Organometallics **1997,** *16,* 3255−3257

Unusual Spin−Spin Interactions across the Coordination Bond in Hexacoordinate Silicon Complexes: Crystal-Structure Coupling Relationship

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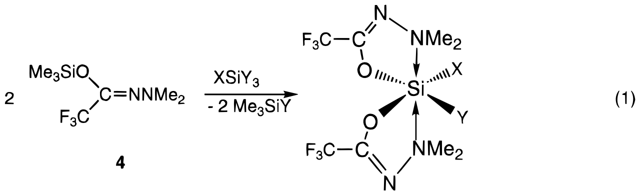
Received April 16, 1997[⊗]

Summary: Two-, three-, and even four-bond coupling constants are reported for the first time across the N→Si coordination bond in neutral, hexacoordinate silicon chelates. Two-bond coupling constants depend critically on bond angles, and three-bond couplings follow a Karplus-type correlation with dihedral angles obtained from X-ray crystallographic analyses.

Hypervalent silicon complexes (coordination numbers of five, six, and even higher), have attracted considerable interest in recent years.[1] Despite this interest, little is known about the nature of the coordination bond. One important aspect of bonding is the ability of the bond to transmit NMR interactions. To this date, however, no nuclear spin−spin interactions across the coordination bond have been reported in hexacoordinate N→Si complexes. We now report the first observation and measurement of coupling constants between ^{1}H or ^{19}F attached directly to silicon, and ^{15}N, ^{13}C, and ^{1}H through two, three, and even four bonds which include the N→Si dative bond.

Complexes **1**−**3** have been prepared in high yields by the reaction shown in eq 1.[2]



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1, X = Ph; Y = F;
2, X = Y = F;
3, X = H, Y = Cl;

^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR spectral data for these complexes are listed in Table 1. It is evident from Table 1 that the *Si*-fluoro atoms in **1** and **2** and the hydrido atom in **3** caused splitting of signals of the *N*Me nitrogen (^{2}J) in the ^{15}N NMR spectra, as well as three-bond splitting of *N*-methyl carbons and four-bond splitting of *N*-methyl protons. This is, to the best of our knowledge, the first report of spin-spin interactions across the N→Si coordinative bond in a hexacoordinate silicon complex. The only other report of such coupling in silicon compounds relates to *penta*coordinate silicon in silatranes and silocanes.[5] The one-bond N→Si couplings expected in these systems could not be measured, due to the low natural abundance of the spin $^{1}/_{2}$ isotopes of the two elements.

The fact that no spin−spin couplings have been reported previously in similar complexes (across the dative N→Si bond) is probably related to the unusual geometry of **1**−**3**. The crystal structures of **1**−**3** have been determined and are depicted in Figure 1.[6] The three complexes have similar general structures, with slightly different bond lengths and angles. Selected bond lengths and angles for **1**−**3** are listed in Table 2.

Relatively few crystal structures have been reported previously for neutral hexacoordinate silicon complexes.[1] Most of these were bis chelates and had essentially a tetrahedral arrangement around silicon, with the coordinated nitrogen ligands "capping" the tetrahedral faces at relatively large distances: N→Si lengths in the range 2.5−3.0 Å.[1,7] In contrast, the bis chelates reported here are essentially octahedral, with the nitrogen ligands in relative *trans* positions. It appears that an octahedral structure is preferred relative to a bicapped-tetrahedral one when the ligands at

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) For recent reviews see: (a) Tandura, S. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley; Chichester, U.K., 1989; p 1241. (c) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17; **1996**, *96*, 927. (d) Corriu, R. J. P. *J. Organomet. Chem.* **1990**, *400*, 81. (e) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (f) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley; Chichester, U.K., 1989; p 839. (g) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds;* Apeloig, Y., Rappoport, Z., Eds.; Wiley: Chichester, U.K., in press.

(2) **3** and a series of analogous complexes were reported previously.[3] **1** and **3** were prepared by mixing **4** with the appropriate $XSiY_3$ compound in a toluene solution under an Ar atmosphere at ambient temperature. **2** was prepared by passing SiF_4[4] through a toluene solution of **4**. The solutions of **1**−**3** were sealed under vacuum and left for several weeks at −10 °C, after which the compounds had crystallized and single crystals suitable for X-ray analysis were obtained. The yields, as judged from the NMR spectra of the solutions, were quantitative. Anal. Calcd for **1**, $C_{14}H_{17}F_7N_4O_2Si$: C, 38.71, H, 3.94, N, 12.90. Found: C, 38.69, H, 4.02, N, 12.84. Anal. Calcd for **2**, $C_8H_{12}F_8N_4O_2Si$: C, 25.54, H, 3.21, N, 14.89. Found: C, 25.52; H, 3.11; N, 14.81.

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(6) Crystallographic data for **1** and **2** were collected at −100 °C on an Enraf-Nonius CAD4 four-circle diffractometer equipped with a homemade low-temperature device. Crystals were mounted on a glass fiber, coated with a drop of perfluorinated polyether, and shock-frozen in the cold nitrogen stream of the low-temperature device.[12] Data for **3** were collected at −80 °C on a Siemens R3 diffractometer. Full details can be found in the Supporting Information. The structures were solved by direct methods[13a] and refined by full-matrix, least-squares iteration against F^2.[13b]

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Table 1. ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR Spectral Data for Complexes 1−3

nucleus	group	δ, ppm[a] (multiplicity, Hz) complex **1**	complex **2**	complex **3**
^{1}H	NMe_a[b]	2.18 (s)	2.86 (t, $^{4}J_{HF} = 1.6$)	2.51 (s)
	NMe_b[b]	3.14 (s)	2.96 (t, $^{4}J_{HF} = 0.7$)	2.34 (s)
	NMe_a'[b]	2.59 (s)	2.89 (t, $^{4}J_{HF} = 1.6$)	2.36 (s)
	NMe_b'[b]	2.62 (d, $^{4}J_{HF} = 2.4$)	2.96 (t, $^{4}J_{HF} = 0.7$)	2.65 (s)
^{13}C	NMe_a[b]	52.7 (s)	50.3 (t, $^{3}J_{CF} = 5.4$)	50.1 (qq)[c]
	NMe_b[b]	49.9 (d, $^{3}J_{CF} = 3.4$)	50.1 (t, $^{3}J_{CF} = 1.4$)	49.6 (qq)[c]
	NMe_a'[b]	49.5 (d, $^{3}J_{CF} = 0.8$)	50.3 (t, $^{3}J_{CF} = 5.4$)	48.7 (qqd,[c] $^{3}J_{CNSiH} = 2.5$)
	NMe_b'[b]	49.3 (d, $^{3}J_{CF} = 9.1$)	50.1 (t, $^{3}J_{CF} = 1.4$)	48.2 (qqd,[c] $^{3}J_{CNSiH} = 1.4$)
^{15}N[d]	N=C	248.4 (s) 251.1 (s)	242.2 (s)	247.3 (s) 249.2 (s)
	NMe	67.8 (d, $^{2}J_{NF} = 9.0$) 63.4 (d, $^{2}J_{NF} = 4.5$)	63.6 (t,$^{2}J_{NF} = 12.2$)	68.4 (d, $^{2}J_{NH} = 10.2$) 65.7 (d, $^{2}J_{NH} = 12.0$)
^{29}Si		−146.1 (d, $^{1}J_{SiF} = 279.7$)	−159.9 (t, $^{1}J_{SiF} = 207.0$)	−136.5 (d, $^{1}J_{SiF} = 344.4$)

[a] All spectra were recorded on a Bruker DMX-500 NMR spectrometer, operating at 500 MHz for the ^{1}NMR measurements. Spectra for **3** were recorded in toluene-d_8 solution and for **1** and **2** in CD_2Cl_2 (^{13}C and ^{1}H) and in $CDCl_3$ (^{15}N and ^{29}Si). ^{13}C and ^{1}H spectra were run at 243 K (slow exchange, see ref 3); ^{15}N and ^{29}Si spectra were run at 298 K. [b] a and b denote geminal methyl groups, located on the same nitrogen; a and a′ (and b, b′) are methyls which interchange first upon increase of temperature.[3] [c] ^{13}C spectra without proton decoupling. qq stands for quartet of quartets and qqd for doublet of qq; qq coupling constants $^{1}J_{CH} = 142$ Hz, $^{3}J_{CNCH} = 4.3$ Hz. [d] δ relative to external $^{15}NH_4Cl$.

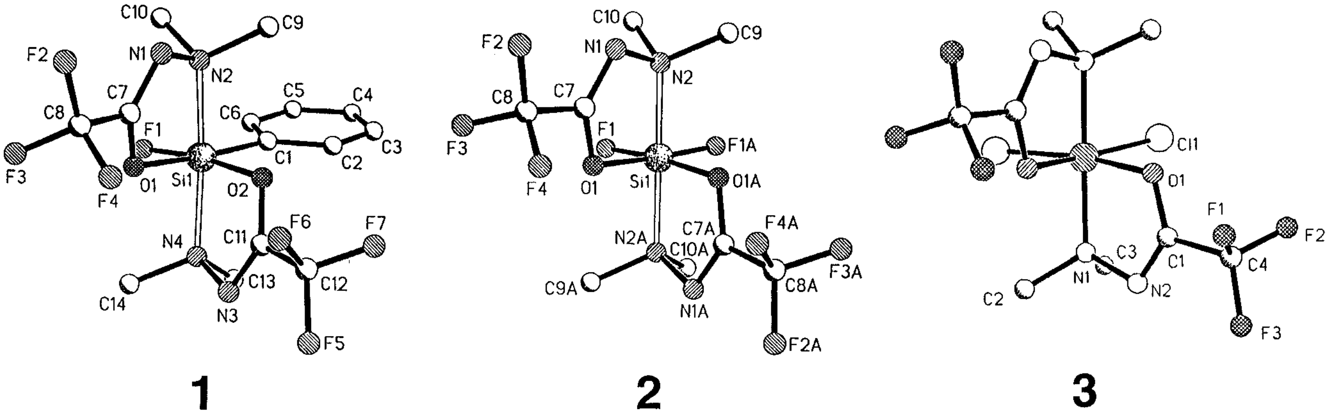

Figure 1. X-ray crystal structures for compounds **1**−**3**.

Table 2. Selected Bond Lengths and Angles for Complexes 1−3[a]

compd	Si−N, Å		Si−O, Å		Si−F [Si−Cl], Å	∠N−Si−N, deg	∠N−Si−F [N−Si−Cl], deg	
1	2.021(3)	2.029(3)	1.826(3)	1.817(2)	1.638(2)	163.62(8)	96.85(11)	91.23(12)
2	1.962(2)	1.962(2)	1.782(2)	1.782(2)	1.615(2)	170.49(14)	95.39(8)	91.12(9)
3[b]	2.002(3)	2.002(3)	1.772(3)	1.772(3)	[2.184(2)]	170.1(2)	[90.64(9)]	[95.20(10)]

[a] Complete crystallographic data are available as Supporting Information. [b] Disorder was found in the crystal structure of **3** between the locations of the hydrido and chloro groups (0.5 Cl population in its unique location), and consequently apparent molecular C_2 symmetry in the crystal was found (*i.e.*, the coordinates of the two chelate cycles are related in the solid state by symmetry and have equivalent geometries). The N−Si−Cl angle is taken to represent the N−Si−H angle, which cannot be measured directly.

silicon are more electronegative. Only one hexacoordinate silicon complex featuring the coordinating nitrogen atoms in *trans* positions was reported previously,[8] with the backbone identical with that in **1**−**3**. Substitution of the O−C(R)=N−NMe_2 sidearm by the more rigid 8-quinolinato group led to an octahedral bis chelate with the coordinating nitrogen atoms assuming *cis* positions.[9] Other complexes with two coordinating nitrogen atoms in a *trans* orientation are known only for the *inter*molecular complexes SiF_4·2(pyridine)[10a] and SiF_4·$2NH_3$.[10b]

The *trans* geometry of the present complexes implies that the N-Si-X (X = H, F) bond angle is close to 90° (Table 2). A near 90° angle appears to be necessary in order to observe measurable two-bond couplings. Indeed, a similar situation was reported for pentacoordinate silicon compounds: silatranes and silocanes, in which $^{2}J(^{15}N-Si-^{1}H)$ decreased from 8 through 4 to 0 Hz upon changing the bond angle from ~90° through ~109.5° to 180°, respectively.[5] This remarkable sensitivity of the two-bond coupling to the bond angle is found also in the present case: in **1** the two N−Si−F angles are 96.9 and 91.2° (Table 2), and the corresponding coupling constants are 4.5 and 9 Hz, respectively. In **3**, a smaller difference in bond angles (90.6 and 95.2°) is found, corresponding to a smaller difference in coupling constants (10.2 and 12.0 Hz, respectively). In **2**, however, the two different angles do not result in the observation of different coupling constants due to fast exchange of the fluoro ligands,[3] leading to a triplet for the ^{15}N signal with average coupling constants.

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Table 3. Dihedral Angles between *Si*-Ligand (F, Cl) and *N*-Methyl Carbons and the Corresponding Three-Bond Coupling Constants

	complex **1**		complex **2**			complex **3**	
N-methyl group	∠F−Si−N−C, deg	$^3J(^{19}F-^{13}C)$, Hz	∠F−Si−N−C, deg	$^3J(^{19}F-^{13}C)$, Hz[b]	interpolated $^3J(^{19}F-^{13}C)$[c]	∠Cl−Si−N−C, deg[d]	$^3J(^1H-^{13}C)$, Hz
a[a]	138.9	0.8	143.08	1.4	0.8	157.4	2.4
b[a]	14.6	9.1	20.02	5.4	8.0	31.9	1.1
a′ [a]	40.4	3.4	49.28		2.2	49.3	0
b′ [a]	−83.9	0	−73.78		0.6	−76.1	0

[a] See footnote *b* in Table 1. [b] Due to fast exchange of fluoro ligands, only two average coupling constants are observed in **2**. [c] Interpolated from Figure 3 and crystallographic dihedral angles. See text. [d] Due to the Cl−H disorder in the crystal of **3** the Cl−Si−N−C dihedral angle is taken to represent the H−Si−N−C angle, which cannot be determined directly.

The above discussion of two-bond coupling constants relates to the ^{15}N NMR spectra. From the ^{13}C NMR spectra (Table 1) information about the dependence of three-bond coupling constants upon geometry is obtained. Table 1 shows, for instance, that in the hydrido complex **3** only two of the four distinct *N*-methyl carbons (at the slow exchange limit temperature[3]) are effectively coupled to the hydrido nucleus. This selectivity is particularly remarkable in view of the fact that *both* of the dimethylamino nitrogens are coupled to the hydrido group. A combination of NMR experiments (undecoupled ^{13}C spectra for **3**, low-temperature ROESY, CH correlation, and long-range CH correlation (COLOC); see Supporting Information) provided unequivocal evidence that the two *N*-methyl carbons in **3**, which were spin-coupled to the Si−*H*, were located on the *same* nitrogen atom.[11]

In contrast, in the monofluoro complex **1** the two major coupling constants are found between the Si−*F* and two of the *N*-methyl groups belonging to *different* nitrogen ligands. These different behaviors of **1** and **3** may be rationalized by reference to the X-ray crystal structures. Table 3 lists the various F(H)−Si−N−Me dihedral angles and the corresponding coupling constants. Assuming that the geometries in solution do not differ substantially from those in the solid state, a Karplus-type correlation is found between ^3J(F−Si−N−C) and the dihedral angles (Figure 2): only those angles which are close to 0 or 180° are associated with measurable coupling constants. No spin interactions are observed in cases of near-90° dihedral angles.

In **2** a direct correlation of three-bond coupling and dihedral angle is not possible, because the two fluoro ligands exchange rapidly and give rise to a triplet with an averaged coupling constant (Table 3). However, the Karplus relationship (Figure 2) obtained for **1** can be used to interpolate the coupling constants in **2** using the crystallographic dihedral angles. The individual expected ^3J(F-Si-N-C) values obtained in this way are listed in Table 3. The calculated average spin-spin couplings for the a, a′ and b, b′ methyl pairs are 1.5 and 4.3 Hz, respectively, in very good agreement with the measured values (1.4 and 5.4 Hz).

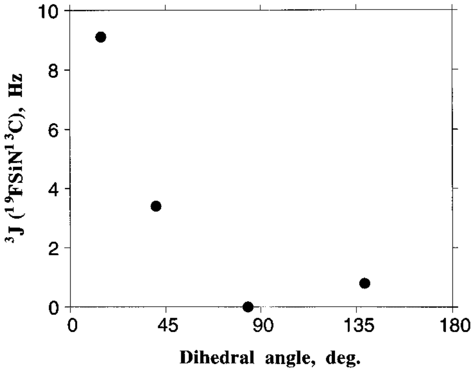

Figure 2. Karplus-type correlation of three-bond coupling constants and the corresponding F−Si−N−C dihedral angles (absolute values) in **1**.

Given the almost octahedral environment of silicon in **3** (Figure 1), we take the Cl-Si-N-C angle as a close approximation of the corresponding H−Si−N−C dihedral angle. It is evident that, as in the fluoro compound **1**, the coupling constants (Table 3) follow a Karplus-type dependence on dihedral angle: in this case a pair of *geminal* methyl groups have dihedral angles which are relatively close to 0 and 180° (31.9 and 157.4°, respectively), and consequently in **3** coupling is observed between the hydrido atom and a pair of *geminal* methyl carbons.

Acknowledgment. We thank the Israeli Ministry of Sciences and Arts and the Israel Science Foundation (administered by the Israel Academy of Sciences and Humanities) for financial support.

Supporting Information Available: Tables of crystal data, fractional coordinates and *U* values, bond distances and angles, anisotropic displacement parameters, hydrogen atom coordinates, completely labeled figures of structures **1**−**3**, and a COLOC specrum of **3** (22 pages). Ordering information is given on any current masthead page.

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(11) Unequivocal evidence of this assignment was obtained by positive identification of the ^{13}C signals for the geminal *N*-methyls, by observation of the long-range coupling $^3J(^{13}CH_3-N-CH_3) = 4.3$ Hz, using 2D-COLOC (see Supporting Information). This result was verified by a ROESY spectrum at 243 K, avoiding exchange cross-signals.

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