EPR Studies on the Addition of Ligated Boryl Radicals to Carbonyl Compounds.

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ABSTRACT. The boron-centred radicals derived from alkenyl NHC-boranes bearing ester substituents were recently found to ring close in *5-endo* mode by addition to the oxygen atoms of the ester substituents. The inference from this was that NHC-boryl radicals might add intermolecularly to carbonyl-containing substrates. Several different NHC-boryl radicals were generated by H-atom abstraction from NHC-ligated trihydroborates. EPR spectroscopy proved that these did indeed add to the oxygen atoms of diarylketones with production of the corresponding bora-ketyl radicals. The same unusual regioselectivity of addition was observed with monoarylketones, but no bora-ketyls were observed with dialkylketones. Similarly, no bora-ketyl adduct radicals were observed with esters; even esters of benzoic acid. EPR spectroscopic evidence suggested that NHC-boryl radicals also added to the O-atoms of aromatic

aldehydes. Amine-boryl and phosphine-boryl radicals were also observed to add to the O-atom of benzophenone with production of the corresponding ketyl radicals.

INTRODUCTION

The chemistry of N-heterocyclic carbene boryl radicals (hereafter NHC-boryl radicals) is proving to be different and diverse.[1] Typically NHC-boryl radicals have π-configurations with most spin density at their B-atoms but accompanied by some spin delocalization into their NHC-rings.[2] They readily undergo self-termination, abstract halogen atoms, and add to C=C bonds.[3] Their reactivity is modulated by steric shielding from substituents on the NHC rings and by the Lewis base strength of these heterocycles.[4]

There are two available sites for a radical $R_nX^\bullet$ (**1**) to add to a carbonyl C=O bond (Scheme 1). In mode (c) addition takes place at the C-atom with production of an O-centered alkoxyl radical **2**. The alternative mode (o) entails addition to the O-atom and generates C-centered ketyl radical **3**.

Scheme 1. Alternative Modes for Radical Additions to Carbonyl Compounds
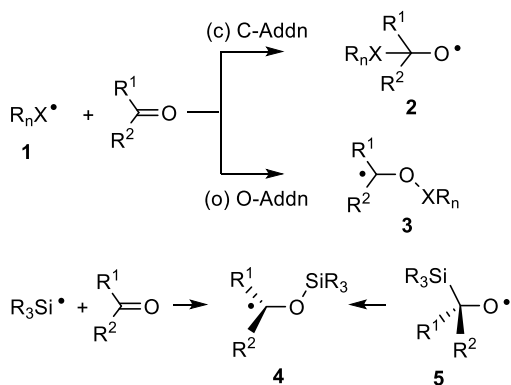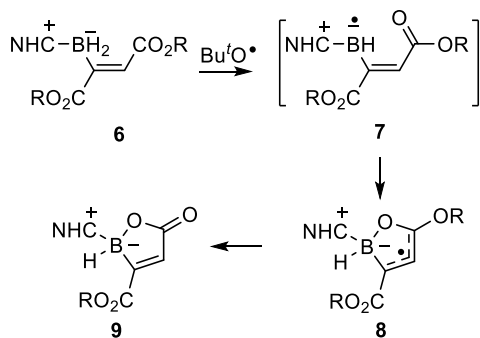
Experimental studies of the regioselectivity and kinetics of additions of C-centered radicals ($R_nC^\bullet$) indicate that mode (c) addition is strongly preferred.[5] Computational studies are in agreement with this.[6] The activation barrier of mode (o) addition was computed to be higher typically by about 3 kcal/mol.[6c] The alkoxyl radicals **2** formed from mode (c) additions to carbonyl compounds are important in combustion and atmospheric chemistry. The main applications of the reaction in preparative chemistry are the elegant Beckwith-Dowd ring expansions[7] that take place with organo-halide-[8] -selenide-[9] and -cobalamin-cycloalkanone[10] precursors and the analogous chain extension process.[11]

The alternative mode (o) addition is comparatively rare and has mainly been observed for radicals centered on elements that are less electronegative than carbon. For example, organosilyl radicals preferentially add to the O-atoms of aldehydes, ketones and even carboxylic acids.[12] The product silyloxyalkyl radicals **4** have been observed by EPR spectroscopy.[13] The hydrosilylation of carbonyl compounds with silicon hydrides has been exploited for the preparation of silyl ethers.[14] It has even been found that trialkylsilyl groups in α-trialkylsilylalkoxyl radicals **5** undergo rapid intramolecular 1,2-migration to trialkylsilyloxyalkyl radicals **4** in the radical Brook rearrangement.[15] Organostannyl and organogermyl radicals also preferentially add in mode (o) to give ketyl type radicals **3**[13c] and this reaction has been exploited synthetically with cyclopropyl ketone reactants.[16]

We recently investigated H-atom abstraction by *t*-butoxyl radicals from NHC-alkenylboranes **6** (Scheme 2). We expected to generate NHC-ligated boraallyl radicals **7**, but EPR spectroscopy demonstrated that 1,2-oxaborole radicals **8** were formed instead.[17] Furthermore, preparative experiments enabled ring closed NHC-boralactones **9** to be isolated.

Scheme 2. *5-Endo* Ring Closure of NHC-boryl Radicals onto Ester Groups.

NHC⁺–B⁻H₂–CO₂R (RO₂C) **6** → [NHC⁺–B•H ... O=C–OR (RO₂C)] **7** → (NHC⁺, B⁻, H, O, OR, RO₂C) **8** → (NHC⁺, B⁻, H, O, O, RO₂C) **9**

$$\text{6} \xrightarrow{\text{Bu}^t\text{O}\bullet} \text{7} \longrightarrow \text{8} \longrightarrow \text{9}$$

It was evident that the NHC-ligated boryl radicals **7** rapidly underwent *5-endo* ring closure onto the O-atom of the terminal ester substituent in what was the intramolecular equivalent of mode (o) addition to carbonyls. These unusual ring closures suggested that intermolecular addition of NHC-ligated boryl radicals to carbonyl compounds in mode (o) might be observable. A key factor in the success of the *5-endo*-cyclizations was the allylic resonance stabilization of the 1,2-oxaborole radicals **8**. It seemed probable that resonance stabilization would also be necessary in the intermolecular version. We undertook an investigation, mainly by EPR spectroscopy, to test radical-mediated reactions of NHC-boranes with various carbonyl-containing substrates. Addition was indeed found to take place regiospecifically in mode (o). We also mapped out the types of substituents on the carbonyl groups that were needed to facilitate this reaction.

RESULTS AND DISCUSSION

NHC-boryl radicals can be conveniently generated by H-atom abstraction from an NHC-ligated trihydroborates by photochemically produced *tert*-butoxyl radicals.[2] The set of NHC-boranes selected for this study (Chart 1) contained the archetype, sterically unhindered, dimethyl compound **10a** and the sterically hindered analogue **10c** with dipp substituents on its imidazolium ring. The parent **10a** is sparingly soluble in hydrocarbon solvents so the much more soluble (3-butyl-1-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate **10b** was also selected.[18] The dihydro-5*H*-pyrrolo[1,2,4]triazolium compound **11** was chosen as having an NHC with a

significantly different Lewis basicity (for **11** the NHC-H has $pK_a = 16.5$; for **10a** the NHC-H has

$pK_a = 23.8$).[19]   The NHC-ligated trihydroborates **10a-10c** were prepared as described

previously.[1b,d,18]

Chart 1. Selected NHC-ligated Trihydroborates
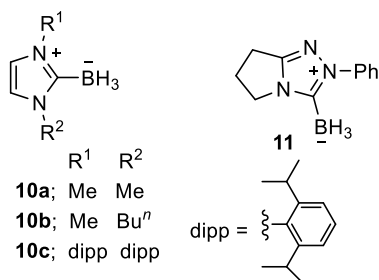
Additions of NHC-boryl Radicals to Diarylketones

In initial experiments the NHC-BH$_3$ (ca. 0.1 mmol) was dissolved or suspended in *tert*-

butylbenzene (0.5 mL) containing ca. 1 equiv of benzophenone and di-*tert*-butyl peroxide

(DTBP, 0.02 mL). The mixture was sonicated and an aliquot (0.02 mL) was placed in a quartz

tube, deaerated by bubbling N$_2$ for 10 min and then irradiated with UV in the resonant cavity of a

9 GHz EPR spectrometer. Spectra were recorded during photolysis at temperatures in the range

240 to 300 K. Good quality but complex EPR spectra were obtained from samples containing

benzophenone with each of **10a**, **10b** and **10c** (see figure 1 (a, a') and Supporting Information

figures S1 and S2). These spectra all showed hyperfine splitting (hfs) from ^{11}B atoms together

with complex patterns from coupling of the unpaired electron (upe) with H-atoms from aryl rings

and the (B)H$_2$ groups (see Table 1). Comparison with literature data for the ketyl radicals

MeOC$^\bullet$Ph$_2$ [$a(4H^o) = 3.3$, $a(4H^m) = 1.3$, $a(2H^p) = 3.7$, $a(CH_3) = 0.2$ G at 294K][20] and HOC$^\bullet$Ph$_2$ [g

$= 2.0030$, $a(4H^o) = 3.2$, $a(4H^m) = 1.3$, $a(2H^p) = 3.6$, $a(H) = 2.8$ G at 298 K][21] signalled that these

were ketyl radicals **16a-c** (Table 1).

Figure 1. 9.5 GHz EPR Spectra from UV Irradiation of NHC-boranes, Ketones and DTBP in PhBu^t Solution.
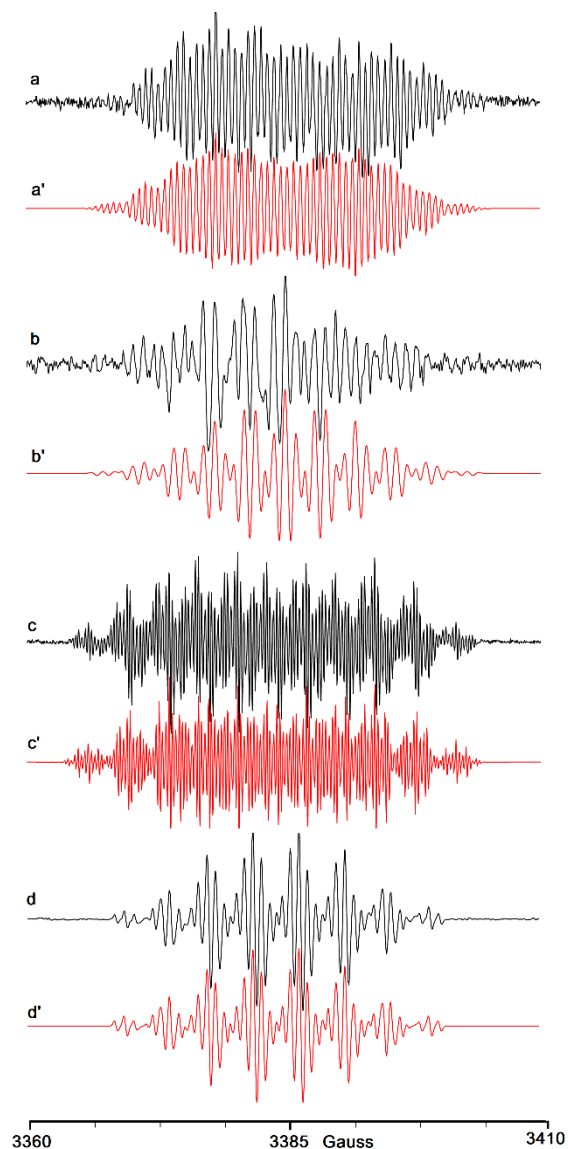
(a) Spectrum of radical **16b** from BnMeNHC-BH$_3$ (**10b**) and benzophenone at 260 K; (a') corresponding simulation; parameters in Table 1.

(b) 2nd Derivative spectrum of radical **17b** from BnMeNHC-BH$_3$ (**10b**) and fluorenone (**13**) at 260 K; (b') corresponding simulation; parameters in Table 1.
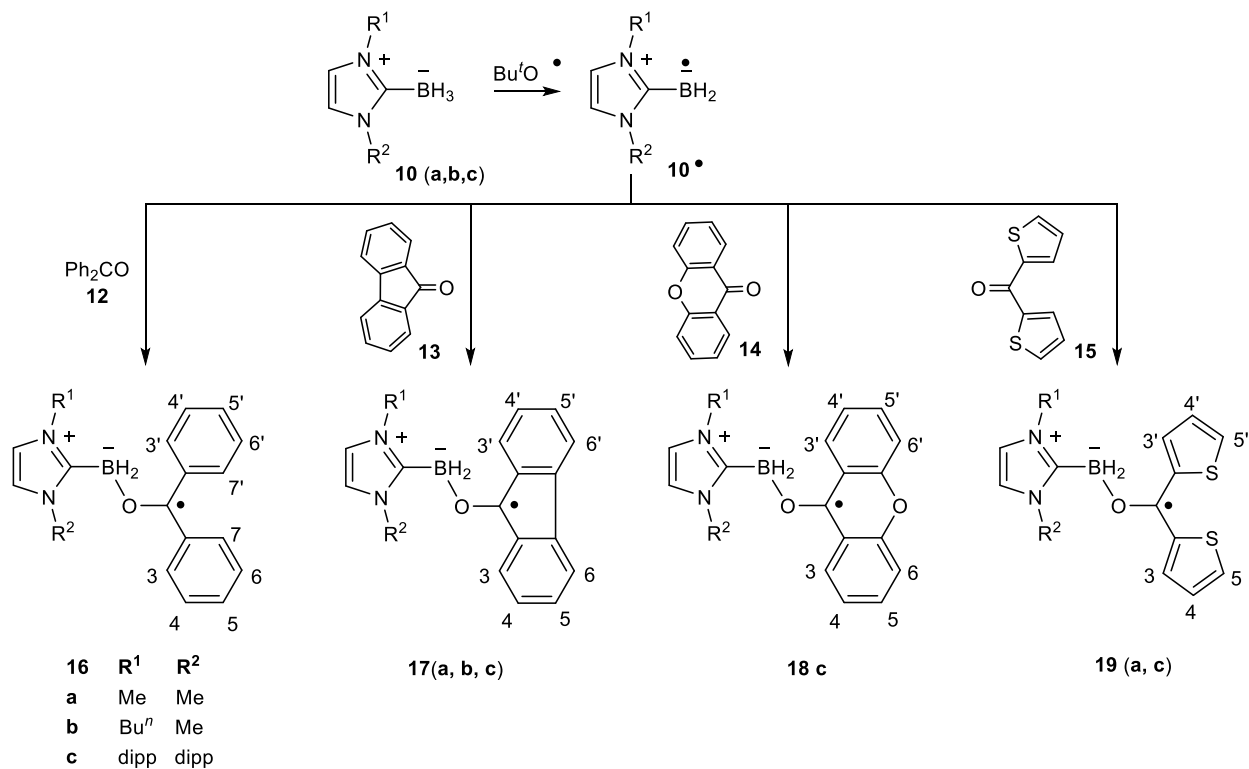
(c) Spectrum of radical **18c** from di-dippNHC-BH$_3$ (**10c**) and xanthone (**14**) at 280 K; (c') corresponding computer simulation; parameters in Table 1.

(d) Spectrum of radical **19c** from di-dippNHC-BH$_3$ (**10c**) and dithienylmethanone **15** at 280 K; (d') corresponding computer simulation; parameters in Table 1.

Similar photolysis experiments were carried out with fluorenone **13** and NHC-reactants **10a-c** and with xanthone **14** and NHC-reactant **10c**. The spectra of the radicals obtained with fluorenone were less well resolved, but satisfactory results were obtained with second-derivative presentation (See Figure 1(b, b') and Supporting Information Figures S3 and S4). A beautifully resolved spectrum (Figure 1c) that persisted for several hours was obtained with xanthone **14**. That the process also worked well with heteroaromatic ketones was demonstrated by the good quality spectra obtained from photolyses of dithienylmethanone (**15**) with **10a** and **10b** (see Figure 1d and Supporting Information Figure S5). Photolyses were also carried out with N,N'-carbonyldiimidazole and **10c** but only the NHC-BH$_2$$^\bullet$ radical was detected. The lack of addition could, however, be due to the poor solubility of the CDI in the benzene solvent. The best fit hfs for all these spectra, obtained from computer simulations, are in Table 1. For the best resolved spectra from xanthone and from dithienylmethanone the parameters for the ^{10}B-isotope were also obtained (Table 1).

That these species were from analogous bora-ketyl radicals **17-19** was supported by DFT computations of the EPR parameters. The Gaussian 09 software suite was employed with the B3LYP functional and the 6-31+G(d) basis set[22] to obtain optimum geometries of the adduct radicals. The EPR parameters were then computed using the triple zeta EPR-iii basis set developed for EPR parameters by Barone.[23] Good correspondence between the experimental and computed hfs was obtained in agreement with the proposed radical structures (Table 1).
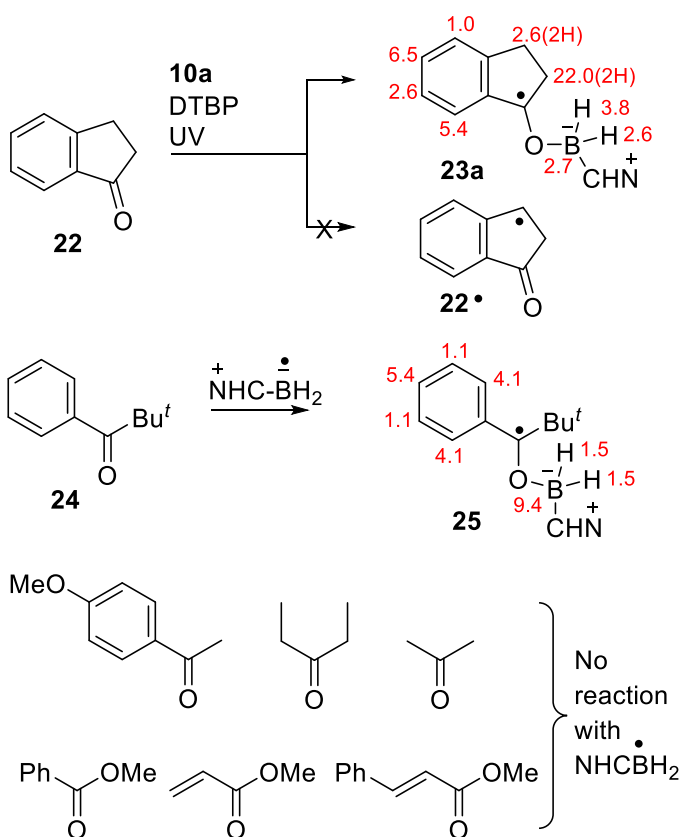
Table 1. Experimental and Computed EPR Parameters for NHC-BH$_2$ Ketyl Radicals.[a]

16 | **R¹** | **R²**
a | Me | Me
b | Buⁿ | Me
c | dipp | dipp

The reaction scheme shows **10 (a,b,c)** converting to **10•** via Bu^{t}O•, then reacting with Ph₂CO **12** → **16**, fluorenone **13** → **17(a, b, c)**, xanthone **14** → **18 c**, and di(2-thienyl)ketone **15** → **19 (a, c)**.

Radical	T/K DFT	$a(^{11}B)$	$a(2H^B)$	$a(H^{3,7,3',7'})$	$a(H^{4,6,4',6'})$	$a(H^{5,5'})$	
16b	260	4.41	0.54	3.02	1.14	3.73	
16a	290	4.43	0.54	3.00	1.12	3.71	
16a	DFT[b]	5.82	1.00	-3.48	1.58	-3.96	
16c	280	4.76	1.16	3.67	0.63	4.91	
		$a(^{11}B)$	$a(2H^B)$	$a(H^{3,5})$	$a(H^{4,6})$		
17b	260	0.67	4.0	1.73 2.35	1.73		
17a	280	< 0.7	3.26	0.69 2.32	0.69		
17a	DFT[b]	-1.6	5.58	-2.89 -3.40	0.91		
17c	280	0.64	3.55	3.55	0.61		
		$a(^{11}B)$	$a(2H^B)$	$a(H^{3,3'})$	$a(H^{5,5'})$	$a(H^{4,4'})$	$a(H^{6,6'})$
18c	280	6.57 2.18(^{10}B)	0.32	4.01	3.76	0.98	0.98
18a	DFT	7.28	-0.36	-4.13	-4.31	1.31	0.74
		$a(^{11}B)$	$a(2H^B)$	$a(H^{3,3'})$	$a(H^{4,4'})$	$a(H^{5,5'})$	
19a	280	5.03 1.68(^{10}B)	< 1.0	5.10	1.03	4.23	
19a	DFT[c]	5.42	-0.26	-5.58	1.60	-5.28	
19c	280	5.29	< 1.0	5.18	1.11	4.42	

| | $1.80(^{10}B)$ | | | | |

<superscript>a</superscript> Hfs in Gauss; note that EPR gives only the magnitude not the sign of hfs. All *g*-factors 2.003 ± 0.001. <superscript>b</superscript> B3LYP/epr-iii//B3LYP/6-31+G(d) (smd(solvent=toluene)). <superscript>c</superscript> B3LYP/cc-pVQZ (smd(solvent=toluene)).

Previous research had shown that, under appropriate conditions, NHC-ligated boranes could directly reduce (hydroborate) ketones to the corresponding alkoxyborates **20** (see Scheme 3) in an ionic process.[24] H-atom abstraction from **20** by the initiating Bu^{t}O$^\bullet$ radicals in our photolyses could then generate the ketyl radicals **21** that we had observed by EPR spectroscopy. This can be ruled out, however, because NHC-boranes do not react with ketones at rt.

Scheme 3. Possible Ionic Hydroboration of Ketones by Ligated Boranes

It is safe to conclude, therefore, that the ketyl radicals **16** to **19** that we detected were produced by direct regioselective addition of the ligated-boryl radicals to the ketones in mode (o).

Additions of NHC-boryl Radicals to Monoaryl- and Dialkyl-ketones and Esters

The formation of the ketyl radicals **16-19** was favoured by the extensive diarylmethyl type resonance delocalization of their unpaired electrons. We next tested a set of ketones selected such that the corresponding ketyl radicals would contain progressively less delocalization. Complex, but well resolved, EPR spectra were obtained during photolyses of indanone **22** and DTBP with the NHC-borane **10a** and with **10b** (See Supporting Information Figures S6 and S7). Analyses of these (see chart 2) indicated they were ketyl radicals **23a** and **23b**. Another

possibility was that the *t*-BuO• radicals had simply abstracted H-atoms from the indanone to generate the resonance stabilized indanyl radical **22•**. However, when a mixture containing only DTBP and indanone was UV irradiated, a completely different spectrum was obtained. This spectrum was very weak and the signal-to-noise ratio was too low for definitive analysis but it was probably the spectrum of radical **22•**. This control experiment supported our original assignments for **23a** and **23b**.

Chart 2. NHC-boryl Radical Reactions with Aryl- and Dialkyl-ketones and Esters

EPR hfs in red (/Gauss).

NHC-boryl radical **10a•** also coupled with 2,2-dimethyl-1-phenylpropan-1-one **24** to afford the corresponding adduct radical **25** (Charts 2, 3 and Supporting Information Figure S8). Interestingly, no reaction took place with 4-methoxyacetophenone showing that steric shielding

from the Bu^t group of **25** was important in stabilizing adduct ketyl radicals. EPR monitoring of similar experiments with acetone and NHC-boranes **10a** and **11** showed only the NHC-boryl radical. With pentan-3-one, EPR detected the pentan-3-one-2-yl radical but no adduct ketyl radical. Ketyl radicals from NHC-boryl radical addition were not spectroscopically observed for any of the esters in Chart 2.

Had addition taken place in mode (c), alkoxyl radicals (**2**) would have been formed. These are not directly detectable by EPR in solution. However, they readily undergo β-scission with release of the most stable alkyl radical and the corresponding ketone. That the released alkyl radicals are easily observed by EPR spectroscopy was demonstrated by detection of methyl radicals in several spectra from β-scission of the primary *t*-BuO$^\bullet$ radicals (see for example Supporting Information Figure S8). Had mode (c) addition taken place with ketone **24** the resulting alkoxyl radical would have rapidly released *t*-Bu$^\bullet$ radicals that would have been easily detected by EPR. Mode (c) addition was not detected in this way for any of the ketones or esters leading to the conclusion that NHC-boryl radicals either select mode (o) addition to carbonyl compounds or fail to react at room temperatures.

Additions of NHC-boryl Radicals to Aldehydes

The formyl H-atom of aldehydes is easily removed, particularly by O-centered radicals, and this is an important route to acyl radicals.[25] Our NHC-boryl radicals are obtained by use of *t*-BuO$^\bullet$ radicals. It seemed probable that on using aldehydes in concert with NHC-BH$_3$ precursors, competition with acyl radical formation would be a problem. The rate constant for H-atom abstraction from NHC-BH$_3$ by *t*-BuO$^\bullet$ radicals was known[1,2,3] to be $k_H \approx 10^8$ M^{-1}s^{-1} at 295 K. The absolute rate constant for H-atom abstraction by *t*-BuO$^\bullet$ radicals from PhCHO was determined by laser flash photolysis[26] to be somewhat less at 6.7×10^7 M^{-1}s^{-1} at 297 K. The

inference was that NHC-boryl radicals might be generated in mixtures of NHC-BH$_3$ and ArCHO with the latter in small excess. EPR experiments were carried out by photolyses of NHC-boranes **10a-c** with benzaldehyde or 4-*t*-butylbenzaldehyde in PhBu-*t* solvent. Di-methyl precursor **10a** was too sparingly soluble such that only spectra of the PhC$^\bullet$O radicals were observed. A weak spectrum with a very poor signal-to-noise ratio was obtained from dipp-precursor **10c** and benzaldehyde. This was probably the adduct radical NHC-BH$_2$-OC$^\bullet$H(Ph) but the spectrum was too insubstantial for definitive analysis. A satisfactory spectrum was recorded on photolysis of Me,Bu^n-precursor **10b** with 4-*t*-butylbenzaldehyde. Analysis of this afforded the following parameters: $a(^{11}B) = 4.5$, $a(1H) = 9.4$, $a(2H) = 1.5$ G at 295 K that probably correspond to the adduct radical NHC-BH$_2$-O-C$^\bullet$H(Ar). We conclude that NHC-boryl radicals do add to aromatic aldehydes but that an alternative route to form boryl radicals, which does not involve H-atom abstraction, is needed for the process to become practicable.

Conformations of β-NHC-bora-ketyl Radicals 16-19

In the adduct bora-ketyl radicals **16** etc. the B-atoms are sited β-to the π-orbitals containing the unpaired electrons. The extent of overlap, and hence the magnitude of $a(^{11}B)$, will depend on the dihedral angle θ between the π-orbital and the O–B bonds **25** (Chart 3). The EPR $a(^{11}B)$ hfs will be governed by a Karplus type relationship equ. (1): [27]

$$a(^{11}B) = A + B\cos^2\theta \qquad\qquad (1)$$

where A and B are constants. The average dihedral angle θ depends on the barrier to internal rotation about the C–O bond and hence also on temperature. It follows that $a(^{11}B)$ could also be temperature dependent.

Chart 3. Conformations of β-NHC-bora-ketyl Radicals
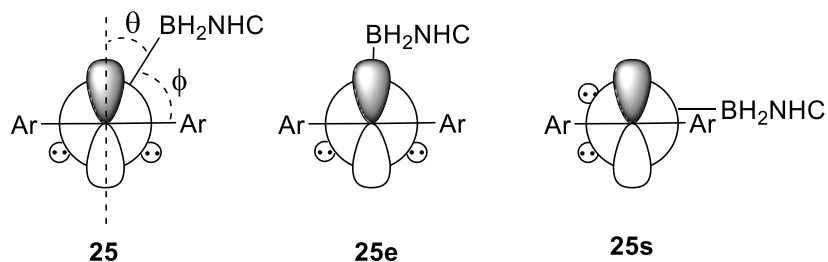
The temperature dependencies of the $a(^{11}B)$ values of the NHC-bora-ketyl radicals were difficult to determine because of the complexity of the EPR spectra. However, satisfactory results were obtained for radical **17c** from fluorenone for which $a(^{11}B)$ decreased from 0.77 to 0.52 G with increasing temperature in the accessible range; for radical **23a** for which $a(^{11}B)$ was invariant at 2.70±0.02 G and for radical **19c** for which $a(^{11}B)$ decreased from 5.18 to 4.98 G as T increased (see Figure 2).

Figure 2. Temperature dependence of $a(^{11}B)$ from EPR spectra of NHC-bora-ketyl radicals in PhBu^t solution.
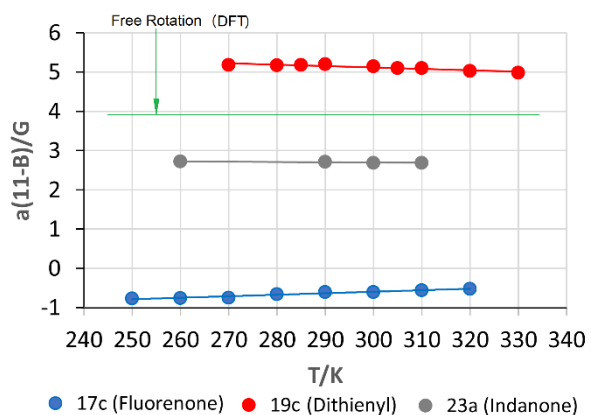
Experimental values for A and B in equ. (1) are not available for boron-containing radicals so DFT computations were carried out with radical **17a** as a model chosen because it has an approximately planar aromatic system. A = -1.6 G and B = 11.1 G were obtained at the B3LYP/EPR-iii//B3LYP/6-31+G(d) level from structures with $\phi = 0$ ($\theta = 90°$) and $\phi = 90$ ($\theta =$

13

0°). For free rotation about the C–O bond the mean value of $\theta = 45°$ and hence from equ. (1) the

hfs for free rotation would be $a(^{11}B)_{45} = 3.95$ G; invariant with temperature. The experimental

$a(^{11}B)$ for radical **19c** decreases towards this as temperature increases (see Figure 2) hence the

preferred conformation of this radical about its C–O bond will be **25e** in which the BH$_2$NHC

group eclipses the aromatic π-orbital. The $a(^{11}B)$ of radical **23a** is invariant and fairly close to

the computed free rotation value of 3.95 G which suggests a very low barrier to internal rotation

in this radical.   For radical **17c**, derived from fluorenone, the $a(^{11}B)$ values *decreased* in

magnitude (0.77 to 0.52 G); diverging more from the free rotation value (3.95 G) as T increased!

This was anomalous because the $a(^{11}B)$ should tend towards the free rotation value as T

increases. Only the magnitudes of hyperfine splittings can be derived from EPR spectra. This

anomalous behaviour implies therefore that $a(^{11}B)$ for radical **17c** must be negative in sign. It

has been plotted in Figure 2 with this assumption and then correctly tends towards the free

rotation value as T increases. It can be deduced that the preferred low temperature conformation

of this radical about its C–O bond will be **25s** in which the BH$_2$NHC group is in the nodal plane

the aromatic π-orbital.

   Judging by the magnitudes of their $a(^{11}B)$ hfs (Table 1) the preferred conformations for the

benzophenone and xanthone adduct radicals **16** and **18** will be eclipsed **25e**. The adduct radical

24 from 2,2-dimethyl-1-phenylpropan-1-one has the largest $a(^{11}B)$ (Chart 2)   It also adopts

conformation **25e** and the bulky *t*-Bu substituent may well inhibit rotation about the C–O bond

thus increasing the size of the barrier such that the BH$_2$-NHC substituent spends more time

eclipsing the π-system.   This accounts for the large $a(^{11}B)$.

   Additions of Amine- and Phosphine-boryl Radicals to Benzophenone

The facile addition of NHC-boryl radicals to diaryl ketones in mode (o) suggested that other ligated boryl radicals might add to ketones in the same way. To test this idea experiments analogous to those above were carried out with benzophenone and 4-dimethylaminopyridine borane (DMAP-BH$_3$, **26a**),[24] 1,8-diazabicyclo[5.4.0]undec-7-ene borane (DBU-BH$_3$, **26b**)[24] and triphenylphosphine-BH$_3$ (**26c**) (see Table 2).

Table 2. Amine-borane and Phosphine-borane Ketyls with Benzophenone^a
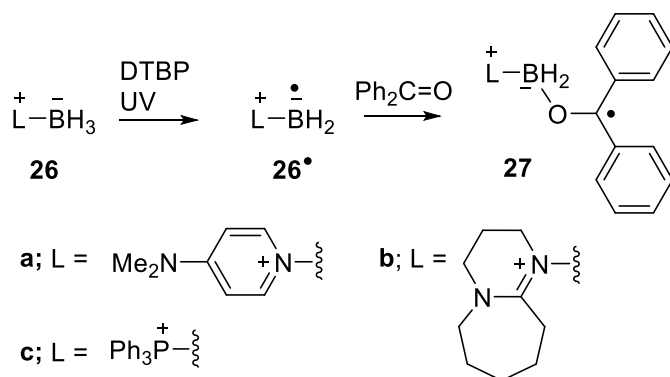
Radical	g-factor	$a(^{11}B)$	$a(2H^p)$	$a(4H^o)$	$a(4H^m)$
27a	2.0030	2.4	3.2	2.3	1.3
27b	2.0029	4.7	3.6	3.0	1.1
27c	2.0038	4.5	3.7	3.2	1.2

^{a} Isotropic spectra at 280 K in PhH; EPR hfs in Gauss

With DMAP-BH$_3$ (**26a**) very weak EPR spectra were obtained from samples in PhBu-t and in benzene (see Supporting Information Figures S9 and S10). Both spectra were simulated with similar EPR parameters which was good evidence the radical was indeed the DMAP-BH$_2$ ketyl adduct **27a**. A good spectrum of adduct ketyl radical **27b** (Supporting information Figure S11) was also obtained with the DBU-ligated borane **26b** and the EPR parameters are in Table 2. UV photolysis of Ph$_3$P-BH$_3$ (**26c**) and DTBP in benzene gave a strong spectrum of a radical with $a(^{31}P) = 41.63$, $a(^{11}B) = 18.81$, $a(2H) = 15.84$ G at 280 K. These parameters are in good

agreement with literature data for the $Ph_3P\text{-}BH_2^{\bullet}$ radical **26c**[$^{\bullet}$].[28] When samples including benzophenone were irradiated, spectra showing both $Ph_3P\text{-}BH_2^{\bullet}$ together with the adduct ketyl radical **27c** were obtained (Supporting Information S13). This spectroscopic data was good evidence that amine-boryl and phosphine-boryl radicals do add in mode (o) to ketones. The EPR spectra were considerably weaker than those obtained from NHC-boryl radicals with benzophenone. It appears therefore that amine-boranes and phosphine boranes add much less efficiently and that the range of suitable carbonyls will be limited.

Two control experiments were carried out with benzophenone and DBU-BH_3 and DMAP-BH_3. Specifically, benzophenone (0.2 mmol), the borane (0.1 mmol) and Bu^tOH (0.1 mmol) were mixed in benzene (1 mL). The Bu^tOH was added to mimic the photolysis reactions, where this is made from DTBP during photolysis. The reactions were monitored by ^{11}B NMR. After 12 h at rt there was no conversion to product and only the starting borane was detected. So ionic hydroboration by **26** to make L–BH_2OCHPh_2 under the EPR conditions can also be discounted.

Conclusions

Un-hindered **10a** and hindered **10c** NHC-boryl radicals added selectively to the O-atoms of mono- and di-arylketones and to aryl-aldehydes. This mode of addition contrasts with that of C-centered radicals that preferentially add to the C-atoms of carbonyl compounds. Mode (o) addition only took place when the adduct ketyl radicals were strongly resonance stabilized by electron delocalization. Significant spin density in the resulting bora-ketyl radicals was associated with the B-atoms that overlapped π-systems encompassing the aromatic rings. A second factor favouring mode (o) addition is the strong B–O bond. Addition in mode (o) was also observed with amine-boryl and phosphine-boryl radicals and benzophenone but was less

efficient. Thus, ligated boryls join the select few radicals that, when summoned by the prospect of delocalized product, show a preference for addition to unsaturated oxygen.

EXPERIMENTAL

DFT Calculations

DFT calculations were carried out using the Gaussian 09 suite of programs. Results were obtained with the B3LYP functional and the 6-311+G(2d,p) or the EPR-iii basis sets were employed with the SMD continuum model with toluene as solvent. Default values of the keywords Alpha, Radii, TSNUM, and TSARE were employed. Vibrational frequency calculations were implemented so that GS (no imaginary frequencies) status could be checked.

EPR Experiments

CW-EPR spectra were obtained at 9.5 GHz with 100 kHz modulation employing a commercial spectrometer fitted with a rectangular ER4122 SP resonant cavity. Stock solutions of each sample (2 to 15 mg) and DTBP (1 equiv. wt/wt) in solvent (0.5 mL) were prepared and sonicated if necessary. An aliquot (0.2 mL), to which any additional reactant had been added, was placed in a 4 mm o. d. quartz tube and de-aerated by bubbling nitrogen for 10 min. Photolysis in the resonant cavity was by unfiltered light from a 500 W super pressure mercury arc lamp. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker SimFonia and/or NIEHS Winsim2002 software packages.[29] EPR signals were digitally filtered and double integrated using the Bruker WinEPR software. The majority of EPR spectra were recorded with 2.0 mW power, 0.3 G_{pp} modulation intensity and a gain of ca. 10^6.

ASSOCIATED CONTENT

Supporting Information. Contains details of EPR experiments and calculations with copies of spectra of all new radicals as well as Cartesian coordinates and energies for DFT computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ToC Graphic:

ligated boryl radicals

bora-ketyls
observed by EPR