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Carbenes

"Abnormal" Addition of NHC to a Conjugate Acid of CAAC: Formation of *N*-Alkyl-Substituted CAAC**

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Dedicated to Professor Dietmar Stalke on the occasion of his 60th birthday

Abstract: The addition reactions of N-heterocyclic carbenes (NHCs) are mostly known to occur through the carbenic centre (C2), which leads to a "normal" adduct. Herein, we report the "abnormal" addition of NHC^{Dip} **1** (1,3-(2,6-$iPr_2C_6H_3$)-imidazole-2-ylidene) to a conjugate acid of cyclic (alkyl)(amino)carbene **2** ($CAAC^{iPr}$ = 1-*i*Pr-3,3,5,5-Me_4-pyrrolinium triflate). Mechanistic study revealed that this reaction proceeded through the in situ formation of 1,3-(2,6-$iPr_2C_6H_3$)-imidazolium cation **4** and *N*-*i*Pr-substituted CAAC **5** followed by the oxidative addition of compound **5** across the C4–H bond (alias backbone C–H) of compound **4**. The in situ formation of compound **5** was also proven by the oxidative addition of it to the N–H group of $iPrNH_2$. DFT calculations also supported the mechanistic findings. A different methodology for the in situ generation of compound **5** by using TMPLi is also described.

Introduction

Since the first isolation of singlet carbenes nearly three decades ago, the chemistry of these species has expanded remarkably.[1] The most prolific examples in this class are the imidazol-2-ylidene-based carbenes, also known as N-heterocyclic carbenes (NHCs) (Figure 1, **I**).[2] The other class of carbenes that are derived from the imidazole moiety are known as abnormal or mesoionic carbenes **II**, in which the carbenic carbon atom is flanked by N and C atoms of the imidazole moiety.[3] Yet another class of carbenes are cyclic (alkyl)(amino)carbenes (CAAC) **III**, in which the carbenic carbon atom is connected to N and C atoms.[4] The addition reactions of NHCs are mostly known to result in a "normal" adduct formation through the involvement of the carbenic carbon centre (C2).[2b] A few exceptions are known,[5] such as those that involve the addition of NHCs to a phosphinidene complex,[6] an N-heterocyclic silylene,[7] and a phosphaalkene.[8] This results in the formation of complexes **IV**–**VI** (Figure 2). Of these species, complexes **V** and **VI** are backbone-functionalized NHCs, whereas **IV** is a conjugate acid of the corresponding NHC.

Figure 1. Generic chemical structures of N-heterocyclic carbene **I**, abnormal or mesoionic carbene **II**, and cyclic(alkyl)(amino)carbene **III** (R = monoanionic organic substituents).

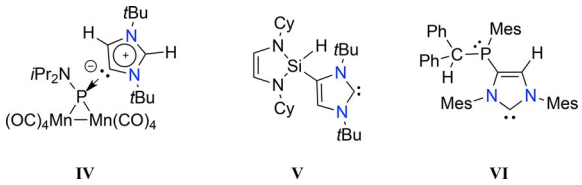

Figure 2. Chemical structures of abnormal addition products **IV**, **V**, and **VI** from the reaction of an NHC with a phosphinidene complex, an N-heterocyclic silylene, and a phosphaalkene, respectively.

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[**] NHC = N-heterocyclic carbene; CAAC = cyclic(alkyl)(amino)carbene

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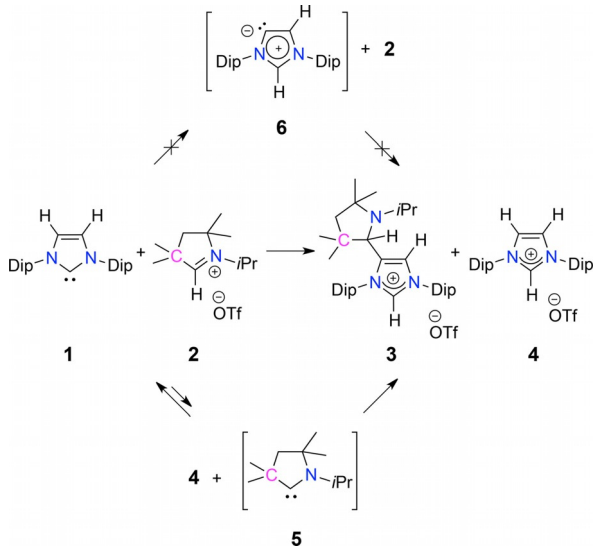
As mentioned above, the normal addition reactions of NHCs are common, whereas the abnormal reactions are rare. Even in such instances the reaction mechanisms are not validated by experimental proof; hence, such reactions are unable to serve as general pathways for the preparation of backbone-functionalized NHCs. The latter are highly desirable and would considerably add to the repertoire of this synthetic family. In this context, it may be mentioned that abnormal addition products are also obtained from the rearrangement of normal addition products or by subsequent reactions.[9] Additionally, the synthesis of backbone-functionalized NHCs has also been reported from a classical NHC precursor by Bertrand et al.[10] In spite of these reports, it has to be mentioned that all these currently available synthetic methodologies have limited functional-group tolerance.

In view of the above, the aim of this work was to study a "general abnormal" addition of NHCs and to completely understand the reaction mechanism that is involved in such an addition. In doing so, we have developed method for the in situ generation of free *N*-alkyl CAAC. This opens up the synthetic preparation of this new family of CAACs, which is extremely important as they are expected to have widely different properties in comparison to their *N*-aryl-substituted analogues; a situation that has already been proven in NHCs.[11]

Results and Discussion

A reaction of **1** and **2** (1:1) in THF led to the formation of backbone-functionalized imidazolium triflate **3** along with 1,3-(2,6-diisopropylphenyl)-imidazolium triflate **4**,[12] a conjugated acid of carbene **1**, in about 9:1 ratio (Scheme 1). Compound **3** was isolated in a pure form (61% yield) by recrystallization of the crude mixture by slow evaporation of *n*-hexane to a saturated THF solution of it.

The ^{1}H NMR spectrum of compound **3** revealed a downfield resonance at $\delta = 9.72$ ppm for the imidazolium C2–H proton.



Scheme 1. Synthesis and possible mechanism for the formation of compound **3**.

The molecular structure of compound **3** was confirmed by single-crystal X-ray diffraction analysis (Figure 3). The calculated N1–C1 and N2–C1 bond lengths, 1.323(3) and 1.333(2) Å, respectively, suggest that the positive charge is delocalized over the two N atoms. A similar situation was found in compound **4** (1.324(4) and 1.333(4) Å).[12] The backbone C2–C3 bond length in compound **3** was 1.357(3) Å, which is slightly larger than that of corresponding bond length in compound **4** (1.333(5) Å).

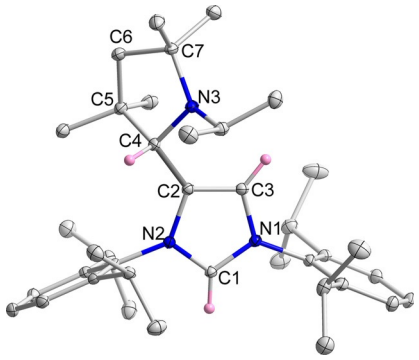


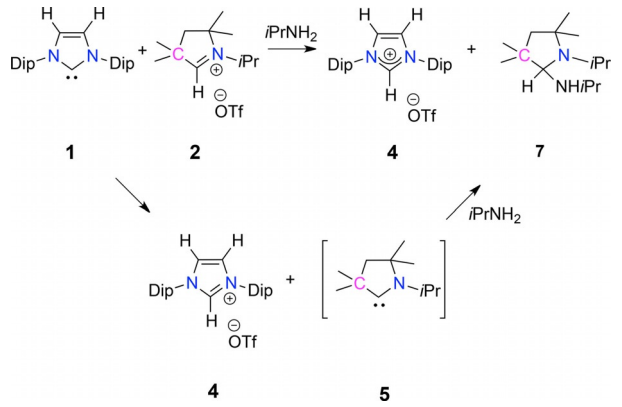
Figure 3. Molecular structure of compound **3**. Thermal ellipsoids at 50% probability level; triflate anion and all hydrogen atoms, except for C1–H, C3–H, and C4–H, were omitted for clarity.

The formation of compound **3** represents an atom economic reaction and can formally be considered as an abnormal addition product of NHC^{Dip} (**1**) to a conjugate acid of CAAC^{iPr} (**2**). The possible pathway for the formation of compound **3** could involve an initial acid–base reaction between compounds **1** and **2**, which would lead to the formation of compounds **4** and **5**. Subsequently, a formal oxidative addition of **5** across the C4–H (alias backbone C–H) of compound **4** would afford compound **3** (Scheme 1).

In contrast, another possible pathway would be the formation of abnormal NHC **6** from NHC^{Dip} **1** by proton transfer (C4–H to C2–H), and its subsequent nucleophilic addition to compound **2** (Scheme 1). This kind of isomerization is known for NHCs;[5a,6] however, the 1,3-hydrogen shift is energetically not favorable.[13]

While comparing the two possibilities outlined above, we considered the fact that compound **4** is formed in the reaction that favors the first pathway. To prove this experimentally, we carried out a reaction between compounds **1** and **2** in the presence of *i*PrNH$_2$ (Scheme 2). The ^{1}H NMR of the crude reaction mixture mostly indicates the formation of compounds **4** and **7**, the latter being an *i*PrNH$_2$ activation product (isolated yield = 78%). To rule out the possibility of formation of compound **7** by nucleophilic amination, we reacted compound **2** with an excess of *i*PrNH$_2$, which resulted in no reaction. It may be mentioned that when we reacted sterically less hindered N-alkyl substituted NHCs, 1,3,4,5-Me$_4$-imidazole-2-ylidene and 1,3-*i*Pr$_2$-4,5-Me$_2$-imidazole-2-ylidene, with compound **2**, normal addition occurred.[14]

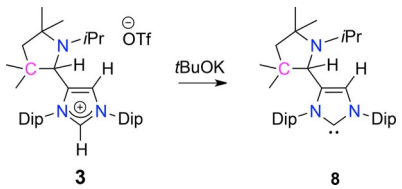
The calculated free energy at the B3LYP/TZVP level of theory[15] for the formation of compounds **4** and **5** from sub-



Scheme 2. Oxidative addition of the in situ generated compound **5** across the N–H bond of $iPrNH_2$.

strates **1** and **2** was marginally endothermic by $\Delta G_{298} = 6.2$ kcal mol^{-1}, which is in line with the estimated pK_a values of the C2–H moiety of compounds **2** (p$K_a = 27.9$) and **4** (p$K_a = 23.3$); however, this is much lower than the energy involved in the isomerization of compound **1** into **6** ($\Delta G_{298} = 14.1$ kcal mol^{-1}).[13] On the other hand, the formation of compound **3** from species **4** and **5** is a thermoneutral reaction ($\Delta G_{298} = 0.6$ kcal mol^{-1}). To further probe the electronic origin of the proton transfer from compounds **2** to **1** to form species **4** and **5**, we performed natural population analysis (NPA) to estimate the charges on the individual atoms and these computed charges on C and H atoms support the proposed mechanism (see the Supporting Information, Figure S24).[15]

After having successfully synthesized the backbone-functionalized imidazolium salt **3**, we prepared the NHC **8** in good yield (81%) by the reaction of compound **3** with KO*t*Bu (Scheme 3). The $^{13}C\{^1H\}$ NMR spectrum exhibited a downfield resonance at $\delta = 221.56$ ppm for the carbenic carbon atom,



Scheme 3. Synthesis of backbone functionalized N-heterocyclic carbene (NHC) **8**.

which is slightly downfield shifted compared with that of compound **2** ($\delta = 220.6$ ppm).[16]

Analysis of the solid-state molecular structure of NHC **8** (Figure 4) revealed that N1–C1 and N2–C1 bond lengths were 1.3685(19) and 1.3779(19) Å, which are very similar to those observed in compound **2** (1.364 and 1.369 Å).[17] Compound **8** was formally considered to result from a tail-to-head coupling between NHC and CAAC. Notably, the reaction of free NHC and CAAC did not occur. The analogous *N*-aryl-substituted pyrrolidinyl-functionalized NHC was reported by Roesky et al. as a side product when $NHC^{Dip}{\cdot}SiCl_2$ was reacted with $CAAC^{Dip}$.[18]

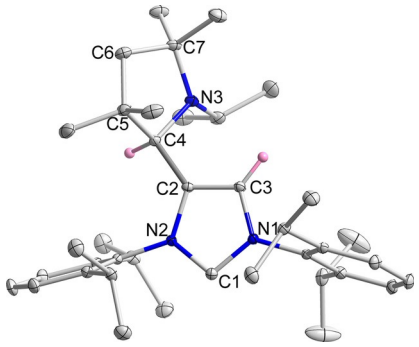


Figure 4. Molecular structure of compound **8**. Thermal ellipsoids at 50% probability level; all hydrogen atoms, except for C3–H and C4–H, were omitted for clarity.

To gain an insight into the electronic structure of compounds **5** and **8** and for their comparison with compounds **5′** and **1**, we estimated the HOMO and LUMO energies and singlet–triplet gap of all these molecules (Figure 5).[15] For *N*-isopropyl CAAC **5**, both the HOMO and LUMO were destabilized compared to *N*-aryl CAAC **5′** owing to the electron-donating *i*Pr group attached to the N centre. In the case of backbone functionalized NHC **8**, the HOMO was mostly delocalized over the σ-donating pyrrolidinyl group and was higher in energy than that of compound **1**. As a result, the pyrrolidinyl-functionalized NHC **8** will be a strong σ-donor ligand, like CAACs, with a smaller singlet–triplet gap than compound **1**.

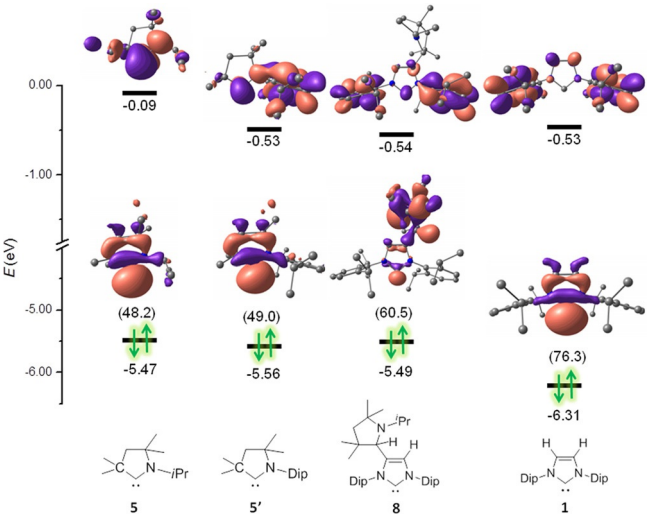
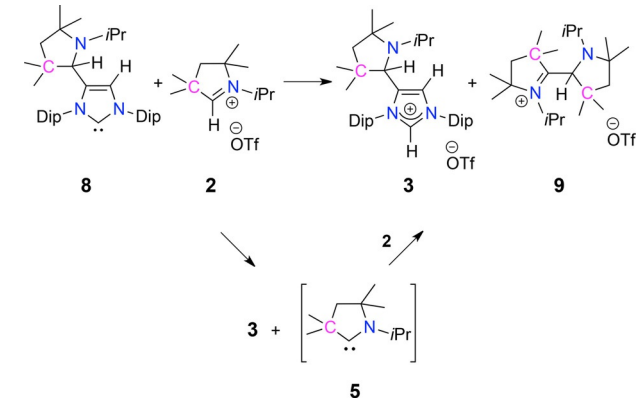


Figure 5. Energy of the HOMO–LUMO (eV) and singlet–triplet (in parentheses; kcal mol^{-1}) gaps of compounds **5**, **5′**, **8**, and **1** calculated at the B3LYP/TZVP level of theory.

To further functionalize the backbone C–H of NHC **8**, we reacted it with compound **2** (Scheme 4). To our surprise, we did not observe the expected product; however, from the crude reaction mixture, we obtained two different types of crystals. Molecular structure determination showed that one of these was compound **3** and the other was compound **9** (Figure 6).



Scheme 4. Reaction of compounds **8** and **2**.

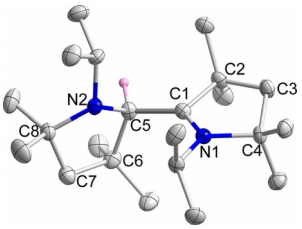
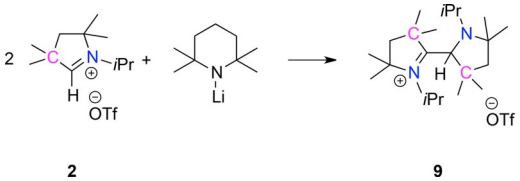


Figure 6. Molecular structure of compound **9**. Thermal ellipsoids at 50% probability level; triflate anion and all hydrogen atoms, except C5–H, were omitted for clarity.

Formation of compound **3** followed the acid–base reaction between compounds **8** and **2**, which we have proved in the case of compounds **1** and **2** (Scheme 1). During the formation of **3**, the concurrent formation of **5** was expected. Most likely owing to the steric hindrance at the backbone of **3**, *N*-isopropyl CAAC **5** was unable to react with it; instead, it underwent an oxidative addition to the C2–H bond of compound **2** to give the coupling product **9**. In support of this proposed pathway, we identified unreacted NHC **8** in the crude reaction mixture after its reaction with compound **2** in a 1:1 ratio. As **5** is formed in situ in the reaction of compound **2** with *N*-aryl-substituted NHCs **1** and **8**, we considered the possibility of generating *N*-isopropyl CAAC **5** by using a readily available base, such as lithium tetramethylpiperidide (TMPLi). Accordingly, the reaction of compound **2** with half an equivalent of TMPLi afforded compound **9** (Scheme 5). This was further evidence for the successful in situ formation of **5** and its subsequent reaction with substrate **2**. Moreover, it was demonstrated that the in situ formed *N*-isopropyl-substituted CAAC **5** reacted with the C–H bond as well as the N–H bond of organosubstrates, which was previously known for *N*-aryl-substituted CAACs.[19]



Scheme 5. Synthesis of compound **9**.

Analysis of the solid-state molecular structural data of compound **9** showed the presence of two different C–N bond lengths (C1–N1 = 1.290(3) Å and C5–N2 = 1.462(2) Å) for the pyrrolidinyl and pyrrolinium moiety, respectively (Figure 6). The distance between the two heterocycles is 1.524 Å, which indicates the presence of a carbon–carbon single bond.

As various compounds derived from CAACs are known to display intriguing electrochemical properties,[20] we investigated the electrochemical properties of compounds **3**, **8**, and **9** by using cyclic voltammetry. Of the three investigated compounds, **9** showed the most well-behaved electrochemical response, as judged by the complete reversibility of the reduction wave at −2.03 V (i_{pc}/i_{pa} ratio close to unity) in THF versus FcH/FcH^+ (Figure 7). We tentatively assigned this wave to the

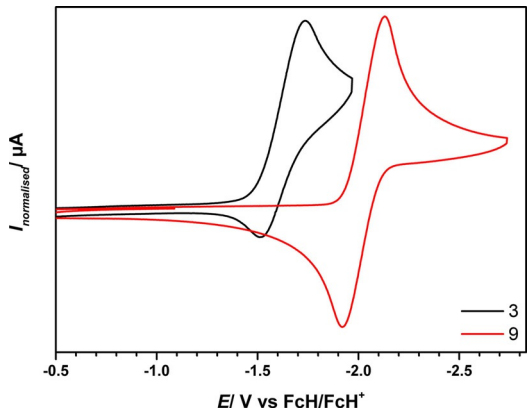
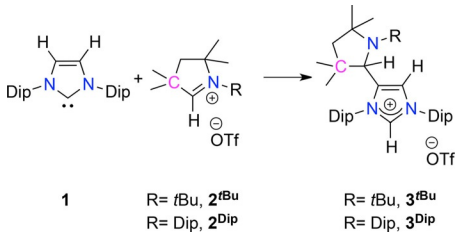


Figure 7. Cyclic voltammogram of compounds **3** (black) and **9** (red) measured in dry, degassed THF at a scan rate of 100 mV s^{-1} with a Bu_4NPF_6 supporting electrolyte (0.1 M) at an approximate concentration of 1 mM, and FcH/FcH^+ was used as an internal standard.

reduction of the cationic pyrrolinium salt to the corresponding neutral radical. Similar measurements on compound **3** showed a reduction peak at −1.73 V, which was positively shifted compared with that of species **9** (Figure 7). However, this reduction step was not reversible owing to the much higher i_{pc} value than i_{pa} value as well as the observation of an additional reoxidation wave at 0.1 V, which appeared in response to the reduction wave at −1.73 V (see the Supporting Information, Figure S22). Additionally, an irreversible oxidation step was observed for compound **3** at 0.88 V. This redox step was also irreversible owing to the almost nonexistent return wave and an additional rereduction peak at −1.09 V (see the Supporting Information, Figure S22). Furthermore, it was observed that the redox stability of compound **3** was rather limited, as all the redox waves changed significantly after a few repeated runs in the cyclic voltammogram. We believe that the difference in the reversibility of the reduction steps in compounds **9** and **3** is related to the existence of a more acidic C–H bond (C2–H) in compound **3**. Upon reduction, an acidic C–H bond is likely to be susceptible to radical H-atom abstraction reactions, which will make the reduction step irreversible. This behavior appeared to be quite general for all kinds of azolium salts. For instance, similar irreversible reduction waves were recently ob-

served for 1,2,3-triazolium salts, which are precursors to mesoionic carbenes.[21] Thus, substitution at the acidic C–H bonds of the azolium salts is likely to be a good strategy to gain access to stable radicals that are based on such carbene precursors. Even though several redox processes were observed for the free carbene **8**, no well-defined electrochemical response was detected for this compound in THF (see the Supporting Information, Figure S23). This observation is a likely indication of the extremely reactive nature of the radicals that are generated upon oxidation or reduction of such free carbenes. A detailed study that is related to elucidating the electronic structure of the aforementioned stable radicals is currently ongoing in our laboratories.

To see the generality of this type of NHC addition reaction to other conjugated acids of CAAC, we reacted carbene **1** with *N*-*t*Bu- and *N*-Dip-substituted pyrrolinium salts $\mathbf{2}^{t\mathrm{Bu}}$ and $\mathbf{2}^{\mathrm{Dip}}$. The initial results revealed the formation of the corresponding abnormal addition products $\mathbf{3}^{t\mathrm{Bu}}$ and $\mathbf{3}^{\mathrm{Dip}}$, both of which are analogues of compound **3** (Scheme 6).[22]



Scheme 6. Synthesis of $\mathbf{3}^{t\mathrm{Bu}}$ and $\mathbf{3}^{\mathrm{Dip}}$.

Conclusion

We have reported an abnormal addition of an NHC to a conjugated acid of CAAC, which serves as an effective route for the synthesis of pyrrolidinyl-functionalized NHCs. These backbone-modified NHCs feature strong σ-donor properties, like CAAC, with a smaller singlet–triplet gap than that of NHCs, and they offer promise as a new kind of ligand for coordination chemistry. The reaction proceeded through an in situ formation of corresponding CAAC under acid-base reaction. DFT calculations supported the mechanistic findings. We have also developed a straightforward strategy for the in situ formation of *N*-isopropyl-substituted CAAC by using a common base, TMPLi. The manifestation of the in situ generation of *N*-alkyl-substituted CAAC (and analogous compounds) enables these species to be used as ligands for the preparation of hitherto unknown *N*-alkyl-CAAC-coordinated transition-metal complexes, which have various applications, particularly in catalysis. These studies are in progress.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: addition reactions · carbenes · density functional calculations · group 14 elements · X-ray diffraction

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