Pergamon

Tetrahedron Letters, Vol. 35, No. 14, pp. 2133-2136, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0283-4

Low Temperature NMR Evidence Shows the Elusive Siliconium Ion is a Further Example of Tautomeric Equilibrium

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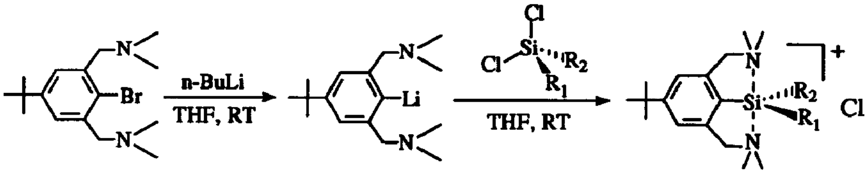
Abstract: Compounds with a potentially pentacoordinated silicon central atom have been synthesized using a new tridentate ligand. Detailed NMR studies have shown, however, that, in contrast to an earlier report[1], each of these species exists in solution as an equilibrium mixture of two equivalent structures in which the central atom is tetracoordinated.

There has been much interest in the preparation and characterization of hypercoordinated and hypervalent silicon compounds over the last two decades.[2,3] The experimentally derived structural and electronic features of these compounds, compared with contemporary theoretical models, further clarify the nature of hypervalency and hypervalent bonding. Recently we have synthesized new silicon compounds with a potentially pentacoordinated central silicon atom. The synthetic sequence outlined in Scheme 1, utilizes a hitherto unreported tridentate ligand 3.[4]



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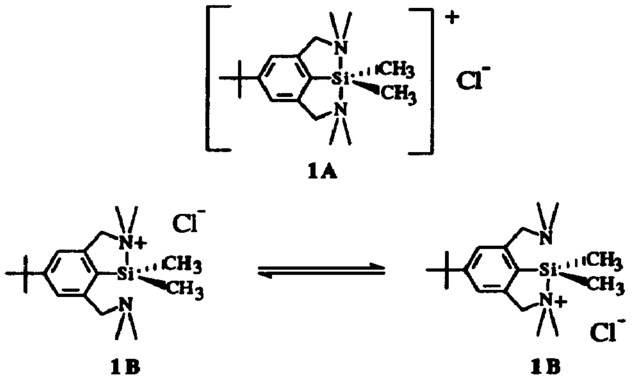
1: $R_1 = R_2 = CH_3$
2: $R_1 = CH_3$
R_2 = vinyl

Scheme 1

The properties of compounds **1** and **2** agree consistently with an ionic nature for the final products. These compounds are soluble in water and other polar protic solvents and insoluble in nonpolar solvents. Their melting points of 246°C (**1**) and 198°C (**2**) are substantially higher compared to structurally similar aryldialkylmonochlorosilanes. They are unusually stable in air and do not solvolyze. Two different ionic structures can be assigned to the final products. One structure is symmetric with both nitrogen atoms simultaneously bonded to the central silicon atom. This structure features a pentacoordinated silicon atom and is a siliconium ion (Structure **1A** in Scheme 2). Such a structure has been assigned to similar compounds recently synthesized by Corriu and coworkers.[1] Alternatively, the compound can exist as an equilibrium mixture of two equivalent asymmetrical structures containing a tetracoordinate silicon atom (Structures **1B** in Scheme 2).



Scheme 2

^{1}H and ^{13}C NMR spectra of **1** were obtained in three different solvents: methanol-*d*$_4$, chloroform-*d* and acetonitrile-*d*$_3$. The ^{1}H spectrum of **1** at room temperature in methanol-*d*$_4$ is shown in Figure 1.

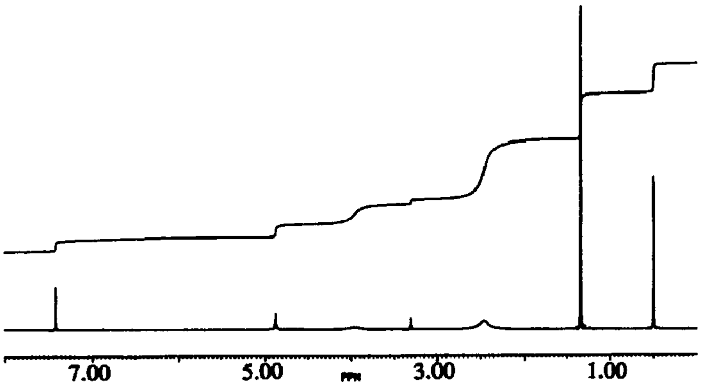


Figure 1. ^{1}H NMR spectrum of compound 1 in methanol-*d*$_4$ at room temperature

At room temperature the peaks for the methyl and methylene groups adjacent to nitrogen are broadened, presumptive evidence for an identity exchange process at the silicon center. As the temperature is decreased, each of these peaks is split into two resonances of equal intensity. The coalescence temperature T_C = 265 K and the methyl and methylene peaks are separated by Δv = 200 Hz. Upon further cooling the average singlet signal for the aromatic protons is also split and generates two singlets of equal intensity. The ^{1}H spectrum of 1 at 180 K is shown in Figure 2.

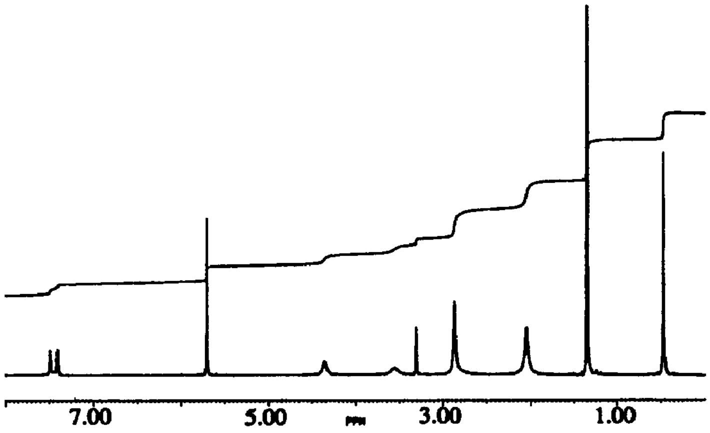


Figure 2. ^1H NMR spectrum of compound **1** in methanol-*d4* at 180 K

The observed pattern at 180 K is indicative of the asymmetrical structure for **1**. Consistent results were obtained from the ^{13}C measurements. At room temperature in the decoupled spectrum, one singlet is observed for the N-CH_3 group, one singlet for the N-CH_2 group and four signals in the aromatic region. At 180 K there are two sets of singlets for both the methyl and methylene groups connected to nitrogen and the aromatic region contains six well distinguished signals (Figure 3).

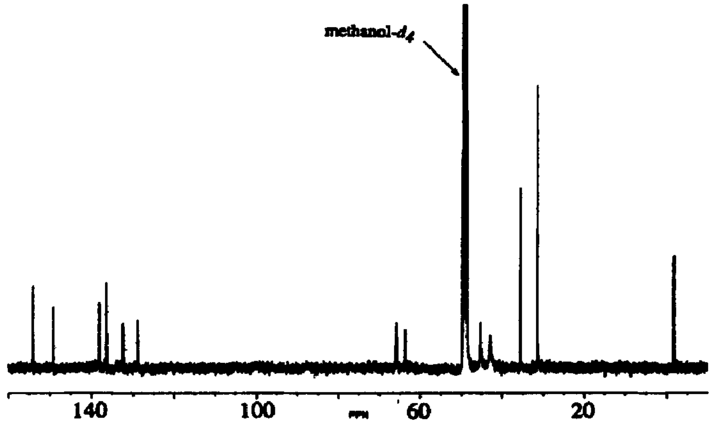


Figure 3. ^{13}C NMR spectrum of compound **1** in methanol-*d4* at 180 K

Similar behavior of **1** was observed in the other two solvents. The coalescence temperature of the N-methyl signals in chloroform-*d* is $T_c = 220$ K with a separation $\Delta v = 134$ Hz. A substantial broadening of the N-methyl and N-methylene peaks was also observed in acetonitrile-*d3* but the coalescence temperature is below the freezing point of the solvent.

The ^{29}Si NMR spectrum of **1** in methanol-*d4* shows a singlet peak at $\delta = 6.57$ ppm (Downfield from TMS, $\delta = 0$ ppm).

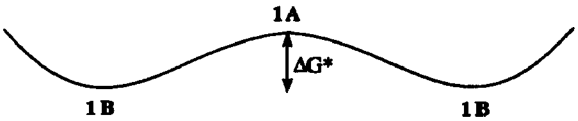


Figure 4. Energy surface for interconversion of tautomers of **1**.

The two equivalent structures with tetracoordinated silicon (**1B**) are involved in a process of rapid interconversion which averages the NMR signals at room temperature. The actual pentacoordinated structure (**1A**) would then be located at the transition state (Figure 4). Kinetic parameters, estimated on the basis of the NMR measurements[5], are collected in Table 1.

Table 1. Kinetic Parameters for Compound 1 in Different Solvents.

Solvent	T_c [K]	k_c [s^{-1}]	ΔG_c* [kJ/mol]
methanol	265	679	50.3
chloroform	220	484	42.1

In summary, our characterization of compound **1** clearly demonstrates the purported "siliconium ion" structure involving pentacoordinated silicon atom is not viable. The structure of compound **1** is reconciled using the double potential well shown in Figure 4. We anticipate that this will be the general case for compounds of this generic type.

Acknowledgement. The authors are grateful to the National Institutes of Health for the support of this research project.

References and Notes

1. Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reye, C. *Angew. Chem. Int. Ed. Engl.* **1993**, *32 (9)*, 1311.
2. Stevenson, W. H.; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340.
3. Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. *Chem. Rev.* **1993**, *93*, 1371-1448.
4. Synthesis of **3**: 2,6-bis(bromomethyl)-4-(1,1-dimethylethyl)bromobenzene[6] (3.50 g, 0.0088 mol) was dissolved in THF (25 mL). Dimethylamine (7.90 g, 0.1754 mol, 22.0 mL of 40% soln. in water) was added to the solution and the resulting mixture was refluxed for 4 h. The layers were separated and the organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under vacuum leaving a yellow solid. The crude material was recrystallized from DMSO and then sublimed (75°C, 0.5 mm Hg) to yield a white crystalline product (2.10 g, 0.0064 mol, 73%). m.p. 98-99°C. ^{1}H NMR (acetone-d_6) δ 7.45 (s, 2H), 3.50 (s, 4H), 2.25 (s, 12H), 1.32 (s, 9H); ^{13}C (acetone-d_6) δ 150.24, 138.87, 127.17, 124.03, 64.49, 45.68, 34.97, 31.52.
5. Gutowsky, H. S.; Holm, C. H.; Saika, A.; Williams, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 4596.
6. Tashiro, M.; Yamato, T. *J. Org. Chem.* **1985**, *50*, 2939.

(*Received in USA* 7 *December* 1993; *accepted* 1 *February* 1994)