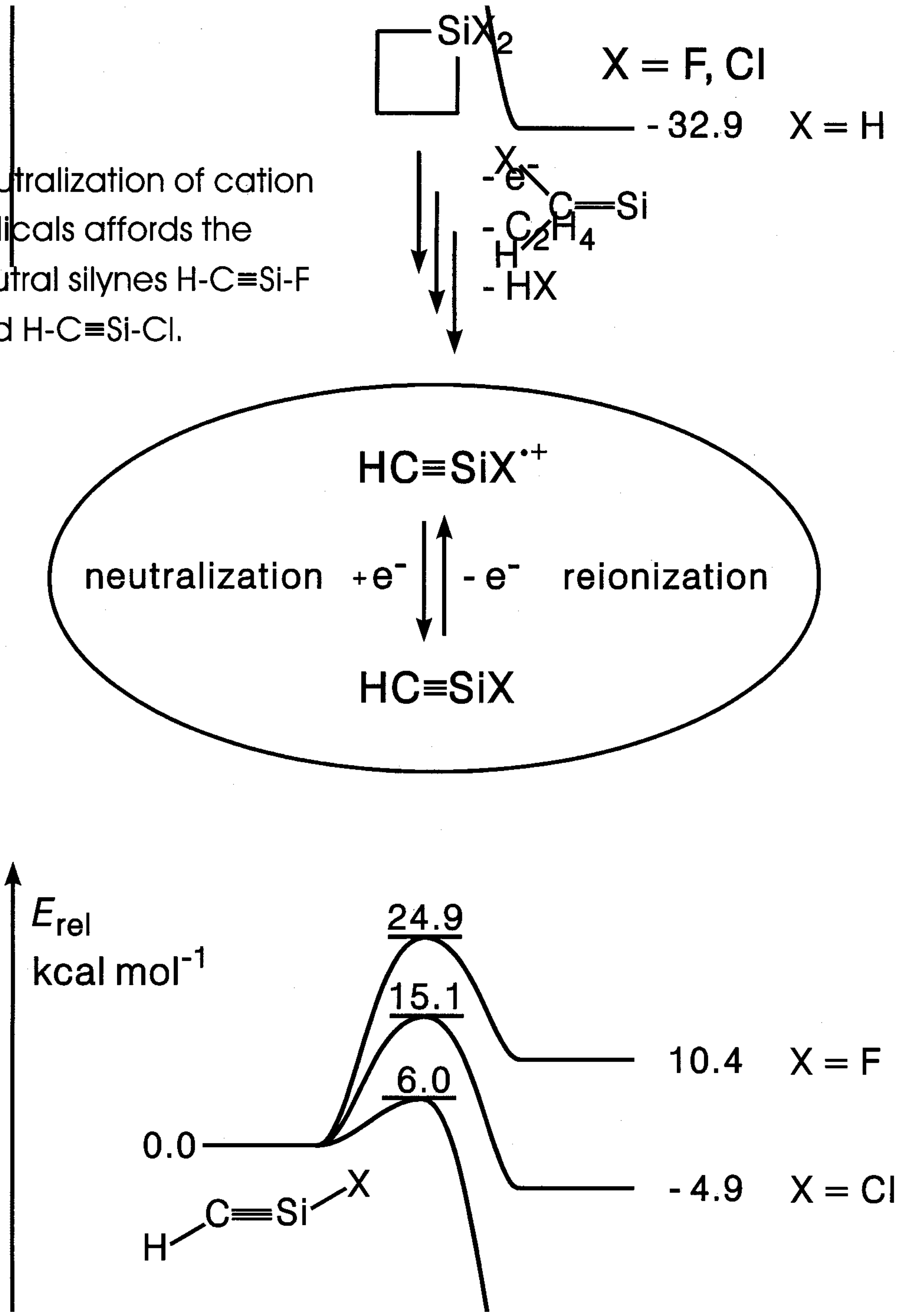


Neutralization of cation radicals affords the neutral silynes H-C≡Si-F and H-C≡Si-Cl.

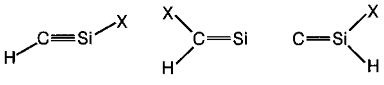
HCSiF and HCSiCl: The First Detection of Molecules with Formal C≡Si Triple Bonds**

Miriam Karni, Yitzhak Apeloig, Detlef Schröder, Waltraud Zummack, Roberto Rabezzana, and Helmut Schwarz*

Dedicated to Professor Jack D. Dunitz
on the occasion of his 75th birthday

The synthesis and isolation of compounds having multiple bonds to silicon has been one of the major challenges in main group chemistry.[1] The first stable compounds with double bonds to silicon were synthesized in 1981,[2] and since then this group of compounds has been studied extensively, both experimentally[3] and theoretically.[4] In contrast, compounds with triply bonded silicon are still largely unknown except for HSi≡N which has been characterized by matrix isolation spectroscopy.[5] The formation of transient $HC\equiv SiCH_3$,[6] HC≡SiCl,[7] and $H_3CSi\equiv SiCH_3$[8] has been suggested but conclusive evidence for the existence of silynes (RC≡SiR) or disilynes (RSi≡SiR) has not yet been presented, and their synthesis remains one of the "holy grails" of silicon chemistry.

One of the major obstacles in the preparation of triply bonded silicon compounds, even as transients, is the existence of more stable isomers.[9, 10] For the $[C,Si,H_2]$ parent system, the silyne **1a** is calculated[11] to be less stable than the silylidene **2a** by 32.9 kcal mol^{-1}, and the barrier for the **1a** → **2a** rearrangement is only 6 kcal mol^{-1};[9a, 14] the isomeric vinylidene **3a** is 85.8 kcal mol^{-1} less stable than **2a**. Accordingly, only **2a** has been detected and characterized spectroscopically in the gas phase,[15] while the shallow wells of the high-energy isomers **1a** and **3a** are beyond the means of the conventional variant of neutralization-reionization (NR)[16] mass spectrometry used in this study.[17]



1a : X = H
1b : X = F
1c : X = Cl

2a : X = H
2b : X = F
2c : X = Cl

3a : X = H
3b : X = F
3c : X = Cl

Theoretical studies by two of us[9] have revealed that substitution affects strongly and even reverses the stability order between formally triply bonded silicon species[18] and their other isomers (Figure 1a). Thus, the fluorosilyne **1b** is predicted to be more stable than its isomers **2b** and **3b** by 10.4 and 48.0 kcal mol^{-1}, respectively. Furthermore, the barrier of 24.9 kcal mol^{-1} associated with the interconversion **1b** → **2b** is significantly larger than for the parent silyne (**1a** → **2a**), suggesting that **1b** is amenable for experimental detection. The situation is similar for X = Cl (Figure 1a) and X = OH.[9a] The dramatic effect of X can be attributed mostly to the high D(Si–F) and D(Si–Cl) bond energies which exceed D(C–F) and D(C–Cl), respectively, while D(Si–H) is smaller than D(C–H).[19]

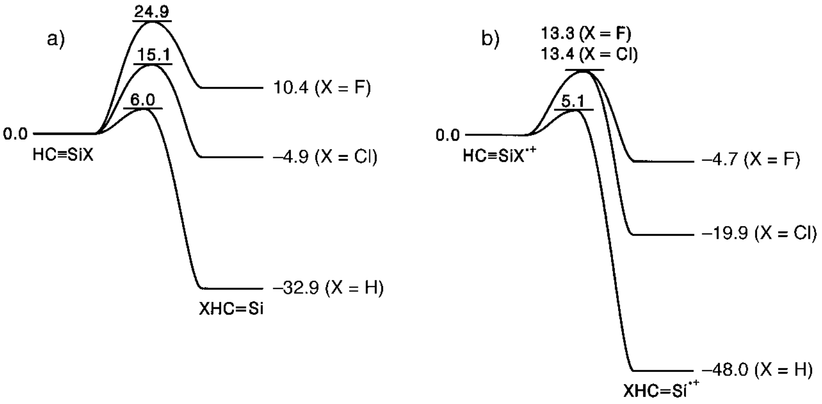


Figure 1. Schematic potential-energy profiles [kcal mol^{-1}] for a) the neutral and b) the cationic [C,H,Si,X] isomers **1** and **2** (X = H, F, Cl) calculated at the QCISD(T)/6-31G** level of theory.

Herein, we examine these theoretical predictions by means of neutralization-reionization (NR) mass spectrometry and provide the first firm evidence for the existence of compounds with formal C≡Si triple bonds. Our experimental approach for generating neutral HC≡SiX is based upon the neutralization of the corresponding radical cations. A prerequisite for such experiments is that the geometry changes occurring upon neutralization of the radical cations **1b**$^{\bullet+}$ and **1c**$^{\bullet+}$ are associated with minor excitations of the neutral species. This condition is fortunately fulfilled, as the calculated energy differences of the vertical versus adiabatic neutralizations of **1b**$^{\bullet+}$ and **1c**$^{\bullet+}$, respectively, are less than 4 kcal mol^{-1}. In conjunction with the significant height of the calculated activation barriers for migration of either X = F or Cl, respectively, the silyne structures may thus be preserved upon neutralization.

Experimentally[20] it is not trivial, however, to generate the desired radical cations **1b**$^{\bullet+}$ and **1c**$^{\bullet+}$ in a straightforward manner and in sufficient yields. Many potential organosilicon precursors do not yield abundant molecular ions but undergo instead facile α cleavages. For example, upon ionization the precursors $(CH_3)_{(4-n)}SiX_n$ ($n = 1-3$; X = F, Cl) show predominant losses of open-shell fragments, producing closed-shell silylium ions which would require an additional homolytic bond cleavage in order to afford the desired radical cations. Consequently, for most halosilanes, the yields of $[C,H,Si,X]^{\bullet+}$ ions are generally low—at most moderate. An efficient

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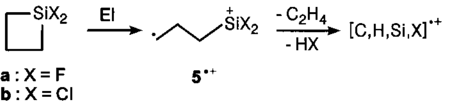
generation of silicon-containing $[C,H,Si,X]^{\bullet +}$ radical cations would require compounds which form abundant molecular ions upon ionization. These open-shell species may then undergo consecutive losses of closed-shell neutral particles leading to the desired $[C,H,Si,X]^{\bullet +}$ ions. The 1,1-dihalosilacyclobutanes **4** (X = F, Cl) fulfill these requirements:[23] ionization of **4** leads to an intense molecular ion, presumably the distonic[24] ion $\mathbf{5}^{\bullet +}$, which subsequently eliminates C_2H_4 and HX to give abundant amounts of $[C,H,Si,X]^{\bullet +}$ ions (Scheme 1).



Scheme 1. Formation and fragmentation of $\mathbf{5}^{\bullet +}$.

The collisional activation (CA) mass spectra of the $[C,H,Si,X]^{\bullet +}$ ions are in full accord with the anticipated connectivities of $\mathbf{1b}^{\bullet +}$ and $\mathbf{1c}^{\bullet +}$ (Figures 2a and 3a, respectively). Thus, the intense SiX^+ fragments are in keeping with the silyne structures as are the other, minor fragments. In particular, the $SiCH_n^+$ ($n = 0, 1$) signals are much more intense than the CH_nX^+ signals, the latter pointing towards the silylidene ions $\mathbf{2b}^{\bullet +}$ and $\mathbf{2c}^{\bullet +}$. We conclude that the majority of the precursor $[C,H,Si,X]^{\bullet +}$ (X = F, Cl) ions have the silyne structures, even though the corresponding silylidenes $\mathbf{2b}^{\bullet +}$ and $\mathbf{2c}^{\bullet +}$ are thermochemically more stable (Figure 2b). This conclusion is also in accordance with the generation of $[C,H,Si,X]^{\bullet +}$ ions by consecutive fragmentation of $\mathbf{5}^{\bullet +}$ (Scheme 1).

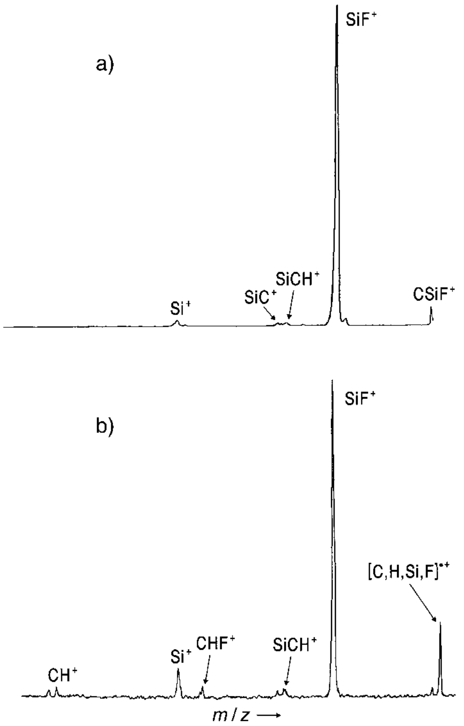


Figure 2. a) Collisional activation (He, 80% transmission) and b) neutralization-reionization (Xe, 80% transmission/O_2, 80% transmission) mass spectra of $[C,H,Si,F]^{\bullet +}$ ions; the precusor ion was generated by electron ionization of 1,1-difluorosilacyclobutane (**4a**) and mass-selected with sectors B(1) and E(1).

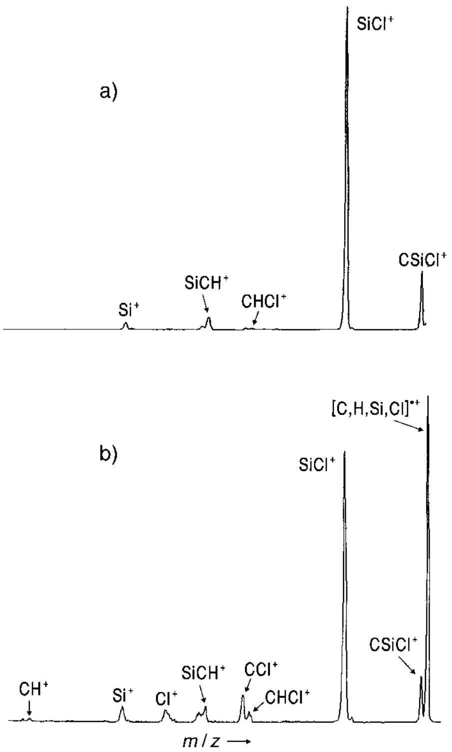


Figure 3. a) Collisional activation (He, 80% transmission) and b) neutralization-reionization (Xe, 80% transmission/O_2, 80% transmission) mass spectra of $[C,H,Si,Cl]^{\bullet +}$ ions; the precursor ion was generated by electron ionization of 1,1-dichlorosilacyclobutane (**4b**) and mass-selected with sectors B(1)

The NR spectra of the $[C,H,Si,X]^{\bullet +}$ (X = F, Cl) ions (Figures 2b and 3b) show pronounced recovery signals due to reionized [C,H,Si,X] molecules, along with the characteristic SiX^+ fragments. The observation of the recovery signals implies that the neutral [C,H,Si,X] species have lifetimes of at least a microsecond. While in a preparative sense, this lifetime may appear to be rather short, it is sufficient to allow for a complete dissipation of internal energy in the internal rovibrational modes for small species such as [C,H,Si,X], which hence can be considered to be stable species as isolated molecules. In analogy to the above interpretation of the CA mass spectra, we therefore conclude that the NR experiments demonstrate the existence in the gas phase of the neutral silynes $HC{\equiv}SiF$ (**1b**) and $HC{\equiv}SiCl$ (**1c**). For X = Cl, however, the CH_nCl^+ fragments ($n = 0, 1$) observed in Figure 3b imply the occurrence of partial rearrangement to the silylidene isomer **2c** (see below).

While the above reasoning is self-consistent, one objection remains. Thus, the observed CA and NR spectra may also be consistent with the interpretation that the precursor ions are $\mathbf{2b}^{\bullet +}$ or $\mathbf{2c}^{\bullet +}$, rather than $\mathbf{1b}^{\bullet +}$ and $\mathbf{1c}^{\bullet +}$, respectively, because the predominance of the SiX^+ ions may simply reflect an energetically favored dissociation channel as suggested by our calculations. Thus, for X = F and Cl, respectively, the fragments $[SiX^+ + CH^\bullet]$ stemming from $HC{\equiv}SiX^{\bullet +}$ are calculated to be 26.9 and 20 kcal mol^{-1}, respectively, more stable[25] than $[HXC + Si^{\bullet +}]$, the lowest energy fragmentation channel of

$HXC{=}Si^{\cdot +}$. For X = Cl this option can be excluded by a further experiment. As shown in Figure 3a, a significant fraction of $[C,H,Si,Cl]^{\cdot +}$ undergoes collision-induced loss of a hydrogen atom to yield the ion $[C,Si,Cl]^{+}$. If the precursor ions were **2c**$^{\cdot +}$, the connectivity of this fragment should be Cl-C-Si, while C-Si-Cl is expected from **1c**$^{\cdot +}$. An experimental distinction of the two connectivities should hence be possible based on the observation of either CCl^{+} (characteristic of Cl-C-Si) or $SiCl^{+}$ (characteristic of C-Si-Cl). To test this point, mass-selected $[C,H,Si,Cl]^{\cdot +}$ ions were collisionally activated, yielding $[C,Si,Cl]^{+}$ fragments which were again mass-selected and subjected to yet another collision event. The corresponding CA/CA spectrum of the $[C,Si,Cl]^{+}$ ions shows an intense $SiCl^{+}$ fragment (100 %) along with less intense signals due to SiC^{+} (10 %) and Si^{+} (10 %), while CCl^{+} is not observed above the noise level of 4 %. Thus, the hydrogen atom loss from $[C,H,Si,Cl]^{\cdot +}$ yields $ClSiC^{+}$ and not $SiCCl^{+}$, indicating that the precursor beam consists of genuine $HC{\equiv}SiCl^{\cdot +}$ (**1c**$^{\cdot +}$) ions.[26] By analogy, we assume that the recovery signal in the NR spectrum of $[C,H,Si,F]^{\cdot +}$ is due to the formation of the silyne **1b**. Finally, this analysis supports the conclusion that the CH_nCl^{+} fragments ($n = 0, 1$) observed in the NR spectrum of $[C,H,Si,Cl]^{\cdot +}$ are due to a collision-induced rearrangement of neutral **1c** to **2c**. This interpretation is also in accord with the lower intensities of CH_nF^{+} in the NR spectrum of $[C,H,Si,F]^{\cdot +}$, because for X = F the neutral silyne is more stable than the silylidene, and the **1b** → **2b** isomerization barrier is higher than for X = Cl (Figure 1a).

In summary, the present results provide the first experimental evidence for the existence of neutral $HC{\equiv}SiX$ (X = F, Cl) molecules with $C{\equiv}Si$ triple bonds. This success calls for experimental studies of related systems by more direct techniques, for example, matrix isolation spectroscopy. Silynes of the type $RC{\equiv}SiX$, where substituents X = F, Cl, or an alkoxy group[9a] maximize thermochemical stability, and where R is a bulky group which increases kinetic stability, for example 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl,[3d] are promising candidates for isolation as long-lived compounds.

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[1] For comprehensive reviews, see: a) *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**; b) *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**.

[2] a) A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, *J. Chem. Soc. Chem. Commun.* **1981**, 191; b) R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343.

[3] a) G. Raabe, J. Michl in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, p. 1015; b) H. Sakurai in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, p. 827; c) T. Müller, W. Ziche, N. Auner in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, p. 857; d) N. Tokitoh, R. Okazaki in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, p. 1063; e) M. Driess, *Adv. Organomet. Chem.* **1996**, *39*, 193; f) R. Okazaki, R. West, *Adv. Organomet. Chem.* **1996**, *39*, 232.

[4] a) Y. Apeloig in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, p. 103; b) Y. Apeloig, M. Karni, T. Müller in *Organosilicon Chemistry II. From Molecules to Materials* (Eds.: N. Auner, J. Weis), VCH, Weinheim, **1996**, p. 263.

[5] G. Maier, J. Glatthaar, *Angew. Chem.* **1994**, *106*, 486; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 473.

[6] M. Urbanová, E. A. Volnina, L. E. Gusel'nikov, Z. Bastl, J. Pola, *J. Organomet. Chem.* **1996**, *509*, 73.

[7] M. Jakoubková, R. Fajgar, J. Tláskal, J. Pola, *J. Organomet. Chem.* **1994**, *466*, 29.

[8] A. Sekiguchi, S. S. Zigler, R. West, J. Michl, *J. Am. Chem. Soc.* **1986**, *108*, 4241.

[9] a) Y. Apeloig, M. Karni, *Organometallics* **1997**, *16*, 310; b) Y. Apeloig, K. Albrecht, *J. Am. Chem. Soc.* **1995**, *117*, 7263.

[10] a) S. Koseki, M. S. Gordon, *J. Phys. Chem.* **1988**, *92*, 364; b) S. Koseki, M. S. Gordon, *J. Phys. Chem.* **1989**, *93*, 118; c) B. T. Colgrove, H. F. Schaefer III, *J. Phys. Chem.* **1990**, *94*, 5593; d) R. Grev, H. F. Schaefer III, *J. Chem. Phys.* **1992**, *97*, 7990.

[11] All calculations were performed using standard routines of Gaussian 94.[12] The energies reported throughout the paper refer to the QCISD(T)/6-31G** level of theory and include corrections for zero point energy (ZPE) scaled by a factor of 0.98.[13]

[12] Gaussian 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, G. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburg, PA, **1995**.

[13] A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502.

[14] For recent calculations of $[C,H_2,Si]$ at other levels of theory, see: a) M. T. Nguyen, D. Sengupta, L. G. Vanquickenborne, *Chem. Phys. Lett.* **1995** *244*, 83; b) R. Stegmann, G. Frenking, *J. Comput. Chem.* **1996**, *17*, 78.

[15] a) K. P. Lim, F. W. Lampe, *Int. J. Mass Spectrom. Ion. Processes* **1990**, *101*, 245; b) R. Srinivas, D. Sülzle, H. Schwarz, *J. Am. Chem. Soc.* **1991**, *113*, 52; c) C. D. Sherrill, H. F. Schaefer III, *J. Phys. Chem.* **1995**, *99*, 1949; d) M. Izuha, S. Yamamoto, S. Saito, *J. Chem. Phys.* **1996**, *105*, 4923.

[16] a) N. Goldberg, H. Schwarz, *Acc. Chem. Res.* **1994**, *27*, 347; b) C. A. Schalley, G. Hornung, D. Schröder, H. Schwarz, *J. Chem. Soc. Rev.* **1998**, *27*, 91.

[17] For an example of the application of more sophisticated variants of this method, see: D. Schröder, C. A. Schalley, N. Goldberg, J. Hrušák, H. Schwarz, *Chem. Eur. J.* **1996**, *2*, 1235.

[18] The term "formal" pays tribute to the fact that the silynes have bent structures, unlike the linear arrangements expected for triple bonds; for a more detailed discussion see ref. [9].

[19] Dissociation energies D in H_3MX (M = C, Si; X = H, F, Cl) [$kcal\,mol^{-1}$]: $D(C-H) = 105$, $D(C-F) = 113$, $D(C-Cl) = 83$, $D(Si-H) = 92$, $D(Si-F) = 152$, $D(Si-Cl) = 110$. Data from: a) S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. Ref. Data Suppl. 1* **1988,** *17*; b) R. Becerra, R. Walsh in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, p. 153.

[20] The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer[21] of BEBE configuration (B stands for magnetic and E for electric sectors). $[C,H,Si,X]^{\cdot +}$ ions (X = F, Cl) were generated by electron ionization (electron energy 70 eV) of the 1,1-dihalosilacyclobutanes **4**; similar results were obtained with other precursors such as $(CH_3)_{(4-n)}SiX_n$ ($n = 1-3$, X = F, Cl). All chlorosilanes were commercially available (ABCR, Karlsruhe), and the fluorides were prepared[22] by treating the neat chlorides with anhydrous ZnF_2. The ions having a kinetic energy of 8 keV were mass-selected using B(1) and E(1), and the respective mass spectra were recorded by scanning B(2). For collisional activation helium was used as collision gas. In the NR experiments,[16,21d] neutralization was

afforded by xenon, and oxygen was used for reionization. The CA/CA mass spectrum of $[C,Si,Cl]^+$ was obtained by daughter ion selection with B2, and recording the subsequent fragmentations by scanning E(2).[21c] All spectra were accumulated and on-line processed with the AMD/Intectra data system; in general 5 to 50 spectra were averaged to improve the signal-to-noise ratio.

[21] a) R. Srinivas, D. Sülzle, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 368; b) R. Srinivas, D. Sülzle, W. Koch, C. H. DePuy, H. Schwarz, *J. Am. Chem. Soc.* **1991**, *113*, 5970; c) D. Schröder, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1995**, *146/147*, 183; d) C. A. Schalley, D. Schröder, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 173.

[22] A. E. Newkirk, *J. Am. Chem. Soc.* **1946**, *68*, 2736.

[23] In analogy, photolysis of **4** (X = Cl) has been speculated to yield neutral **1c**, see ref. [7].

[24] For a definition and examples for distonic ions: R. L. Smith, P. K. Chou, H. I. Kenttämaa in *The Structure and Dynamics of Organic Ions* (Eds.: T. Baer, C. Y. Ng), Wiley, London, **1996**, p. 197.

[25] According to the experimental data in ref. [19a], the preference for SiF^+ formation is only 16 kcal mol^{-1}. However, we trust our calculated value of 26.9 kcal mol^{-1}. A similar discrepancy between calculated and experimental energetics of SiF^+ was reported earlier, see: E. W. Ignacio, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 7439.

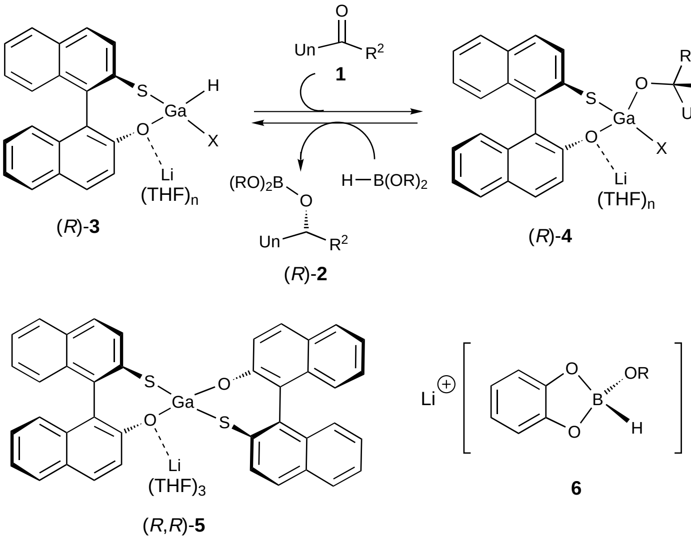
[26] While the fragmentations of $[Si,C,Cl]^+$ leading to $[SiCl^+ + C]$ and to $[Si^+ + CCl]$ may also be attributed to the mere energetic preference of these exit channels ($\Sigma\Delta H_f^0 = 386$ and 388 kcal mol^{-1}, respectively), compared to those for the formation of $[SiC^+ + Cl]$ ($\Sigma\Delta H_f^0 = 416$ kcal mol^{-1}) or $[Si + CCl^+]$ ($\Sigma\Delta H_f^0 = 405$ kcal mol^{-1}), of the higher energy channels only SiC^+ is observed experimentally, but not the lower energy fragment CCl^+; data taken from refs. [19a,b,27].

[27] A. E. Ketvirtis, D. K. Bohme, A. C. Hopkinson, *J. Phys. Chem.* **1995**, *99*, 16121.

Catalytic Enantioselective Reduction of Ketones by a Chiral Gallium Complex and Catecholborane**

Alan Ford and Simon Woodward*

Practical catalytic reduction of prochiral ketones to secondary alcohols of high enantiopurity is indispensable to many organic preparations. Oxazaborolidine-catalyzed BH_3 reduction[1] and ruthenium-catalyzed transfer hydrogenation[2] are effective for the reduction of $R^1C(O)R^2$ **1** provided an appropriate difference, steric or electronic, exists between the groups. As steric differences cannot always be realized, alternative catalysts that sense electronic differences between the groups in addition to steric requirements are highly desirable. In a seminal paper Noyori described the use of [LiAlH(OEt)(BINOL dianion)] (BINOL = 2,2′dihydroxy-1,1′-binaphthyl) in stoichiometric amounts to effect an electronically controlled hydride addition to **1** (R^1 = unsaturated unit, R^2 = alkyl).[3] We have used the principles of "hard" and "soft"[4] Lewis acids and bases to attempt a catalytic analogue of this reagent. Monothiobinaphthol (MTB)[5] and $LiGaH_4$[6] were selected as the "soft" ligand/catalyst combination and catecholborane as a "hard" terminal hydride source to promote only the removal of alkoxide products and not the chiral ligand from **4** (Scheme 1). While a range of spectator ligands gave moderate selectivities (X = OMe (72% *ee*), 2-S-$C_{10}H_7$ (72% *ee*), 1,2-$HOCH_2CH_2SH$ (24% *ee*)), a mixture of $LiGaH_4$ and two MTB ligands proved particularly effective for a range of ketones (Table 1); the mixture was characterized in the solid state as **5**, which is isostructural with the gallium–BINOL catalysts of Shibasaki.[7]



Scheme 1. Reduction of ketone **1** with a complex of MTB and LiGaH4 (Un = unsaturated unit) as well as with the complex **5** and the borate **6**.

These reactions are technically simple, stirring the reaction is not essential and any cryostat or even a domestic freezer suffices for cooling. At catalyst loadings below 2.5 mol% the enantioselectivity falls: At 1 mol% (−25 °C) **1a** is reduced in 86% *ee* and with 0.5 mol% (0 °C) in 72% *ee*. Pre-storage of solutions of $LiGaH_4$/2MTB at ambient temperature for two

Table 1. Enantioselective reduction of ketones **1** by **5** (2.5 mol%) and catecholborane (1.1 equiv) by method B (see experimental section, unless otherwise stated).

Ketone	R^1	R^2	Yield [%]	*ee* [%]
a	Ph	Me	89–95[a]	89–91[a]
b	Ph	Et	96	93
c	Ph	*n*Bu	80	92
d	Ph	*i*Bu	65	92
e	4-BrPh	Me	80	87
f	4-MePh	Me	95	87
g	2-furyl	*n*-C_6H_{13}	76	81
h	PhCH=CH	Me	70	75
i	EtC≡C	Me	60	63

[a] Using methods A–C.

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