How to cite: *Angew. Chem. Int. Ed.* **2020**, *59*, 10523–10526
International Edition: doi.org/10.1002/anie.202003799
German Edition: doi.org/10.1002/ange.202003799

VIP **Lewis Acids** *Very Important Paper*

Synthesis of a Counteranion-Stabilized Bis(silylium) Ion

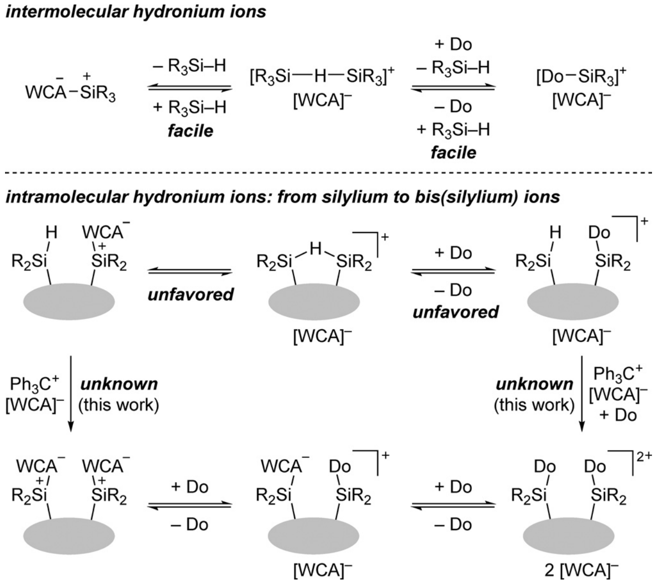
*Qian Wu+, Avijit Roy+, Guoqiang Wang, Elisabeth Irran, Hendrik F. T. Klare, and Martin Oestreich**

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 two-fold 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.

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

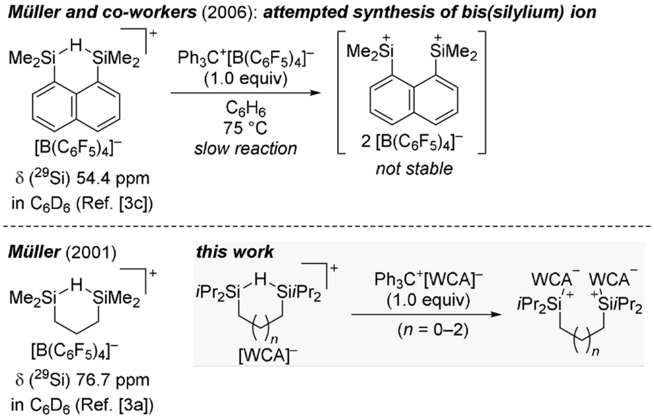
---

[*] 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.

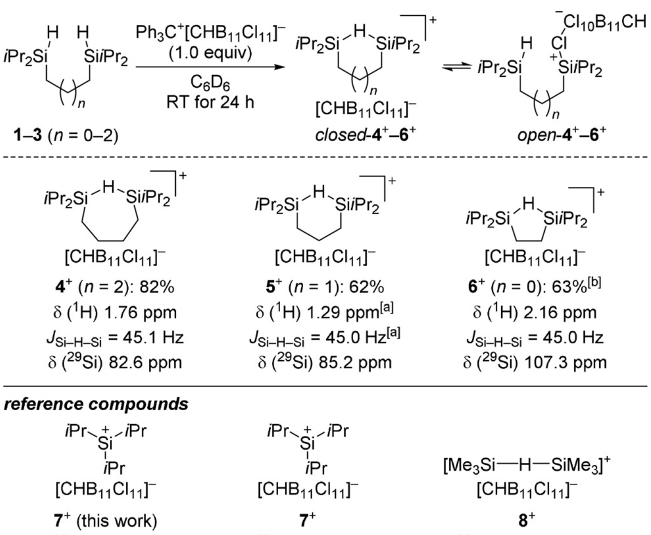
[++] X-ray crystal-structure analysis.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202003799.



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

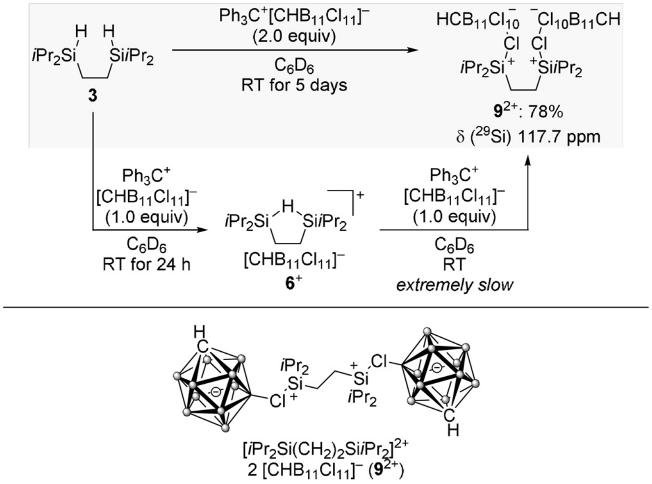
isopropyl and *tert*-butyl groups usually hamper such processes.[9c,d] For this reason, we opted for the bis(hydrosilanes) **1**–**3** with $i\mathrm{Pr_2Si}$ moieties (Scheme 3, top); their straightforward preparation is outlined in the Supporting Information. The chemical stability of the counteranion is of utmost importance in silylium-ion chemistry,[10] and $[\mathrm{B(C_6F_5)_4}]^-$ previously used by Müller is not suitable for the given challenge.[3c,11] We decided to go with $[\mathrm{CHB_{11}Cl_{11}}]^-$,[12] one of the least coordinating and most robust carborate counteranions.[10,13] Reacting precursors **1**–**3** with the corresponding trityl salt $\mathrm{Ph_3C[CHB_{11}Cl_{11}]}$ in $\mathrm{C_6D_6}$ 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 $\mathrm{C_6D_6}$ and *n*-pentane. The remainder was fully dissolved in 1,2-$\mathrm{C_6D_4Cl_2}$, and the homogeneous solution was subjected to NMR analysis (Scheme 3). Running those reactions directly in 1,2-$\mathrm{C_6D_4Cl_2}$ 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-$\mathrm{C_6D_4Cl_2}$. CPMAS = cross polarization and magic-angle spinning. [a] Determined by a ^{1}H/^{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 $i\mathrm{Pr_3Si^+}$ (**7**$^+$)[12b] and known $[(\mathrm{Me_3Si})_2(\mu\text{-H})]^+$ (**8**$^+$)[2a] both having $[\mathrm{CHB_{11}Cl_{11}}]^-$ 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**$^{+[2a]}$ ($\delta(^{29}\mathrm{Si})$ approx. 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 atoms in ethylene-tethered silylium ion **6**$^+$ ($n = 0$) are significantly more deshielded with $\delta(^{29}\mathrm{Si}) = 107.3$ ppm. This value lies between those of related hydronium ions and $\delta(^{29}\mathrm{Si}) = 130.4$ ppm of $i\mathrm{Pr_3Si[CHB_{11}Cl_{11}]}$ (**7**$^+$) in 1,2-$\mathrm{C_6D_4Cl_2}$ 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 ($\mathrm{C_6H_6}$ or 1,2-$\mathrm{C_6H_4Cl_2}$ versus $[\mathrm{CHB_{11}Cl_{11}}]^-$). Importantly, a low free energy difference was only found between *closed*-**6**$^+$ and *open*-**6**$^+$ ($\Delta G = 1.3\ \mathrm{kcal\,mol^{-1}}$). This means that the counteranion-stabilized open form of **6**$^+$ is energetically accessible in $\mathrm{C_6H_6}$ solution. Conversely, *open*-**4**$^+$ and *open*-**5**$^+$ do not exist in solution state ($\Delta G = 3.9$ and $5.5\ \mathrm{kcal\,mol^{-1}}$, respectively). This trend was the same but more pronounced for the NMR solvent 1,2-$\mathrm{C_6D_4Cl_2}$ ($\Delta G = 8.1$ for **4**$^+$, 9.4 for **5**$^+$, and $4.7\ \mathrm{kcal\,mol^{-1}}$ 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 $\mathrm{Ph_3C[CHB_{11}Cl_{11}]}$ 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 $\mathrm{Ph_3C[CHB_{11}Cl_{11}]}$ afforded the dication **9**$^{2+}$ in 78% yield (gray box). We explain this dramatic difference by the poor solubility of the reactants in $\mathrm{C_6D_6}$; 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 $i\mathrm{Pr_3Si^+}$ ion **7**$^+$ (Scheme 3, bottom), the cationic silicon centers are each stabilized by one of the counteranion's chlorine



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

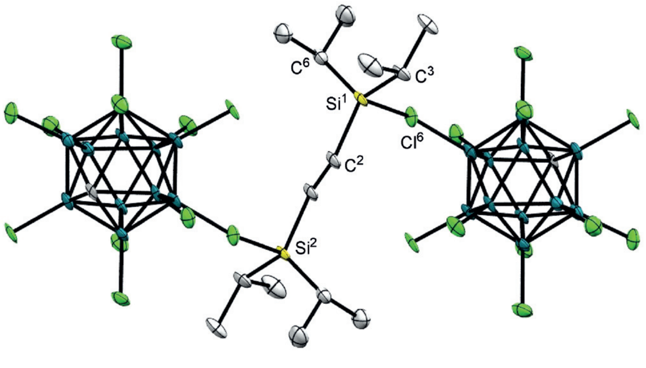
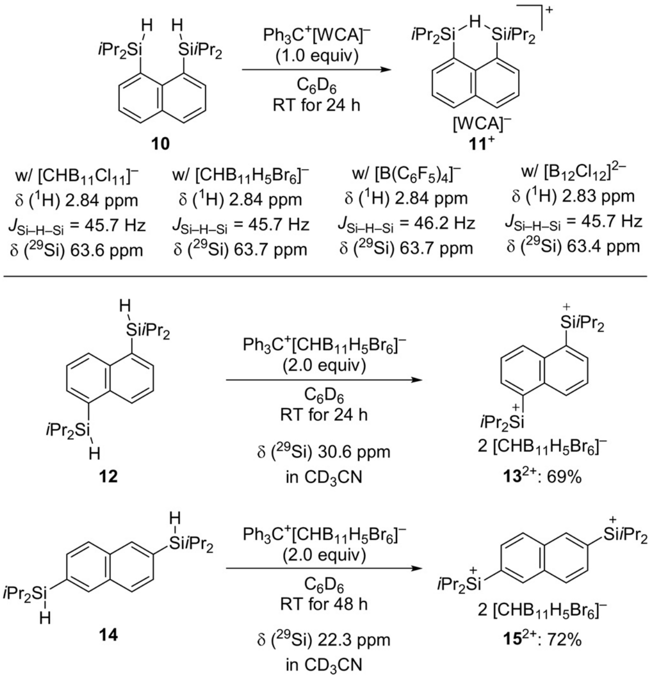


Figure 1. Molecular structure of bis(silylium) ion **9**$^{2+}$ (thermal ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Si^1–Cl^6 2.3411(15), Si^1–C^2 1.866(4), Si^1–C^3 1.855(5), Si^1–C^6 1.858(4) and C^2-Si^1-C^3 112.68(19),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

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 $i\mathrm{Pr}_3\mathrm{Si}^+$ (**7**$^+$) (2.33 Å).[2a]

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** was converted into the stable hydronium ions **11**$^+$ in high yields with various trityl salts Ph$_3$C[WCA] (Scheme 5, top). The aryl substitution typically brings about an upfield shift of about $\Delta\delta(^{29}\mathrm{Si}) = 20$ ppm.[9b,c] Relative to $\delta(^{29}\mathrm{Si}) = 85.2$ ppm for **5**$^+$, approx. $\delta(^{29}\mathrm{Si}) = 63.5$ ppm for **11**$^+$ independent of the weakly coordinating counteranion is in excellent agreement with this.

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.



Scheme 5. Regioisomeric naphthalene-based bis(hydrosilanes) as precursors for bis(silylium) ions. Unless noted otherwise, all NMR spectra were recorded in 1,2-$C_6D_4Cl_2$.

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 bridge, 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.

Conflict of interest

The authors declare no conflict of interest.

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. Y. 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; *Angew. Chem.* **2013**, *125*, 1608–1611; 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. Melaimi, F. P. Gabbaï, *Adv. Organomet. Chem.* **2005**, *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. Comput. 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.

Manuscript received: March 13, 2020
Accepted manuscript online: March 26, 2020
Version of record online: April 17, 2020