Chemical Shielding Tensors for a Silicon−Carbon Double Bond

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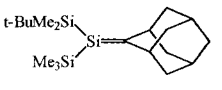
Measurements of NMR chemical shielding tensors (CST) have been important in aiding the understanding of the nature of the chemical bond and in particular for multiple bonding involving heavier main group elements. Chemical shielding tensors have been reported and interpreted for compounds containing Si=Si,[1] P=P,[2] Sn=Sn,[3] C=P, and C≡P[4] bonds. Although stable silenes, $R_2Si{=}CR'_2$, have been known since 1981,[5] no information on the ^{29}Si or ^{13}C tensors in these molecules is available. Here we report the *first experimental determination and theoretical calculations*[6] *of the solid-state NMR chemical shielding tensors for a silene*, (tBuMe$_2$Si)(Me$_3$Si)Si=2-Ad (**1**),[7] as well as theoretical calculations for simpler model systems (**2**−**6**) (Table 1). We find a large anisotropy of the CST, indicating a highly asymmetric electron distribution around the Si=C bond, which is typical for a genuine classical π-bond.



1

$R_2Si{=}CR'_2$

2 R = R' = H
3 R = R' = Me
4 R = H$_3$Si, R' = Me

$Me_2Si{=}SiMe_2$

5

$Me_2C{=}CMe_2$

6

Table 1. Calculated and Observed Chemical Shift Tensors[a,b]

	^{29}Si values[c]					
	δ_{iso}[m]	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$[n]	CSA[18]
1, experimental	50.3[f]	149.9	20.2	−14.5	164.3	147.0
(tBuMe$_2$Si)Me$_3$Si**Si**=Ad, **1**[d]	55.5[g]	165.4[g]	16.3[g]	−15.2[g]	180.5[g]	164.8[g]
	(72.2)	(198.2)	(22.4)	(−4.1)	(189.0)	(202.3)
(tBuMe$_2$**Si**)Me$_3$SiSi=Ad, **1**[d]	5.8[h]	27.8	12.4	−22.7	50.5	32.9
(tBuMe$_2$Si)Me$_3$**Si**Si=Ad, **1**[d]	−9.7[i]	0.8	−14.2	−15.8	16.6	15.8
H$_2$Si=CH$_2$ (**2**)	59.6	264.3	−15.4	−70.1	334.4	307.1
	(70.4)	(286.2)	(−18.6)	(−56.4)	(342.6)	(323.7)
Me$_2$Si=CMe$_2$ (**3**)	85.2	202.6	58.9	−5.8	208.4	176.1
	(90.7)	(214.0)	(53.0)	(5.1)	(208.9)	(185.0)
(H$_3$Si)$_2$Si=CMe$_2$ (**4**)	42.8	173.1	−8.8	−36.1	209.2	195.6
	(59.5)	(206.0)	(−2.6)	(−25.0)	(231.0)	(219.8)
Me$_2$Si=SiMe$_2$ (**5**)[j]	87.8	182.9	71.0	9.7	173.2	142.5
	(96.3)	(189.0)	(89.3)	(10.6)	(178.5)	(139.1)
	^{13}C values[e]					
	δ_{iso}[m]	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$[n]	CSA[18]
1, experimental	197[k]	382	160	49	333.0	277.5
1, calculated	197.4[g]	371.5[g]	192.8[g]	28.0[g]	343.5[g]	261.1[g]
	(219.8)	(419.3)	(209.8)	(30.3)	(389.0)	(299.3)
H$_2$Si=CH$_2$ (**2**)	103.1	251.9	65.7	−8.2	260.0	223.1
	(117.6)	(281.9)	(78.5)	(−7.7)	(289.6)	(246.5)
Me$_2$Si=CMe$_2$ (**3**)	119.6	243.8	96.1	19.1	224.7	186.2
	(134.2)	(268.9)	(113.5)	(20.2)	(248.7)	(202.1)
(H$_3$Si)$_2$Si=CMe$_2$ (**4**)	179.0	363.3	160.5	13.3	350.0	276.4
	(201.4)	(411.1)	(177.4)	(15.6)	(395.5)	(314.5)
Me$_2$C=CMe$_2$ (**6**), experimental[l]	123	222	119	29	193	152
Me$_2$C=CMe$_2$ (**6**)	127.3	220.9	124.4	36.8	184.1	140.3
	(133.9)	(232.6)	(133.9)	(35.3)	(197.3)	(148.0)

[a] At GIAO-MP2/6-311+G(2df,p)//B3LYP/6-31(d). Values in parentheses are at GIAO−B3LYP/6-311+G(2df,p)//B3LYP/6-31(d). [b] Relative to TMS. [c] For the Si=C silicon atom. [d] Atom in bold indicates the atom for which the values are given. [e] For the Si=C carbon atom. [f] 51.7 ppm in C$_6$D$_6$ solution.[7] [g] GIAO−B3LYP values corrected according to GIAO-MP2 calculations for **4**; i.e., δ (**1**, corrected) = δ(**1**, B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d)) + [δ(**4**, MP2/6-311+G(2df,p)//B3LYP/6-31(d)) − δ(**4**, B3LYP/6-311+G(2df,p)//B3LYP/6-31(d))]. [h] Measured value: 1.0 ppm (both in the solid state (using MAS/NMR) and in C$_6$D$_6$[7]). [i] Measured values: −14.8 ppm (MAS/NMR, solid state), −14.5 ppm (in C$_6$D$_6$ solution).[7] [j] Planar structure.[22] [k] 196.8 ppm in C$_6$D$_6$ solution.[7] [l] Zilm, K.W: Conlin, R. T.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6672. [m] $\delta_{iso} = (1/3)(\delta_{11} + \delta_{22} + \delta_{33})$. [n] $\Delta\delta = \delta_{11} - \delta_{33}$.

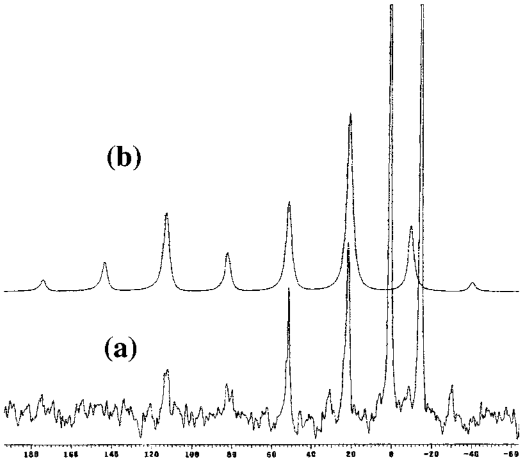


Figure 1. Slow-spinning, CPMAS ^{29}Si NMR of **1**. (a) Observed spectrum. (b) Computer fitting for the resonance of the Si=C silicon atom.

Experimental measurements were carried out by the slow-spinning CP/MAS technique,[8] yielding sidebands which were analyzed by the Herzfeld−Berger method[9] to determine the tensor elements (Table 1). Determination of the ^{29}Si tensor components was straightforward. Figure 1 shows an experimental spectrum and the corresponding computer simulation using the values (ppm) $\delta_{11} = 149.86$, $\delta_{22} = 20.23$, $\delta_{33} = -14.45$. Determination of the ^{13}C shielding tensor components for the doubly bonded carbon atom in **1** proved much more difficult, because of overlapping peaks from other carbon atoms in the molecule and poor cross-polarization from protons to the ^{13}C=(Si) atom. Matching of the spinning sidebands allowed estimation of the ^{13}C CST, but with error limits of ±5 ppm (95% confidence). The isotropic (δ_{iso}) ^{29}Si and ^{13}C chemical shifts of **1** in the solid state, of 50.3 and

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(8) In a drybox, ∼100 mg of **1** was placed in an airtight 7-mm ZrO$_2$ rotor. Measurements were made on a Varian Unity 300-MHz (proton) NMR spectrometer operating at a sample frequency of 59.587 MHz (for ^{29}Si), with a Doty Scientific Inc. probe. Spinning speed was 1−3 kHz, the CP mixing time was 5.0 ms followed by a 4 s delay; the pulse width was 6.5 μs. The spectra were referenced to external (Me$_3$Si)$_4$Si and Me$_4$Si for ^{29}Si and ^{13}C, respectively. Analysis of the sidebands to obtain the CST was done on a Sun SPARC 5 workstation using the STARS program, version 2.

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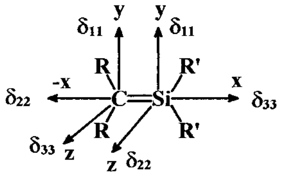

Figure 2. Orientation of the principal shielding tensor components.

197 ppm respectively (see Table 1), are very similar to those observed for a solution of **1** in C_6D_6 (51.7 and 196.8 ppm).[7]

To allow the assignment of the CST we have carried out quantum mechanical calculations[10a] for **1** and for the model compounds **2**−**6**. The geometries of **1**−**6** were fully optimized[10b] using the hybrid-density functional (DFT) method[10c] using the B3LYP functional[10d] with the 6-31G(d) basis set[10a] (denoted as B3LYP/6-31G(d)). The NMR chemical shielding tensors were calculated[10a] using the GIAO (Gauge Included Atomic Orbitals) method[11] coupled with the hybrid-DFT[10c,d] and the 6-311+G(2df,p) basis set,[10a] using the B3LYP/6-31G(d) optimized geometries[10e] (these calculations are denoted as GIAO-B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d)). For **2**−**6** we have also performed GIAO calculations coupled with the perturbative second-order Möller−Plesset theory, that is, using the GIAO-MP2 method[12] (denoted as GIAO-MP2/6-311+G(2df,p)//B3LYP/6-31(d)).

The calculated CST of **1**−**6** are given in Table 1, and their directions in space are defined in Figure 2. The agreement between the calculated[13] and experimentally measured tensors for **1** is generally good (Table 1). Thus, the calculations predict the isotropic ^{29}Si and ^{13}C signals of the Si=C bond in **1** as precisely as ±1−5 ppm, but there are larger deviations in the individual tensors. Particularly large deviations of 33 and −21 ppm are found for the ^{13}C chemical tensor components δ_{22} and δ_{33}. We think that these large theoretical−experimental differences result from experimental difficulties in determining the δ_{22} and δ_{33} values due to signal overlaps in the ^{13}C NMR spectra, and not from errors in the calculations. Thus, both GIAO-B3LYP and GIAO-MP2 calculations predict very accurately the ^{13}C δ_{22} and δ_{33} values in ethylenes (e.g., see **6**, Table 1) and the ^{29}Si tensor components in **1** (with maximal errors for δ_{11} of ∼15 ppm at MP2[13]).

The most strongly deshielded tensor component, δ_{11}, (for both C and Si) is associated with the in-plane axis (i.e., in the XY plane) perpendicular to the Si=C vector (Figure 2). The applied magnetic field causes rotation along this axis and mixes the σ(Si=C) bonding electrons with the π^*(Si=C) orbital and the π(Si=C) electrons with σ^*(Si=C), leading to the observed strong anisotropic deshielding.[14] IGLO (Individual Gauge for Localized Orbitals)[15] calculations indicate that the σ(Si=C) → π^*(Si=C) interaction contributes to the deshielding significantly more than the alternative π(Si=C) → σ^*(Si=C) mixing.[16] The orientation of the δ_{22} and δ_{33} components for the doubly bonded carbon and silicon atoms are different. For the doubly bonded carbon atom the most shielded component is δ_{33} which is aligned perpendicularly to the molecular plane, while the intermediate δ_{22} component is aligned along the Si=*C* axis. These axis orientations are similar to those found for C=C[17] and Si=Si[1] doubly bonded compounds. In contrast, for the silicon atom the orientation of the δ_{22} and δ_{33} CST components is different from that in C=C or in Si=Si compounds; the most shielded component δ_{33} is aligned along the Si=C axis, while δ_{22} is aligned perpendicularly to the molecular plane (Figure 2).

Comparison of the calculated tensor values for **1**−**6** (Table 1) leads to the following conclusions: (1) Substitution of the silene with silyl or alkyl, R and R′ groups (i.e., **3** and **4**) does not change the orientation of the shielding tensor components relative to the molecular frame but strongly affects the magnitude of the components (Table 1). (2) The ^{13}C NMR chemical shifts for the doubly bonded C atom in silenes **1** and **4** show the largest CSA[18] of 261 and 276 ppm, respectively, significantly larger than for **2** and **3** (223 and 186 ppm) or for ethylene **6** (140 ppm). This is consistent[14] with the much longer UV absorption maximum of **1** (322 nm)[7] relative to **2** (258 nm)[19] and the 2 eV lower ionization potential of **1**[20a] relative to **2**.[20b] The unusually large ^{13}C CSA of **1** and **4** can be related to their mode of substitution with alkyl (at C) and silyl (at Si) groups, which reduces the polarity of the C=Si bond relative to that of **2** and **3**.[7] This localizes the π^* and the σ^* Si=C orbitals more on C and less on Si (in $H_2C=SiH_2$ both π^* and σ^* are strongly localized at the more electropositive Si[7]). In contrast, but consistent with the above interpretation, the ^{29}Si chemical shift in **1** shows a relatively small CSA (165 ppm), in particular relative to **2** (307 ppm).[21] (3) The ^{13}C CSA in alkyl substituted silenes is larger than in the analogous alkenes; for example, **3** (186 ppm) versus **6** (140 ppm). (4) The ^{29}Si CSA for silene **3** (176 ppm) is larger than for the similarly substituted planar $Me_2Si=SiMe_2$, **5**, (146 ppm).[22]

In conclusion, the measured and calculated tensor components in silenes indicate the presence of a genuine Si=C π-bond. Our results parallel closely those for alkenes[17] and disilenes,[1] which also display marked deshielding of the δ_{11} tensor component, resulting in large CSA values, often >200 ppm for C and >150 ppm for Si.

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[21] The difference in *r*(Si=C) between **2** (171 pm) and **1** (174 pm) increases the CSA for both Si and C by 5−7 ppm, a smaller change than in disilenes (12−14 ppm for a similar change in *r*(Si=Si)[1]).

[22] Planar $Me_2Si=SiMe_2$ lies only 1 kcal/mol (at B3LYP/6-31G(d)//B3LYP/6-31(d)) above the fully optimized trans-bent $Me_2Si=SiMe_2$.