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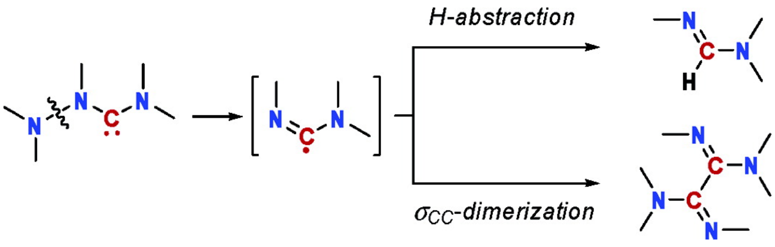

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# Evidence for Radical Fragmentations from Persistent Singlet Carbenes

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In the last 15 years, our understanding of carbene chemistry has advanced dramatically.[1] In particular, starting from the pioneering push−pull phosphinosilylcarbenes **A**[2a] and push−push N-heterocyclic carbenes **B**[2b] (Figure 1), the availability of a variety of stable singlet carbenes[3,4] has allowed for spectacular achievements both in organic[5] and organometallic[6] chemistry. More insights have also been gained for typical carbene reactivity (such as dimerization,[7] cyclopropanation,[8] 1,2-,[9] and 1,3-[10] migration reactions) that could thus far only be investigated for the transient species.

In this perspective, we report here the preparation and characterization of persistent aminohydrazinocarbenes **C**[11] as well as evidence for their spontaneous radical fragmentation. Notably, the fragmentation of carbenes has been much less investigated than their isomerization or dimerization.[12−14] Moss made significant contributions in the heterolytic cleavage of transient alkoxyhalocarbenes,[12] and Warkentin recently demonstrated that the apparent 1,2- and 2,3-sigmatropic rearrangements of allyloxymethoxycarbenes occur via homolytic $\beta$-scission of the transient carbenes (Scheme 1).[13b−f]

We first investigated carbene **2a**, replacing one of the di*iso*propylamino substituent of $(i\text{-Pr})_2N-\ddot{C}-N(i\text{-Pr})_2$[15] by an hydrazino group of similar steric hindrance. The required formamidinium precursor **1a** was prepared in good yield by condensing the appropriate silylhydrazine and chloroformamidinium chloride (Scheme 2). Deprotonation of **1a** by lithium hexamethyldisilazane (LiHMDS) at −78 °C in deuterated THF cleanly afforded the corresponding carbene **2a**, as unambiguously deduced from $^{13}C$ NMR spectroscopy ($\delta$ 228 ppm).[16]

Although $(i\text{-Pr})_2N-\ddot{C}-N(i\text{-Pr})_2$ is indefinitely stable at room temperature, carbene **2a** rapidly fragments at −22 °C, following first-order kinetics ($t_{1/2} \approx 20$ min), affording tri*iso*propylformamidine **3** along with methylenemethylamine **4**.[17]

To gain more insight into this $\beta$-fragmentation reaction,[18] DFT calculations were carried out on the model carbene **2*** at the B3LYP/6-31G** level of theory.[19] In agreement with the experimental observations, the rearrangement was predicted to be highly exothermic (−33.6 kcal mol$^{-1}$), and a cyclic transition state **TS$_{\mathbf{frag}}$** could be located on the closed-shell surface 26.0 kcal mol$^{-1}$ higher in energy than the reactive conformer of **2*** (Figure 2).

Accordingly, at first glance, the fragmentation reaction could be predicted to be concerted and asynchronous, the N−N and C−H bonds being elongated in the transition state by 40 and 20%, respectively, compared to those of the carbene **2***.

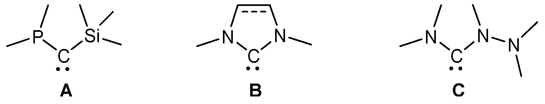
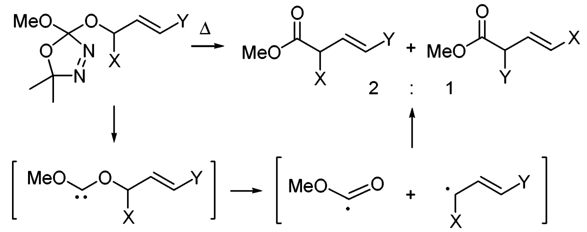


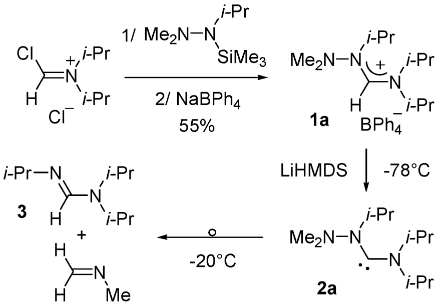
***Figure 1.*** Schematic representation of carbenes **A**−**C**.

***Scheme 1***



(X = Ph, Y = H) or (X = H, Y = Ph)

***Scheme 2***



Interestingly, the stability and rearrangement pathway of aminohydrazinocarbenes were found to be dependent on the substitution pattern of the N$_\beta$ atom. Indeed, deprotonation of the formamidinium salt **1b** afforded the corresponding carbene **2b** that could be observed without degradation up to −10 °C.[16] The half-life time of **2b** ($t_{1/2} \approx 2.5$ h at −5 °C) is significantly larger than that of **2a**, and carbene **2b** affords, upon warm up, not only formamidine **3** but also hexa*iso*propyloxamidine **5** in a 6:4 ratio (Scheme 3). The structure of **5** was established spectroscopically and unambiguously confirmed by an X-ray diffraction study.[19] The formation of oxamidine **5** most likely results from the N−N homolytic fragmentation of **2b** followed by $\sigma$-(C−C) dimerization of the resulting aminoimidoyl radicals $(i\text{-Pr})N{=}\dot{C}-N(i\text{-Pr})_2$ **6**.[20,21] Such a radical rearrangement is not surprising in view of the weakness of NN single bonds (i.e., 40 kcal mol$^{-1}$ for hydrazines).

To confirm the feasibility of such a radical pathway for the fragmentation of **2***, the resulting aminyl and aminoimidoyl radicals were optimized at the UB3LYP/6-31G** level, and the N−N bond energy for carbene **2*** ($\Delta E$) was thereby estimated at 27.8 kcal mol$^{-1}$ (eq 1).[22] Because of favorable entropic factors, the corresponding $\Delta G$ value for this dissociative radical process is only 14.4 kcal mol$^{-1}$ at 25 °C, which is lower than the value predicted for the formation of **3*** via a concerted process ($\Delta G^{\ddagger} = 26.0$ kcal mol$^{-1}$

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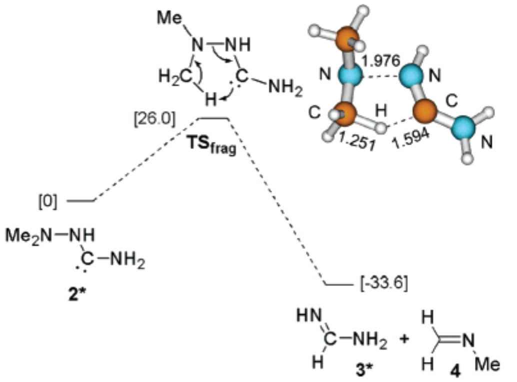
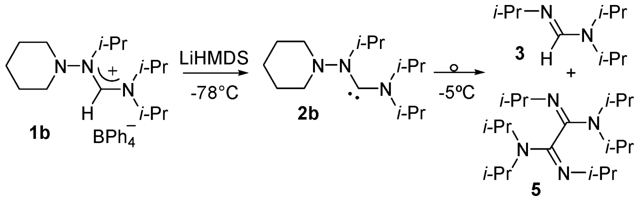
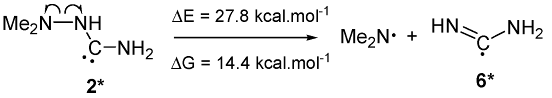


***Figure 2.*** Closed-shell surface of the model aminohydrazinocarbene **2*** computed at the B3LYP/6-31G** level (total energies $E$ relative to the carbene **2*** including ZPE correction and expressed in kilocalories per mole, distances given in angstroms).

***Scheme 3***



at 25 °C). Accordingly, the concomitant formation of **3** and **5**, observed experimentally, can result either from competitive closed-shell/radical fragmentation of **2b** or more likely from radical fragmentation of **2b** followed by competitive H-abstraction/$\sigma$-dimerization of the ensuing aminoimidoyl radical **6**.



$$\mathrm{Me_2N{-}NH{-}\ddot{C}{-}NH_2}\ (\mathbf{2^*}) \xrightarrow[\Delta G = 14.4\ \mathrm{kcal.mol^{-1}}]{\Delta E = 27.8\ \mathrm{kcal.mol^{-1}}} \mathrm{Me_2N^{\bullet}} + \mathrm{HN{=}\dot{C}{-}NH_2}\ (\mathbf{6^*}) \qquad (1)$$

In conclusion, acyclic aminohydrazinocarbenes have been prepared and spectroscopically characterized in solution at low temperature. Their $\beta$-fragmentation upon warm up affords the first evidence for a homolytic fragmentation for a persistent singlet carbene.[23−25] The possible involvement of such radical pathways in other carbene reactions is currently under investigation.

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**Supporting Information Available:** Full experimental and computational details, spectroscopic data, and X-ray crystallographic data for **1b** and **5** (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) To a first approximation, this value can be considered as the energy required for homolytic fragmentation of **2***, although it might be slightly larger if this dissociation involves a transition state, as predicted for (di)hydroxycarbenes.[13d]

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