60 kOe, which is very close to the expected value of 7.0 $N\mu_B$ for a parallel alignment of the magnetic moments of two $Ru^{III}$ and one $Mn^{II}$ ion. Furthermore, a characteristic hysteresis loop is observed at 1.85 K but with negligible remanent magnetization (0.06 $N\mu_B$) and coercive field (6 Oe). Although ferromagnetic $Ru^{III}-Mn^{II}$ interaction was also observed in two-dimensional $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$ via the oxalato bridges, no long-range ordering occurs down to 2 K.[4] We are currently investigating related 3d–4d and 4d–5d systems in order to understand the origin of the ferromagnetic behavior in **2**.

*Experimental Section*

**1**: *trans*-$Ph_4P[Ru^{III}(acac)_2Cl_2]$[12] (355 mg, 0.5 mmol) and KCN (325 mg, 5.0 mmol) were heated in refluxing methanol (30 mL) for 24 h. The solution was evaporated to dryness, and the residue was dissolved in $CH_2Cl_2$ (10 mL). After filtration, the product was precipitated as a dark purple solid by adding diethyl ether. Yield: 225 mg (65 %). Crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution of **1** in $CH_2Cl_2$. IR (KBr): $\tilde{\nu}_{CN} = 2099\ cm^{-1}$; UV/Vis ($CH_3CN$): $\lambda_{max}$ ($lg\varepsilon$) = 349 (3.76), 407 sh (3.16), 540 (3.22); elemental analysis (%) calcd for $C_{36}H_{34}N_2O_4RuP$: C 62.60, H 4.96, N 4.06; found: C 62.96, H 5.05, N 4.21.

**2**: A mixture of $MnClO_4 \cdot 6H_2O$ (36 mg, 0.1 mmol) and **1** (69 mg, 0.1 mmol) was stirred in methanol (30 mL) at room temperature. The solution was filtered after 3 h, and slow evaporation of the filtrate afforded dark purple crystals. Yield: 34 mg (45 %). IR (KBr): $\tilde{\nu}_{CN} = 2125\ cm^{-1}$; elemental analysis (%) calcd for $Ru_2MnN_4C_{24}O_8H_{28}$: C 38.05, H 3.73, N 7.40; found: C 38.24, H 3.82, N 7.56.

Received: February 26, 2001
Revised: May 25, 2001 [Z16686]

[1] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**.
[2] a) K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **1997**, *45*, 283–373; b) T. Iwamoto in *Comprehensive Supramolecular Chemistry*, *Vol. 6* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 643–690; c) W. D. Grieber, D. Babel, *Z. Naturforsch. B* **1982**, *87*, 832; d) V. Gadet, T. Mallah, I. Castro, P. Veillet, M. Verdaguer, *J. Am. Chem. Soc.* **1992**, *114*, 9213; e) T. Mallah, S. Thiébaut, M. Verdaguer, P. Veillet, *Science* **1993**, *262*, 1554; f) H. Miyasaka, H. Ieda, N. Matsumoto, N. Re, R. Crescenzi, C. Floriani, *Inorg. Chem.* **1998**, *37*, 255; g) K. V. Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki, K. S. Murray, *Inorg. Chem.* **1997**, *36*, 5006; h) H. Miyasaka, N. Matsumoto, N. Re, E. Gallo, C. Floriani, *Inorg. Chem.* **1997**, *36*, 670; i) N. Re, E. Gallo, C. Floriani, H. Miyasaka, N. Matsumoto, *Inorg. Chem.* **1996**, *35*, 5964; j) M. Ohba, H. Ōkawa, N. Fukita, Y. Hashimoto, *J. Am. Chem. Soc.* **1997**, *119*, 1011; k) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani, *J. Am. Chem. Soc.* **1996**, *118*, 981; l) M. Ohba, N. Maruono, H. Ōkawa, T. Enoki, J.-M. Latour, *J. Am. Chem. Soc.* **1994**, *116*, 11566; m) M. S. El Fallah, E. Rentschler, A. Caneschi, R. Sessoli, D. Gatteschi, *Angew. Chem.* **1996**, *108*, 2081; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1947; n) H. Miyasaka, N. Matsumoto, H. Ōkawa, N. Re, E. Gallo, C. Floriani, *Angew. Chem.* **1995**, *107*, 1565; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1446; o) S. Ferlay, T. Mallah, J. Vaissermann, F. Bartolomé, P. Veillet, M. Verdaguer, *Chem. Commun.* **1996**, 2481; p) M. Ohba, H. Ōkawa, T. Ito, A. Ohto, *J. Chem. Soc. Chem. Commun.* **1995**, 1545.
[3] a) J. Larionova, R. Clérac, J. Sanchiz, O. Kahn, S. Golhen, L. Ouahab, *J. Am. Chem. Soc.* **1998**, *120*, 13088; b) G. Rombaut, S. Golhen, L. Ouahab, C. Mathonière, O. Kahn, *J. Chem. Soc. Dalton Trans.* **2000**, 3609.
[4] J. Larionova, B. Mombelli, J. Sanchiz, O. Kahn, *Inorg. Chem.* **1998**, *37*, 679.
[5] F. M. Crean, K. Schug, *Inorg. Chem.* **1984**, *23*, 853.
[6] J. L. Manson, W. E. Buschmann, J. S. Miller, *Angew. Chem.* **1998**, *110*, 815; *Angew. Chem. Int. Ed.* **1998**, *37*, 783.
[7] a) Crystal data for **1** ($C_{36}H_{34}N_2O_4RuP$): $M_r = 690.72$, dark purple prisms, monoclinic, space group $P2_1/c$ (no. 14), $a = 7.727(8)$, $b = 27.541(8)$, $c = 15.645(9)$ Å, $\beta = 103.13(8)°$, $V = 3242(3)$ Å$^3$, $F(000) = 1420.00$, $Z = 4$, $\rho_{calcd} = 1.415\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 5.74\ cm^{-1}$. Data were measured on a Rigaku AFC7R diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation and a 12-kW rotating anode generator at 28.0 °C. Of the 3670 reflections measured, 3298 were unique ($R_{int} = 0.053$), and 1403 with $I > 2\sigma(I)$ were observed. Data were corrected for Lorentzian and polarization effects. The structure was solved by direct methods (SHELXS86), and the full-matrix least-squares refinement converged to $R = 0.094$ and $R_w = 0.077$ with a GOF of 3.91. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161807 (**1**) and -161808 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[8] H. Matsuzawa, Y. Ohashi, Y. Kaizu, H. Kobayashi, *Inorg. Chem.* **1988**, *27*, 2981.
[9] Crystal data for **2** ($Ru_2MnN_4C_{24}O_8H_{28}$): $M_r = 757.59$, dark purple blocks, tetragonal, space group $P4_2/n$ (no. 86), $a = 13.6900(7)$, $c = 8.1530(5)$ Å, $V = 1528.0(1)$ Å$^3$, $F(000) = 747.00$, $Z = 2$, $\rho_{calcd} = 1.646\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 14.31\ cm^{-1}$. Data were collected at 25.0 °C. Of the 9457 reflection measured, 1862 were unique ($R_{int} = 0.034$), and 1091 with $I > 1.50\sigma(I)$ were observed. Data were corrected for Lorentzian and polarization effects. The structure was solved by direct methods (SIR92), and the full-matrix least-squares refinement converged to $R = 0.036$ and $R_w = 0.021$ with a GOF of 1.18.[7b]
[10] B. N. Figgis, P. A. Reynolds, K. Murray, B. Moubaraki, *Aust. J. Chem.* **1998**, *51*, 229, and references therein.
[11] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**, p. 228.
[12] T. Hasegawa, T. C. Lau, H. Taube, W. P. Schaefer, *Inorg. Chem.* **1991**, *30*, 2912. $Ph_4PCl$ was used instead of $Ph_4AsCl \cdot x\,H_2O$.

## A Silyl Cation with a Three-Center Si-H-Si Bond**

Thomas Müller*

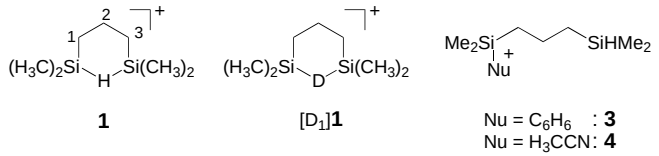
Three-center, two-electron bonds involving hydrogen as a bridging atom are a common feature in the chemistry of early main group metals. Several hydrido-bridged carbocations were identified by low-temperature NMR spectroscopy.[1] It was predicted that the isoelectronic silylium ions will even interact with methane,[2] and it was suggested that such interactions between a positively charged silicon atom and appropriately arranged alkyl groups on its substituents can be

[*] Dr. T. Müller
Institut für Anorganische Chemie der Goethe Universität Frankfurt
Marie-Curie-Strasse 11, 60439 Frankfurt am Main (Germany)
Fax: (+49) 69-798-29188
E-mail: Dr.Thomas.Mueller@chemie.uni-frankfurt.de

[**] Presented in part at ISOS XII, May 23rd–28th 1999, Sendai, Japan. This work was supported by the Deutsche Forschungsgemeinschaft and the German Israeli Foundation (GIF). The author thanks Mrs. R. Meyer for the synthesis of starting materials, Prof. H.-U. Siehl for fruitful discussions and Prof. N. Auner for continuing support.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

used to stabilize a silylium ion by intramolecular solvation.[3] More suitable for such interactions than C–H bonds are the Si–H bonds of silanes. Due to the higher lying σ-bonding orbital, the interaction with the empty 3p(Si) orbital is more favorable. Recently, Wrackmeyer et al. gave convincing NMR evidence for the presence of an Si-H-B bridge in silylated vinylboranes.[4] Here we report the synthesis of silyl cation **1** having a symmetrical Si-H-Si bridge, a previously unknown structural motif in organosilicon chemistry.[5]




**1** [D$_1$]**1** Nu = $C_6H_6$ : **3** Nu = $H_3CCN$: **4**

The silyl cation **1** is formed by a hydride transfer[6] from 2,6-dimethyl-2,6-disilaheptane (**2**) to trityl tetrakis(pentafluorophenyl)borate (TPFPB) in [D$_6$]benzene at room temperature. The orange-red color of the trityl salt instantaneously disappears, and the reaction mixture separates into two layers. The upper layer containing triphenylmethane was separated from the reaction mixture. $^1$H, $^{13}$C, $^{29}$Si, and $^{19}$F NMR spectra of the lower layer confirm the exclusive formation of the symmetrical cation **1**.[7]

The unusually shielded $^1$H NMR signal for the SiH group in **1** ($\delta(^1H^{br}) = 1.47$, $\Delta\delta = -2.43$ relative to **2**) is indicative of the hydrogen-bridged structure.[8] The $^{13}$C{$^1$H} NMR spectrum shows, besides the signals for the anion, only three signals corresponding to C$^2$ ($\delta = 18.1$), C$^{1/3}$ ($\delta = 14.9$), and the methyl groups ($\delta = -4.0$; see Table 1 and Supporting Information). The single, deshielded $^{29}$Si NMR signal at $\delta = 76.7$[8] splits in the $^1$H-coupled spectrum into a broad doublet with an unusually small coupling constant ($^1J_{Si,H} = 39$ Hz, Figure 1a, b). The $^{29}$Si signal of the deuterated cation [D$_1$]**1**[9] is split into a triplet with $^1J_{Si,D} = 6.3$ Hz (Figure 1c), as expected for the gyromagnetic ratio $\gamma_H/\gamma_D$.[10] In arene solvents, the $^{29}$Si NMR signal of **1** shows only minor solvent dependence ($\delta(^{29}Si) = 77.1$ in [D$_8$]toluene). This indicates only small interactions between the silyl cation and the solvent; in particular, the formation of a silylated arenium ion **3** can be excluded, since for trialkylsilyl-substituted arenium ions solvent effects of $\Delta\delta = 10$ or more are reported.[6a, 11, 12] In contrast, when acetonitrile is added to a solution of **1** in [D$_6$]benzene, the silylated nitrilium ion **4** is formed, as shown by two $^{29}$Si NMR signals at $\delta = 32.3$ and $-14.2$ (d, $^1J_{Si,H} = 180.6$ Hz).[13]

Table 1. Measured and calculated (in parenthesis) chemical shifts of silyl cations **1** and **5b**; $|^1J(Si,H)|$ values in square brackets.

| Compound | Si | C$^1$ | C$^2$ | C$^3$ | H$^{br}$ |
|---|---|---|---|---|---|
| **1**[a] | 76.7 [39 Hz] | 14.9 | 18.1 | 14.9 | 1.47 |
| **1**[b] | 77.0 | 15.2 | 18.5 | 15.2 | 1.40 |
| **1**[c] | (88.0) | (18.6) | (22.9) | (18.6) | |
| **5b**[c] | (347.9, −13.3) | (36.4) | (16.0) | (25.3) | |
| **1**[d] | (96.5) | (20.7) | (25.7) | (20.7) | |
| **1**[e] | (93.4 [−43.8 Hz[g]]) | (18.3) | (23.4) | (18.3) | |
| **1**[f] | (87.4) | | | | |

[a] In [D$_6$]benzene at 300 K. [b] In [D$_8$]toluene at 300 K. [c] At the GIAO/MPW1PW91/6-311G(3d,p)//MP2/6-311G(d,p) level, $\sigma(^{13}C, TMS) = 187.51$, $\sigma(^{29}Si, TMS) = 339.97$.[23, 24] [d] At the SOS/DFPT/IGLO/PW91/BasisIII//B3LYP/6-311G(d,p) level, $\sigma(^{13}C, TMS) = 183.6$, $\sigma(^{29}Si, TMS) = 346.7$.[25, 26] [e] At the GIAO/MPW1PW91/6-311G(3d,p)//B3LYP/6-311G(d,p) level, $\sigma(^{13}C, TMS) = 186.90$, $\sigma(^{29}Si, TMS) = 338.76$.[23, 24] [f] At the GIAO/MP2/6-311G(2df,p)(Si), 6-31G(d)(C,H)//MP2/6-311G(d,p) level, $\sigma(^{29}Si, TMS) = 370.61$.[23, 27] [g] $^1J(Si,H)$ calculated by the SOS/DFPT/IGLO method utilizing the Perdew–Wang exchange with Perdew correlation functional and the basis set III on geometries optimized at the B3LYP/6-311G(d,p) level.[25, 26]

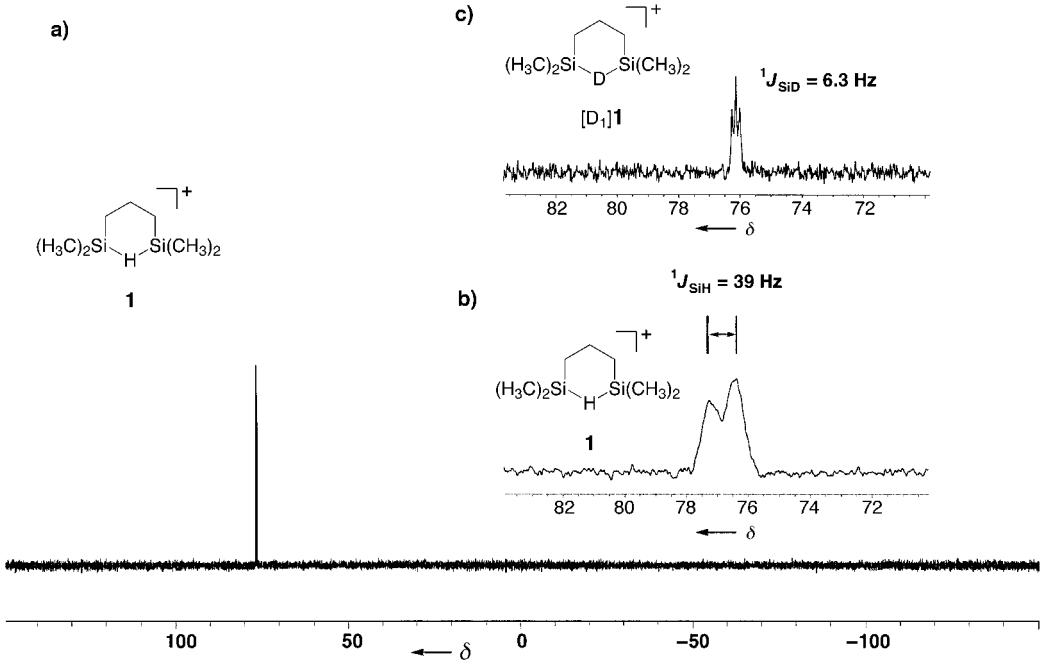
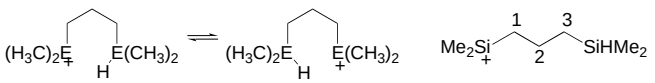



Figure 1. a) $^{29}$Si{$^1$H} INEPT NMR spectrum (79.5 MHz) of **1** at 300 K. b) $^{29}$Si INEPT+ NMR spectrum (49.5 MHz) of **1** at 300 K. c) $^{29}$Si{$^1$H} INEPT NMR spectrum (49.5 MHz) of [D$_1$]**1** at 300 K.

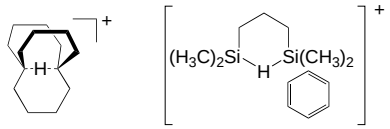
The number of observed NMR signals is in agreement with the symmetrical structure **1**, but a fast degenerate 1,5-H shift which interconverts two open silylium ions **5** can not be a priori excluded. The carbocation **6** was shown to be a rapidly equilibrating system with a barrier of about 5 kcal mol$^{-1}$ for




E = Si : *syn, syn* **5a** E = C : **6** *anti, anti* **5b**

  1433-7851/01/4016-3034 $ 17.50+.50/0 

the 1,5-H shift, and the symmetry reflected in the NMR spectra at higher temperatures is therefore time-averaged.[1i, 14] Low-temperature NMR studies at $-40\,^{\circ}C$ with **1** in [$D_8$]toluene showed no kinetic line broadening of the $^{29}Si$ NMR signal,[15a] and this suggests a barrier of less than 8.5 kcal mol$^{-1}$ for a conceivable degenerate 1,5-H shift in **5**.[15b] An analysis of the NMR data[16, 17] and the use of deuterium isotope effects on the NMR chemical shift,[14b, 18, 19] however, provide conclusive arguments for the static structure **1** and against an equilibrating system **5**: 1) The time-averaged $^{29}Si$ NMR signal for equilibrating **5** is expected to be at about $\delta =$ 168 (average of 348 and $-13$, calculated for **5b**; Table 1).[16] 2) The expected value of the time-averaged coupling constant $^1J_{Si,H}$ for **5** is about 90 Hz (average of 180 ($RSiHMe_2$) and 0 Hz ($RSiMe_2^+$)).[16a] 3) The hexadeuterated cation $[(H_3C)_2Si(CH_2)_3SiH(CD_3)_2]^+$ ([$D_6$]**1**) exhibits two $^{29}Si$ NMR signals ($\delta = 77.01, 76.78$), that is, the intrinsic isotope effect on the chemical shift is $\Delta\delta^{int} = -0.23$ and it is constant over the whole accessible temperature range. This is consistent only with a single minimum potential (i.e., structure **1**).[14b, 18] 4) When a 1:1 mixture of cations **1** and [$D_1$]**1** is generated, a $^2H$ NMR signal at 1.77 is recorded for the bridging deuterium atom in [$D_1$]**1**; hence, the primary deuterium isotope effect on the chemical shift is $\Delta\delta(^1H,^2H) = -0.30$.[19a] Negative $\Delta\delta(^1H,^2H)$ values indicate a single-minimum potential[19b] and are found for symmetrically hydrogen-bridged carbocations. For example, the tricyclic cation **7** has $\Delta\delta(^1H,^2H) = -0.10$.[1k]




**7** **8**

The experimental characterization of **1** is strongly corroborated by quantum mechanical calculations[20] at the hybrid density functional[21] B3LYP/6-311G(d,p) + ZPVE level of theory. At this level, **1** is more stable than the *anti*, *anti* conformer **5b** by 24.0 kcal mol$^{-1}$. The *syn*, *syn* conformer **5a** is not a stationary point on the potential energy surface but collapses without a barrier to the symmetrical, cyclic isomer **1**. The calculated dipole moment of **1** is rather small due to its symmetrical structure; in contrast, silylium ions like **5b** have dipole moments more than an order of magnitude larger ($\mu$(**1**) = 0.61, $\mu$(**5b**) = 10.4 Debye, at the B3LYP/6-311G(d,p) level). Consequently, solvation has a considerable effect on the relative energy of both isomers, but it does not change the relative stability order. Thus, according to SCRF theory[22] at the B3LYP/6-311G(d,p) level, the energy difference for **1** and **5b** decreases to 15.7 kcal mol$^{-1}$, whereby cyclic **1** is more stable.

The association energy $E_A$ between **1** and benzene, as calculated for the complex **8**, is relatively small ($E_A =$ 3.7 kcal mol$^{-1}$). Therefore, it is unlikely that this complex exists at ambient temperature, and **1** is best described as a free silyl cation with no direct coordination to the solvent, in agreement with the negligible solvent effects on $\delta(^{29}Si)$ in aromatic hydrocarbons.

Calculations of NMR data[23–27] at several levels of theory (see Table 1) predict $\delta(^{29}Si) = 87-96$ for **1**, near to the observed value. In addition, density functional calculation of $^1J_{Si,H}$ at the SOS/IGLO/DFPT/PP/BasisIII level[25, 26] predict for **1** a small $|^1J_{Si,H}|$ value of 43.8 Hz, in agreement with the experiment.

The calculated structure of **1** (Figure 2a) clearly reveals the existence of the three-center Si-H-Si bond. Compound **1** adopts a regular chair conformation with long Si–H bonds

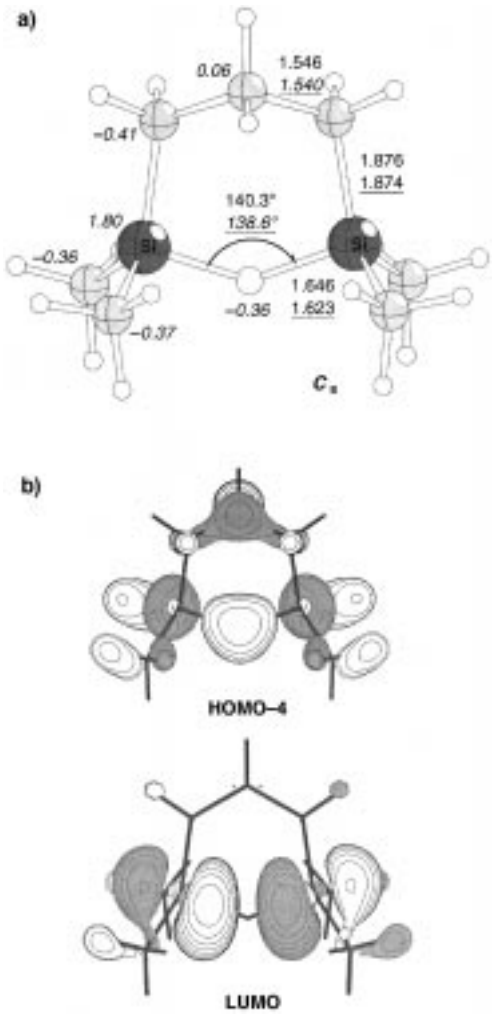



Figure 2. a) Calculated structure (at B3LYP/6-311G(d,p) and MP2/6-311G(d,p) (underlined) levels) and charge distribution (italics; NBO analysis[28] at B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) level) of **1**. b) Orbital plots of the occupied MO (HOMO – 4) and of the nonbonding MO (LUMO) of the Si-H-Si bond.[29]

(1.646 Å), and the positive charge is distributed over the two silicon atoms, while negative charge is accumulated at the bridging hydrogen atom (see Figure 2a), as expected for a three-center, two-electron bond with high electron density on the $\mu$-H atom in the bonding orbital, and a LUMO which is centered predominantely on the two silicon atoms (Figure 2b).

Received: March 22, 2001 [Z16829]

  1433-7851/01/4016-3035 $ 17.50+.50/0 

[1] a) R. P. Kirchen, T. S. Sorensen, *J. Chem. Soc. Chem. Commun.* **1978**, 769; b) R. P. Kirchen, T. S. Sorensen, K. J. Wagstaff, *J. Am. Chem. Soc.* **1978**, *100*, 6761; c) R. P. Kirchen, N. Okazawa, K. Ranganayakulu, A. Rauk, T. S. Sorensen, *J. Am. Chem. Soc.* **1981**, *103*, 597; d) R. P. Kirchen, K. Ranganayakulu, B. P. Singh, T. S. Sorensen, *Can. J. Chem.* **1981**, *59*, 2173; e) R. P. Kirchen, T. S. Sorensen, K. J. Wagstaff, A. M. Walker, *Tetrahedron* **1986**, *42*, 1063; f) R. P. Kirchen, T. S. Sorensen, *J. Am. Chem. Soc.* **1979**, *101*, 3240; g) P. Buzek, P. von R. Schleyer, H. Vancik, D. E. Sunko, *J. Chem. Soc. Chem. Commun.* **1991**, 1538; h) T. S. Sorensen, S. M. Whitworth, *J. Am. Chem. Soc.* **1990**, *112*, 8135; i) F. Sun, T. S. Sorensen, *J. Am. Chem. Soc.* **1993**, *115*, 77; j) J. E. McMurry, C. N. Hodge, *J. Am. Chem. Soc.* **1984**, *106*, 6450; k) J. E. McMurry, T. Lectka, C. N. Hodge, *J. Am. Chem. Soc.* **1989**, *111*, 8867; l) J. E. McMurry, T. Lectka, *Acc. Chem. Res.* **1992**, *25*, 47.

[2] C. Maerker, J. Kapp, P. von R. Schleyer in *Organosilicon Chemistry: From Molecules to Materials*, *Vol. II* (Eds.: N. Auner, J. Weis), VCH, Weinheim, **1995**, p. 329.

[3] C.-H. Ottoson, D. Cremer, *Organometallics* **1996**, *15*, 5309.

[4] B. Wrackmeyer, O. L. Tok, Y. N. Bubnov, *Angew. Chem.* **1999**, *111*, 214; *Angew. Chem. Int. Ed.* **1999**, *38*, 124.

[5] For preliminary reports on a solid-state structure of a related compound, see P. D. Lickiss, P. C. Masangane, Abstracts Paper ISOS XII (Sendai, Japan), **1999**, 2A14 and P. D. Lickiss, P. C. Masangane, Abstracts 34th Organosilicon Symposium (White Plains, NY), **2001**, C-16.

[6] Review: a) P. D. Lickiss in *The Chemistry of Organosilicon Compounds*, *Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, p. 557; examples of silylium ions: b) J. B. Lambert, Y. Zhao, *Angew. Chem.* **1997**, *109*, 389; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 400; c) T. Nishinaga, Y. Izukawa, K. Komatsu, *J. Am. Chem. Soc.* **2000**, *122*, 9312; d) A. Sekiguchi, T. Matsuno, M. Ichinohe, *J. Am. Chem. Soc.* **2000**, *122*, 11250.

[7] Spectroscopic data of **1**-[$B(C_6F_5)_4$]: $^1$H NMR (400.14 MHz, [$D_6$]benzene, 300 K, $\delta(C_6D_5H) = 7.20$): $\delta = 1.47$ (br s, 1H, SiHSi), 1.32 (m, 2H, $H^2$), 0.43 (m, 4H, $H^{1/3}$), 0.07 (s, 12H, $(H_3C)_2Si$); $^{13}$C{$^1$H} NMR (100.63 MHz, [$D_6$]benzene, 300 K, $\delta(C_6D_6) = 128.0$): $\delta = 149.0$ (d, $^1J(C,F) = 241.5$ Hz, *o*-$C_6F_5$), 139.2 (d, $^1J(C,F) = 251.6$ Hz, *p*-$C_6F_5$), 137.0 (d, $^1J(C,F) = 251.6$ Hz, *o*-$C_6F_5$), 125.2 (br, *ipso*-$C_6F_5$), 18.1 (s, $C^2$), 14.9 (s, $C^{1/3}$), $-4.0$ (s, $CH_3$); $^{29}$Si NMR (79.50 MHz, [$D_6$]benzene, 300 K; $\delta((H_3C)_2SiHCl) = 11.1$, external): $\delta = 76.7$ (d, $^1J(Si,H) = 39$ Hz); $^{19}$F NMR (254.2 MHz, [$D_6$]benzene, 300 K; $\delta(CF_2Cl_2) = 0$, external): $\delta = -136.9$ (d, 2F, $J(F,F) = 8.4$ Hz, *m*-F), $-167.7$ (t, 1F, $J(F,F) = 20.7$ Hz, *p*-F), $-171.5$ (t, 2F, $J(F,F) = 16.8$ Hz, *o*-F).

[8] $\delta(^1H^{br})$ and $\delta(^{29}Si)$ are only slightly temperature dependent: $\Delta\delta(^1H^{br}) = -0.06$ (300 K, 263 K); $\Delta\delta(^{29}Si) = -0.6$ (300 K, 243 K).

[9] Spectroscopic data of [$D_1$]**1** (for $^1$H, $^{13}$C, and $^{19}$F NMR data, see ref. [7]): $^2$H NMR (38.40 MHz, [$D_6$]benzene, 300 K, $\delta(C_6D_6) = 7.20$): $\delta = 1.77$ (br s); $^{29}$Si{$^1$H} NMR (49.49 MHz, [$D_6$]benzene, 300 K, $\delta((H_3C)_2SiHCl) = 11.1$, external): $\delta = 76.2$ (t, $^1J(Si,D) = 6.3$ Hz).

[10] N. M. Sergeyev, *NMR* **1990**, *22*, 31.

[11] a) J. B. Lambert, S. Zhang, S. M. Ciro, *Organometallics* **1994**, *13*, 2430; b) C. Maerker, P. von R. Schleyer in *The Chemistry of Organosilicon Compounds*, *Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, p. 513.

[12] Removal of the solvent from the solution of **1** leads to an oily glue, which dissolves in aromatic hydrocarbons to give a two-phase solution again.

[13] For NMR data of silylnitrilium ions, see a) G. A. Olah, S. C. Narang, B. G. B. Gupta, R. Malhotra, *J. Org. Chem.* **1979**, *44*, 1247; b) M. Kira, T. Hino, H. Sakurai, *Chem. Lett.* **1993**, 153; c) S. R. Bahr, P. Boudjouk, *J. Am. Chem. Soc.* **1993**, *115*, 4514; d) Z. Xie, D. J. Liston, T. Jelinek, V. Mitro, R. Bau, C. A. Reed, *J. Chem. Soc. Chem. Commun.* **1993**, 384; e) T. Müller, R. Meyer, D. Lennartz, H.-U. Siehl, *Angew. Chem.* **2000**, *112*, 3203; *Angew. Chem. Int. Ed.* **2000**, *39*, 3074.

[14] a) N. E. Okazawa, T. S. Sorensen, *Can. J. Chem.* **1985**, *60*, 2180; b) H.-U. Siehl, *Adv. Phys. Org. Chem.* **1987**, *23*, 63.

[15] a) Below $-40\,^\circ$C the solution solidifies. b) Calculated for $T = 230$ K, with a shift difference of the interchanging silicon atoms of $\Delta\delta = 360$ (calculated for **5b**; see Table 1) at 49.5 MHz.

[16] a) For a similar analysis for carbocations, see: G. A. Olah, A. M. White, *J. Am. Chem. Soc.* **1969**, *91*, 5801. b) For a fast equilibrium between two equivalent forms of **3** the time-averaged $^{29}$Si NMR signal is expected to be at $\delta = 45.2$ (av of 102.4 and $-12.1$, calculated for **3** at the SOS/DFPT/IGLO/PW91/BasisIII//B3LYP/6-311G(d,p) level). The activation energy for such a process, however, is expected to be greater than 20.5 kcal mol$^{-1}$ (the interaction energy between benzene and **5b**, calculated at the B3LYP/6-311 + G(d,p) + ZPVE) level). However, this process is no longer fast on the $^{29}$Si NMR timescale at room temperature, and therefore the $^{29}$Si NMR spectra of static **3** should be observable.

[17] All attempts to record an IR spectrum of **1**, either dissolved in $C_6D_6$ or without solvent, led to inconclusive results, most probably due to decomposition of **1** in the IR cell.

[18] M. Saunders, P. von R. Schleyer, J. Chandrasekhar in *Rearrangements in Ground and Excited States* (Ed.: P. de Mayo), Academic Press, San Diego, **1980**, chap. 1.

[19] a) The primary isotope effect is defined as $\Delta\delta(^1H,^2H) = \delta(^1H) - \delta(^2H)$; b) L. J. Altman, D. Laungani, G. Gunnarsson, H. Wennerström, S. Forsén, *J. Am. Chem. Soc.* **1978**, *100*, 8264.

[20] a) All calculations were performed with Gaussian 94, Revisions C2 – E2, and Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**; b) calculations at the MP2/6-311G(d,p) level of theory gave similar results; that is, the energy difference between **1** and **5b** is 27.4 kcal mol$^{-1}$; see also Figure 2 for a comparison of geometries.

[21] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* **1993**, *98*, 5612; d) a recent monograph: W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, **2000**.

[22] Self-consistent reaction field (SCRF) calculations were performed with the Onsager model and an assumed relative permittivity of $\varepsilon_r = 80$. a) M. W. Wong, M. J. Frisch, K. B. Wiberg, *J. Am. Chem. Soc.* **1991**, *113*, 4776; b) M. W. Wong, K. B. Wiberg, M. J. Frisch, *J. Am. Chem. Soc.* **1992**, *114*, 1645.

[23] GIAO: a) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789; b) K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1982**, *104*, 5667; c) J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497.

[24] a) K. B. Wiberg, *J. Comput. Chem.* **1999**, *20*, 1299; b) C. Adamo, V. Barone, *Chem. Phys. Lett.* **1997**, *274*, 242; c) J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* **1996**, *54*, 16533.

[25] SOS/IGLO/DFPT: a) V. G. Malkin, O. L. Malkina, M. E. Casida, D. R. Salahub, *J. Am. Chem. Soc.* **1994**, *116*, 5898; b) V. G. Malkin, O. L. Malkina, L. A. Erikson, D. R. Salahub in *Modern Density Functional Theory* (Eds.: J. M. Seminario, P. Politzer), Elsevier, Amsterdam, **1995**, p. 273; c) V. G. Malkin, O. L. Malkina, D. R. Salahub, *Chem. Phys. Lett.* **1996**, 261, 335.

[26] a) J. P. Perdew, Y. Wang, *Phys. Rev. B* **1986**, *33*, 8800; b) J. P. Perdew, *Phys. Rev. B* **1986**, *34*, 7406; c) W. Kutzelnigg, U. Fleischer, M. Schindler, *NMR* **1990**, *23*, 165.

[27] MP2/GIAO: a) J. Gauss, *J. Chem. Phys.* **1993**, *99*, 3629.

[28] NBO 4.0: E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **1996**; A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

[29] Calculated from the B3LYP/6-311G(d,p) density by using the Molden program: G. Schaftenaar, J. H. Noordik, *J. Comput. Aided Mol. Des.* **2000**, *14*, 123.


  1433-7851/01/4016-3036 $ 17.50+.50/0 