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Reactions of *N*-heterocyclic carbenes (NHCs) with one-electron oxidants: possible formation of a carbene cation radical†

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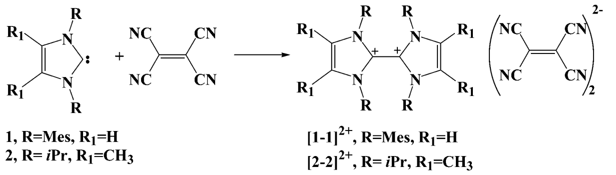
One-electron oxidation of *N*-heterocyclic carbenes (NHCs) has been carried out using oxidising agents such as tetracyanoethylene (TCNE) and ferrocenium $[\mathrm{Cp_2Fe}]^+$; the formation of carbene radical cations is postulated.

Carbenes are neutral molecules with a dicoordinate carbon atom having two non-bonding electrons.[1,2] *N*-heterocyclic carbenes (NHCs) have attracted attention due to their numerous applications in synthetic organic chemistry.[3,4] NHCs are highly basic, and as a ligand they are strong electron donors and poor π-electron acceptors. NHCs have been used in transition metal chemistry to stabilise low[2] and, more recently, high[5,6] oxidation state metal complexes.

We recently reported the reactivity of NHCs with simple reagents, including protic sources[7] and the hydrogen atom.[8] Electrochemical studies have been reported describing the *reduction* of NHCs,[9] but we note that simple one-electron *oxidation* reactions of NHCs have not been identified.[10] Here we report the reaction of NHCs with one-electron oxidants such as tetracyanoethylene (TCNE) and ferrocenium $[\mathrm{Cp_2Fe}]^+$. The oxidation of two NHCs has been explored using cyclic voltammetry.

TCNE is a strong organic electron acceptor[11] and readily forms stable salts containing $[\mathrm{TCNE}]^{\cdot-}$ or its π-stacked dimer $[\mathrm{TCNE}]_2^{2-}$.[12] TCNE-containing compounds have been central to the development of molecules with metallic[13] and superconducting[14] properties. Since NHCs are good *carbon-based* electron donors and TCNE is a good *carbon-based* electron acceptor, we began our studies examining their reactivity.

Treatment of 1,3-*bis*-(2,4,6-trimethylphenyl)-imidazol-2-ylidene,[15] **1**, or 1,3-*bis*-(isopropyl)-4,5-dimethylimidazol-2-ylidene,[16] **2**, with TCNE in THF solution results in the formation of an insoluble red material. The red, air-sensitive solids were characterised by IR and NMR spectroscopy as well as by mass spectrometry.† Elemental analyses on the reaction products are consistent with a material containing a 1:1 ratio of **1** or **2** with TCNE (Scheme 1). The products are diamagnetic and their ^{1}H NMR spectra exhibit signals that are downfield from the corresponding resonances in either **1** or **2**. The signals are consistent with a symmetrical carbene fragment. The IR data for both compounds show two strong ν_{CN} absorptions at 2191(s) and 2147(s) cm^{-1} consistent with the formation of the dianion π-$(\mathrm{TCNE})_2^{2-}$.[17] These signals are markedly different from neutral TCNE which has ν_{CN} absorptions at 2257(s) and 2219(s) cm^{-1}.[18] Formation of the complex anion is also supported by the ^{13}C NMR spectra, where the resonance corresponding to the ethyleneic carbon is observed at 68 ppm, upfield from that observed for TCNE at 110 ppm.[17] Electrospray mass spectrometry studies on the solids dissolved in THF solution showed distinct peaks in the positive mode at 304 and 180 amu for the products derived from **1** and **2** respectively. Under similar conditions **1** and **2** exhibit peaks at 305 and 181 amu, corresponding to the $[\mathrm{M + H}]^+$ ion. Taken in total, the spectroscopic data suggest the formation of the symmetrical dications $[\mathbf{1–1}]^{2+}$ and $[\mathbf{2–2}]^{2+}$. We note that peaks at 304.5 and 180.5, anticipated due to the isotopic pattern of the dications $[\mathbf{1–1}]^{2+}$ and $[\mathbf{2–2}]^{2+}$, respectively, are not observed and this suggests breaking of the *C–C* bonds under the experimental conditions. Finally, the dication $[\mathbf{2–2}]^{2+}$ has previously been isolated from a nucleophilic substitution reaction,[19] and the ^{1}H and ^{13}C NMR features reported are in accord with our data.



Scheme 1 Reaction of NHCs with TCNE.

Formation of $[\mathbf{1–1}]^{2+}$ and $[\mathbf{2–2}]^{2+}$ can be rationalised by the generation of the transient radical cations $[\mathbf{1}]^{\cdot+}$ or $[\mathbf{2}]^{\cdot+}$. Carbene radical cations have been postulated as intermediates in the electrochemical oxidation of diazo compounds.[20] Dimerisation of the radical cation produces the observed dicationic products. These species feature prominently in the chemistry of organic molecules in superacidic media.[21,22]

We were unable to spectroscopically confirm the radical cation intermediate, and hence we turned to computational studies to shed light on its structure. Computational studies were performed using the Gaussian 98 package of programs with the UB3LYP functional.[23] The 6–31G** basis set was used to optimise the structures of **2**, $[\mathbf{2}]^{\cdot+}$ and $[\mathbf{2–2}]^{2+}$. The results of this study are presented in Fig. 1. The most notable feature of the radical cation is the high spin density concentrated on the carbenic carbon. The shape of the SOMO suggests the potential of dimerisation through *C–C* bond formation. Also notable is that the C–N bond length is shorter for $[\mathbf{2}]^{\cdot+}$ compared to neutral carbene **2**. There is an increase in the $\mathrm{N_1–C_2–N_2}$ bond angle as expected according to VSEPR theory (Table 1).[24]

At least two routes leading to the formation of $[\mathbf{2–2}][\mathrm{TCNE}]_2$ are possible. *Route 1* involves dimerisation of two radical cations $[\mathbf{2}]^{\cdot+}$. *Route 2* is a stepwise reaction that involves initial formation of radical cation $[\mathbf{2}]^{\cdot+}$ followed by reaction with **2** to produce $[\mathbf{2–2}]^{\cdot+}$ which is then oxidised to give the dication.

Reactions of **1** or **2** with either $[\mathrm{Cp_2Fe}][\mathrm{PF_6}]$ or $[\mathrm{Cp_2Fe}][\mathrm{BF_4}]$ were also performed (Scheme 2). Upon mixing, a slow colour change from dark green to reddish brown was observed. After removal of the solvent, the resulting coloured solids were washed with hexane. Ferrocene was identified in these washings and the

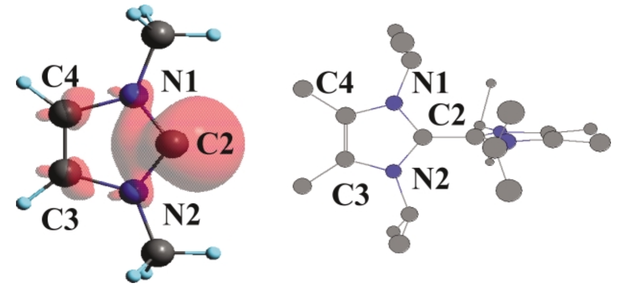


Fig. 1 Total electron spin density of $[\mathbf{2}]^{\cdot+}$ and the calculated structure of $[\mathbf{2–2}]^{2+}$ (hydrogen atoms omitted for clarity).

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† Electronic supplementary information (ESI) available: spectroscopic data, calculated atomic coordinates and cyclic voltammograms. See http://www.rsc.org/suppdata/cc/b3/b314110a/

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Table 1 Selected calculated bond lengths (Å) and angles (°) for **2**, $[\mathbf{2}]^{\cdot+}$, and $[\mathbf{2}\text{–}\mathbf{2}]^{2+}$

Parameter	**2**	$[\mathbf{2}]^{\cdot+}$	$[\mathbf{2}\text{–}\mathbf{2}]^{2+}$ (calc.)	$[\mathbf{2}\text{–}\mathbf{2}]^{2+}$ (exp.)[19]
C_2–N_2	1.379	1.337	1.370	1.351(3)
N_2–C_3	1.416	1.423	1.395	1.370(3)
C_3–C_4	1.371	1.381	1.390	1.363(4)
C_2–C_2	—	—	1.462	1.463(3)
N_1–C_2–N_2	102.3	111.6	107.7	108.4(2)
C_2–N_3–C_3	112.9	107.2	109.0	108.6(2)
N_2–C_3–C_4	105.9	106.9	107.1	107.4(2)
N_1–C_2–C_2–N_2	—	—	90.04	88.1

remaining hexanes-insoluble materials were characterised by NMR spectroscopy. The principal compounds identified in these solids were the imidazolium salts [**1**-H][PF_6], [**1**-H][BF_4], [**2**-H][PF_6], and [**2**-H][BF_4], respectively. The identity of these compounds was confirmed through the preparation of original samples of the imidazolium species synthesised *via* protonation and anion exchange reactions. The reactivity of **1** and **2** with [Cp_2Fe][PF_6] or [Cp_2Fe][BF_4] is significantly different from the reaction observed for TCNE. We speculate that the difference is readily explained by noting that the reaction is *heterogeneous* and *slow*. Under these conditions, at any given time only a small amount of radical cation is generated, thus precluding the dimerisation reaction, and alternate routes of reactivity are possible, namely abstraction of hydrogen atom from other sources, such as the solvent.[25]

Further exploration of the electrochemical oxidation of these NHCs in THF solution was performed using cyclic voltammetry. Both **1** and **2** demonstrate irreversible oxidations (Ep_{ox}) at 1 mV and −30 mV, respectively, *vs.* SCE when oxidised using a glassy carbon electrode. The kinetics of the electrode reaction appear to be slow and thus hindered the use of ferrocene as an internal standard for calibration and coulometric analysis. Unoxidised carbene from the solution reacts with ferrocenium produced and destroys the reliability of the redox couple. In addition, the carbenes slowly react with solvent/electrolyte over the course of the experiment which could complicate the coulometry of these species. Calibration was performed using ferrocene as an *external* standard and, therefore, the potentials obtained are to be regarded as estimates until further studies with other internal standards resistant to reaction with these carbenes are performed.

In conclusion, one-electron oxidation of NHCs has been carried out using different oxidising agents. Data consistent with a radical cation intermediate were obtained in reactions with TCNE producing dimeric dications. Reactions between **1** or **2** with ferrocenium produce imidazolium ions as the major products, suggesting hydrogen atom abstraction reactions.

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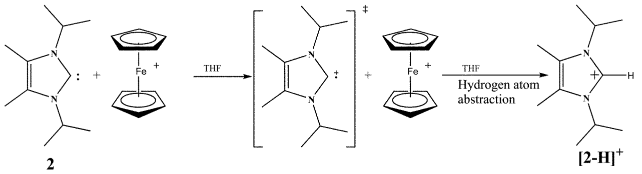

2

[2-H]$^+$

Scheme 2 Reaction of **2** with [Cp_2Fe]$^+$.

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