A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
www.angewandte.org

Accepted Article

Title: Synthesis of a Counteranion-Stabilized Bis(silylium) Ion

Authors: Qian Wu, Avijit Roy, Guoqiang Wang, Elisabeth Irran, Hendrik F.T. Klare, and Martin Oestreich

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202003799
Angew. Chem. 10.1002/ange.202003799

Link to VoR: http://dx.doi.org/10.1002/anie.202003799
http://dx.doi.org/10.1002/ange.202003799

WILEY-VCH

Synthesis of a Counteranion-Stabilized Bis(silylium) Ion

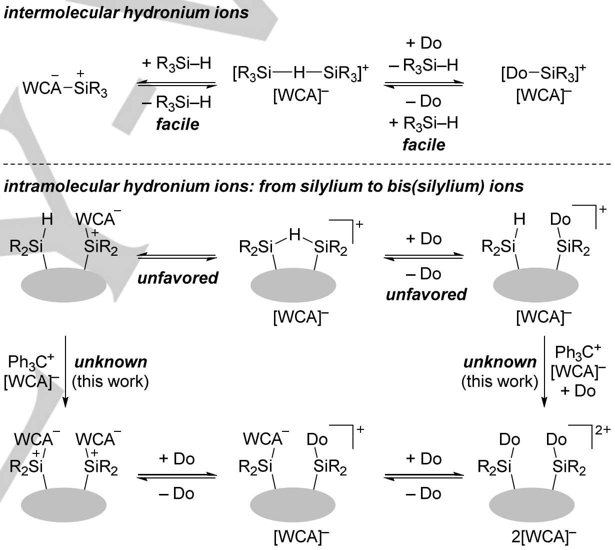
Qian Wu[+], Avijit Roy[+], Guoqiang Wang, Elisabeth Irran, Hendrik F. T. Klare, and Martin Oestreich*

Dedicated to Professor Paul Knochel on the occasion of his 65th birthday

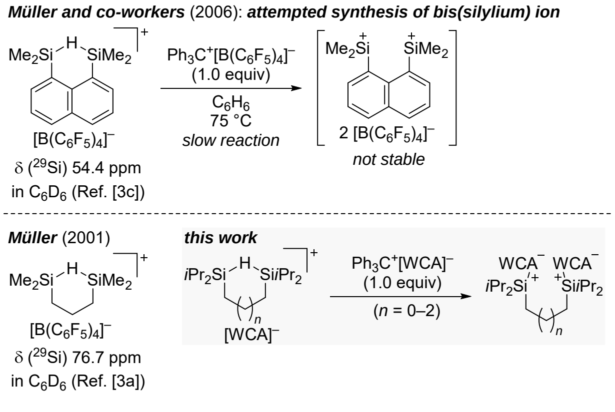
Abstract: The preparation of a molecule with two alkyl-tethered silylium-ion sites from the corresponding bis(hydrosilanes) by twofold hydride abstraction is reported. The length of the conformationally flexible alkyl bridge is crucial as otherwise the hydride abstraction stops at the stage of a cyclic bissilylated hydronium ion. With an ethylene tether, the open form of the hydronium-ion intermediate is energetically accessible and engages in another hydride abstraction. The resulting bis(silylium) ion has been NMR spectroscopically and structurally characterized. Related systems based on rigid naphthalen-*n*,*m*-diyl platforms can only be converted into the dications when the positively charged silylium-ion units are remote from each other (1,8 versus 1,5 and 2,6).

A common way of stabilizing silylium ions is by Lewis pair formation with σ-basic molecules to yield onium ions.[1] Under certain circumstances, that is with no such Lewis base present in the reaction medium, even an Si–H bond can lend stabilization to a silylium ion in the form of a three-center, two-electron (3c2e) Si–H–Si bond (Scheme 1, top).[2–4] If intermolecular, this is a weak interaction, and the hydrosilane in these hydronium ions is usually supplanted by the arene used as the solvent.[2] Conversely, the situation changes when a tethered Si–H bond is geometrically accessible (Scheme 1, bottom). Several cyclic hydronium ions have already been described, and their spectroscopic and crystallographic characterization established that these are free in the sense that neither the solvent nor the counteranion coordinates to either of the silicon atoms.[3]

These systems are actually fairly stable, and the abstraction of another hydride with the trityl salt $Ph_3C[B(C_6F_5)_4]$ to access a bis(silylium) ion is, if at all, slow. A likely reason could be the stereoelectronic inaccessibility of the Si–H bond engaged in the aforementioned 3c2e bond. An attempt by Müller and co-workers did not enable the isolation of such a species (Scheme 2, top).[3c] The targeted dication was too reactive and immediately decomposed the borate counteranion. The close proximity of the cationic centers attached to the rigid naphthalen-1,8-diyl platform is presumably part of the problem. Müller had reported another six-membered ring system with an aliphatic backbone before (Scheme 2, bottom).[3a] We anticipated that smaller or larger ring sizes would make the formation of the Si–H–Si unit less favorable (gray box), thereby allowing for donor-mediated ring opening and eventually facile hydride abstraction (Scheme 1, bottom). The aliphatic linker would further equip the dication with the necessary conformational flexibility to accommodate the positive charges and Lewis pair formation with bulky donor molecules. We disclose here the synthesis of a bis(silylium) ion, a new class of bidentate[5] silicon superelectrophiles[6] for potential application in catalysis[7] or as receptors.[8]



Scheme 1. Inter- and intramolecular hydronium ions, and the generation of bis(silylium) ions from those cyclic systems. WCA = weakly coordinating anion. Do = donor, typically solvent molecule.



Scheme 2. Attempted and planned synthesis of counteranion-stabilized bis(silylium) ions.

---

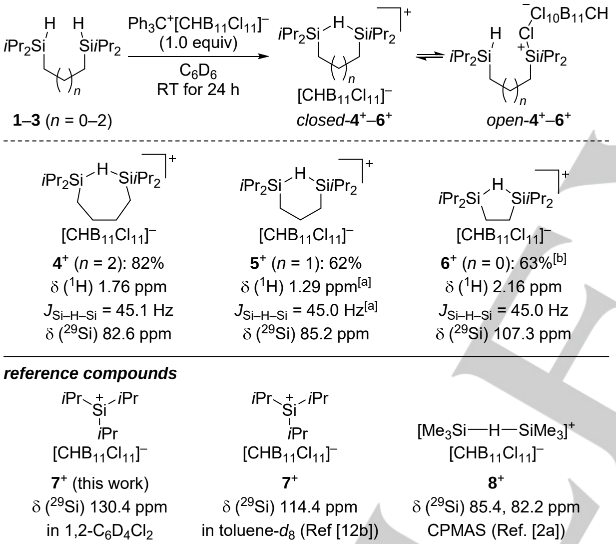
[*] Dr. Q. Wu,[+] A. Roy,[+] Dr. G. Wang, Dr. E. Irran,[++] Dr. H. F. T. Klare, Prof. Dr. M. Oestreich
Institut für Chemie, Technische Universität Berlin
Strasse des 17. Juni 115, 10623 Berlin (Germany)
E-mail: martin.oestreich@tu-berlin.de
Homepage: http://www.organometallics.tu-berlin.de

[+] These authors contributed equally to this work.

[++] X-ray crystal-structure analysis.

Supporting information for this article is given via a link at the end of the document.

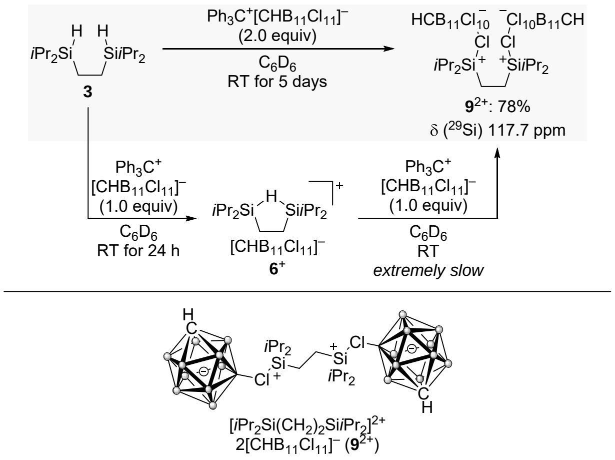
The choice of substituents at the silicon atom is crucial for the successful generation of heteroleptic silylium ions as substituent redistribution reactions often produce complex mixtures.[9] The alkyl-substituted precursors required for the present study are inherently afflicted with this problem but isopropyl and *tert*-butyl group usually hamper such processes.[9c,9d] For this reason, we opted for the bis(hydrosilanes) **1**–**3** with *i*Pr$_2$Si moieties (Scheme 3, top); their straightforward preparation is outlined in the Supporting Information. The chemical stability of the counteranion is of utmost importance in silylium-ion chemistry,[10] and $[B(C_6F_5)_4]^-$ previously used by Müller is not suitable for the given challenge.[3c,11] We decided to go with $[CHB_{11}Cl_{11}]^-$,[12] one of the least coordinating and most robust carborate counteranions.[10,13] Reacting precursors **1**–**3** with the corresponding trityl salt $Ph_3C[CHB_{11}Cl_{11}]$ in C_6D_6 resulted a biphasic suspension that contained silylium ions **4**$^+$–**6**$^+$ (Scheme 3, top). For characterization, the phases were separated and the remaining slurry was washed with a few drops of C_6D_6 and *n*-pentane. The remainder was fully dissolved in 1,2-$C_6D_4Cl_2$, and the homogeneous solution was subjected to NMR analysis (Scheme 3). Running those reactions directly in 1,2-$C_6D_4Cl_2$ was far less clean.



Scheme 3. Synthesis and NMR spectroscopic characterization of cyclic hydronium ions. Unless noted otherwise, all NMR spectra were recorded in 1,2-$C_6D_4Cl_2$. CPMAS = cross polarization and magic-angle spinning. [a] Determined by a $^1H/^{29}Si$-1D-CLIP-HSQMBC NMR experiment. [b] The molecular structure of *closed*-**6**$^+$ was determined by an X-ray diffraction analysis but its quality prevents its publication (see the Supporting Information). The CIF file was deposited with The Cambridge Crystallographic Data Centre as a personal communication (CCDC 1990361).

The collected ^{29}Si NMR data were correlated with independently prepared *i*Pr$_3$Si$^+$ (**7**$^+$)[12b] and known $[(Me_3Si)_2(\mu\text{-}H)]^+$ (**8**$^+$)[2a] both having $[CHB_{11}Cl_{11}]^-$ as counteranion (Scheme 3, bottom). The silylium ions **4**$^+$ and **5**$^+$ with a butylene (*n* = 2) or a propylene (*n* = 1) tether show chemical shifts similar to Reed's acyclic hydronium ion **8**$^+$[2a] (approx. δ (^{29}Si) 84 ppm) and Müller's system (cf. Scheme 2, bottom).[3a] We therefore concluded that these are best represented as cyclic systems *closed*-**4**$^+$ and *closed*-**5**$^+$, respectively. In turn, the silicon atom in ethylene-tethered silylium ion **6**$^+$ (*n* = 0) is significantly more deshielded with δ (^{29}Si) 107.3 ppm. This value lies between those of related hydronium ions and δ (^{29}Si) 130.4 ppm of *i*Pr$_3$Si$[CHB_{11}Cl_{11}]$ (**7**$^+$) in 1,2-$C_6D_4Cl_2$ and could therefore be an average resonance signal. To learn whether this is due to an equilibrium between the closed and counteranion- or solvent-stabilized open forms of **6**$^+$, we performed theoretical calculations at the B3LYP-D3(BJ)/cc-PVTZ+(PCM, benzene)//B3LYP-D3(BJ)/6-31G(d,p)+(PCM, benzene) level of theory.[14–16] Generally, these computations revealed that, out of those three, the closed forms represent the energetic minimum while the solvent adducts of the open forms are higher in energy than those of the counteranion (C_6H_6 or 1,2-$C_6H_4Cl_2$ versus $[CHB_{11}Cl_{11}]^-$). Importantly, a low free energy difference was only found between *closed*-**6**$^+$ and *open*-**6**$^+$ (ΔG = 1.3 kcal mol^{-1}). This means that the counteranion-stabilized open form of **6**$^+$ is energetically accessible in C_6H_6 solution. Conversely, *open*-**4**$^+$ and *open*-**5**$^+$ do not exist in solution state (ΔG = 3.9 and 5.5 kcal mol^{-1}, respectively). This trend was the same but more pronounced for the NMR solvent 1,2-$C_6D_4Cl_2$ (ΔG = 8.1 for **4**$^+$, 9.4 for **5**$^+$, and 4.7 kcal mol^{-1} for **6**$^+$). This is in line with VT NMR measurements which did not indicate any change in the stabilization mode (closed forms only). The computed NMR chemical shifts agree with those obtained experimentally (see the Supporting Information).

Based on the above reasoning, we predicted that ethylene-tethered **6**$^+$ would be more likely to participate in another hydride abstraction than **4**$^+$ and **5**$^+$ with longer alkyl bridges. Indeed, **4**$^+$ and **5**$^+$ did not react with $Ph_3C[CHB_{11}Cl_{11}]$ any further. However, the reaction of **6**$^+$ with the trityl salt was extremely slow, furnishing the desired bis(silylium) ion **9**$^{2+}$ in small quantities along with byproducts (Scheme 4). In turn, direct treatment of bis(hydrosilane) **3** with 2.0 equiv of $Ph_3C[CHB_{11}Cl_{11}]$ afforded the dication **9**$^{2+}$ in 78% yield (gray box). We explain this dramatic difference by the poor solubility of the reactants in C_6D_6; preformed, solid **6**$^+$ is less prone to undergo the hydride abstraction than in-situ-formed, dissolved **6**$^+$.[17] The new bis(silylium) ion was fully characterized by NMR spectroscopy, and its molecular structure was determined by X-ray single-crystal analysis (Figure 1).[18] Different from the previously reported solvent-stabilized *i*Pr$_3$Si$^+$ ion **7**$^+$ (Scheme 3, bottom), the cationic silicon centers are each stabilized by one of the counteranion's chlorine atoms. The *anti* conformation of the coordinated silicon centers is likely a consequence of both steric and charge–charge repulsion. The average C–Si–C angle is 116.4° and, hence, closer to a trigonal planar (120.0°) than a tetrahedral (109.5°) coordination geometry. The Si–Cl bond (2.341 Å) is longer than that of a typical covalent Si–Cl bond (2.072 Å) and even longer than that in 1,2-$C_6D_4Cl_2$-stabilized *i*Pr$_3$Si$^+$ (**7**$^+$) (2.33 Å).[2a]



Scheme 4. One-step and two-step approaches to bis(silylium) ion.

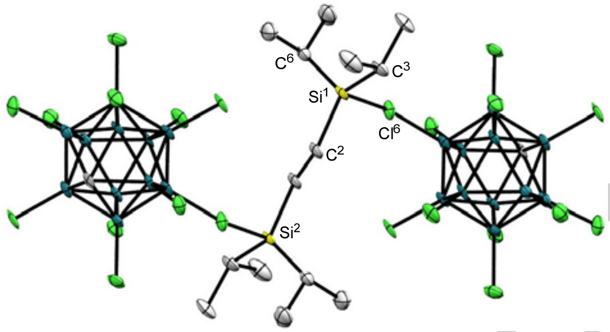
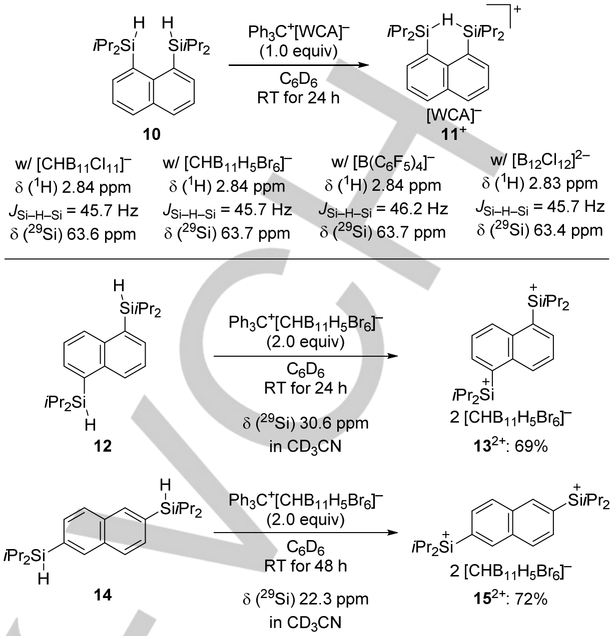


Figure 1. Molecular structure of bis(silylium) ion **9**$^{2+}$ (thermal ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Selected bond length (Å): Si^1–Cl^6 2.3411(15), Si^1–C^2 1.866(4), Si^1–C^3 1.855(5), Si^1–C^6 1.858(4). Selected bond angle (°): C^2–Si^1–C^3 112.68(19), C^2–Si^1–C^6 116.25(19), C^3–Si^1–C^6 120.2(2).

We then turned towards a reinvestigation of Müller's naphthalen-1,8-diyl system but were also not able to generate the corresponding bis(silylium) ion (cf. Scheme 2, top).[3c] Precursor **10** converted into the stable hydronium ions **11**$^+$ in high yield with various trityl salts Ph$_3$C[WCA] (Scheme 5, top). The aryl substitution typically brings about an upfield shift of about Δδ (^{29}Si) 20 ppm.[9b,9c] Relative to δ (^{29}Si) 85.2 ppm for **5**$^+$, approx. δ (^{29}Si) 63.5 ppm for **11**$^+$ independent of the weakly coordinating counteranion is in excellent agreement with this.



Scheme 5. Regioisomeric naphthalene-based bis(hydrosilanes) as precursors for bis(silylium) ions. Unless noted otherwise, all NMR spectra were recorded in 1,2-C$_6$D$_4$Cl$_2$.

As the *peri* substitution pattern is potentially thwarting the establishment of another positive charge, we subjected regioisomeric bis(hydrosilanes) **12** and **14** to the one-step procedure (Scheme 5, bottom). However, we found that the counteranion had a profound effect on the dication formation of these regioisomers; **13**$^{2+}$ and **15**$^{2+}$ did not form with [CHB$_{11}$Cl$_{11}$]$^-$ as the counteranion. In turn, the reaction of **12** and **14** with 2.0 equiv of Ph$_3$C[CHB$_{11}$H$_5$Br$_6$] afforded the bis(silylium) ions **13**$^{2+}$ and **15**$^{2+}$, respectively in good yields. Due to their poor solubility even in highly polar arene solvents, these bis(silylium) ions were characterized by NMR spectroscopy as the acetonitrile adducts.

The present work demonstrates that the generation of long-sought bis(silylium) ions is possible, provided that the two positive charges can dodge each other. This can either be achieved by conformational flexibility of the tether between those sites or by an appropriate predefined distance in rigid systems. The length of the flexible tether is crucial as it determines the stability of intermediate cyclic hydronium ions. With an ethylene brigde, the open form of such a hydronium ion exists in equilibrium to undergo another hydride abstraction. The new bis(silylium) ion has been characterized by NMR spectroscopy and X-ray diffraction. Future work will be directed towards the application of such superelectrophilic bidentate Lewis acids in catalysis or as receptors.[5]

Acknowledgements

A.R. gratefully acknowledges the Berlin Graduate School of Natural Sciences and Engineering for a predoctoral fellowship

(2018−2021). Q.W. and G.W. thank the Alexander von Humboldt Foundation (2017−2019) and the China Scholarship Council (2019−2020), respectively, for postdoctoral fellowships. The work was also funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany´s Excellence Strategy – EXC 2008 – 390540038 – UniSysCat. All theoretical calculations were performed at the High-Performance Computing Center (HPCC) of Nanjing University. We also thank Dr. Sebastian Kemper (TU Berlin) for expert advice with the NMR measurements. M.O. is indebted to the Einstein Foundation Berlin for an endowed professorship.

Keywords: bidentate interaction • carboranes • density functional calculations • Lewis acids • silylium ions

[1] For general reviews of silylium ion chemistry, see: a) V. Y. Lee, *Russ. Chem. Rev.* **2019**, *88*, 351–369; b) V. Ya. Lee, A. Sekiguchi in *Organosilicon Compounds*, *Vol. 1* (Ed.: V. Ya. Lee), Academic Press, Oxford, **2017**, pp. 197–230; c) T. Müller in *Structure and Bonding, Vol. 155* (Ed.: D. Scheschkewitz), Springer, Berlin, **2014**, pp. 107–162; d) T. Müller in *Science of Synthesis: Knowledge Updates 2013/3* (Ed.: M. Oestreich), Thieme, Stuttgart, **2013**, pp. 1–42.

[2] For intermolecular bissilylhydronium ions, see: a) S. P. Hoffmann, T. Kato, F. S. Tham, C. A. Reed, *Chem. Commun.* **2006**, 767–769; b) M. Nava, C. A. Reed, *Organometallics* **2011**, *30*, 4798–4800; c) S. J. Connelly, W. Kaminsky, D. M. Heinekey, *Organometallics* **2013**, *32*, 7478–7481.

[3] For intramolecular bissilylhydronium ions, see: a) T. Müller, *Angew. Chem. Int. Ed.* **2001**, *40*, 3033–3036; *Angew. Chem.* **2001**, *113*, 3123–3126; b) A. Sekiguchi, Y. Murakami, N. Fukaya, Y. Kabe, *Chem. Lett.* **2004**, *33*, 530–531; c) R. Panisch, M. Bolte, T. Müller, *J. Am. Chem. Soc.* **2006**, *128*, 9676–9682; d) A. Y. Khalimon, Z. H. Lin, R. Simionescu, S. F. Vyboishchikov, G. I. Nikonov, *Angew. Chem. Int. Ed.* **2007**, *46*, 4530–4533; *Angew. Chem.* **2007**, *119*, 4614–4617; e) A. Schäfer, M. Reißmann, A. Schäfer, M. Schmidtmann, T. Müller, *Chem. Eur. J.* **2014**, *20*, 9381–9386; f) L. Albers, J. Baumgartner, C. Marschner, T. Müller, *Chem. Eur. J.* **2016**, *22*, 7970–7977; g) L. Albers, S. Rathjen, J. Baumgartner, C. Marschner, T. Müller, *J. Am. Chem. Soc.* **2016**, *138*, 6886–6892.

[4] For gas-phase studies, see: a) M. Savoca, J. Langer, O. Dopfer, *Angew. Chem. Int. Ed.* **2013**, *52*, 1568–1571; b) M. A. R. George, M. Savoca, O. Dopfer, *Chem. Eur. J.* **2013**, *19*, 15315–15328; c) M. A. R. George, O. Dopfer, *Int. J. Mass Spectrom.* **2019**, *435*, 51–60.

[5] For authoritative overviews of bidentate Lewis acids, particularly isoelectronic bisboranes, see: a) W. E. Piers, G. J. Irvine, V. C. Williams, *Eur. J. Inorg. Chem.* **2000**, 2131–2142; b) M. Melami, F. P. Gabbaï, *Adv. Organomet. Chem.* **2015**, *53*, 61–99; c) L. Schweighauser, H. A. Wegner, *Chem. Eur. J.* **2016**, *22*, 14094–14103.

[6] For a recent review on Lewis superacids, see: L. Greb, *Chem. Eur. J.* **2018**, *24*, 17881–17896.

[7] For the application of silylium ions in catalysis, see: a) J. C. L. Walker, H. F. T. Klare, M. Oestreich, *Nat. Rev. Chem.* **2020**, *4*, 54–62; b) P. Shaykhutdinova, S. Keess, M. Oestreich in *Organosilicon Chemistry : Novel Approaches and Reactions* (Eds.: T. Hiyama, M. Oestreich), Wiley-VCH, Weinheim, **2019**, pp. 131–170; c) A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2012**, *51*, 4526–4528; *Angew. Chem.* **2012**, *124*, 4602–4604.

[8] For an example, see: N. Lühmann, H. Hirao, S. Shaik, T. Müller, *Organometallics* **2011**, *30*, 4087–4096.

[9] For substituent redistribution of silylium ions, see: a) A. Schäfer, M. Reissmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem. Int. Ed.* **2011**, *50*, 12636–12638; *Angew. Chem.* **2011**, *123*, 12845–12848; b) A. Schäfer, M. Reissmann, S. Jung, A. Schäfer, W. Saak, E. Brendler, T. Müller, *Organometallics* **2013**, *32*, 4713–4722; c) K. Müther, P. Hrobárik, V. Hrobáriková, M. Kaupp, M. Oestreich, *Chem. Eur. J.* **2013**, *19*, 16579–16594; d) L. Omann, B. Pudasaini, E. Irran, H. F. T. Klare, M.-H. Baik, M. Oestreich, *Chem. Sci.* **2018**, *9*, 5600–5607; e) K. Bläsing, R. Labbow, D. Michalik, F. Reiß, A. Schulz, A. Villinger, S. Walker, *Chem. Eur. J.* **2020**, *26*, 1640–1652.

[10] For recent reviews of weakly coordinating anions, see: a) S. P. Fisher, A. W. Tomich, S. O. Lovera, J. F. Kleinsasser, J. Guo, M. J. Asay, H. M. Nelson, V. Lavallo, *Chem. Rev.* **2019**, *119*, 8262–8290; b) I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, *Angew. Chem. Int. Ed.* **2018**, *57*, 13982–14024; *Angew. Chem.* **2018**, *130*, 14178–14221; c) T. A. Engesser, M. R. Lichtenthaler, M. Schleep, I. Krossing, *Chem. Soc. Rev.* **2016**, *45*, 789–899.

[11] M. F. Ibad, P. Langer, A. Schulz, A. Villinger, *J. Am. Chem. Soc*. **2011**, *133*, 21016–21027.

[12] a) Z. Xie, C.-W. Tsang, E. T.-P. Sze, Q. Yang, D. T. W. Chan, T. C. W. Mak, *Inorg. Chem.* **1998**, *37*, 6444–6451; b) C.-W. Tsang, Q. Yang, E. T.-P. Sze, T. C. W. Mak, D. T. W. Chan, Z. Xie, *Inorg.Chem.* **2000**, *39*, 5851–5858; c) A. Hepp, R. Labbow, F. Reiß, A. Schulz, A. Villinger, *Eur. J. Inorg. Chem.* **2018**, 2905–2914.

[13] a) C. A. Reed, *Acc. Chem. Res.* **2010**, *43*, 121–128; b) C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 133–139.

[14] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[15] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* **2011**, *32*, 1456–1465.

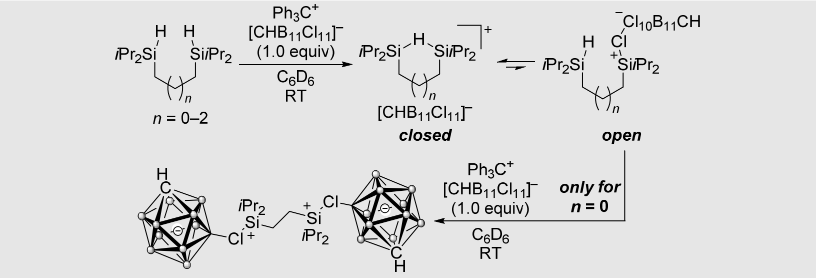
[16] J. Tomasi, M. Persico, *Chem. Rev.* **1994**, *94*, 2027–2094.

[17] The one-step protocol was also applied to bis(hydrosilanes) **1** and **2** but reactions were messy. With **1**, substituent redistribution occurred to considerable extent,[9] and *i*Pr$_3$Si[CHB$_{11}$Cl$_{11}$] (**7**[CHB$_{11}$Cl$_{11}$]) was found as the major product.

[18] CCDC 1989781 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Suggestion for the Entry for the Table of Contents

COMMUNICATION



*Q. Wu, A. Roy, G. Wang, E. Irran, H. F. T. Klare, M. Oestreich**

Page No. – Page No.

Synthesis of a Counteranion-Stabilized Bis(silylium) Ion

Supercharged. A single silylium ion is hard to handle but what about two of these superelectrophiles in one molecule in close proximity? Depending on the distance between these Lewis acidic sites, such a previously elusive bidentate Lewis acid can be accessible, characterized, and stored at room temperature.