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## Trisubstituted Geminal Diazaalkenes Derived Transient 1,2-Carbocations

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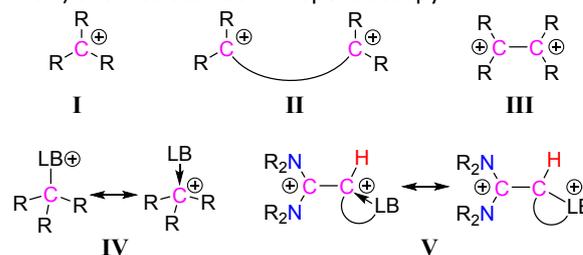
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**Coulombic repulsion between two adjacent cation centres of 1,2-carbocations are known to decrease with  $\pi$ - and/or  $n$ -donor substituents by the positive charge delocalization. Here we report the delocalization of positive charge of transient 1,2-carbocations having one H-substituent by an intramolecular base-coordination. *N*-heterocyclic olefin (NHO) derived 2-pyrrolidinyl appended trisubstituted geminal diazaalkenes were employed for the generation of transient 1,2-carbocations through a 2-e chemical oxidation process. We have also studied the 1-e oxidation reaction of trisubstituted geminal diazaalkenes (electrochemically and chemically) and also studied them by insitu EPR spectroscopy.**

Monocarboxocations, **I** (Scheme 1) are a ubiquitous class of organic intermediates which have been very well-studied over a century, to gain understanding of chemical reactivity, reaction mechanisms and also to address their stability.<sup>1</sup> In parallel to the well-studied monocarbocations, the chemistry of carbocations, **II** (Scheme 1), an important class of compounds, has also been developed.<sup>2</sup> Among carbocations, 1,2-carbocations, **III** (Scheme 1) possess strong Coulombic repulsion between two adjacent cationic centres and therefore,

the isolation of 1,2-carbocations are extremely challenging in addition to the synthetic difficulties that are present.<sup>3</sup> Chemists have been considering to overcome the challenge of Coulombic repulsion by designing substituents that allow a delocalization of the positive charges using  $\pi$ - and/or  $n$ -donor substituents.<sup>4</sup> In contrast to carbocations,<sup>5</sup> partially H-substituted, 1,2-carbocations using any combination of  $n$ -donor,  $\pi$ -, or neutral-substituents are sparse.<sup>6</sup> Theoretical calculations on ethylene dication, a fully H-substituted 1,2-carbocation has been reported.<sup>7</sup> Carbocations are known to form an adduct with Lewis base, **IV** (Scheme 1) even in a reversible manner to delocalize the positive charge.<sup>8,9</sup> This strategy is what we present to delocalize the positive charge in the case of 1,2-carbocations. Accordingly, herein we report the preparation of trisubstituted geminal diazaalkene-derived intramolecular base-stabilized dications **V** (Scheme 1) by a 2-e oxidation process. These systems have one H-substituent. We also report the electrochemistry of the trisubstituted geminal diazaalkenes involving its 1-electron oxidation (electrochemical as well as chemical) and also studied EPR spectroscopy.



**Scheme 1** Chemical structures of I-V (R = monoanionic ligand, LB = Lewis base)

We have considered 2-pyrrolidinyl as a substituent for trisubstituted geminal diazaalkenes considering that the *N*-centre of 2-pyrrolidinyl moiety can have the possibility for an intramolecular base-coordination to the putative 1,2-dications. Accordingly, we performed a 1:1 reactions of **1**<sup>10</sup> and **2**<sup>R11</sup> to afford the formation of **3**<sup>R</sup> (Scheme 2).<sup>12</sup>

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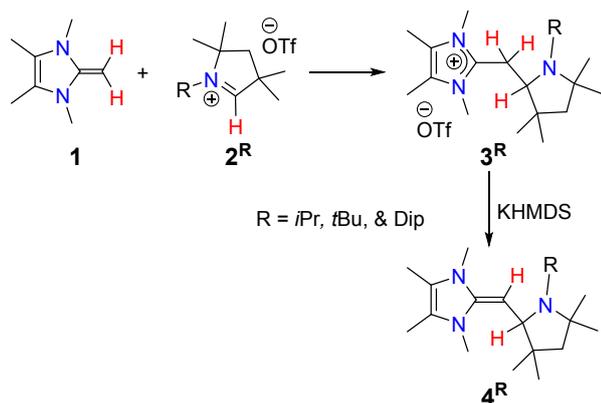
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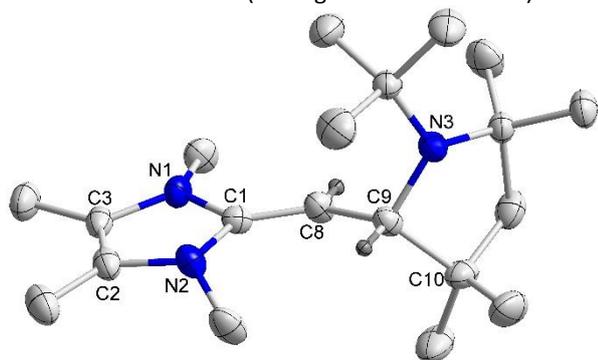
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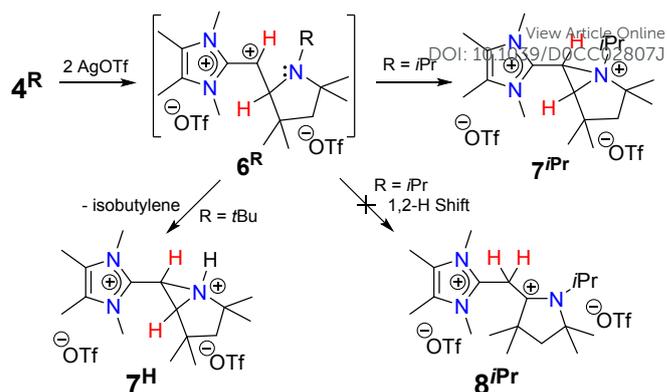
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 ‡ Electronic Supplementary Information (ESI) available: Experimental details, NMR spectra, X-ray crystallographic data and theoretical details. CCDC 1951977 (**1**-HOTf), 1951948 (**3**<sup>Pr</sup>), 1951949 (**3**<sup>Bu</sup>), 1951950 (**3**<sup>ip</sup>), 1951953 (**4**<sup>Bu</sup>), 1951954 (**4**<sup>ip</sup>), 1951955 (**7**<sup>Pr</sup>), 1951956 (**7**<sup>H</sup>), 1951957 (**9**), and 1951958 (**10**). For ESI and crystallographic data in CIF see DOI: 10.1039/x0xx00000x.

Scheme 2 Synthesis of **3<sup>R</sup>** and **4<sup>R</sup>**

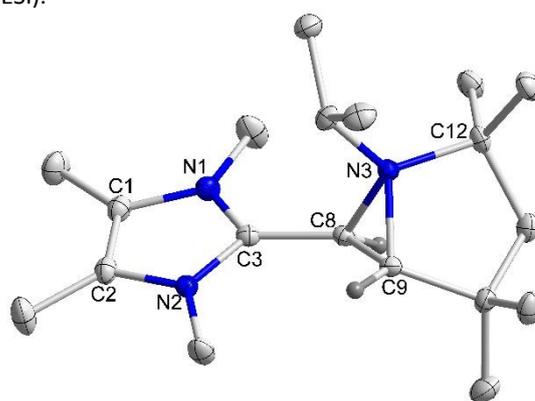
During the course of the reaction between **1** and **2<sup>R</sup>** we observed the formation of a small amount of pentamethylimidazolium triflate salt along with the desired monocations, **3<sup>R</sup>**.<sup>13</sup> Subsequent treatment of **3<sup>R</sup>** with KHMDS afforded the target alkenes **4<sup>R</sup>** (Scheme 2).<sup>12</sup> The <sup>1</sup>H NMR spectrum of **4<sup>iPr</sup>** displays two equal intensity doublets at  $\delta = 2.86$  ppm and 4.03 ppm with a coupling constant of  $^3J_{(1H,1H)} = 10.7$  Hz for allylic- and vinylic-*H*, respectively. Analysis of the single crystal structure of **4<sup>tBu</sup>** (Figure 1) shows the central olefinic carbon-carbon bond length (1.350(3) Å) is shorter than that of **1** (1.357 Å).<sup>10</sup> Frontier molecular orbitals analysis of **4<sup>iPr</sup>** and **4<sup>tBu</sup>** by DFT calculations reveal that the HOMO is mostly localized at the H-substituted olefinic carbon-centre. On the other hand, the LUMO is mainly delocalized across the olefin moiety of the backbone of NHC-scaffold (see Figures S24-S25 in ESI).<sup>12</sup>

Figure 1 Solid state molecular structure of **4<sup>tBu</sup>** with thermal ellipsoids at 50% probability level. All H atoms except at C8 and C9 are omitted for clarity.

Subsequently, the reaction of **4<sup>iPr</sup>** and **4<sup>tBu</sup>** with two equivalents of AgOTf was carried out (Scheme 3).<sup>12</sup> In the case of **4<sup>iPr</sup>**, the 1,3-dication **7<sup>iPr</sup>** was obtained in a good yield through a plausible intramolecular base coordination to the initially formed transient 1,2-carbocation, **6<sup>iPr</sup>**.<sup>14</sup> We didn't observe any 1,2-hydrogen shifted product **8<sup>iPr</sup>** though it is 22.1 kcal/mol lower in Gibbs free energy with respect to **7<sup>iPr</sup>**. The <sup>1</sup>H NMR spectrum of **7<sup>iPr</sup>** exhibits two equal intensity doublets at  $\delta = 4.64$  ppm and 4.39 ppm with a coupling constant of  $^3J_{(1H,1H)} = 6.6$  Hz for C-*H* of aziridinium-moiety of **7<sup>iPr</sup>**.

Scheme 3 2-Electron chemical oxidation of **4<sup>R</sup>** under the formation of **7<sup>R</sup>**

The molecular structure of **7<sup>iPr</sup>** confirms the formation of the 1-azabicyclo-[3.1.0]-hexan-1-ium-moiety<sup>15</sup> (Figure 2). The formulated structure of **7<sup>iPr</sup>** is further supported by the natural bond orbital (NBO) analysis.<sup>12</sup> The two carbon-nitrogen bond lengths of **7<sup>iPr</sup>** (1.534(18) and 1.496(19) Å) of the aziridinium moiety are different due to the non-identical environments at the carbon centres involved. This is similar to the reported 1-azabicyclo-[3.1.0]-hexan-1-ium-moiety where the two carbon-nitrogen bond lengths of the aziridinium moiety are quite different (1.520 and 1.490 Å).<sup>15(a)</sup> The central C3–C8 bond length is 1.472(19) Å which is slightly shorter than that of the corresponding dication derived from NHC-CAAC heterodimers (1.482 to 1.491 Å)<sup>10(a), 16</sup> and diamido carbene-pyran-heterodimers (1.510 Å)<sup>17</sup> suggesting the effective delocalization of positive charge at the C8-centre by an intramolecular base-coordination under the formation of the aziridinium motif. Natural population analysis (NPA) of **4<sup>iPr</sup>** and **7<sup>iPr</sup>** indicates donation of electron from N3 to the C8 centre (N3 has a charge of value  $-0.143$  in **7<sup>iPr</sup>** compared to  $-0.269$  as in **4<sup>iPr</sup>**, see Table S2 in ESI).<sup>12</sup>

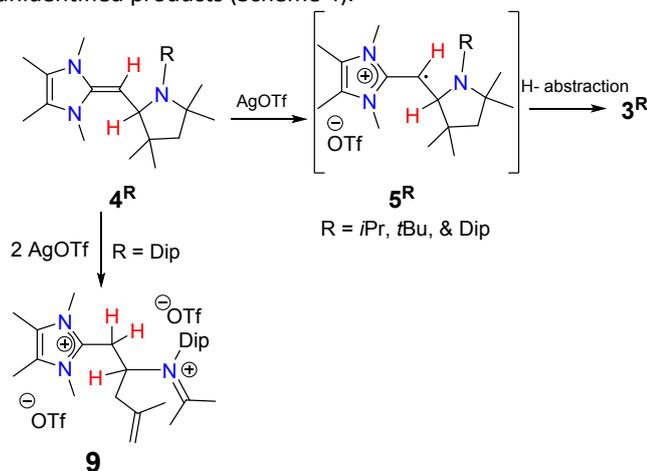
Figure 2 Solid state molecular structure of **7<sup>iPr</sup>** with thermal ellipsoids at 50% probability level. Two triflate anion and all H atoms except at C8 and C9 were omitted for clarity.

On two electron chemical oxidation of **4<sup>tBu</sup>** with AgOTf the 1,3-dication **7<sup>H</sup>** was obtained by the elimination of isobutylene from the *N-t*Bu moiety<sup>11b</sup> through an initially formed transient 1,2-carbocation **6<sup>tBu</sup>** (Scheme 3). The elimination of isobutylene from **7<sup>tBu</sup>** is favorable by  $-4.2$  kcal/mol in Gibbs free energy.<sup>12</sup> The central C3–C8 bond length of **7<sup>H</sup>** is 1.487(3) Å (see

Figure S6 in ESI) which is longer than the corresponding distance found in **7<sup>iPr</sup>** (1.4721(19) Å).

To address the nature of the 2-e oxidation of **4<sup>iPr</sup>** and **4<sup>tBu</sup>** whether it is stepwise or simultaneous we performed cyclic voltammetry investigations. As expected, these two compounds display oxidation steps at negative potentials (see Figures S8 and S10, and Table S1 in ESI).<sup>12</sup> The first oxidation of **4<sup>iPr</sup>** and **4<sup>tBu</sup>** occurred at -0.87 and -0.91 V, respectively in THF/0.1 M Bu<sub>4</sub>NPF<sub>6</sub> versus the FcH/FcH<sup>+</sup> couple. A second oxidation is observed for **4<sup>iPr</sup>** and **4<sup>tBu</sup>** at +0.10 and -0.03 V, respectively. The substituents thus only have a negligible influence on the redox potentials of these compounds. **4<sup>iPr</sup>** displays a third oxidation step that is likely related to the oxidation of new products formed after the second oxidation step. As expected for these extremely electron-rich olefins, they can only be reduced at potentials more negative than -3 V. The shape of voltammograms point to irreversible redox steps (see Figures S8 and S10 in ESI). Scanning only the first oxidation step, and varying the scan rates did not have a significant influence on the reversibility of the first oxidation step (Figures S9 and S11 in ESI). The irreversibility is likely related to reactions involving the reactive C-H olefinic bond (see Schemes 3 and 4).

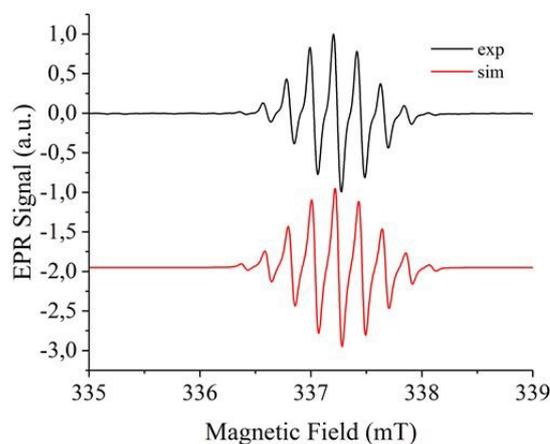
Subsequently, we performed a 1-e chemical oxidation of **4<sup>iPr</sup>** and **4<sup>tBu</sup>** with an equivalent amount of AgOTf which leads to the formation of a H-abstracted product, **3<sup>iPr</sup>** and **3<sup>tBu</sup>** from an initially formed radical cation<sup>18</sup> **5<sup>iPr</sup>** and **5<sup>tBu</sup>** along with other unidentified products (Scheme 4).



**Scheme 4** One electron oxidation of **4<sup>R</sup>** and two electron oxidation of **4<sup>Dip</sup>**

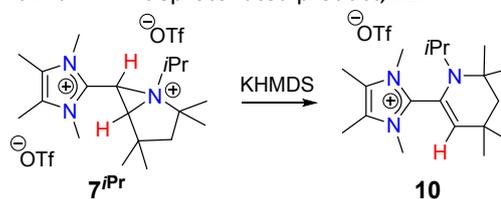
We were unable to detect the radical cation **5<sup>iPr</sup>** and **5<sup>tBu</sup>** even after immediate measurements of the insitu generated species through solution state EPR spectroscopy. To enhance the limited stability of the radical cation we considered *N*-Dip substituted trisubstituted diazaalkene **4<sup>Dip</sup>** which was prepared in an analogous way to that of **4<sup>iPr</sup>** and **4<sup>tBu</sup>** (Scheme 2).<sup>12</sup> The results from the cyclic voltammetry investigations of **4<sup>Dip</sup>** (see Figures S12 and S13, and Table S1 in ESI) is close to that of **4<sup>iPr</sup>** and **4<sup>tBu</sup>**. Chemical oxidation of **4<sup>Dip</sup>** with one equivalent of AgOTf displayed an EPR signal which could be simulated by considering hyperfine couplings to three <sup>14</sup>N (*A*(<sup>14</sup>N, MHz) = 5.77, 6.04, 5.03) and two <sup>1</sup>H nuclei (*A*(<sup>1</sup>H, MHz) = 6.00, 6.07) (Figure 3). This signal decayed in ca. 2 minutes. Attempts were

made to reproduce these experimental parameters at various levels of theory with several modifications by considering **5<sup>Dip</sup>** as the structure of the radical. However, in all these calculations, the hyperfine coupling to the central <sup>1</sup>H nuclei was much larger than the experimentally observed value (see ESI).<sup>12</sup> Consideration of a hypothetical molecule with an O-atom inserted between the central C-H bond delivered calculated hyperfine couplings that are much closer to the experimentally observed values. Even though we cannot unambiguously assign the structure of the observed radical, we can say with a fair amount of confidence that it is likely a radical that has a nuclei without any appreciable nuclear spin inserted between the central C-H bond. More importantly, this observation indirectly points to the formation and the existence of **5<sup>Dip</sup>**. Furthermore, the formation of **3<sup>Dip</sup>** from the chemical oxidation of **4<sup>Dip</sup>** also suggests the initial formation of the radical cation **5<sup>Dip</sup>** and then subsequent hydrogen atom abstraction most likely from the solvent. In contrast to **4<sup>iPr</sup>** and **4<sup>tBu</sup>**, the 2-e oxidation of **6<sup>Dip</sup>** leads to an isolation of very low yield of the dication **9** with a concurrent cleavage and rearrangement of the 2-pyrrolidine scaffold.<sup>19</sup>



**Figure 3** Experimentally obtained and simulated EPR spectra after the insitu oxidation of **4<sup>Dip</sup>** with AgOTf.

At the end, to see the fate of **7<sup>iPr</sup>** with base we reacted it with KHMDS and observed the formation of **10** through deprotonation followed by an aziridinium ring expansion<sup>20</sup> (Scheme 5).<sup>12</sup> In a similar reaction condition, compound **7<sup>H</sup>** leads to a aziridinium N-H deprotonated product, **11**.<sup>12</sup>



**Scheme 5** Synthesis of **10**.

In the <sup>1</sup>H NMR, the presence of a singlet at  $\delta = 5.54$  indicated the olefinic proton. The central C1–C8 bond distance in **10** is 1.4843(18) Å which is longer than that of the central C–C bond distance of **7<sup>iPr</sup>** (1.4721(19) Å) (see Figure S7 in ESI).<sup>12</sup>

In conclusion, we have disclosed a strategy for the delocalization of positive charge of a transient H-substituted

1,2-carbocation by an intramolecular base coordination. We obtained the transient 1,2-carbocation from 2-pyrrolidinyl substituted geminal diamino trisubstituted alkenes which has been derived from *N*-heterocyclic olefin (NHO) and conjugated acid of cyclic(alkyl)(amino)carbene (CAAC). Moreover, we have also studied the one electron oxidation of these geminal diamino trisubstituted alkenes which shows a limited stability of the corresponding radical cations. We feel that the strategy disclosed in this work will be effective for the generation of a variety of other transient 1,2-carbocations.

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### Conflicts of interest

The authors declare no competing financial interests.

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## TOC

Coulombic repulsion between two adjacent cation centres of 1,2-carbocations are known to decrease with  $\pi$ - and/or  $n$ -donor substituents by the positive charge delocalization. Here we report the delocalization of positive charge of 1,2-carbocations having one H-substituent by an intramolecular base-coordination. 2-pyrrolidinyl appended trisubstituted geminal diazaalkenes is employed for the synthesis of intramolecular base-stabilized dicationic species under 2-e oxidation.

