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Silylium Cations

Synthesis of a Silylium Zwitterion[**]

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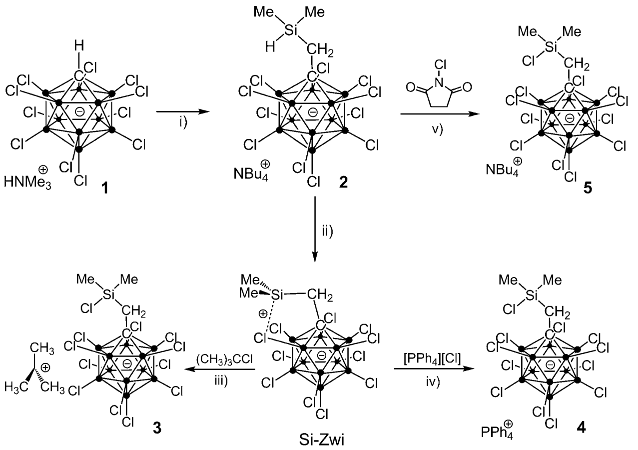
The pursuit of isolable silylium cations (R_3Si^+, where R is an alkyl, aryl, or a similar univalent substituent) has challenged the boundaries of existing chemical concepts and the boundaries of the known synthetic methods.[1–3] Silylium cations are some of the strongest Lewis acids known. Their similarity to their lighter congener carbocations (R_3C^+) had spurred the intrigue but they turned out to be more resistant to isolation than carbocations.[1] Only at the turn of the last century was it possible to prepare compounds that can be viewed as R_3Si^+ salts or their close approximations.[2–7]

The key to the success in R_3Si^+ preparation is the recognition of the need for a weakly coordinating anion (WCA) that is maximally inert and minimally basic.[8] The class of anions that has so far best fulfilled these requirements is comprised of the various halogenated carborane anions ($[HCB_{11}X_{11}]^-$, where X = halogen, H, or alkyl), which are remarkably robust and versatile WCAs.[3,9,10] Only very bulky triaryl silylium cations, such as Mes_3Si^+ (Mes = mesityl = 2,4,6-$Me_3C_6H_2$) have been unambiguously characterized as a discrete three-coordinate cation planar at Si, with the $[HCB_{11}Me_5Br_6]^-$ counterion for the only solid-state structure.[7,11] Trialkylsilylium cations have only been isolated as very weak adducts, coordinated typically to a halogen atom on the carborane anion, an arene solvent, or a trialkylsilane.[4–6,12–14] These salt-like compounds $[R_3Si][HCB_{11}X_{11}]$ have some of the highest levels of acidity achievable in well-defined systems under preparatory laboratory conditions and their full potential is yet to be exploited.[15] As an example of their unique capacity, they have recently been utilized as catalysts for the very challenging C–F conversion reactions of aliphatic and aromatic compounds.[16,17]

Silylium cations can be particularly useful in synthesis where abstraction of a halide or pseudohalide is critical for generation of a new highly unsaturated cation.[3,18,19] Their chloride-abstracting ability is far superior[2] to that of the commonly used Ag^+ and is free of redox complications.

To contrast with the two-component cation–anion combinations, we wished to explore the possibility of a single-component, neutral molecule endowed with the Lewis acidity of a silylium cation. Preferably, such a molecule would cleanly convert into a robust WCA upon halide abstraction and not generate another by-product. There are currently no neutral Lewis acids of silylium-class strength that fit this description. Classical strong inorganic Lewis acids (for example, $AlCl_3$, SbF_5) result in anions that are relatively coordinating, prone to rearrangements, and/or are redox non-innocent.

Tris(pentafluorophenyl)boron $[B(C_6F_5)_3]$ is a notable non-oxidizing Lewis acid that has found widespread use,[20,21] but it does not have the Lewis acidity of a silylium-like cation. The tris(perfluoroalkoxy)aluminum Lewis acid $Al(OC(CF_3)_3)_3$ is a powerful example,[22,23] although this construction is not immune to degradation and redistribution. We envisaged a zwitterion in which the silylium cation site is connected to the anionic carborane core by an inert covalent linker. The silane precursor anion **2** (Scheme 1) was synthesized by deprotonation of the carbon vertex of the known $[Me_3NH][HCB_{11}Cl_{11}]$ (**1**) followed by alkylation with $ClCH_2SiMe_2H$. We recently reported similar alkylation reactions of $[HCB_{11}Cl_{11}]^-$ with simple alkyl iodides.[24] The desired precursor anion $[HSiMe_2CH_2CB_{11}Cl_{11}]^-$ was isolated as its tetrabutylammonium salt **2** in excellent yield.



Scheme 1. Syntheses: i) Treatment of **1** with NaH and $ClCH_2SiMe_2H$ in THF for 48 h at 40°C followed by precipitation of **2** with $[nBu_4N]Cl$. ii) $[Ph_3C][B(C_6F_5)_4]$ in a 3:2 toluene/1,2-difluorobenzene mixture with precipitation of Si-Zwi. iii) Treatment of Si-Zwi with *tert*-butyl chloride in liquid SO_2 at −70°C. iv) Trapping of Si-Zwi with $[Ph_4P][Cl]$ in dichloromethane to form the $[ClSiMe_2CH_2CB_{11}Cl_{11}]^-$ anion. v) Independent synthesis of the $[ClSiMe_2CH_2CB_{11}Cl_{11}]^-$ anion by treatment of **2** with N-chlorosuccinimide in dichloromethane.

Treatment of **2** with $[Ph_3C][B(C_6F_5)_4]$ in a toluene/1,2-difluorobenzene mixture resulted in the abstraction of the silicon-bound hydride by the Ph_3C^+ cation and precipitation of the desired zwitterion Si-Zwi, which was isolated in 46% yield upon workup. Under slow diffusion conditions, this reaction produced a single crystal suitable for a structural

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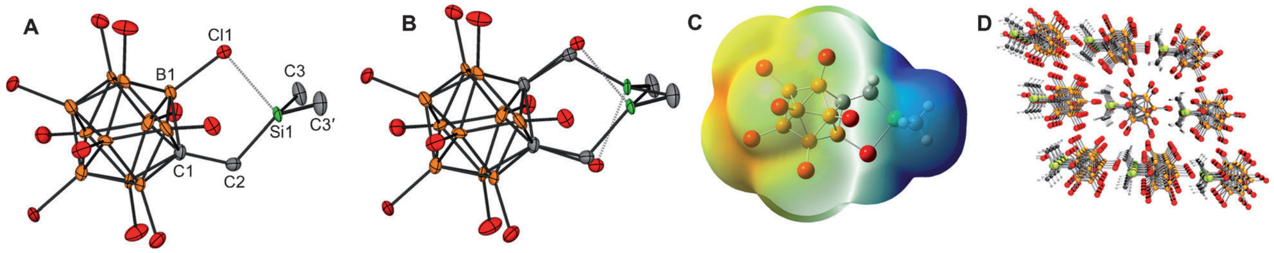

Figure 1. A) ORTEP diagram of the structure of Si-Zwi in the solid state. Si1⋯Cl1 2.304(8) Å; sum of C-Si-C angles 351(2)°. B) ORTEP diagram of the observed disorder in the crystal, consisting of two superimposed orientations of the molecule related by a 180° rotation around a pseudo-C_2 axis passing through the center of the cage and the silicon site. In both instances the ellipsoids were set at 50% probability, with the hydrogen atoms omitted for clarity. C) Charge density plot for Si-Zwi. D) Three-dimensional packing diagram of Si-Zwi in the crystal.

study by X-ray diffractometry (XRD). The solid-state structure contained crystallographic disorder derived from the random swapping of the C1-C2-Si1(C3)$_2$ and B1-Cl1-Si1(C3)$_2$ moieties (Figure 1 A, B). The silylium center in Si-Zwi is stabilized by the weak coordination of a proximal chlorine atom located at a distance of 2.304(8) Å. The significant silylium character of Si-Zwi is supported by only modest pyramidalization at Si: sum of C-Si-C angles around Si is 351(2)°. These parameters are similar to those found in adducts of R_3Si^+ cations with chlorocarboranes.[3] For example, the Si−Cl distance was found to be 2.3044(13) Å or 2.2815(11) Å (two crystallographically independent ion pairs) in $Et_3Si[HCB_{11}H_5Cl_6]$,[25] 2.323(3) Å in $i$$Pr_3Si[HCB_{11}H_5Cl_6]$[12] and 2.334(3) Å in $Et_3Si[HCB_{11}Cl_{11}]$,[13] whereas the values for the sum of the C-Si-C angles in these compounds fall into 345–351° range.

Si-Zwi proved to be unexpectedly poorly soluble in 1,2-difluorobenzene, a solvent that is typically quite capable of dissolving organic salts of carborane anions. We were able to shed light on the low solubility and on the observed disorder in the solid-state through density functional theory (DFT) calculations on an isolated gas-phase molecule of Si-Zwi. The calculated structure matched the XRD structure closely, lending extra credence to the model of the crystallographic disorder, and revealed a nearly C_{2v}-symmetric distribution of charge density in Si-Zwi (Figure 1 C). We posit that it is the origin of the crystallographic disorder: Si-Zwi packs in the crystal as though it were a C_{2v}-symmetric molecule. The dipole moment of Si-Zwi is very high (15.2 D, by DFT) and the "head-to-tail" packing with alternating stacking of layers (Figure 1 D) presumably results in a high lattice energy that disfavors dissolution.

DFT calculations on the gas phase Si-Zwi also accurately predicted its ^{29}Si NMR chemical shift. Si-Zwi resonated at $\delta = 137.4$ ppm in the solid-state ^{29}Si NMR spectrum; DFT calculation yielded $\delta = 140.7$ ppm. The degree of the downfield ^{29}Si NMR chemical shift has been used to characterize the degree of silylium character. The Si-Zwi value is farther downfield than the values for adducts of R_3Si^+ with chlorocarboranes and is comparable to $[Me_3Si][EtCB_{11}F_{11}]$ ($\delta = 138$ ppm), for which ionicity was demonstrated in the melt.[26] Consistent with the postulated significant silylium character, the lowest unoccupied molecular orbital (LUMO) of Si-Zwi is predominantly based on silicon (Supporting Information, Figure S17, and table of contents graphic).

Si-Zwi rapidly reacted with $(CH_3)_3CCl$ in liquid SO_2 at −70 °C to produce the $[(CH_3)_3C]^+$ cation complemented by the $[ClSiMe_2CH_2CB_{11}Cl_{11}]^-$ anion (compound **3**, Scheme 1). The identity of the anion was confirmed by independent syntheses (Scheme 1): $[Ph_4P][ClSiMe_2CH_2CB_{11}Cl_{11}]$ (**4**) was cleanly obtained in the reaction of Si-Zwi with $[Ph_4P][Cl]$, while the reaction of **2** with N-chlorosuccinimide produced $[nBu_4N][ClSiMe_2CH_2CB_{11}Cl_{11}]$ (**5**). Compounds **3**, **4**, and **5** were quite soluble in liquid SO_2 or dichloromethane (for **4** and **5**). The *tert*-butyl cation in **3** was identified in SO_2 solution at −60 °C or below based on the characteristic resonances[27,28] in the $^{13}C\{^1H\}$ ($\delta = 334.5$ and 49.0 ppm) and ^1H ($\delta = 4.53$ ppm) NMR spectra.[29] This reaction demonstrates the prowess of Si-Zwi as a powerful Lewis acid and that the WCA generated from Si-Zwi upon chloride abstraction is compatible with a reactive carbocation. Our findings demonstrate the potential for design of powerful charge-neutral Lewis acids based on zwitterionic construction with the carborane cage as the anionic component. This approach is conceptually related to the use of neutral carborane radical $MeCB_{11}Me_{11}$ as a one-electron oxidant that converts to a weakly coordinating anion upon accepting an electron.[30,31]

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[1] J. B. Lambert, L. Kania, S. Zhang, *Chem. Rev.* **1995**, *95*, 1191.
[2] C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 325.
[3] C. A. Reed, *Acc. Chem. Res.* **2010**, *43*, 121.
[4] C. A. Reed, Z. Xie, R. Bau, A. Benesi, *Science* **1993**, *262*, 402.
[5] J. B. Lambert, S. Zhang, *J. Chem. Soc. Chem. Commun.* **1993**, 383.
[6] J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917.
[7] K.-C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin, J. B. Lambert, *Science* **2002**, *297*, 825.
[8] I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116; *Angew. Chem. Int. Ed.* **2004**, *43*, 2066.
[9] S. Körbe, P. J. Schreiber, J. Michl, *Chem. Rev.* **2006**, *106*, 5208.
[10] E. S. Stoyanov, K.-C. Kim, C. A. Reed, *J. Am. Chem. Soc.* **2006**, *128*, 8500.

[11] A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem.* **2011**, *123*, 12845; *Angew. Chem. Int. Ed.* **2011**, *50*, 12636.

[12] Z. Xie, J. Manning, R. W. Reed, R. Mathur, P. D. W. Boyd, A. Benesi, C. A. Reed, *J. Am. Chem. Soc.* **1996**, *118*, 2922.

[13] S. P. Hoffmann, T. Kato, F. S. Tham, C. A. Reed, *Chem. Commun.* **2006**, 767.

[14] M. F. Ibad, P. Langer, A. Schulz, A. Villinger, *J. Am. Chem. Soc.* **2011**, *133*, 21016.

[15] H. F. T. Klare, M. Oestreich, *Dalton Trans.* **2010**, *39*, 9176.

[16] C. Douvris, O. V. Ozerov, *Science* **2008**, *321*, 1188.

[17] O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldridge, J. S. Siegel, *Science* **2011**, *332*, 574.

[18] E. S. Stoyanov, S. P. Hoffmann, M. Juhasz, C. A. Reed, *J. Am. Chem. Soc.* **2006**, *128*, 3160.

[19] J. D. Egbert, R. M. Bullock, D. M. Heinekey, *Organometallics* **2007**, *26*, 2291.

[20] G. Erker, *Dalton Trans.* **2005**, 1883.

[21] W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345.

[22] L. O. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quiñones, V. Brecht, I. Krossing, *Angew. Chem.* **2008**, *120*, 7772; *Angew. Chem. Int. Ed.* **2008**, *47*, 7659.

[23] A. Kraft, N. Trapp, D. Himmel, H. Böhrer, P. Schlüter, H. Scherer, I. Krossing, *Chem. Eur. J.* **2012**, *18*, 9371.

[24] R. Ramírez-Contreras, O. V. Ozerov, *Dalton Trans.* **2012**, *41*, 7842.

[25] C. Douvris, C. M. Nagaraja, C.-H. Chen, B. M. Foxman, O. V. Ozerov, *J. Am. Chem. Soc.* **2010**, *132*, 4946.

[26] T. Küppers, E. Bernhardt, R. Eujen, H. Willner, C. W. Lehmann, *Angew. Chem.* **2007**, *119*, 6462; *Angew. Chem. Int. Ed.* **2007**, *46*, 6346.

[27] T. Kato, C. A. Reed, *Angew. Chem.* **2004**, *116*, 2968; *Angew. Chem. Int. Ed.* **2004**, *43*, 2908.

[28] F. Scholz, D. Himmel, H. Scherer, I. Krossing, *Chem. Eur. J.* **2013**, *19*, 109.

[29] Warming up the SO_2 solution of **3** to ambient temperature resulted in decomposition, although the diminished ^1H NMR resonance of $[(CH_3)_3C]^+$ could still be observed at 20 °C. Apparently, strong acid formation takes place, from the similarity of new downfield signals to the spectrum of F_3CSO_3H in liquid SO_2. It is not clear whether degradation is owing to interaction with SO_2, adventitious impurities, or the anion. Kato and Reed[27] also only observed $[(CH_3)_3C][HCB_{11}Me_5Br_6]$ in solution at $-60\,°C$.

[30] I. Zharov, B. T. King, Z. Havlas, A. Pardi, J. Michl, *J. Am. Chem. Soc.* **2000**, *122*, 10253.

[31] M. J. Ingleson, M. F. Mahon, A. S. Weller, *Chem. Commun.* **2004**, 2398.