Apparent 1,2-Silyl Migrations in Aromatic Carbenes Occur by Intermolecular Silyl Exchanges

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In the past few years, carbene chemistry has undergone a profound revolution with the appearance of stable singlet carbenes **1**−**6**[1−6] in the literature. However, the true carbenic nature of these species remains a highly debatable topic.[7]
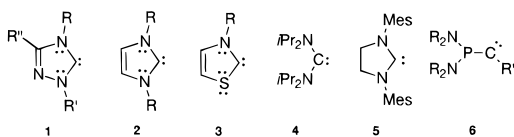
It is now well established that the 1,2-migration is a fundamental reaction for singlet carbenes and occurs via a unimolecular concerted mechanism.[8] Alternative intermolecular pathways such as those involving carbene-olefin π-complexes[9] have recently been ruled out.[10] 1,2-Hydrogen migrations in aromatic carbenes cannot proceed through an intramolecular process in the plane of the ring, since this mechanism would impose the crossing of two orbitals with the same symmetry as shown in the correlation diagram (Figure 1a). An alternative possibility, which has been studied theoretically,[11] involves the interaction of the N−H bond with the out of plane p_π orbital of the carbene. This process induces a deformation of the ring and thus the loss of the electronic delocalization of the nitrogen lone pairs (Figure 1b).
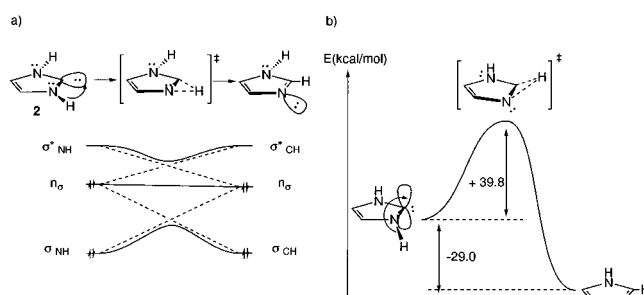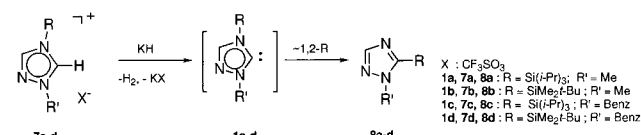

Figure 1. (a) Correlation diagram of the in-plane 1,2-H-migration for aromatic carbenes of type **2**. (b) Energy diagram of the calculated out of plane 1,2-H-migration for **2**.

Scheme 1

Heinemann et al. demonstrated that even though the reaction would be exothermic (−26.1 kcal/mol at the RHF/MP2DSQ level[11a] and −29 kcal/mol at the DFT/B3LYP level[11b]), the carbene **2** (R = H) should be kinetically stable toward 1,2-shifts, since the activation energy of this rearrangement is high (+46.8 kcal/mol,[11a] +39.8 kcal/mol[11b]). Recently, Maïer et al. obtained similar results for the thiazolylidene system **3** (R = H) ($\Delta H = -34.0$ kcal/mol, $E^\ddagger = +42.3$ kcal/mol).[11c]

Here, we report that 1,2 migrations can occur for aromatic carbenes of type **1**, but via intermolecular processes.

Since the ability of silyl groups to migrate is well established, we chose to prepare 1*H*-4-silyl-1,2,4-triazolium salts (**7a**−**d**)[12] as precursors of the corresponding heterocyclic carbenes **1a**−**d** (Scheme 1). Deprotonation of salts **7a**−**d**, with various bases, readily occurred at 0 °C, as shown by the disappearance of the corresponding ^{1}H NMR signal. Interestingly, no ^{13}C NMR signal in the range expected for carbene centers (∼200 ppm)[13] was observed; instead, the signals for the quaternary carbon atoms appeared around 155 ppm. Moreover, the ^{29}Si NMR signals were shifted to high field ($\Delta\delta \approx 35$ ppm) compared to those observed for the triazolium precursors **7a**−**d**. After workup, the products **8a**−**d** were isolated in 42−81% yields and were fully characterized;[12] a single-crystal X-ray diffraction study for compound **8a** was performed. 1*H*-5-Silyl-1,2,4-triazoles **8a**−**d** formally result from the 1,2-migration of the silyl group from nitrogen to the carbene center of the transient derivatives **1a**−**d**.

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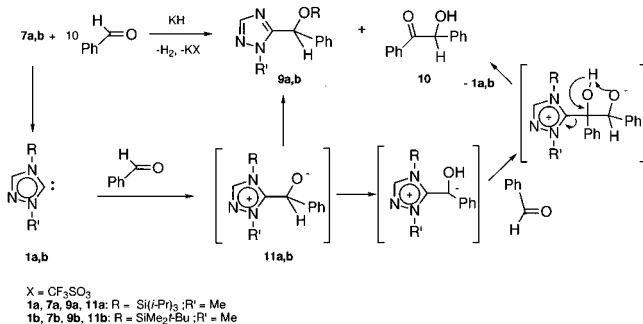
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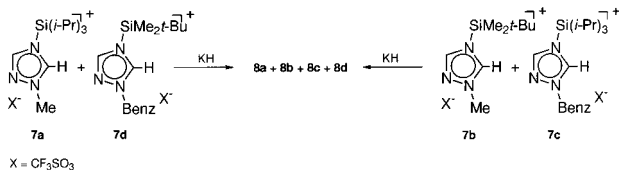
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(12) Physical and spectroscopic data for selected compounds. For **7a**: ^{1}H NMR (CD$_3$CN) δ 1.25 (d, ^3J(H−H) = 7.2 Hz, 18 H, C*H*$_3$CH), 1.77 (sept., ^3J(H−H) = 7.2 Hz, 3 H, CHSi), 4.23 (s, 3 H, CH$_3$N), 8.72 (s, 1 H, CH), 9.49 (s, 1 H, CH); ^{13}C NMR (CD$_3$CN) δ 10.8 (s, CHSi), 16.9 (s, *C*H$_3$CH), 38.9 (s, CH$_3$N), 120.4 (q, ^1J(C−F) = 320.1 Hz, CF$_3$), 144.7 (s, CH), 146.5 (s, CH); ^{29}Si NMR (CD$_3$CN) δ +41.4; mp 77 °C. For **8a**: ^{1}H NMR (C$_6$D$_6$) δ 1.04 (d, ^3J(H−H) = 7.1 Hz, 18 H, C*H*$_3$CH), 1.29 (sept., ^3J(H−H) = 7.1 Hz, 3 H, CHSi), 3.45 (s, 3 H, CH$_3$N), 8.13 (s, 1 H, CH); ^{13}C NMR (C$_6$D$_6$) δ 12.4 (s, CHSi), 18.6 (s, *C*H$_3$CH), 37.4 (s, CH$_3$N), 152.0 (s, CH), 155.3 (s, CSi); ^{29}Si NMR (C$_6$D$_6$) δ +1.2; MS (DCI, NH$_3$) *m/z* = 240 (M + 1); mp 40−42 °C. For **9a**: ^{1}H NMR (CDCl$_3$) δ 0.99 (d, ^3J(H−H) = 3.9 Hz, 18 H, C*H*$_3$CH), 1.17 (sept., ^3J(H−H) = 3.9 Hz, 3 H, CHSi), 3.69 (s, 3 H, CH$_3$N), 6.30 (s, 1 H, CHOSi) 7.21−7.42 (m., 5 H, C$_6$H$_5$), 7.73 (s, 1 H, CH); ^{13}C NMR (CDCl$_3$) δ 12.0 (s, CHSi), 17.9 (s, *C*H$_3$CH), 36.1 (s, CH$_3$N), 69.9 (s, CHOSi), 125.1, 126.8, 127.7, 128.4 (C$_6$H$_5$), 149.7 (s, CH), 155.9 (s, *C*-CHOSi); ^{29}Si NMR (C$_6$D$_6$) δ +19.0; MS (DCI, NH$_3$) *m/z* = 346 (M + 1). For **12'**: ^{1}H NMR (CD$_3$CN) δ 0.05 (s, 6 H, CH$_3$Si), 1.12 (s, 9 H, CH$_3$C), 7.60−8.02 (m, 15 H, C$_6$H$_5$); ^{13}C NMR (CD$_3$CN) δ −4.6 (s, CH$_3$Si), 18.4 (s, CH$_3$*C*), 26.7 (s, *C*H$_3$C), 120.2 (q, ^1J(C−F) = 320.3 Hz, CF$_3$), 123−141 (m, C$_6$H$_5$), 154.3 (s, CSi).

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Scheme 2

X = CF₃SO₃
1a, 7a, 9a, 11a: R = Si(i-Pr)₃ ;R' = Me
1b, 7b, 9b, 11b: R = SiMe₂t-Bu ;R' = Me
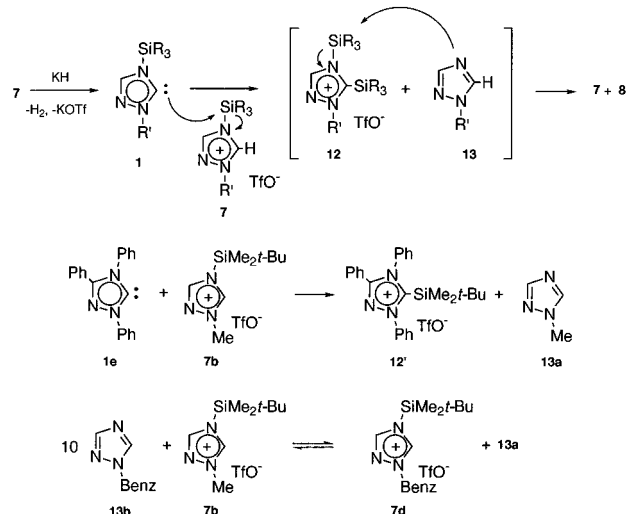
Scheme 3

X = CF₃SO₃

All attempts to spectroscopically characterize carbenes **1a–d** failed, even when monitoring the deprotonation reaction at −78 °C. To prove that the 1,2-migration occurred from the expected transient carbenes, **1a,b** were generated in the presence of a large excess of benzaldehyde. The resulting products **9a,b** (66−72% yields) and **10** (19−15%) have been fully characterized;[12] a single-crystal X-ray diffraction study for **10** was performed. Hetero-cycles **9a,b** clearly result from the attack of the nucleophilic carbenes **1a,b** at the carbonyl group leading to the zwitterion **11a,b**, followed by migration of the silyl group. On the other hand, **10** is the product of the coupling of two benzaldehyde molecules, which is reminiscent of the Breslow benzoin conden-sation catalyzed by thiazolylidene, the first experimental evidence for the transient formation of aromatic carbenes[14] (Scheme 2).

The next question was the intra- or intermolecular nature of the rearrangement of carbenes **1a–d** into triazoles **8a–d**. Depro-tonation of a 1/1 mixture of triazolium salts **7a** and **7d**, bearing different substituents at both nitrogen atoms, led to a mixture of the four rearrangement products **8a–d**, which were identified by ¹H NMR and GC/MS of the bulk reaction mixture. Starting from a 1/1 mixture of triazolium salts **7b,c**, the same products **8a–d** were obtained (Scheme 3). We then checked that in solution no exchange reactions of the silyl groups occurred between the triazolium salts **7a,d**, and between **7b,c**. Similarly, no silyl group exchanges occurred between the triazoles **8a–d**. These results as a whole prove that carbenes **1a–d** were formed by deproto-nation of triazolium salts **7a–d** and that the formation of triazoles **8a–d** resulted from an intermolecular process.

It was then of interest to gain greater insight into the mechanism of this intermolecular rearrangement. Aromatic carbenes are very good nucleophiles.[7d] Therefore, a nucleophilic attack of a carbene of type **1** on the silyl group of a starting cation **7** could result in the formation of the *C*- and *N*-silyl-substituted triazolium salt **12**,

Scheme 4

along with triazole **13** (Scheme 4). Compounds **12** and **13** could then react together via a nucleophilic attack of the nitrogen of **13** at the *N*-silyl group of the cation **12**, affording the rearrangement product **8** and regenerating the starting salt **7**. The first step is supported by the reaction of the stable carbene **1e** with triazolium salt **7b** at 0 °C, which led to the *C*-silylated triazolium salt **12′** and triazole **13a**.[12] The second part of the postulated mechanism has been modelized by reacting the triazole **13b** with the *N*-silylated triazolium **7b**. A large excess of **13b** was necessary to displace the equilibrium toward the formation of **7d** and **13a**, and the reaction only occurred at room temperature. Therefore, it could be surprising that derivatives **12** and **13** were not detected by monitoring the reaction of the cations **7** with KH at low temperature; however, it is quite clear that the sterically congested triazolium salt **12** is much more reactive than the model compound **7b** (Scheme 4).

In conclusion, 1,2-migrations can occur for aromatic carbenes such as **1a–d**, but via intermolecular processes in contrast to all known transient carbenes.[10] This rearrangement implies the carbene and an electrophilic partner. This is reminiscent of the specific behavior of the stable carbenes **1–5** toward dimerization, for which the protonated form of the carbene is also involved.[15,16]

Supporting Information Available: Experimental procedures, physi-cal and spectroscopic data for all new compounds; X-ray structures, tables of crystal and intensity collection data, position and thermal parameters, and interatomic distances for derivatives **8a** and **10** (21 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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