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Tris(dimethylamino)silylium ion: structure and reactivity of a dimeric silaguanidinium†

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Although several strategies for the stabilization of silylium ions have been established, "π-stabilization" with directly attached π-donor heteroatoms at silicon has not been developed yet. Hydride abstraction from $(Me_2N)_3SiH$ generates dicationic $[(Me_2N)_3Si^+]_2$ in solution and in the solid state – constituting the dimer of an elusive silaguanidinium ion. This compound can be synthesized on a gram scale and is compatible with common organic solvents. However, it readily undergoes spontaneous electrophilic silylation of electron-rich aromatic compounds or initiates a catalytic hydro-defluorination reaction.

Silylium ions $[R_3Si^+]$ are tricoordinated, positively charged silicon species with enormous electrophilicity.[1] They may be stabilized with suitable external donors and form adducts like silylated oxonium,[2] nitrilium[3] or phosphonium[2c] ions. In less coordinating environments, they even attract weaker donors such as aromatic solvents,[4] weakly coordinating anions,[3b,5] silanes[6] and silicon halides.[7] Silylium ions can also be stabilized by intramolecular donor coordination, as has been demonstrated for nearby arene,[8] olefin,[9] C–F,[8b,10] Si–H, Si–F and Si–C,[11] Fe(II),[12] chalcogen[13] and B–Cl[14] groups. As the third strategy, thermodynamic stabilization by direct attachment of π-donors (π-stabilization) was already suggested in 1977.[15] Theoretical studies have revealed the significant impact of such donors and consistently identified the amino group as the most efficient for π-stabilization.[15,16] It was found that the hydride ion and fluoride ion affinities of $Si(NMe_2)^{3+}$ (Fig. 1a) in comparison to the parent SiH_3^+ are reduced by 311 and 251 kJ mol^{-1}, respectively.[16c,f] Although this resonance stabilization amounts to only 40% in comparison to the analog carbocation (the well-known guanidinium), it is clearly superior to the stabilization in commonly used alkyl/aryl-substituted silylium ions.[16c] Despite such encouraging predictions, the synthetic realization of threefold amino- or other heteroatom substituted silylium ions is still missing in the literature. One attempt by reacting $(Me_2N)_3SiCl$ with $AlCl_3$ was reported in 1980, but it led solely to donor–acceptor complex formation (Fig. 1b).[17] Preliminary studies on tris(dimethylamino)silicon perchlorate were mentioned in a review article by Lambert, but any details remained unpublished.[18] The formation of a threefold sulfur-substituted silylium ion was indicated by conductivity measurements, but no further evidence was provided.[19] Structurally related, twofold amino-substituted silylium ions were obtained in the form of silaimidazolium ions, but no solid state structure was reported.[20] A formal dimeric species of a monoamino-substituted silylium ion was generated by the double protonation of a cyclodisilazane (Fig. 1c).[21]

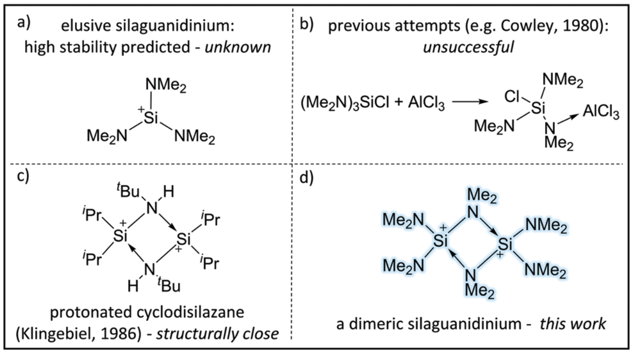

Fig. 1 (a) The elusive silaguanidinium, (b) a previously attempted synthesis and (c) the structurally closest species to the (d) dimeric silaguanidinium presented in this work.

Herein, we describe the synthesis and characterization of a threefold amino-substituted silylium ion in its dimeric form in solution and in the solid state (Fig. 1d). It can be handled in common organic solvents but retains some of the peculiar reactivity known for silylium ions.

When commercially available $(Me_2N)_3SiH$ and $[Ph_3C][B(C_6F_5)_4]$ were mixed in *o*-dichlorobenzene and stored at room temperature overnight, colorless crystals formed from solution (Scheme 1). After removal of triphenylmethane by washing with *n*-pentane,

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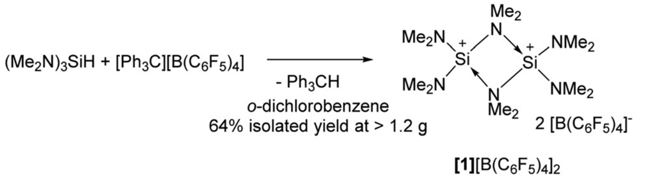

Scheme 1 Synthesis of compound [**1**][B(C_6F_5)$_4$]$_2$ by hydride abstraction.

[**1**][B(C_6F_5)$_4$]$_2$ was isolated in 64% yield on a >1.2 g scale. The purity of the product was verified by ^{1}H-, ^{13}C-, ^{11}B-, ^{19}F- and ^{29}Si-NMR spectroscopy, ESI(+)-MS and elemental analysis. ESI(+)-MS indicated a monomeric, cationic species, $(Me_2N)_3Si^+$, in the gas phase ($m/z = 160.13$). However, in a solution of *o*-difluorobenzene, two singlets at 3.57 ppm and 2.70 ppm in a 1 : 2 ratio were detected by ^{1}H-NMR spectroscopy, revealing two different types of Me_2N-groups. Surprisingly, there was a ^{29}Si-NMR chemical upfield shift of −30.6 ppm compared to the parent $(Me_2N)_3SiH$ (−25.4 ppm), thus in a shift range typically found for tetracoordinate silicon. The ^{29}Si-NMR chemical shift of the monomeric species $(Me_2N)_3Si^+$ was previously calculated as 42.1 ppm.[16c] An experimental ^{29}Si-NMR shift of −30.8 ppm (C_6D_6) for [$(Me_2N)_3Si$][B(C_6F_5)$_4$] was mentioned as a personal communication in the same manuscript. Based on chemical shift calculations of the water adduct $(Me_2N)_3Si^+OH_2$ (−20.8 ppm), the authors concluded that rather the water adduct must have been observed. However, this interpretation would not agree with the two sets of Me_2N-groups found herein. X-ray structural analysis of [**1**][B(C_6F_5)$_4$]$_2$ provided the answer (Fig. 2). Single crystals suitable for X-ray diffraction were obtained directly from a saturated *o*-dichlorobenzene solution or by performing the reaction in toluene and recrystallizing the resulting oil in dichloromethane.

Two units of [$(Me_2N)_3Si$]$^+$ dimerize in a head-to-tail fashion, forming a Si_2N_2 tetracycle, analogous to isoelectronic $Al_2(NMe_2)_6$.[22] The silicon atoms are coordinated by two terminal and two bridging dimethylamino groups. The coordination sphere around silicon is distorted-tetrahedral with N–Si–N bond angles between 116° (terminal/terminal), 113° (terminal/bridged) and 94° (bridged/bridged). The Si(1)–N(5)–Si(2) plane *vs.* the Si(1)–N(6)–Si(2) plane has a fold angle of 16°. The terminal Si–N bond lengths with 1.66 Å are significantly shorter than common Si–N single bonds (1.75 Å).[23] In contrast, the bridging Si–N bonds with 1.87 and 1.85 Å are clearly elongated and much longer than in structurally related, double protonated cyclodisilazane (1.79 Å, Fig. 1c).[21] This observation indicated a significant stabilization of the cationic charge at silicon due to the threefold donation of the free electron pairs from nitrogen to silicon, raising the question whether dissociation might be detectable at elevated temperature. Therefore, VT-NMR-spectroscopy in *o*-dichlorobenzene was performed up to 120 °C. However, no change in lineshape or product composition could be observed, revealing a substantial dimerization free energy. To support the experimental results, the respective association enthalpy and free energy were computed at the highly accurate DLPNO-CCSD(T)/cc-pVQZ level of theory.[24] In a vacuum, the dimerization process is not favored ($\Delta H = 111$ kJ mol^{-1}, $\Delta G = 181$ kJ mol^{-1}), whereas upon consideration of solvation (*o*-dichlorobenzene, COSMO-RS), the process gets indeed favored decisively ($\Delta H_{sol} = -104$ kJ mol^{-1}, $\Delta G_{sol} = -35$ kJ mol^{-1}). Energy decomposition analysis for the two interacting closed shell monomeric units $(Me_2N)_3Si^+$ revealed 54% orbital and 6% London dispersive attraction besides – despite the dicationic nature – 40% electrostatic attraction.[25] These results are inverse to dimerizing neutral aminosilanes, constituting 60% electrostatic and 40% orbital + London dispersive contributions.[26] ETS-NOCV analysis disclosed the orbitals that contribute mainly to this efficient dimerization.[27] As expected, the interaction between the lone pair at the bridging nitrogen atom and the p_z(Si)/σ^*(Si–N)-type acceptor orbital at silicon plays a major role (ETS-NOCV1, Fig. S1, ESI†). However, the second interaction was found, in which the terminal nitrogen lone pairs also contribute as electron density donors (ETS-NOCV2, Fig. S1, ESI†). Although the tendency for dimerization should be diminished due to the π-stabilization within the monomeric $(Me_2N)_3Si^+$ units, the three amino groups favor dimerization by mutually pushing their intermolecular donor capability through intrafragment Y-conjugation (LP(N) → π^*(Si–N)) and negative hyperconjugation (LP(N) → σ^*(Si–N)) at the same time.[16c,28] Intriguingly, this might be an additional cause for the higher intrinsic basicity of silaguanidine in comparison to guanidine.[16c]

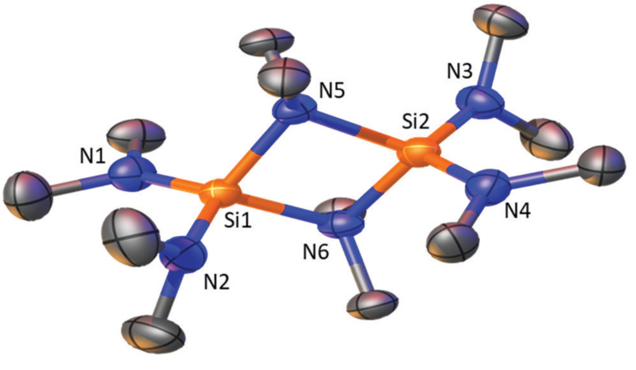

Fig. 2 Molecular structure of [**1**]$^{2+}$ (anions and hydrogen atoms are omitted for clarity). Ellipsoids 50% probability, selected bond lengths [Å] and angles [deg.]: Si(1)–N(1): 1.661(4), Si(1)–N(2): 1.656(4), Si(1)–N(5): 1.849(3), Si(1)–N(6): 1.871(4), Si(1)–Si(2): 2.7231(15), N(1)–Si(1)–N(2): 116.3(2), N(5)–Si(1)–N(6): 85.10(15), N(1)–Si(1)–N(5): 113.00(17), and Si(1)–N(5)–Si(2): 94.30(15).

Having established theoretical insights, the stability and reactivity of [**1**][B(C_6F_5)$_4$]$_2$ were considered. The dication appeared stable towards organic solvents like dichloromethane, toluene, benzene, chlorobenzene, fluorobenzene, *o*-dichlorobenzene and *o*-difluorobenzene at room temperature. The Lewis acidity of [**1**][B(C_6F_5)$_4$]$_2$ was assessed by adduct formation with triethylphosphine oxide according to the Gutmann–Beckett method.[29] Addition of 2 eq. of Et_3PO to 1 eq. of [**1**][B(C_6F_5)$_4$]$_2$ in CD_2Cl_2 yielded a clean adduct, [Et_3PO–Si(NMe_2)$_3$][B(C_6F_5)$_4$], with a ^{31}P-NMR chemical shift of $\delta = 85.2$ ppm ($\Delta\delta^{31}$P *vs.* free Et_3PO = 34.2 ppm).[30] The induced shift change $\Delta\delta^{31}$P is indeed smaller than that for carbon-substituted silylium ions ($\Delta\delta^{31}$P = 40–45 ppm),[31] indicating a tamed effective[32] Lewis acidity due to π-stabilization – thus spectroscopically supporting the computed diminished ion affinities. Although the Lewis acidity within [**1**]$^{2+}$ is decreased

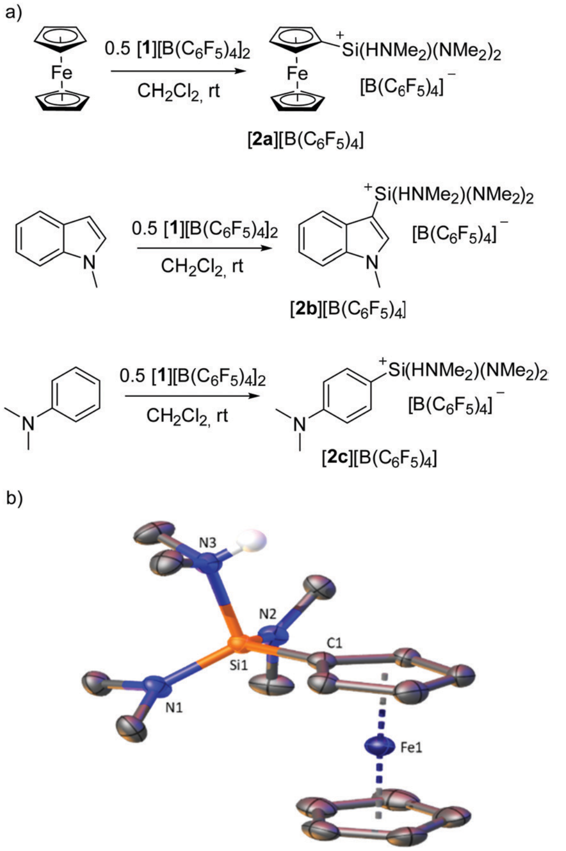

Fig. 3 (a) Reactivity of [**1**][$B(C_6F_5)_4$]$_2$ towards electron-rich aromatic compounds. Full conversion was verified by ^{1}H-NMR signal integration. (b) Molecular structure of [**2a**][$B(C_6F_5)_4$]$_2$. The $B(C_6F_5)_4$ anion and hydrogen atoms are omitted for clarity. Ellipsoids 50% probability, selected bond lengths [Å]: Si(1)–N(1): 1.682(2), Si(1)–N(2): 1.687(2), Si(1)–N(3): 1.895(2), and Si(1)–C(1): 1.835(2).

by both the intra- and intermolecular donation effects, it still initiates a catalytic hydrodefluorination reaction. With 6 mol% of [**1**][$B(C_6F_5)_4$]$_2$, 1-adamantyl fluoride was fully converted to adamantane in the presence of Et_3SiH within <12 h at rt. Finally, the reaction of [**1**][$B(C_6F_5)_4$]$_2$ towards electron-rich aromatic compounds was tested on an NMR scale. An immediate electrophilic aromatic silylation of ferrocene in CD_2Cl_2 was observed under very mild conditions, providing the protonated product salt [**2a**][$B(C_6F_5)_4$] (see Fig. 3a and b for its molecular structure). In analogy, the reaction of [**1**][$B(C_6F_5)_4$]$_2$ towards *N*-methyl indole gave the C3-silylation product [**2b**][$B(C_6F_5)_4$] in perfect regioselectivity. With dimethylaniline, a highly regioselective *para*-silylation to [**2c**][$B(C_6F_5)_4$] was observed.[33] Such spontaneous and quantitative conversions are remarkable, since Friedel–Crafts type electrophilic aromatic silylations usually suffer from competing protodesilylation back-reactions.[34]

A common strategy to shift the equilibrium to the product side is the addition of proton-scavengers. Obviously, the amino groups in [**1**][$B(C_6F_5)_4$]$_2$ have two favorable effects. (1) The silylation products provide a Brønsted basic site by themselves, making the substitution reaction thermodynamically more favorable. (2) The nucleophilic attack of the aromatic at silicon might be concerted with an intramolecular hydrogen transfer process to nitrogen, thus potentially lowering the transition state energy. Although catalytic variants with $(Me_2N)_3SiH$ and $B(C_6F_5)_3$ or [Ph_3C^+] as initiators have remained unsuccessful thus far, this stoichiometric methodology already provides an attractive method for the construction of more complex silanes, given the multitude of functionalization methods available for the Si–N bond.[35]

The present study provides first insights into the stabilization of silylium ions with directly attached π-donors (π-stabilization). It describes the formal dimer of an elusive silaguanidinium ion, isoelectronic to $Al_2(NMe_2)_6$ or related compounds, which have been known for several decades.[22,36] This dicationic compound is obtained from commercial reagents and is easy to handle in common organic solvents, but still exhibits reactivity reminiscent of silylium ions. Interestingly, it undergoes spontaneous electrophilic aromatic substitutions of electron-rich aromatics – potentially caused by means of ligand–element cooperativity.

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Conflicts of interest

There are no conflicts to declare.

References

1 T. Müller, in *Functional Molecular Silicon Compounds I: Regular Oxidation States*, ed. D. Scheschkewitz, Springer International Publishing, Cham, 2014, pp. 107–162.
2 (*a*) M. Kira, T. Hino and H. Sakurai, *J. Am. Chem. Soc.*, 1992, **114**, 6697–6700; (*b*) Z. Xie, R. Bau and C. A. Reed, *J. Chem. Soc., Chem. Commun.*, 1994, 2519–2520; (*c*) M. Driess, R. Barmeyer, C. Monsé and K. Merz, *Angew. Chem., Int. Ed.*, 2001, **40**, 2308–2310; (*d*) S. C. Bourke, M. J. Maclachlan, A. J. Lough and I. Manners, *Chem. – Eur. J.*, 2005, **11**, 1989–2000.
3 (*a*) S. R. Bahr and P. Boudjouk, *J. Am. Chem. Soc.*, 1993, **115**, 4514–4519; (*b*) C. A. Reed, Z. Xie, R. Bau and A. Benesi, *Science*, 1993, **262**, 402–404; (*c*) M. Ichinohe, H. Fukui and A. Sekiguchi, *Chem. Lett.*, 2000, 600–601; (*d*) A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler and T. Müller, *Organometallics*, 2013, **32**, 4713–4722.
4 (*a*) J. B. Lambert and S. Zhang, *J. Chem. Soc., Chem. Commun.*, 1993, 383–384; (*b*) J. B. Lambert, S. Zhang, C. L. Stern and J. C. Huffman, *Science*, 1993, **260**, 1917–1918; (*c*) M. F. Ibad, P. Langer, A. Schulz and A. Villinger, *J. Am. Chem. Soc.*, 2011, **133**, 21016–21027.
5 (*a*) Z. Xie, D. J. Liston, T. Jelinek, V. Mitro, R. Bau and C. A. Reed, *J. Chem. Soc., Chem. Commun.*, 1993, 384–386; (*b*) Z. Xie, J. Manning, R. W. Reed, R. Mathur, P. D. W. Boyd, A. Benesi and C. A. Reed, *J. Am. Chem. Soc.*, 1996, **118**, 2922–2928; (*c*) A. Avelar, F. S. Tham and C. A. Reed, *Angew. Chem., Int. Ed.*, 2009, **48**, 3491–3493; (*d*) M. Kessler, C. Knapp, V. Sagawe, H. Scherer and R. Uzun, *Inorg. Chem.*, 2010, **49**, 5223–5230.
6 (*a*) S. P. Hoffmann, T. Kato, F. S. Tham and C. A. Reed, *Chem. Commun.*, 2006, 767–769; (*b*) M. Nava and C. A. Reed, *Organometallics*, 2011, **30**, 4798–4800.
7 M. Lehmann, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2009, **48**, 7444–7447.
8 (*a*) S. Duttwyler, Q. Q. Do, A. Linden, K. K. Baldridge and J. S. Siegel, *Angew. Chem., Int. Ed.*, 2008, **47**, 1719–1722; (*b*) P. Romanato, S. Duttwyler, A. Linden, K. K. Baldridge and J. S. Siegel, *J. Am. Chem. Soc.*, 2011, **133**, 11844–11846.
9 T. Müller, C. Bauch, M. Ostermeier, M. Bolte and N. Auner, *J. Am. Chem. Soc.*, 2003, **125**, 2158–2168.
10 P. Romanato, S. Duttwyler, A. Linden, K. K. Baldridge and J. S. Siegel, *J. Am. Chem. Soc.*, 2010, **132**, 7828–7829.

11 (*a*) T. Müller, *Angew. Chem., Int. Ed.*, 2001, **40**, 3033–3036; (*b*) A. Sekiguchi, Y. Murakami, N. Fukaya and Y. Kabe, *Chem. Lett.*, 2004, **33**, 530–531; (*c*) R. Panisch, M. Bolte and T. Müller, *J. Am. Chem. Soc.*, 2006, **128**, 9676–9682; (*d*) N. Lühmann, H. Hirao, S. Shaik and T. Müller, *Organometallics*, 2011, **30**, 4087–4096.

12 (*a*) H. F. T. Klare, K. Bergander and M. Oestreich, *Angew. Chem., Int. Ed.*, 2009, **48**, 9077–9079; (*b*) K. Müther, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme and M. Oestreich, *J. Am. Chem. Soc.*, 2011, **133**, 12442–12444; (*c*) K. Müther, P. Hrobárik, V. Hrobáriková, M. Kaupp and M. Oestreich, *Chem. – Eur. J.*, 2013, **19**, 16579–16594.

13 N. Kordts, S. Kunzler, S. Rathjen, T. Sieling, H. Grossekappenberg, M. Schmidtmann and T. Muller, *Chem. – Eur. J.*, 2017, **23**, 10068–10079.

14 R. Ramírez-Contreras, N. Bhuvanesh, J. Zhou and O. V. Ozerov, *Angew. Chem., Int. Ed.*, 2013, **52**, 10313–10315.

15 Y. Apeloig and P. v. R. Schleyer, *Tetrahedron Lett.*, 1977, **18**, 4647–4650.

16 (*a*) Y. Apeloig, S. A. Godleski, D. J. Heacock and J. M. McKelvey, *Tetrahedron Lett.*, 1981, **22**, 3297–3300; (*b*) S. A. Godleski, D. J. Heacock and J. M. McKelvey, *Tetrahedron Lett.*, 1982, **23**, 4453–4456; (*c*) U. Pidun, M. Stahl and G. Frenking, *Chem. – Eur. J.*, 1996, **2**, 869–876; (*d*) J. Rissler, M. Hartmann, C. M. Marchand, H. Grützmacher and G. Frenking, *Chem. – Eur. J.*, 2001, **7**, 2834–2841; (*e*) T. Müller, *Silicon Chem.*, 2007, **3**, 123–130; (*f*) D. G. Gusev and O. V. Ozerov, *Chem. – Eur. J.*, 2011, **17**, 634–640.

17 A. H. Cowley, M. C. Cushner and P. E. Riley, *J. Am. Chem. Soc.*, 1980, **102**, 624–628.

18 J. B. Lambert, L. Kania and S. Zhang, *Chem. Rev.*, 1995, **95**, 1191–1201.

19 (*a*) J. B. Lambert, W. J. Schulz, J. A. McConnell and W. Schilf, *J. Am. Chem. Soc.*, 1988, **110**, 2201–2210; (*b*) N. Tokitoh, T. Imakubo and R. Okazaki, *Tetrahedron Lett.*, 1992, **33**, 5819–5822.

20 (*a*) S. Ishida, T. Nishinaga, R. West and K. Komatsu, *Chem. Commun.*, 2005, 778–780; (*b*) A. Schäfer, A. Schäfer and T. Müller, *Dalton Trans.*, 2010, **39**, 9296–9303.

21 U. Kliebisch, U. Klingebiel, D. Stalke and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 915–916.

22 J. K. Ruff, *J. Am. Chem. Soc.*, 1961, **83**, 2835–2839.

23 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1–S19.

24 C. Riplinger and F. Neese, *J. Chem. Phys.*, 2013, **138**, 034106.

25 (*a*) M. v. Hopffgarten and G. Frenking, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 43–62; (*b*) L. Zhao, M. Hermann, W. H. E. Schwarz and G. Frenking, *Nat. Rev. Chem.*, 2019, **3**, 48–63.

26 N. Kramer, C. Jöst, A. Mackenroth and L. Greb, *Chem. – Eur. J.*, 2017, **23**, 17764–17774.

27 M. P. Mitoraj, A. Michalak and T. Ziegler, *J. Chem. Theory Comput.*, 2009, **5**, 962–975.

28 (*a*) A. Gobbi and G. Frenking, *J. Am. Chem. Soc.*, 1993, **115**, 2362–2372; (*b*) C. M. Marchand, U. Pidun, G. Frenking and H. Grützmacher, *J. Am. Chem. Soc.*, 1997, **119**, 11078–11085.

29 (*a*) U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem./Chem. Mon.*, 1975, **106**, 1235–1257; (*b*) M. A. Beckett, G. C. Strickland, J. R. Holland and K. Sukumar Varma, *Polymer*, 1996, **37**, 4629–4631.

30 The connectivity of $Et_3PO–Si(NMe_2N)^{3+}$ was verified crystallographically for the reaction product of Et_3PO and $(Me_2N)_3SiOTf$, with identical NMR spectra for the cation.

31 H. Großekappenberg, M. Reißmann, M. Schmidtmann and T. Müller, *Organometallics*, 2015, **34**, 4952–4958.

32 L. Greb, *Chem. – Eur. J.*, 2018, **24**, 17881–17896.

33 Y. Ma, B. Wang, L. Zhang and Z. Hou, *J. Am. Chem. Soc.*, 2016, **138**, 3663–3666.

34 S. Bähr and M. Oestreich, *Angew. Chem., Int. Ed.*, 2017, **56**, 52–59.

35 (*a*) R. Fessenden and J. S. Fessenden, *Chem. Rev.*, 1961, **61**, 361–388; (*b*) P. Neugebauer, B. Jaschke and U. Klingebiel, *The Chemistry of Organic Silicon Compounds*, John Wiley & Sons, 2001, vol. 3, pp. 429–469; (*c*) K. Kraushaar, D. Schmidt, A. Schwarzer and E. Kroke, in *Adv. Inorg. Chem.*, ed. A. Michele and E. Rudi van, Academic Press, 2014, vol. 66, pp. 117–162.

36 M. Veith, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1–14.