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A Carbene–GeI$_2$ Adduct: Model of the Non-Least-Motion Pathway for Dimerization of Singlet Carbenes

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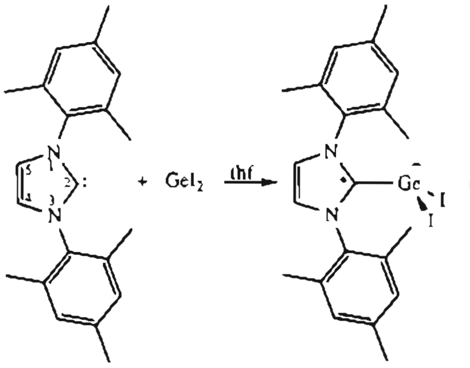
We have previously reported the syntheses, characterizations, and isolation of stable nucleophilic carbenes.[1,2] These imidazol-2-ylidenes have singlet ground states[3] and offer a convenient opportunity to observe the direct reactivity of carbenes with various reagents[4,5] in the absence byproducts from carbene generation and without the need to mask the carbene in the form of a "cryptocarbene" [6] precursor.

The dimerization of singlet carbenes is believed to follow a non-least-motion pathway that involves the attack of the occupied in-plane σ lone pair of one singlet carbene center on the out-of-plane vacant p orbital of a second carbene as shown in Scheme I.[7-11]

This non-least-motion pathway for singlet carbene dimerization has been investigated in detail using quantum mechanical models; however, chemical models for species along the reaction coordinate have not been available for direct study. A related non-least-motion pathway for phosphonium ylide formation from PH$_3$ and $^1A_1$:CH$_2$ was investigated by Trinquier and Mâlrieu.[12] These workers identified the adduct of triphenylphoshine and germanium dichloride that was characterized by Bokii et al.[13] as a structural model for phosphonium ylide formation.

We used germanium diiodide as a model for a singlet carbene in reaction with 1,3-dimesitylimidazol-2-ylidene (**1**). Reaction of **1** with GeI$_2$ in tetrahydrofuran (thf) quantatively afforded the carbene–germene adduct **2** as a yellow crystalline material (eq 1).[14]



1 **2**

(1)

Adduct **2** melts at 210–214 °C, which is substantially higher than the melting point for the free carbene (150–155 °C). The ring protons in the 4- and 5-positions of the imidazole ring resonate at lower field in adduct **2** than in carbene **1** (Δδ: 0.60 in C_6D_6, 0.56 in thf-d_8). This downfield shift suggests an increase in positive charge and π-delocalization in **2** as compared to **1**. The carbene center in **1** is shifted upfield by 60.88 ppm when bonded to the germanium center of **2**. These NMR data support a structure for **2** in which the newly formed C–Ge bond is not a true double bond but rather highly polarized as indicated in eq 1.

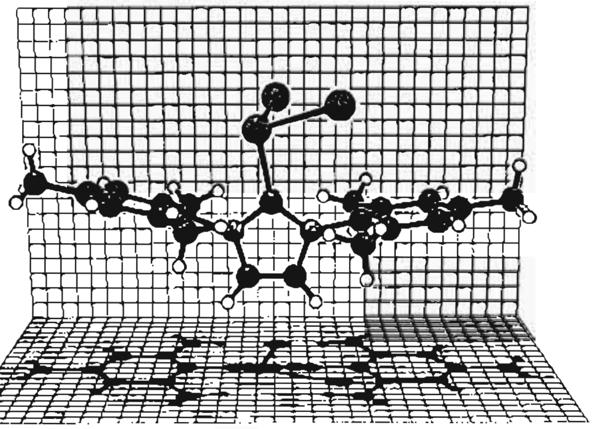
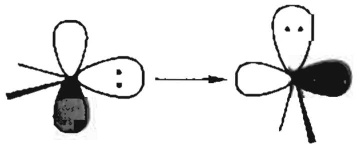


Figure 1. KANVAS[16] drawing of 2

Scheme I



The X-ray structure of **2** was determined on a crystal grown by cooling a toluene/hexane solution.[15] The geometry of **2** is

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[†] Contribution No. 6414.

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(14) Germanium diiodide (0.505 g, 1.54 mmol) and 1,3-dimesitylimidazol-2-ylidene (**1**) (0.450 g, 1.48 mmol) were mixed in thf (20 mL), and the mixture was stirred for 6 h. The solvent was removed from the resulting cloudy yellow solution to afford 0.95 g of crude adduct **2**. The crude product was extracted into toluene, and the extract was filtered, concentrated, and cooled to –25 °C to produce yellow plates of **2** (0.620 g, 65%), mp 210–214 °C. ^{1}H NMR (C_6D_6): δ 2.05 (s, 6 H, *p*-CH$_3$), 2.08 (s, 12 H, *o*-CH$_3$), 5.88 (s, 2 H, NCH), 6.69 (s, 4 H, *m*-H). ^{1}H NMR (thf-d_8): δ 2.20 (s, 12 H, *o*-CH$_3$), 2.33 (s, 6 H, *p*-CH$_3$), 7.02 (s, 4 H, *m*-H), 7.60 (s, 2 H, NCH). ^{13}C NMR (thf-d_8): δ 18.92 (s, *o*-CH$_3$), 21.20 (s, *p*-CH$_3$), 125.83 (s, NCH), 130.29 (s, mesityl $C_{3,5}$), 134.59 (s, mesityl C_1), 136.11 (s, mesityl $C_{2,6}$), 140.98 (s, mesityl C_4), 158.81 (s, NCN). Anal. Calcd for $C_{21}H_{24}N_2GeI_2$: C, 39.98; H, 3.83; N, 4.44. Found: C, 40.17; H, 3.79; N, 4.13.

(15) Crystal data for **2** at –65 °C with Mo Kα radiation: a = 1625.0(2), b = 1760.9(2), c = 1627.5(2) pm; orthorhombic, *Pccn*, Z = 8; μ(Mo) = 39.28 cm^{-1}, 1717 unique reflections with $I > 3\sigma(I)$. The final R factors were R = 0.051 and R_w = 0.038. The largest residual electron density in the final difference Fourier map was 0.73 e/Å^3, near one of the iodines. Further details of the crystal structure are available in the supplementary material.

(16) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A.J.A. (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.

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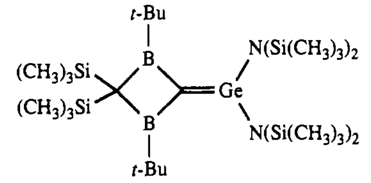
Table I. Selected Bond Lengths (pm) and Angles (deg) in **2** and Related Structures[a]

property	**1**	**2**	1,3-diphenylimidazolium ion[18c]
$r(C_2–N_{1(3)})$	136.5(4), 137.1(4)	136.8(15), 133.9(14)	133.6
$r(C_4–C_5)$	133.1(5)	132.3(17)	133.9
$r(N_{1(3)}–C_{5(4)})$	138.1(4), 137.8(4)	140.1(16), 138.7(15)	138.0
$r(N_{1(3)}$–mesityl)	144.1(4), 144.2(4)	143.3(15), 143.6(15)	143.2 (phenyl)
$r(C_2–Ge)$		210.2(12)	
r(Ge–I)		263.9(2), 268.1(2)	
$\theta(N_1–C_2–N_3)$	101.4(2)	107.0(10)	109.2
$\theta(C_{5(4)}–N_{1(3)}–C_2)$	112.8(3), 112.8(3)	108.0(10), 110.0(10)	108.0
$\theta(N_{1(3)}–C_{5(4)}–C_{4(5)})$	106.5(3), 106.5(3)	109.0(10), 107.0(10)	106.5
$\theta(C_2–N_{1(3)}$–mesityl)	121.8(2), 122.6(2)	132.0(10), 124.0(10)	126.6 (phenyl)
$\theta(Ge–C_2–N_{1(3)})$		137.0(10), 116.0(10)	
$\theta(C_2–Ge–I)$		100.2(4), 95.4(3)	
θ(I–Ge–I)		99.43(6)	

[a] The numbering scheme for all compounds is as indicated for **1**.

illustrated with the KANVAS[16] drawing in Figure 1. The germanium center is distinctly pyramidal with C–Ge–I angles of 95.4 and 100.1° and a I–Ge–I angle of 99.4°. The Ge–C bond in **2** is 210.2 pm, which is much longer than that in the adduct from Berndt's cryptocarbene and a divalent germanium center **3** ($r_{C–Ge}$ = 182.7 pm)[6] or the fluorenylidene derivative **4** ($r_{C–Ge}$ = 180.6 pm).[17] The pyramidalization of the germanium and the length and orientation of the C–Ge bond indicate a highly charge-separated structure for **2** as suggested by NMR data. The ring internal angle at C_2 in **2** (Table I) has opened from that in the carbene to one more like an imidazolium ion.[18] One final feature of the structure of **2** that is apparent from the direct view in Figure 1 is the offset of the C–Ge bond from the pseudo-C_2 axis which passes through the former carbene center of the imidazole fragment. The deviation from this ideal orientation is 12° and most likely results from a steric interaction of the iodines and the mesityl substituents. The germanium center is 18 pm out of the imidazole-ring plane.

The geometry of nucleophilic carbene adduct **2** is dramatically different from those of the more olefin-like adducts **3**[6] and **4**[17,19] that are derived formally from electrophilic carbene precursors and bear more electropositive substituents at germanium. Not only are the geometries of the two adducts very different but the charge separation about the C–Ge bond is reversed. Differences in iodine ylides derived from nucleophilic carbenes and electrophilic carbenes have been noted previously.[4] Together, adducts **2** and **3** or **4** illustrate the different reactivity that is found for nucleophilic carbenes as compared to electrophilic carbenes.



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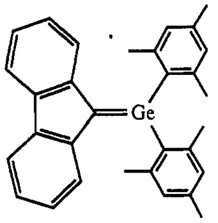

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Finally, the highly pyramidal geometry observed for the germanium center in **2** makes this adduct a model for an intermediate structure in the non-least-motion pathway of singlet carbene dimerization (Scheme I) and provides experimental support for this reaction pathway.[7-11]

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Supplementary Material Available: A textual description of the X-ray crystallographic determination of **2**, tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles, and ORTEP drawings (8 pages). Ordering information is given on any current masthead page.

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(18) For structures of representative imidazolium ions see: (a) 1,3-Dimethylimidazolium chloride (ref 2, supplementary material). (b) 1,3-Diadamant-1-ylimidazolium tetraphenylborate (ref 1, supplementary material). (c) 1,3-Diphenylimidazolium perchlorate (Luger, P.; Ruban, G. *Z. Kristallogr.* **1975**, *142*, 177). (d) Langer, V.; Huml, K.; Reck, G. *Acta Crystallogr., Sect. B* **1982**, *38*, 298. (e) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753.

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