



# An air-stable N-heterocyclic carbene iminoxyl borate radical zwitterion†

Cite this: *Chem. Commun.*, 2018, 54, 6824

Youngsuk Kim <sup>ab</sup> and Eunsung Lee <sup>\*abc</sup>

Received 18th February 2018,  
Accepted 26th March 2018

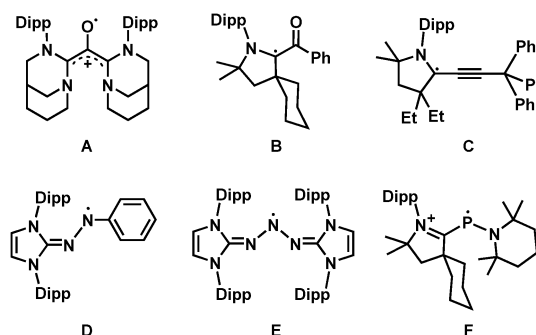
DOI: 10.1039/c8cc01399c

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**A remarkably stable radical zwitterion derived from N-heterocyclic carbene nitric oxide and  $B(C_6F_5)_3$  is reported. The presented radical was generated by steric and electronic protection of the nitric oxide moiety using  $B(C_6F_5)_3$ , which secured its stability toward air and moisture. An analogous yet less stable radical derived from  $C(C_6H_5)_3$ <sup>+</sup> is also synthesized and characterized.**

Stable organic radicals are of great interest to chemists since they offer fundamental understanding of reactive intermediates, as well as they have numerous applications as functional materials.<sup>1</sup> While the majority of organic radicals are thermodynamically and kinetically unstable, there are several kinds of stable organic radicals, namely triarylmethyl, nitroxyl, and hydrazyl radicals, for example.<sup>2</sup> In the past decade, N-heterocyclic carbenes (NHCs)<sup>3</sup> have been introduced to stabilise various organic radicals and radical ions,<sup>4</sup> as a variety of previously inaccessible organic radicals have been successfully prepared and characterised with the aid of NHCs.<sup>5</sup> To date, NHC-stabilised carbonyl (A and B),<sup>6</sup> propargyl (C),<sup>7</sup> aminyl (D and E),<sup>8</sup> phosphinyl (F),<sup>9</sup> and many other organic radicals have been isolated or spectroscopically characterised by the groups of Bertrand, Roesky, Curran, and many others (Scheme 1).<sup>10</sup> These radicals were successfully stabilised due to the  $\pi$ -accepting properties of NHCs that delocalise the spin density,<sup>11</sup> as well as the steric protection of the bulky NHC substituents.<sup>12</sup>

In this context, our group recently reported the synthesis of persistent iminoxyl radicals derived from NHCs with nitric oxide.<sup>10a,13</sup> The iminoxyl radical **1** was quite stable in the solid



**Scheme 1** Selected examples of organic radicals stabilised by NHC (Dipp = 2,6-diisopropylphenyl).

state; however, in the solution phase, it slowly decomposed even under an inert atmosphere of nitrogen. Here we report the synthesis and characterisation of a remarkably stable radical zwitterion **2** obtained from the steric protection of **1** using tris(pentafluorophenyl)borane ( $B(C_6F_5)_3$ ) (Scheme 2).

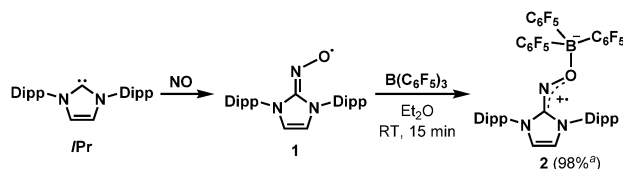
The radical **2** can be synthesised in high yield by mixing equimolar amounts of **1** and  $B(C_6F_5)_3$  in diethyl ether solution under a  $N_2$  atmosphere. The reaction mixture turned dark brown immediately, and after 15 minutes, volatiles were removed under vacuum. After washing the resulting solid using *n*-pentane, **2** was isolated as a dark brown solid in 98% yield. It is notable that a similar reactivity was recently reported for the (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) radical with  $B(C_6F_5)_3$ .<sup>14</sup> The molecular structure of **2** was unambiguously determined using single crystal X-ray crystallography (Fig. 1). The bond lengths of C1–N3 (1.339(2) Å) and N3–O1 (1.344(2) Å) indicate a bond order of 1.5. The (imidazole ring)–N3–O1–B1 group is planar, which also suggests delocalisation of the radical through  $\pi$ -conjugation. The structural parameters of **2** were well reproduced using density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level of theory. The Wiberg bond orders were calculated for the C1–N3 (1.49), N3–O1 (1.44), and O1–B1 (0.86) bonds, which were consistent with the structure obtained from single crystal X-ray analysis. The experimental electron paramagnetic resonance

<sup>a</sup> Center for Self-assembly and Complexity, Institute for Basic Science (IBS), Pohang, 37673, Republic of Korea

<sup>b</sup> Department of Chemistry, Pohang University of Science and Technology, Pohang, 37673, Republic of Korea. E-mail: eslee@postech.ac.kr

<sup>c</sup> Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang, 37673, Republic of Korea

† Electronic supplementary information (ESI) available: Experimental details, EPR spectra, X-ray crystal data, DFT calculation results. CCDC 1823243 and 1823244. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc01399c



**Scheme 2** Synthesis of the radical zwitterion **2** from IPr (1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) and NO (nitric oxide). <sup>a</sup> Isolated yield.



**Fig. 1** Molecular structure of **2** from X-ray crystallography. The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules (*n*-pentane) were omitted for clarity.

(EPR) spectrum shows a complex splitting pattern (Fig. 2), which was well reproduced in the simulated spectra. DFT calculations suggest that the N3 atom has the largest spin density (44%), consistent with the largest hyperfine coupling constant on N3 (23.4 MHz). The calculation also shows that the singly occupied molecular orbital (SOMO) of **2** is delocalised over the molecular plane (Fig. S1, ESI<sup>†</sup>). The UV-vis absorption spectrum of **2** in benzene at room temperature shows a peak at  $\lambda_{\text{max}} = 448 \text{ nm}$  (Fig. S8, ESI<sup>†</sup>). The cyclic voltammogram of **2** reveals one reversible redox peak at  $E_{1/2} = -0.022 \text{ V}$  (versus saturated Ag/AgCl electrode), showing that **2** is a weak oxidant (Fig. S13, ESI<sup>†</sup>).

It is notable that **2** shows remarkable stability toward air and moisture. For example, a solution of **2** in wet technical-grade benzene was monitored using UV-vis, which showed no detectable decomposition over 12 days (Fig. 3). In addition, **2** was stable even under silica chromatographic conditions as the benzene solution of **2** was still EPR active even after the filtration through silica gel under air (Fig. S6, ESI<sup>†</sup>).

After discovering the remarkable stability of the radical **2**, we were curious whether the radical cation **3** with almost equivalent steric bulk is also stable or not. When **1** was treated with a stoichiometric amount of trityl tetrakis(pentafluorophenyl)borate



**Fig. 2** Experimental (bottom) and simulated (top) EPR spectra of **2** ( $g = 2.0107$ ; hyperfine coupling constants:  $a(^{14}\text{N}) = 23.4, 9.1, 6.9 \text{ MHz}$ ,  $a(^{11}\text{B}) = 6.7 \text{ MHz}$ ,  $a(^1\text{H}) = 5.3, 3.6 \text{ MHz}$ ,  $a(^{19}\text{F}) = 2.6, 1.7 \text{ MHz}$ ).



**Fig. 3** Decay of the radicals **2** and **3** in wet benzene solution under air; monitored by UV-vis.



**Scheme 3** Synthesis of the radical cation **3**. <sup>a</sup> Isolated yield.

( $\text{Ph}_3\text{C}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ ) in diethyl ether solution under a  $\text{N}_2$  atmosphere, the color of the reaction mixture changed immediately to dark brown (Scheme 3). After 5 minutes, the product was precipitated by the addition of *n*-pentane, and subsequently washed to yield **3** as a dark brown solid (96%). Single crystal X-ray crystallographic analysis revealed the molecular structure of **3** with the  $\text{B}(\text{C}_6\text{F}_5)_4^-$  counteranion (Fig. 4). The planar molecular structure and bond lengths of C1–N3 (1.339(1) Å) and N3–O1 (1.361(1) Å) of **3** were almost identical with the structure of **2**. The calculated Wiberg bond lengths of C1–N3 (1.50), N3–O1 (1.38), and O1–C2 (0.87) bonds of **3** were also similar with those of **2**. On the other hand, the experimental and simulated EPR spectra of **3** were very different from those of **2** due to the absence of nearby boron and fluorine atoms (Fig. 5). The UV-vis spectrum of **3** in benzene was recorded at room temperature, which showed a peak at  $\lambda_{\text{max}} = 458 \text{ nm}$  (Fig. S9, ESI<sup>†</sup>). In contrast to **2**, **3** is a quite strong oxidant as its cyclic



**Fig. 4** Molecular structure of **3** from X-ray crystallography. The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.



Fig. 5 Experimental (bottom) and simulated (top) EPR spectra of **3** ( $g = 2.0098$ ; hyperfine coupling constants:  $a(^{14}\text{N}) = 26.6, 9.3, 7.5$  MHz,  $a(^1\text{H}) = 10.2, 6.6$  MHz).

voltammogram shows one reversible redox peak at  $E_{1/2} = 0.582$  V versus sat. Ag/AgCl (Fig. S14, ESI<sup>†</sup>). One-electron reduction of **3** using decamethylferrocene also resulted in the neutral oxime compound (see the ESI<sup>†</sup>). Interestingly, **3** was much more sensitive toward air and moisture than **2** as the half-life of **3** in wet technical-grade benzene was approximately 35 minutes (Fig. 3).

Therefore, simply protecting the radical center using a bulky substituent did not guarantee the stability of the radical. DFT calculations at the B3LYP/6-31G(d,p) level using the SMD solvation model showed that the trityl group is not binding strongly enough to the oxygen atom of **1** compared to the  $\text{B}(\text{C}_6\text{F}_5)_3$  group. The standard free energy of the dissociation of the  $\text{B}(\text{C}_6\text{F}_5)_3$  group from **2** is energetically uphill by  $12.6 \text{ kcal mol}^{-1}$  in benzene solution, while the trityl group of **3** required only  $1.4 \text{ kcal mol}^{-1}$  for dissociation (Fig. S2, ESI<sup>†</sup>). Additional calculations using  $\text{BPh}_3$  and  $\text{C}(\text{C}_6\text{F}_5)_3^+$  groups also suggested that the introduction of electron-withdrawing fluorine atoms makes huge difference in the dissociation energies, as perfluorinated substituents have much higher electrophilicity (see the ESI<sup>†</sup>). The dissociation of the trityl group from **3** was also evidenced by the crossover experiment: adding 2 equivalents of  $\text{B}(\text{C}_6\text{F}_5)_3$  to a solution of **3** successfully generated **2** along with the trityl group as observed by EPR (Fig. S7, ESI<sup>†</sup>) and UV-vis (Fig. S12, ESI<sup>†</sup>).

In summary, two different radicals **2** and **3** were synthesised from **1** and  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ , respectively. The radical zwitterion **2** showed remarkable stability toward air, moisture, and even toward silica. On the other hand, **3** showed limited stability upon exposure to air and moisture, showing a half-life of about 35 minutes in wet benzene solution. The difference of stability is mainly because the trityl moiety of **3** binds weaker than the  $\text{B}(\text{C}_6\text{F}_5)_3$  group of **2** to the oxygen, as analysed *via* DFT calculations. With the help from the novel properties of NHCs, this work clearly shows a successful example of designing a stable radical. Possible applications of the stable radical **2** are currently under active investigation.

This work was supported by Institute for Basic Science (IBS) [IBS-R007-D1]. The X-ray diffraction experiment with synchrotron radiation was performed at the Pohang Accelerator Laboratory (Beamline 2D).

## Conflicts of interest

There are no conflicts to declare.

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