Polysilane Reactions

Cationic Si–H–Si Bridges in Polysilanes: Their Detection and Targeted Formation in Stable Ion Studies

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Abstract: The ionization of 1,1-dihydridocyclopentasilane 7 has been found to yield the cyclic polysilylnilsilyl cation 8 instead of the expected hydrogen-substituted silylium ion 6. The silyl cation 8 is stabilized by the formation of an intramolecular Si–H–Si bridge, which also provides the thermodynamic driving force for its formation. In general, the preference for the formation of Si–H–Si bridges can be used to scavenge and identify transient intermediates in the Lewis acid induced rearrangement of polysilanes. The validity of this concept has been demonstrated for one central step in this chemistry, the ring-contraction reaction of cyclohexasilanes to form silylcyclopentasilanes.

Introduction

Several well-characterized examples of silylium ions, tricoordinated silyl cations of the general formula $R_3Si^+$, are known.[1–8] Commonly, all of these cations are substituted with three bulky aryl groups to prevent bimolecular reactions with nucleophiles.[9] Even the replacement of only one of the aryl groups by a smaller alkyl or even a hydrogen substituent triggers a rich consecutive chemistry.[1,2] For example, in a previous investigation we noticed the surprising formation of the triaryl-substituted silyl cation 1 from the reaction of dihydridosilane 2 with the trityl cation.[10] Cation 1 is formed presumably by the reaction of the incipiently formed cation 3 with the solvent benzene and arenium ion 4 is a likely intermediate (Scheme 1).

This observation clearly reveals the principal difficulties in the synthesis of hydrogen-substituted silylium ions of type 5.[11–13] Nevertheless, the secondary silylium ions 5 are an interesting class of compounds. On the one hand, being isoelectronic with hydridoboranes, they are perfect reagents for hydrosilylation reactions. On the other hand, in principle, secondary silylium ions can be regarded as protonated silylenes, which opens the field for a complementary chemistry based on proton-transfer reactions to sterically hindered Lewis bases (Scheme 2).

Hence, the above-mentioned reactivity was our impetus for an investigation into the synthesis of secondary silylium ions of type 5. As a viable target cation, we chose the oligosilylnilsilyl cation 6. The results of density functional calculations[14,15] predicted a substantial stabilization of the cation 6 through a combination of favorable $\alpha$- and $\beta$-silyl effects. In detail, according to isodesmic reaction (1), the cyclic cation 6 is more stable than dimethylsilyl, Me$_2$Si + H, by $\Delta E = 141$ kJ mol$^{-1}$ (at the M06-2X/6-311 + G(d,p) level of theory). Moreover, in the past, the 1,1,4,4-tetrakis(trimethylsilyl)tetrasilane-1,4-diyi unit proved to be a well-suited scaffold for the steric protection of reactive main group centers.[16–19]

Although the number of applications of silyl cations in synthesis and catalysis has increased in recent years,[1,2,20,21] experimental investigations of polysilylnilsilyl-substituted silyl cations,
such as cation 6, are rather scarce. This is even more surprising as these cations are believed to be important intermediates in skeletal rearrangement reactions of oligosilanes[22] and a deeper understanding of their nature and reactivity could pave the way to a controlled and directed modification of oligo- and polysilanes.[23–30] Exploratory investigations by Lambert and Zhang revealed the thermolability of even such small representatives as tris(trimethylsilyl)isilylum, (Me₃Si)₃Si⁺[31–34] Subsequently, Sekiguchi and co-workers demonstrated the tendency of dialkyl-oligosilyl cations to undergo 1,2-methyl shifts[35] and our group reported recently on the involvement of polysilyanlylsilyl or germapolysilyansilyl cations as intermediates in sila-Wagner–Meerwein rearrangements of polysilanes and germopolysilanes.[36–37] Common to all the studied polysilyl compounds is their high reactivity, unusual for silyl cations, and their pronounced tendency to undergo skeletal rearrangement reactions. The only examples of polysilyl cation salts that are stable at room temperature are the highly stabilized representatives of aromatic[38,39] and homoaromatic species[40–41].

Against this background, we describe herein our attempts to prepare the secondary silylum ion 6 and its unexpected rearrangement reaction to give the intramolecular hydrogen-bridged silylum ion 8 (Scheme 3). As the main driving force for the rearrangement reaction we identified the formation of the Si–H–Si linkage in cation 6.[1,2,42,43] In addition, we demonstrate that the targeted formation of this type of intramolecular Si–H–Si bridge can be used for the stabilization and verification of cationic intermediates in the skeletal rearrangements of oligosilyansilyl cations.

Results and Discussion

The reaction of cyclo-oligosilane 7 with trityl tetrakis(pentafluorophenyl)borate, (Ph₃C)₄B(C₆F₅)₄ (9), in benzene under ambient conditions resulted in the formation of a mixture of products, as indicated by numerous signals of variable intensity in the ²⁹Si(¹H) INEPT NMR spectrum. However, a set of five ²⁹Si NMR signals (δ(²⁹Si) = 95.5, −4.6, −14.9, −31.2, and −126.3 ppm) dominated. To prevent side-reactions due to the reactivity demonstrated by other secondary silylum ions (Scheme 1), we changed the solvent to chlorobenzene. Chlorobenzene is known to coordinate to silylum ions through the chlorine atom, which excludes arenium-ion-like reactivity.[11] After changing the solvent to chlorobenzene and lowering the temperature (T = −20 °C), the same reaction gave a set of NMR spectra that indicated the selective formation of a single compound (see Figure 1). The polysilyanlylsilyl cation formed was identified by five ²⁹Si NMR signals with chemical shifts very close to those obtained in benzene (δ(²⁹Si) = 95.3, −4.6, −15.2, −31.7, and −127.7 ppm). In the ¹H–²⁹Si HMBC spectrum, the most deshielded resonance at δ(²⁹Si) = 95.3 ppm shows a cross-peak with a broad ¹H NMR signal at δ(¹H) = 1.10 ppm (1H; Figure 1). In the proton-coupled ²⁹Si INEPT NMR spectrum, this resonance appears as a doublet of multiplets with a coupling constant of J(SiH) = 46 Hz. The deshielded ²⁹Si NMR resonance and the size of the Si–H coupling constant (J) are characteristic of Si–H–Si linkages in silicon cations.[44] In addition, the high-field signal at δ(²⁹Si) = −127.7 ppm indicates the presence of tetrasilyl-substituted silicon atoms.[44] These distinctive ²⁹Si NMR spectroscopic features clearly rule out the targeted formation of the hydrogen-substituted silylum 6. The additional ²⁹Si NMR resonances at δ(²⁹Si) = −15.2 and −31.7 ppm could be assigned to SiMe₂ groups by their characteristic NMR chemical shifts and by their correlation with ¹H NMR signals with a relative intensity of six hydrogen atoms. Additional NMR spectroscopic analysis of the silicon cation formed finally revealed the bicyclic structure 8 with the bridging Me₃Si–H–SiMe₂ unit as the most prominent structural feature.

Further support for the identification of cation 8 came from the close agreement between calculated ²⁹Si NMR chemical shifts (GIAO/M06/L6-31G(2d,p)) for a molecular structure optimized by DFT calculations at the M06-2X/6-311+G(d,p) level of theory (see Figure 2) and the experimental data (see Table 1).[14,15,45] In particular, the calculated ²⁹Si NMR chemical shifts and J(SiH) coupling constants of the characteristic symmetric SiMe₂–H–SiMe₂ unit (δ(²⁹Si)calc = 99.5 ppm; J(SiH)calc = 44 Hz) agree convincingly with the experimental parameters obtained in chlorobenzene (δ(²⁹Si)exp = 95.3 ppm; J(SiH)exp = 46 Hz). Even though solutions of polysilyanlylsilyl cation 8 with different weakly coordinating anions, such as [B(C₆F₅)₄]⁻, [B₂Cl₂(CF₃)₃]⁻, or [Al([OCl(CC₆F₅)₃])₃]⁻, in several aresnes or halogenated aresnes were prepared, no single crystals suitable for X-ray crystal analysis were obtained.

The isomerization reaction of silylum ion 6 to give the hydrogen-bridged cation 8 was further investigated by means of DFT calculations.[14,15] Although the secondary silylum ion 6 was found to be a minimum, the hydrogen-bridged cation 8 was predicted to be significantly more stable (by ΔE = −67 kJ mol⁻¹, Figure 3). The formation of the Si–H–Si linkage is the main thermodynamic driving force for this reaction as its formation from its non-bridged isomer 10e was calculated to be exothermic by ΔE = −77 kJ mol⁻¹. In addition, we identified a possible reaction channel connecting both cations (Figure 3). Along this reaction path we located five intermediate silyl cations, 10a–e, which are interconverted by 1,3-methyl shifts (Figure 3). These interconversions proceed via
four-membered cyclic transition states. Transfer of the methyl group may occur in an antara- or suprafacial manner with regard the migrating methyl group. The antarafacial transition states are very high in energy, with energy barriers of $\Delta E = 98–113$ kJ mol$^{-1}$. In contrast, a possible reaction channel connecting the cations 6 and 8 in which the methyl groups shift in a suprafacial way reveals barriers of only $\Delta E = 25–33$ kJ mol$^{-1}$ (Figure 3, see the Supporting Information for the predicted structures of the transition states and intermediates). Such 1,3-methyl shifts are common in silyl cation chemistry. Seminal contributions by Eaborn et al. disclosed the occurrence of such 1,3-methyl shifts during the solvolysis of tris(trimethylsilyl)methylsilyl halides.  

Table 1. Experimental and calculated (italic) NMR parameters for polysilanyl cations 8 and 19. Calculated data for the secondary silylium ion 6 and the hydrogen-bridged cation 18 are provided for comparison.

| Compd | $\delta$ [ppm] (1,$\text{J}(\text{SiH})$) [Hz] |
|-------|------------------------------------------|
| 8     | $\delta_1(\text{Si}^1)$ $\delta_2(\text{Si}^2)$ $\delta_3(\text{Si}^3)$ $\delta_4(\text{Si}^4)$ $\delta_5(\text{Si}^5)$ $\delta_6(\text{Si}^6)$ $\delta_7(\text{Si}^7)$ $\delta_8(\text{SiMe}_3)$ $\delta_9(\text{H}^3)$ |
| 8$^{[a]}$ | $-127.7$ $-31.7$ $-31.7$ $-127.7$ $-15.2$ $95.3$ $95.3$ $-4.6$ $1.10$ |
| 8$^{[b]}$ | $-128.8$ $-32.9$ $-31.9$ $-128.8$ $-16.4$ $94.1$ $94.1$ $-5.9$ |
| 8$^{[c]}$ | $-126.2$ $-31.2$ $-31.2$ $-126.2$ $-14.9$ $95.5$ $95.5$ $-4.6$ $1.01$ |
| 8$^{[d]}$ | $-135.1$ $-25.9$ $-25.9$ $-135.1$ $-5.7$ $99.5$ $95.5$ $-2.0$ $1.81$ |
| 8$^{[e]}$ | $-43.3$ $-24.9$ $-24.9$ $-43.3$ $594.5$ $2.8$ |
| 19$^{[f]}$ | $-107.5$ $-35.3$ $-33.0$ $64.1$ $-33.4$ $78.1$ $-0.7$ $-1.07$ |
| 19$^{[g]}$ | $-120.8$ $-32.4$ $-34.3$ $61.2$ $-34.7$ $66.7$ $0.7$ $-0.14$ |
| 18$^{[h]}$ | $52.2$ $-19.8$ $-32.9$ $52.2$ $-19.8$ $32.9$ $1.0$ $-1.75$ |

[a] At 253 K in C$_6$D$_5$Cl. [b] At 258 K in o-C$_6$H$_4$Cl$_2$ with [D$_7$]acetone capillary. [c] At 303 K in C$_6$D$_6$. [d] Calculated at M06L/S6-31G(d,p)/M06-2X/6-311+G(d,p). [e] Calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level. [f] At 233 K in C$_6$D$_5$Cl.
Related 1,3-methyl migrations are important steps in skeletal rearrangement processes of polysilanyl cations and in inter- and intramolecular substituent exchange reactions in silylium ions.\[7,8, 36, 37\] Recently, we disclosed a similar rearrangement of the closely related silyl cation 11.\[42\]

In general, the potential energy surface along the reaction coordinate is predicted by the calculations to be rather shallow with only small activation barriers for the subsequent methyl shifts (Figure 3). The rate-determining step is the exothermic formation of cation 8. This step involves an overall energy barrier of $\Delta E = 33$ kJ mol$^{-1}$, which is in qualitative agreement with the fast formation of cation 8 at temperatures as low as $T = -20$ °C. These experiments are interesting in their own right as they clearly demonstrate the high reactivity of secondary silylium ions, which prevents their detection, isolation, and characterization even under carefully controlled reaction conditions. They also indicate the high mobility of alkyl groups in polysilanyl cations. In addition, a more general implication of this chemistry emerges. There is a clear preference for polysilanyl cations to form Si–H–Si bridges, which stabilize these systems significantly, allow their spectroscopic characterization, and in some cases even their isolation. For example, silyl cation 10e, a conformer of cation 8 that does not contain the Si–H–Si unit, is markedly less stable than cation 8 by $\Delta E = 77$ kJ mol$^{-1}$.

This fact suggests that the lifetime of fleeting intermediates in this type of rearrangement can be extended significantly by using appropriately designed starting materials, which allow the formation of Si–H–Si linkages in an auto-scavenger reaction. These intermediates then can be verified and identified spectroscopically. Such experiments would provide important insights into the actual rearrangement mechanism.

This concept has been demonstrated for the rearrangements of cyclohexasilanes 12 to yield silylcyclopentasilanes 13 (Scheme 4).\[26, 28–30\] This reaction is a prototype for ring-contraction reactions mediated by strong Lewis acids, which are important tools for the skeletal modification of polysilanes. The reaction is thought to proceed via cyclohexasilanyl cations 14, which undergo ring contraction to cyclopentasilanyl silyl cations 15, followed by trapping by a nucleophile to give neutral cyclopentasilane derivatives 13.\[29\] Although we found that the reaction of 12a to 13a is also catalyzed by 1 mol% of trityl tetakis(pentafluorophenyl)borate (9) in dichloromethane or benzene as solvent (Scheme 4), we were unable to detect cationic intermediates in stoichiometric reactions with trityl borate 9 under ambient conditions at $T = -20$ °C. Subsequently, we studied the reaction of hydrogen-substituted cyclohexasilane

Figure 3. a) Suggested reaction path for the isomerization reaction of the secondary silylium ion 6 to give the bicyclic bis-silylyridonium ion 8. b) Calculated reaction coordinate for this reaction (energies $E^{rel}$ and free enthalpies $G^{298 \, \text{rel}}$ (in kJ mol$^{-1}$) at 298 K and 0.1013 MPa are computed relative to compound 6 at the M06-2X/6-311 + G(d,p) level of theory).

Scheme 4. Lewis acid-catalyzed rearrangement of cyclohexasilanes 12 to give silylcyclopentasilanes 13 (a: $R^1 = R^2 = R^3 = \text{Me}$; b: $R^1 = R^2 = \text{SiMe}_3$, $R^3 = \text{Me}$; c: $R^1 = R^2 = R^3 = \text{SiMe}_3$). Reaction conditions for 12a: Lewis acid: Ph$_3$C$^+$; solvent: CD$_2$Cl$_2$ or C$_6$D$_6$; for 12b: Lewis acid: AlCl$_3$, solvent: cyclohexane; for 12c: Lewis acid: AlCl$_3$, solvent: cyclohexane).\[24, 41\]
16, which smoothly generated the cation even at low temperatures. The $^{29}$Si NMR spectra of the reaction of compound 16 with trityl borate 9 in toluene recorded at $T = -40°C$ suggest the generation of cationic species. The number of $^{29}$Si NMR signals and their NMR chemical shifts indicate the formation of toluene complexes of rearranged silylcyclopentasilanyl cations as the main products in this reaction. Significant formation of side- or decomposition products prevented, however, a reliable structural assignment (see the Supporting Information).

Finally, the use of 1,4-dihydridocyclohexasilane 17 as the starting material for cation generation provided deeper insights into the rearrangement of the cyclohexasilanes (Scheme 5). The ionization of compound 17 was easily accomplished by removal of the first hydride with trityl tetrakis(pentafluorophenyl)borate (9) in chlorobenzene at low temperatures. Based on the previously suggested mechanism (Scheme 4), the formation of two different cations, the symmetric cyclohexasilanyl cation 18 and the cyclopentasilanyl silyl cation 19, could be expected as a result of the auto-scavenger reaction by the remote Si–H functionality (Scheme 5).

The $^{29}$Si NMR spectra recorded at $T = -40°C$ clearly show the predominant formation of one cationic compound. The number and intensity of the $^{29}$Si NMR signals in the inverse-gated $^{29}$Si{1H} NMR spectrum indicate that this compound contains seven different silicon atoms. Two low-field doublets at $\delta^{(29)Si} = 78.1$ and 64.1 ppm with characteristic small $J$ coupling constants of $J(SiH) = 39$ and 43 Hz show the formation of a cation with an unsymmetrically substituted Si–H–Si bridge (see Figure 4 and Table 1). In addition, the $^1$H–$^{29}$Si HMQC NMR spectrum shows a correlation between both low-field resonances with a broad $^1$H NMR signal at an unusually high field for Si–H and Si–H–Si groups ($\delta^1H = -1.07$ ppm). Analysis of the signal multiplicity resulting from long-range Si–H couplings and of the $\delta^{(29)Si}$-NMR chemical shifts of the remaining signals suggest the structure of cyclopentasilanyl silyl cation 19 as the predominantly formed cation. This assignment is supported by the close agreement between calculated $^{29}$Si NMR chemical shifts (GIAO/M06L/6-311G(2d,p)) and the experimental data (see Table 1). Solutions of 19[B(C$_6$F$_5$)$_4$] in chloroben-

![Figure 4. $^{29}$Si INEPT NMR spectrum (99.31 MHz, 233 K, C$_6$D$_5$Cl) of cyclopentasilanyl silyl cation 19 obtained from the reaction of cyclohexasilane 17 with trityl tetrakis(pentafluorophenyl)borate 9.](image-url)
zene are marginally stable at temperatures around $T = -40 \, ^\circ C$. After several hours and at higher temperatures, significant decomposition occurs.

It is particularly noteworthy that no characteristic $^{29}\text{Si}$ NMR signals due to the formation of the symmetric cation 18 were detected (see Table 1 for the theoretical prediction). The absence of significant amounts of cation 18 in the reaction mixture is interesting, because the results of calculations suggest that its formation from the primarily formed cyclohexasilanyl cation 20 is exothermic by $\Delta E = -52 \, \text{kJ mol}^{-1}$ (Scheme 5). Evidently, the ring contraction reaction of cation 20 to give the five-membered ring cation 21 is faster than the formation of the Si–H–Si linkage to form the symmetric cation 18. In contrast, the lifetime of compound 21 is longer, which allows for the formation of the unsymmetrical Si–H–Si-bridged cation 19, which is the most stable isomer in the series of cations 18–21. As a consequence, the predominant formation of cation 19 indicates that cation 20 is either not an intermediate in this reaction and the ring contraction to form cation 21 occurs simultaneously with ionization or, at most, it is a high-lying intermediate with a very low barrier to rearrangement to give cyclopentasilanylsilyl cation 21. This example shows that the formation of cations with an intramolecular Si–H–Si linkage can be detected straightforwardly by NMR spectroscopy and that this feature can be applied in auto-scavenging reactions to reveal important details of otherwise complex reaction sequences in cationic rearrangement reactions of oligo- and polysilanes.

Conclusion

Our attempts to synthesize the hydrogen-substituted polysilanylsilyl ion 6 by hydride transfer reaction from the corresponding cyclic dihydrido-oligosilane 7 resulted in the selective and clean formation of the rearranged bis-silylated hydronium ion 8. This result demonstrates the strong tendency of polysilanylsilyl cations to undergo skeletal rearrangement reactions and indicates the superior thermodynamic stability of polysilanylsilyl cations stabilized by the formation of a Si–H–Si linkage. In addition, our findings suggest that the lifetime of fleeting intermediates in skeletal rearrangement reactions of polysilanylsilyl cations can be extended significantly by using appropriately designed starting materials, which allow the targeted formation of Si–H–Si bridges in an auto-scavenging reaction. This concept has been successfully demonstrated for one of the key steps in the Lewis acid catalyzed rearrangement reactions of poly- and oligosilanes, the cyclohexasilane/silylcyclopentasilane ring-contraction reaction. By using the appropriately substituted dihydridecyclosilane 17 as the starting material, we identified solely the product 19 of the auto-scavenging reaction of the cyclopentasilanylsilyl cation 21. This result provides strong evidence for a synchronous ionization/rearrangement reaction pathway without passing through a cyclohexasilanylsilyl cation intermediate. We are currently investigating the scope of the targeted formation of cations featuring a Si–H–Si bridge for mechanistic studies in Lewis acid initiated skeletal rearrangement reactions of poly- and oligosilanes.
Synthesis of hydrogen-bridged bis-silyl borate 8[B(C,F,)] from dihydridocyclopentasilane 7 in dichlorobenzene: Dihydridocyclopentasilane 7 (50 mg, 1 equiv, 0.10 mmol) and trityl tetrakis(pentafluorophenyl)borate (9; 92 mg, 1 equiv, 0.10 mmol) were evacuated in different Schlenk flasks for 1 h and then dissolved in 1,2-dichlorobenzene (1 mL). The solution of trityl tetrakis(pentafluorophenyl)borate (9) was cooled to −15 °C in an EtOH/N₄ bath. The silane was added through a Teflon tube and the reaction mixture stirred at T = −15 °C for 2 h. The solution was then transferred into an NMR tube and stored at T = −25 °C overnight. The NMR spectra were recorded at T = −15 °C with an external [D₆]jacetone lock. Data for cation 8: ²⁹Si[H] NMR (99.31 MHz, 253 K, C₆D₅Cl): δ = 95.3 (Si), −4.6 (2 × SiMe₅), −15.2 (Si), −31.7 (Si), −127.7 ppm (Si).

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[1] T. Müller in Structure and Bonding, Vol. 155 (Ed.: Scheschkewitz), Springer, Heidelberg, 2014, pp. 107.
[2] T. Müller in Science of Synthesis Knowledge Updates, Vol. 3 (Ed.: M. Oestreich) Thieme, Stuttgart, 2013, pp. 1.
[3] J. B. Lambert, Y. Zhao, Angew. Chem. Int. Ed. Engl. 1997, 36, 400; Angew. Chem. 1997, 109, 389.
[4] T. Müller, Y. Zhao, J. B. Lambert, Organometallics 1998, 17, 278.
[5] J. B. Lambert, Y. Zhao, H. Wu, C. T. Buehler, J. Am. Chem. Soc. 1999, 121, 5001.
[6] K. C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin, J. B. Lambert, Science, 2002, 297, 825.
[7] A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase, T. Müller, Angew. Chem. Int. Ed. 2011, 50, 12636; Angew. Chem. 2011, 123, 12845.
[8] A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler, T. Müller, Organometallics 2013, 32, 4713.

The only example of a characterized diarylalkylsilylium ion is bis(2,4,6-trisopropoxyphenyl)silylum, see ref. [8].

C. Gerdes, W. Saak, D. Haase, T. Müller, J. Am. Chem. Soc. 2013, 135, 10353.

[9] The only example of a characterized diarylalkylsilylium ion is bis(2,4,6-trisopropoxyphenyl)silylum, see ref. [8].

C. Marschner, Angew. Chem. Int. Ed. Engl. 2013, 52, 1605; Angew. Chem. 2012, 104, 1636.

[12] To the best of our knowledge, the only report on an experimental detection of a secondary silylium ion is that of argon-tagged dimethylsilylum in the gas phase: A. F. Dellaise, M. T. Scerba, T. Leclacta, M. A. Johnson, Chem. Phys. Lett. 2013, 568, 9–13.

[13] All calculations were performed by using the Gaussian 09 program, Gaussian 09 Revision B.01, J. M. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fuke, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Chabalowski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian Inc., Wallingford CT 2009.

[14] For details, see the Supporting Information.

[15] H. Arp, J. Baumgartner, C. Marschner, T. Müller, J. Am. Chem. Soc. 2013, 135, 5632.

[16] H. Arp, J. Baumgartner, C. Marschner, P. Zark, T. Müller, J. Am. Chem. Soc. 2012, 134, 6409.

[17] J. Hnila, J. Baumgartner, C. Marschner, L. Albers, T. Müller, Organometallics 2013, 32, 2004.

[18] Review: C. Marschner, Eur. J. Inorg. Chem. 2015, 3805.

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

[20] T. Stahl, H. F. T. Klare, M. Oestreich, ACS Catal. 2013, 3, 1578.

[21] C. Marschner in Structure and Bonding, Vol. 155 (Ed.: Scheschkewitz), Springer, Heidelberg, 2014, pp. 163.

[22] M. Ishikawa, M. Kumada, J. Chem. Soc. D. 1969, 567b.

[23] M. Ishikawa, M. Kumada, J. Chem. Soc. D. 1970, 157a.

[24] M. Ishikawa, J. Iyoda, H. Ikeda, K. Katoke, T. Hashimoto, M. Kumada, J. Am. Chem. Soc. 1981, 103, 4845.

[25] M. Ishikawa, M. Watanabe, J. Iyoda, H. Ikeda, M. Kumada, Organometallics 1982, 1, 317.

[26] T. A. Blinka, R. West, Organometallics 1996, 5, 128.

[27] J. Fischer, J. Baumgartner, C. Marschner, Science 2005, 310, 825.

[28] H. Wagner, A. Wallner, J. Fischer, M. Flock, J. Baumgartner, C. Marschner, Organometallics 2007, 26, 6704.

[29] R. Fischer, J. Baumgartner, G. Kickelbick, K. Hassler, C. Marschner, Monatsh. Chem. 2006, 137, 613.

[30] J. B. Lambert, S. Zhang, J. Chem. Soc. Chem. Commun. 1993, 383.

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Previouse xamples of compounds with Si–C0/H–C0/Si 2e–3c bonds have been found, for intramolecular variants, see: a) T. Müller, Angew. Chem. Int. Ed. 2001, 40, 3033–3036; Angew. Chem. 2001, 113, 3123–3126; b) R. Panisch, M. Bolte, T. Müller, J. Am. Chem. Soc. 2006, 128, 9676–9682; c) 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; d) A. Sekiguchi, Y. Murakami, N. Fukaya, Y. Kabe, Chem. Lett. 2004, 33, 530–531; e) N. Kordts, C. Borner, R. Panisch, W. Saak, T. Müller, Organometallics 2014, 33, 1492–1498; for intermolecular variants, see: f) S. P. Hoffmann, T. Kato, F. S. Tham, C. A. Reed, Chem. Commun. 2006, 767–769; g) M. Nava, C. A. Reed, Organometallics 2011, 30, 4798–4800; h) S. J. Connelly, W. Kaminsky, D. M. Heinekey, Organometallics 2013, 32, 7478–7481.

The five calculated 29Si NMR chemical shifts of cation 8 correlate linearly with the experimental data measured in chlorobenzene: δ(29Si)calc = (1.044 ± 0.038) ppm, δ(29Si)exp = (0.735 ± 3.109) ppm; R² = 0.991.

The seven calculated 29Si NMR chemical shifts of cation 19 correlate linearly with the experimental data measured in chlorobenzene: K(29Si)calc = (1.006 ± 0.052) ppm, K(29Si)exp = (2.744 ± 3.114) ppm; R² = 0.984.

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