at 600 nm) of the N-heteroaryl-borane radical derived from **2** in the presence of different concentrations of $CHCl_3$.

rate constants obtained for N-heteroaryl boranes **1**–**3** versus the corresponding aminopyridine derivatives **1′**–**3′** can be also useful for a better understanding of this selectivity for the hydrogen-abstraction process (Table 1). The hydrogen-abstraction rate constants are noticeably higher for N-heteroaryl boranes, that is, 0.21×10^8 versus 2.2×10^8 M^{-1} s^{-1} for **3′** and **3**, respectively. This can be ascribed to higher α(C–H) BDE compared to (B–H) BDE. The (B–H) BDE is lower than the α(C–H) BDE by about 15 kcal mol^{-1}, thereby demonstrating that the radical hydrogen abstraction occurs mainly from (B–H) in Equation (1) (see Table 1; for **1**: 81.3 vs. 96.8 kcal mol^{-1} for (B–H) and α(C–H); for **2**: 82.2 vs. 95.0 kcal mol^{-1} for B–H and α(C–H); for **3**: 81.9 vs. 95.4 kcal mol^{-1} for B–H and α(C–H), respectively). The α-(C–H) BDEs are found quite similar for **1**–**3** and **1′**–**3′**, thus demonstrating a weak influence of the borane substitution on this latter parameter.

$$t\text{Bu–O}^\bullet + \mathbf{L} \rightarrow \text{BH}_3 \rightarrow t\text{Bu–OH} + \mathbf{L} \rightarrow \text{BH}_2^\bullet \qquad (1)$$

Structure of the N-heteroaryl-borane radicals: Aliphatic amine boranes have relatively strong B–H bonds (for $Et_3N{\cdot}BH_3$, the bond-dissociation energy is

101 kcal mol^{-1}),[6,10b] and the derived amine boryl radicals are bent σ radicals with a high spin density on boron.[2–3]

For the recently proposed NHC-boranes, weaker B−H bonds are found (around 88 kcal mol^{-1}).[8a] Due to the empty π orbital on the central carbene carbon atom of NHC-boryl radicals, a significant spin delocalization from the boron atom into the NHC ligand was noted.[8a,b,9] Such radicals are planar π-type radicals similar to a benzyl radical. The spin densities at boron were calculated at 0.4–0.5 depending on the NHC structure.[9,11b] For N-heteroaryl-borane radicals, a similar behavior is found with planar π-type radicals, that is, in Figure 4, a significant spin delocalization from the boron atom into the N-heteroaryl ligand is found for the singly occupied molecular orbital (SOMO). The spin densities are also quite similar to NHC-boryls, namely, 0.35, 0.37, and 0.32 for **1**, **2**, and **3**, respectively. Interestingly, the pyridine substituent at the 4-position significantly affects the spin density.

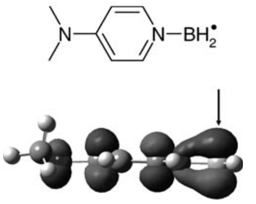


Figure 4. The SOMO characterizing the boryl radical derived from **1**. The boron atom is indicated by an arrow.

Reactivity of the N-heteroaryl-borane radicals: The direct observation of boryl radicals in laser flash photolysis experiments allows convenient access to their reactivity for important processes in small-molecule radical chemistry. Analysis of the time dependence of the spectra provided rate constants for their onward reactions with alkenes, oxygen, alkyl halides, and diphenyliodonium hexafluorophosphate (Figure 3B). The results are gathered in Table 2. As very high rate constants are found for the boryl radical/O_2 interactions (Table 2), the subsequent kinetic experiments with other molecules were carried out under argon.

Reactivity towards double bonds: Concerning the addition to methylacrylate (MA), the boryl radicals derived from **1**–**3** exhibit high addition rate constants (k_{add}). Interestingly, the rate constant of interaction with a carbonyl group (acetone) is found to be $<5\times10^5\,\text{M}^{-1}\text{s}^{-1}$ for the radical derived from **2**. This probably indicates that the reaction with MA corresponds to the addition onto the double bond. For the radical derived from **2**, k_{add} is close ($1.4\times10^8\,\text{M}^{-1}\text{s}^{-1}$) to that found previously for the triethylamine boryl radical ($1.3\times10^8\,\text{M}^{-1}\text{s}^{-1}$).[11a] This latter species was characterized by the highest reported addition rate constant for boryl radicals. The boryl radicals derived from **1**–**3** are also characterized by much higher k_{add} than the aminoalkyl radicals derived from **1′**–**3′** (by a factor of at least 100). All these results highlight the very high reactivity of the new proposed species towards addition processes. For addition to an electron-rich alkene (i.e., ethyl vinyl ether (EVE)), the rate constants are below $5\times10^5\,\text{M}^{-1}\text{s}^{-1}$ for all radicals. The combination of a fast addition to an electron-poor alkene (i.e., MA) and a slow addition to an electron-rich alkene (EVE) suggests that N-heteroaryl-borane radicals may be nucleophilic. Interestingly, for the addition to MA, the reactivity decreases along the series **2**>**1**≈**3**. This is in full agreement with the lower ionization potential determined for the boryl radical of **2** (Table 2). The calculated reaction exothermicity for the addition to MA was quite similar for the investigated heteroaryl-borane radicals, which is in agreement with a low influence of the enthalpy factor to explain the difference of reactivity in the **1**–**3** series (−59, −62, −60 kJ mol^{-1} for the addition to MA of the radicals derived from **1**, **2**, and **3**, respectively at the UB3LYP/6-31+G* level).

Oxidation of boryl radicals with $Ph_2I^+PF_6^-$: Because boryl radicals are characterized by low ionization potentials, their oxidation by iodonium salts (i.e., Ph_2I^+), which exhibit low reduction potentials (around −0.2 V) and are often used to oxidize radicals,[12] is expected. Indeed, the rate constants for the chemical oxidation of N-heteroaryl-borane radicals with $Ph_2I^+PF_6^-$ are very high and close to the diffusion limit ($k\approx10^9\,\text{M}^{-1}\text{s}^{-1}$; Table 2). This is also in line with the nucleophilic character of these radicals.

Reactivity towards alkyl halides: The study of the reactions of N-heteroaryl-borane radicals with alkyl halides can be important for a better understanding of their reactivity. The rate constants (k_{Cl} or k_I) for reactions with $CHCl_3$, CH_2Cl_2, or C_3H_7I are gathered in Table 2. The reactivity with $CHCl_3$ or C_3H_7I decreased in

Table 2. Interaction rate constants of the boryl radicals derived from **1**–**3** or aminoalkyl radicals from **1′**–**3′** with various additives at RT in acetonitrile/di-*tert*-butylperoxide solvent (MA and EVE stand for methylacrylate and ethyl vinyl ether, respectively).

	k_{add} ($R^{\bullet}$/MA) [$10^7\,\text{M}^{-1}\text{s}^{-1}$]	k_{add} ($R^{\bullet}$/EVE) [$10^5\,\text{M}^{-1}\text{s}^{-1}$]	k'_{add} ($R^{\bullet}/O_2$) [$10^8\,\text{M}^{-1}\text{s}^{-1}$]	k_{Cl} ($R^{\bullet}/CHCl_3$)[a] [$10^6\,\text{M}^{-1}\text{s}^{-1}$]	k_I ($R^{\bullet}/C_3H_7I$) [$10^7\,\text{M}^{-1}\text{s}^{-1}$]	k_{ox} ($R^{\bullet}/Ph_2I^+$) [$10^9\,\text{M}^{-1}\text{s}^{-1}$]
1	3.5	<1	>7	1.5	3.2	2.5 (4.9[b])
2	14		>7	3.8	5.5	2.0 (4.7[b])
3	2.4		>7	0.4	0.3	0.5 (4.9[b])
1′	<0.05		>7			
2′	0.14		>7	<0.05	<0.005	
3′	0.15		>7			

[a] For CH_2Cl_2, rate constants of $<5\times10^5\,\text{M}^{-1}\text{s}^{-1}$ are found for **1**–**3**. [b] Ionization potential at the UB3LYP/6-31+G* level in eV.

the order **2** > **1** > **3**; a similar order was found previously for the addition to MA (see above). The high reactivity of the radical derived from **2** is consistent with the addition properties shown above. For the reaction with CH_2Cl_2, quite low rate constants are found ($k_{Cl} < 5\times10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, i.e., they do not react fast enough to be measured with our LFP setup). The charge transfer from the boryl radicals to $CHCl_3$ might explain in part their much higher reactivity towards $CHCl_3$ compared to CH_2Cl_2. Significant polar effect can be involved. The process probably corresponds to a halogen-abstraction reaction as propyl radicals are observed by ESR-ST in the photolysis of di-*tert*-butylperoxide in the presence of **2** and C_3H_7I (Figure S1 in the Supporting Information).

N-Heteroaryl boranes as efficient coinitiators: To highlight the high reactivity of the boryl radicals proposed here, their initiating ability in thermally and photochemically induced polymerization were also investigated.

N-Heteroaryl boranes in photoinitiating systems: The free-radical polymerization (FRP) kinetics were examined by measuring the monomer consumption (here trimethylolpropane triacrylate, or TMPTA) in photoinitiated experiments using benzophenone (BP) as the photoinitiator in both the absence and presence of N-heteroaryl-borane coinitiators. The polymerization efficiencies of these type II systems were studied by measuring the conversion of TMPTA versus time (Figure 5).

The photopolymerization can be induced by BP alone (Figure 5A, curve a) but this is not a very efficient process. An inhibition time of 20 s was found. In that case, the initiation is ascribed to an abstraction of a labile hydrogen from the monomer (i.e., TMPTA) by the benzophenone triplet state (i.e., ^{3}BP). In contrast, addition of the N-heteroaryl-borane coinitiators **1**–**3** (1 % w/w) significantly improved the rate of polymerization (Figure 5A, curves b, c, and d; no inhibition time was observed). This suggests that initiating radicals were generated from hydrogen abstraction by ^{3}BP, which behaves like an alkoxy radical. Since the concomitantly generated ketyl radicals are not efficient polymerization-initiating structures, the boryl radicals are assumed to be the main initiating structures for acrylate polymerization. This is in good agreement with their high addition rate constants to an MA acrylate unit (Table 2). In laminate, the most promising coinitiator is **2**, with a polymerization rate higher than **1** or **3**. At $t = 5$ s, the conversions were 18 % for BP/**2** and only about 7 % for BP/**1** and BP/**3**. Albeit slightly lower, the polymerization rates with **1**–**3** are quite close to that noted when using BP/ethyl dimethylaminobenzoate (EDB); EDB is a well-known reference amine coinitiator.[12d]

Any FRP process is usually strongly inhibited by O_2. This is related to the conversion of both initiating and propagat-

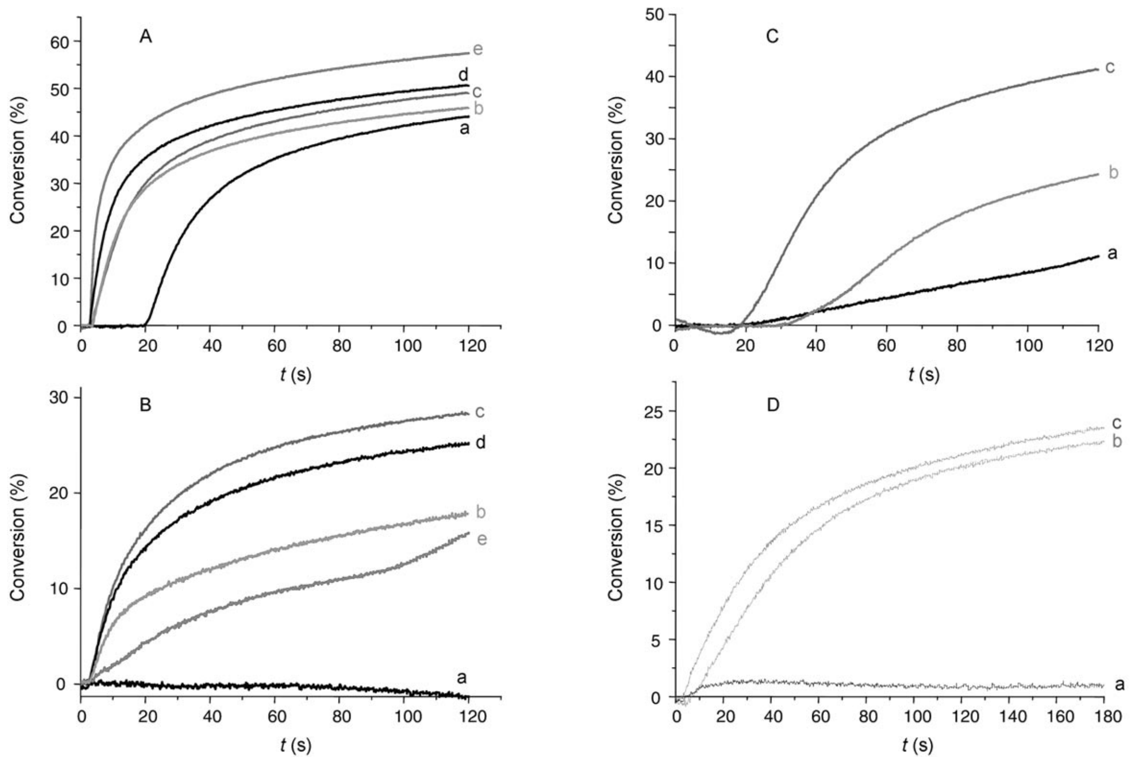


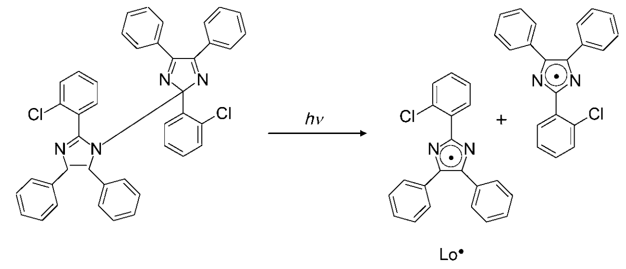
Figure 5. A) Radical photopolymerization ability of various BP/coinitiator couples (1 % w/w; in TMPTA, in laminate; irradiation Xe–Hg lamp filtered for $\lambda > 300$ nm): e) EDB, b) **1**, d) **2**, c) **3**, and a) without coinitiator. B) Radical photopolymerization ability of various BP/coinitiator couples (1 % w/w; in TMPTA, under air): e) EDB, b) **1**, d) **2**, c) **3**, and a) without coinitiator. C) Radical photopolymerization ability of various *o*-Cl-HABI/coinitiator couples (1 % w/w; in TMPTA, under air): c) **2**, a) without coinitiator, and b) without *o*-Cl-HABI. D) Radical photopolymerization ability of various CQ/coinitiator couples (3 % w/w; in TMPTA, under air; diode laser irradiation 473 nm): b) **1**, c) **3**, and a) without coinitiator.

ing radicals to stable peroxyls, which no longer participate in the propagation process. The development of new systems for FRP in aerated conditions is actually very important. In Figure 5B, BP/N-heteroaryl boranes are found to be much better initiating systems than BP/EDB (using BP or N-heteroaryl borane alone, no polymerization process is observed under air in the selected conditions). As found previously for other boranes ($\mathbf{L}\rightarrow BH_3$; $\mathbf{L}$ = amine or phosphine), this can be related to the ability of N-heteroaryl boranes to convert peroxyls into new initiating boryl radicals [Eq. (2)]:[10]

$$R{-}OO^{\bullet} + \mathbf{L} \rightarrow BH_3 \rightarrow R{-}OOH + \mathbf{L} \rightarrow BH_2^{\bullet} \qquad (2)$$

Equation (2) explains the better ability of **1**–**3** compared to EDB to overcome the oxygen inhibition in FRP. Using camphorquinone (CQ) in visible-light photoinitiating systems under air (diode laser irradiation at 473 nm), efficient processes are only observed with CQ/N-heteroaryl boranes, that is, no polymerization reaction is observed with CQ alone (Figure 5D). This is also in agreement with the hydrogen-abstraction reaction between ^{3}CQ and the boranes that results in the formation of initiating radicals. These results can be worthwhile for selected irradiation conditions that require visible light.

Interestingly, it is found that lophyl radicals (Lo$^{\bullet}$) generated by photolysis of 2,2′-di(*ortho*-chlorophenyl)-4,4′,5,5′-tetraphenylbiimidazole (*o*-Cl-HABI) (Scheme 1)[10a] can abstract hydrogen atoms from N-heteroaryl boranes [Eq. (3)], thus leading to quite efficient *o*-Cl-HABI/N-heteroaryl-borane-initiating systems (Figure 5C).



Scheme 1. Lo$^{\bullet}$ radicals generated from the photolysis of *o*-Cl-HABI.

$$Lo^{\bullet} + \mathbf{L} \rightarrow BH_3 \rightarrow Lo{-}H + \mathbf{L} \rightarrow BH_2^{\bullet} \qquad (3)$$

N-Heteroaryl boranes in thermal initiating systems: As expected from the above results, N-heteroaryl boranes/Ph_2I^+ have been found to be efficient polymerization-initiating systems for the FRP of TMPTA even at RT and under air (Figure 6A). The polymerization processes are highly exothermic. For N-heteroaryl boranes, the reactivity decreased along the order **2**>**1**>**3**. The same order is found for the oxidation potential (E_{ox}; Table 1) of the N-heteroaryl boranes investigated here, thereby providing evidence that a redox process is probably involved. In ESR-ST experiments, Ph$^{\bullet}$ are clearly observed (a_N = 14.6 G; a_H = 2.6 G; Figure 6B) during the organoborane/Ph_2I^+ interactions, which is in full agreement with a reduction of the iodonium salt. The overall mechanism is depicted in Scheme 2. As already known, Ph$^{\bullet}$ is an initiating radical.[13] It can also abstract a hydrogen atom from a N-heteroaryl borane with the concomitant formation of a boryl radical. The boryl is then oxidized by Ph_2I^+, thereby leading to a chain process with a reformation of Ph$^{\bullet}$. In polymerization under air, the conversion of peroxyls into boryl radicals [Eq. (2)] must be also taken into account to explain the observed high efficiency.

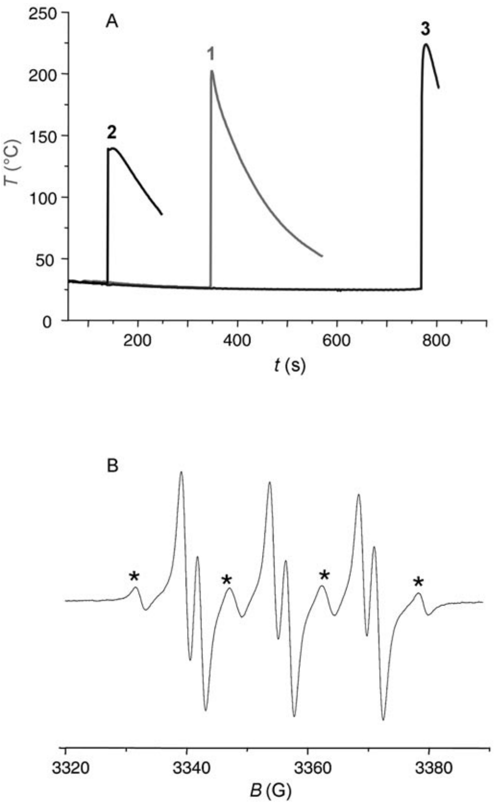
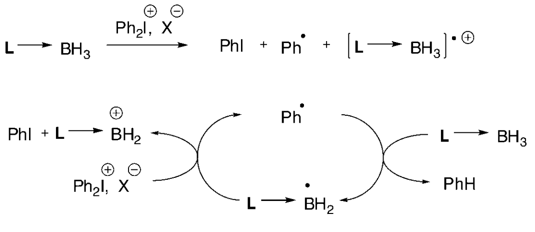


Figure 6. A) Sample temperature versus time for the polymerization of TMPTA initiated by the various N-heteroaryl borane/Ph_2I^+ couples (1% w/w; under air) at RT. B) ESR spectrum observed in spin0trapping experiments (using PBN) for the adduct that results from the **1**/Ph_2I^+ interaction in acetonitrile (the stars indicated an unidentified minor adduct).



Scheme 2. N-Heteroaryl boranes in thermal initiating systems.

Conclusion

In the present paper, the formation, the structure, and the reactivity of an interesting class of radicals derived from N-heteroaryl boranes has been investigated. High rate constants of radical formation through hydrogen abstraction are found to be in agreement with the low B–H BDE of the starting compounds.[21] The nucleophilic character of the radicals is associated with a high addition rate constant to electron-deficient alkenes (such as acrylates). Some selected examples of applications of N-heteroaryl-borane radicals as polymerization-initiating structures are provided. Their use in organic synthesis will be presented in forthcoming studies as a broader scope of application can be expected.[22] This can also open perspectives on other types of radicals.

Experimental Section

The investigated borane complexes: The borane complexes **1**–**3** were synthesized from well-known procedures (the synthesis procedures are given in the Supporting Information); the corresponding aminopyridines (**1′**–**3′**) were also investigated for comparison. Benzophenone (BP) or camphorquinone (CQ) were used as model photoinitiators (Aldrich). Ethyl dimethylaminobenzoate (EDB; Esacure EDB from Lamberti) was chosen as a reference amine coinitiator. 2,2′-Di(*ortho*-chlorophenyl)-4,4′,5,5′-tetraphenylbiimidazole (*o*-Cl-HABI) was obtained from Tokyo Chemical Industry (TCI-Europe). Methylacrylate (MA), ethyl vinyl ether (EVE), diphenyl iodonium hexafluorophosphate (Ph_2I^+), as well as the different alkyl halides, were obtained from Aldrich.

Laser flash photolysis experiments: Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd:YAG laser ($\lambda_{exc}=355$ nm, 9 ns pulses; energy reduced down to 10 mJ, from Powerlite 9010 Continuum) and an analyzing system that consisted of a pulsed xenon lamp, a monochromator, a fast photomultiplier, and a transient digitizer.[14] tBu–O$^\bullet$ are easily generated at 355 nm by the direct cleavage of di-*tert*-butylperoxide.[14b]

ESR spin-trapping experiments: This ESR technique (ESR-ST) is recognized as a powerful means for the identification of radical centers.[15] The radicals were generated under the polychromatic light exposure of a Xe–Hg lamp (Hamamatsu, L8252, 150 W) of BoCs in di-*tert*-butyl peroxide/acetonitrile (50:50); 6 mm quartz cylindrical ESR tubes were used and the samples were argon purged 15 min prior to measurements. The irradiation was carried out inside the cavity (TE102) of the spectrometer through a filter to cut off the light below 310 nm. The generated radicals were trapped by phenyl *N-tert*-butyl nitrone (PBN). The ESR spectra simulations were carried out with WINSIM software.[16]

Redox potentials and DFT calculations:[17] See the Supporting Information.

Photopolymerization experiments: For film-polymerization experiments, a given photoinitiator (PI) was dissolved into a bulk formulation based on trimethylolpropane triacrylate (TMPTA from Cytec).[18] The laminated films (20 μm thick) were deposited on a BaF_2 pellet and irradiated with polychromatic light (Xe–Hg lamp, Hamamatsu, L8252, 150 W). The evolution of the double-bond content was followed by real-time FTIR spectroscopy (Nexus 870, Nicolet) at RT. These experiments were carried out both in laminated and under air conditions.[19] A weak stable turbidity was noted in TMPTA polymerization experiments.

Thermal polymerization experiments: The polymerization was carried out in a pillbox for a sample of 1 g. The progress of the exothermic polymerization was followed by monitoring the sample temperature using a thermocouple connected to a DaqPro-5300 (resolution 0.1 °C) instrument. A magnetic stirrer was in contact with the pillbox to ensure a good homogeneity of the sample. The addition of the organoboranes into the formulation corresponded to time $t=0$ s. As most polymerization reactions rapidly take place with the release of a large amount of heat, it has been shown[20] that the increase of the temperature is directly proportional to the monomer conversion. However, as the setup used here is not adiabatic, the relationship between the conversion and the temperature is only valid for the first steps of the polymerization process.

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