31 °C, $CDCl_3$] 1.5–2.0 (br, $\overline{PdCH_2CH_2CH_2CH_2}$, 8 H), 1.32 (d, $^2J_{P-H}$ = 6 Hz, PCH_3, 12 H), 7.23 (m, PPh, 10 H). Anal. Calcd for $C_{20}H_{30}P_2Pd$: C, 54.7; H, 6.9. Found: C, 54.9; H, 6.9.

Acknowledgment. This work was partly supported by U.S.–Japan Cooperative Science Program jointly sponsored by the National Science Foundation and the Japan Society for the Promotion of Science and by the National Science Foundation (Grant CHE-79-04814).

Registry No. *cis*-$PdEt_2(PMe_2Ph)_2$, 77881-06-2; *trans*-$PdEt_2(PMe_2Ph)_2$, 75108-70-2; *trans*-$PdEt_2(PEt_3)_2$, 60885-31-6; *trans*-$PdEt_2(PEt_2Ph)_2$, 75108-73-5; $\overline{Pd(CH_2CH_2CH_2CH_2})(PMe_2Ph)_2$, 82871-37-2; *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$, 79075-56-2; $PdCl_2(PMe_2Ph)_2$, 15616-85-0; $Li(CH_2)_4Li$, 2123-72-0; *cis*-$PdMe_2(PMe_2Ph)_2$, 82871-38-3; *trans*-$PdMe_2(PMe_2Ph)_2$, 82916-00-5.

Organometallic Chemistry. 19. Correlation of ^{29}Si to ^{13}C NMR Chemical Shifts in Analogous Compounds. Application in Attempted Preparation of Silicenium Ions[1]

George A. Olah* and Leslie D. Field

Hydrocarbon Research Institute, Department of Chemistry, University of Southern California,
Los Angeles, California 90089

Received April 27, 1982

Although the parallel between ^{29}Si NMR chemical shifts in silicon compounds and ^{13}C NMR chemical shifts in the analogous carbon compounds has been recognized, no systematic study was made to explore the relationship. We have carried out such a study extending the relationship from tetraalkyl-substituted silanes to polarized trimethylsilyl halides in search for still elusive stable silicenium ions. Due to the high affinity of silicon for oxygen and fluoride (or chloride), methods used for the preparation of stable carbocations were not applicable. Using bromosilanes and aluminum tribromide, in methylene bromide solution, strongly polarized donor–acceptor complexes of $Me_3Si^{\delta+}Br \rightarrow {}^{\delta-}AlBr_3$ were observed but no free silicenium ions.

Although many long-lived carbenium ions (trivalent carbocations) have been prepared and studied as stable entities in solution,[2] the analogous silicenium ions (trivalent sila cations, R_3Si^+) have never been directly observed in solution or in the solid state. Silicenium ions are well-known in the gas phase as high abundance fragments in the mass spectra of organosilicon compounds.[3] In solution, silicenium ions have been proposed as reaction intermediates in many organosilicon reactions,[4] but attempts directed toward the preparation of stable silicenium ions have been so far unsuccessful.[5] Even under conditions developed for the preparation and study of stable carbocations[2] (low-nucleophilicity systems, low temperatures), the extreme affinity of silicon for oxygen, fluorine, and chlorine usually results in the reaction of solvents (even SO_2, SO_2ClF) and/or reagents (Lewis acid halides, superacidic systems) with the developing electrophilic silicon center (i.e., to yield silyl fluorides, fluorosulfates, trifluoromethyl sulfates, etc.).

The most valuable analytical tool employed to study stable carbocations has been ^{13}C NMR spectroscopy since this permits direct observation of the cationic center. The sensitivity of ^{13}C chemical shifts[6] and coupling constants to changes in hybridization, geometry, and charge density provides specific information concerning the nature of the carbocation. Our interest in the possible preparation of silicenium ions and the need for techniques to characterize such compounds has prompted us to examine the parallels between ^{29}Si chemical shifts in silicon compounds and ^{13}C chemical shifts in the analogous carbon compounds. Close analogies of silicon chemical shifts with carbon chemical shifts have earlier been realized in the case of methyl-substituted silanes.[7]

The Correlation of ^{13}C Chemical Shifts to ^{29}Si Chemical Shifts

Several theoretical treatments of nuclear screening and chemical shift have been developed, but, as yet, no approach provides generally satisfactory values for chemical shifts. The present understanding of chemical shift is based principally on Ramsey's formulation,[8] which disects nuclear screening into diamagnetic and paramagnetic contributions. The paramagnetic term reflects the influence of other atoms (and their electrons) in the molecule on the local magnetic environment of a nucleus; for the lighter nuclei such "substituent effects" are the dominant contributions to chemical shifts. Roberts et al.[9] found that the ^{15}N chemical shifts in amines and related compounds correlate linearly to the ^{13}C chemical shifts of structurally identical hydrocarbons, i.e., $\delta(^{15}N)$ in $R_1R_2R_3N$ and $\delta(^{13}C)$ in $R_1R_2R_3CH$. This implies that the same structural fac-

---

(1) Part 18 see: Olah, G. A.; Garcia-Luna, A. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5036–5039.

(2) For comprehensive reviews see: Olah, G. A. *Top. Curr. Chem.* **1979**, *80*, 19–88.

(3) Weber, W. P.; Felix, R. A.; Willare, A. K. *Tetrahedron Lett.* **1970**, 907–910 and references therein.

(4) (a) Flowers, M. S.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968**, 419–423. (b) West, R. *Int. Symp. Organosilicon Chem., Sci. Commun.* **1965**, 1–13. (c) Sommer, L. H.; Evans, F., *J. Am. Chem. Soc.* **1954**, *76*, 1186–1187. (d) Sommer, L. H.; Bailey, D. L.; Coulf, J. R.; Whitmore, F. C. *Ibid.* **1954**, *76*, 801–803.

(5) (a) Olah, G. A.; O'Brien, D. H.; Lin, C. Y. *J. Am. Chem. Soc.* **1969**, *91*, 701–706. (b) Brook, A. G.; Pannell, A. K. *Can. J. Chem.* **1970**, *48*, 3679–3693. (c) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 4942–4943. (d) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *Ibid.* **1980**, *102*, 624–628.

(6) See for instance: "NMR and the Periodic Table", Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978.

(7) Kintzinger, J. P. In "NMR—Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1981; Vol. 17.

(8) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699–703.

(9) (a) Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 2495–2500. (b) Duthaler, R. O.; Williamson, K. L.; Giannini, D. D.; Bearden, W. H.; Roberts, J. D. *Ibid.* **1977**, *99*, 8406–8412. (c) Duthaler, R. O.; Roberts, J. D. *Ibid.* **1978**, *100*, 3889–3895. (d) *Ibid.* **1978**, *100*, 3882–3889.

0276-7333/82/2301-1485$01.25/0 © 1982 American Chemical Society

Table I. ^{13}C Chemical Shifts for Carbon Compounds[a] (X = C) and ^{29}Si Chemical Shifts[b] for their Silicon Analogues (X = Si)

compd	$\delta(^{13}C)$	$\delta(^{29}Si)$	compd	$\delta(^{13}C)$	$\delta(^{29}Si)$
1, Me_4X	27.9	0.0	**19**, H_3XBr	10.2	−49.0
2, Me_3XH	25.2	−15.5	**20**, H_2XBr_2	21.6	−30.4
3, Me_2XH_2	16.1	−37.3	**21**, $HXBr_3$	12.3	−43.3
4, $MeXH_3$	5.9	−65.2	**22**, H_3XI	−20.5	−83.3
5, XH_4	−2.1	−93.1	**23**, H_2XI_2	−53.8	−99.6
6, Me_3XCl	65.3	30.3	**24**, HXI_3	−139.7	−175.9
7, Me_2XCl_2	85.2	32.2	**25**, Cl_3XBr	67.8	−34.3
8, $MeXCl_3$	95.0	12.5	**26**, Cl_2XBr_2	35	−50.7
9, XCl_4	96.7	−20.0	**27**, $ClXBr_3$	5.1	−69.8
10, Me_3XBr	60.7	26.4	**28**, Cl_2XI_2	(22.4)[c]	−75.4
11, Me_2XBr_2	58.3	19.9	**29**, $ClXI_3$	(−160)[c]	−245.9
12, XBr_4	−28.5	−92.7	**30**, Br_3XI	(−75)[c]	−149.5
13, Me_3XI	42.0	8.9	**31**, Ph_3XH	62.0	−17.0
14, $PhXH_3$	21.0	−60.0	**32**, XI_4	−292.3	−346.2
15, Ph_2XH_2	37.0	−33.0	**33**, H_3XF	75.4	−17.4
16, H_3XCl	25.1	−36.1	**34**, Br_2XI_2	(−133)[c]	−212.3
17, H_2XCl_2	54.2	−11.0	**35**, $BrXI_3$	(−190)[c]	−280.1
18, $HXCl_3$	77.7	−9.6			

[a] ^{13}C chemical shifts, ppm from Me_4Si (taken from ref 13a and 13b). [b] ^{29}Si chemical shifts, ppm from TMS (taken from ref 6, pp 313–314). [c] Calculated using the additive chemical shift relationship of Litchman and Grant.[15]

tors that determine ^{13}C chemical shifts also determine ^{15}N chemical shifts. In a similar way, ^{17}O chemical shifts show a linear correlation to ^{13}C chemical shifts in structurally analogous compounds,[7] and ^{29}Si chemical shifts parallel ^{27}Al shifts in isoelectronic tetrahaloaluminates.[10] The ^{11}B chemical shifts of trigonal boron compounds have been found[11] to correlate linearly to the ^{13}C chemical shifts of carbenium ions, i.e., $\delta(^{11}B)$ in $R_1R_2R_3B$ against $\delta(^{13}C)$ in $R_1R_2R_3C^+$. The existence of such correlations clearly leads to a better understanding of the effect of substituents and geometry on the magnetic environment of nuclei in general. The vast amount of ^{13}C data accumulated for well-characterized carbon compounds permits the direct transposition of structural and geometric information to the compounds of other elements via the chemical shift relationships.

Scholl, Maciel, and Musker[12] showed that ^{29}Si chemical shifts in alkylsilanes could be expressed by eq 1, where A_i

$$\delta(^{29}Si) = \delta(^{29}Si)_{SiH_4} + A_i$$

are additive shift parameters for the *i*th carbon attached to silicon. This equation closely parallels the equation of Grant and Paul[13] that describes ^{13}C chemical shifts in alkanes.

The ^{29}Si chemical shift range for alkylsilanes spans only ca. 60 ppm from a total shift range of some 500 ppm for known ^{29}Si shifts. When the analysis is not restricted to alkylsilanes, the ^{29}Si chemical shifts of silicon compounds (SiXX′X″X‴) in general follow the same shielding trends observed in their carbon analogues (CXX′X″X‴) (Table I, Figure 1).

Considering the entire range of ^{29}Si chemical shifts, Figure 1 shows an overall correspondence between the carbon and silicon shieldings. Even though a large (but by no means exhaustive) variety of substituents (halogens, alkyl, aryl, oxygen, hydrogen, etc.) has been considered (Table I), the observed correlation indicates that the same factors which *dominate* carbon shieldings also *dominate* silicon shieldings.

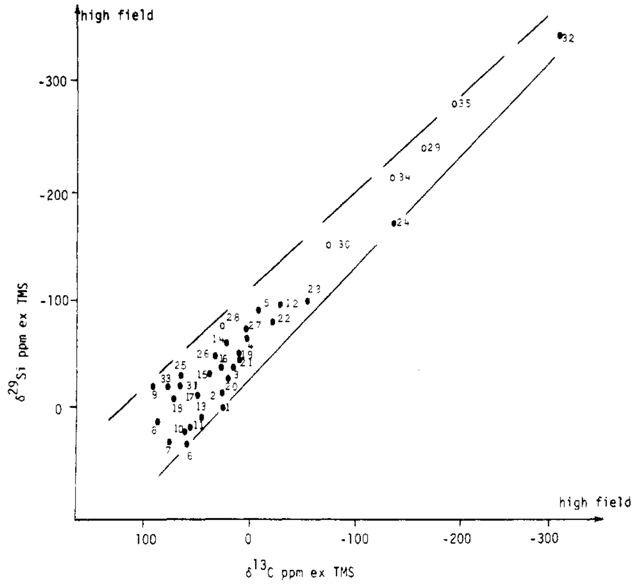


Figure 1. Correlation of ^{13}C chemical shifts in carbon compounds with ^{29}Si chemical shifts in their silicon analogues: solid circles, literature data; open circles, ^{13}C shifts from the additivity relationship of Litchman and Grant.[15]

Table II. Variation of $\delta(^{29}Si)$ with increasing Electron-withdrawing Ability of Substituents

compd	$\delta(^{29}Si)$[a]	compd	$\delta(^{29}Si)$[a]
Me_3SiOMe	17.2	$Me_3SiOSO_2CF_3$	46.6
$Me_3SiOCOCH_3$	21.5	$MeSiOSO_2F$	52
$Me_3SiOCOCF_3$	34.2		

[a] Ppm from external Me_4Si.

Electron-Deficient Silicon Compounds

Among structurally related silanes, there are trends in ^{29}Si chemical shifts that parallel the trends in ^{13}C shifts of carbon compounds. For example, in carbon compounds, the development of positive charge causes a downfield shift of the charged center. Similarly, in a series of related silanes, $\delta(^{29}Si)$ moves downfield as the electron-withdraw-

---

(10) Niemann, U.; Marsmann, H. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *308*, 202.

(11) (a) Spielvogel, B. F.; Nutt, W. R.; Izydore, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 1609–1610. (b) Spielvogel, B. F.; Purser, J. M. *Ibid.* **1971**, *93*, 4418–4426. (c) Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3089–3103. (d) Odom, J. D.; Moore, T. F.; Goetze, R.; Nöth, H.; Wrackmeyer, B. *J. Organomet. Chem.* **1979**, *173*, 15–32.

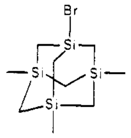
(12) Scholl, R. L.; Maciel, G. E.; Musker, W, K. *J. Am. Chem. Soc.* **1972**, *94*, 6376–6385.

(13) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984–2990.

(14) (a) "Carbon-13 NMR Spectroscopy"; Stothers, J. B., Ed.; Academic Press: New York, 1972. (b) "^{13}C-NMR Spectroscopy"; Breitmaier, E., Voelter, W., Eds.; Verlag Chemie: Weinheim/Bergstr., 1974.

(15) Litchman, W. M.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 1400–1407.

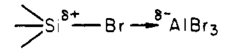
Table III. Effect of Lewis Acids on the ^{29}Si Chemical Shift of Trialkylsilyl Halides

silane	Lewis acid (equiv)	solvent	$\delta(^{29}Si)$ [a]
Me_3SiI		CH_2I_2	10.5
	BI_3 (3)	CH_2I_2	11.1
Me_3SiBr		CH_2Br_2	27.3
	BBr_3	neat	28.0
	BBr_3 (1.2)	CH_2Br_2	46.0
	$TaBr_5$ (satd)	CH_2Br_2	28.0
	$AlBr_3$ (1.2)	PBr_3	45.5
	$AlBr_3$ (1.2)	CS_2	43.5
	$AlBr_3$ (3)	CS_2	54.2
	$AlBr_3$ (3)	CH_2Br_2	62.7
Me_3SiCl		CH_2Cl_2	30.4
	$AlCl_3$ (1.2)	CH_2Cl_2	32.4
		CH_2Cl_2	2.4, 23.1
	$AlBr_3$ (satd)	CH_2Br_2	2.0, 74

[a] Ppm from Me_4Si (neat); 25 °C; ca 30% v/v.

ing ability of substituents increases (Table II). This trend parallels the reactivity of these compounds as electrophilic silylating agents, consistent with the increasing development of positive charge at silicon.

In weakly coordinating solvents (e.g., methylene chloride, methylene bromide), Lewis acids apparently form complexes with trialkylsilyl halides and the ^{29}Si resonance of the silicon nucleus is shifted to lower field with respect to the parent compounds. In the case of trialkylsilyl bromides there is a substantial deshielding of the silicon nucleus in the presence of $AlBr_3$. ^{29}Si chemical shifts ca. 76 ppm are characteristic of these compounds, and these are among the most highly deshielded ^{29}Si resonances yet reported. We attribute this to the formation of a highly polarized complex (I). The polarized complex I can also undergo rapid equilibration involving a very small concentration of free ion pairs formed by the dissociation of the complex. However, the observed NMR data cannot distinguish either of the two possibilities.



The structure I is, however, consistent with the observation that the line width of the ^{27}Al NMR resonance of $AlBr_3$ in CH_2Br_2 decreases from 1250 to 950 Hz in the presence of trimethylsilyl bromide. Such a reduction in the line width of the resonance of a quadrupolar nucleus is expected for the formation of a pseudotetrahedral environment about the ^{27}Al nucleus (tetrahedral $AlBr_4^-$ has a line width of ca. 20Hz in CH_2Br_2).

Expected ^{29}Si Shifts of Silicenium Ions

If the chemical shift relationship developed above for neutral tetrahedral silanes and carbon compounds is extended to the trigonal trivalent cations, then the chemical shifts for silicenium ions can be predicted from their carbenium ion analogues. Such an extension is not unprecedented since the relationship which correlates $\delta(^{11}B)$ to $\delta(^{13}C)$ can be extended from tetrahedral to trigonal compounds.[11e]

The $\delta(^{13}C)$ for the *tert*-butyl cation (330 ppm) leads to a predicted $\delta(^{29}Si)$ for the trimethylsilicenium ion (Me_3Si^+) within the range 225–275 ppm. Similarly, $\delta(^{13}C)$ for trityl cation leads to a predicted $\delta(^{29}Si)$ for triphenylsilicenium ion (Ph_3Si^+) within the range 100–150 ppm. These considerations make it clear that no long-lived trivalent silicon cation has yet been observed.

Due to the high affinity of silicon for oxygen and halogen donors, as well as limited Si–C $d\pi$–$p\pi$ overlap, it is doubtful that long-lived, stable trivalent silicon cations can be observed in solution with systems applied for carbocations. We are continuing studies to overcome these difficulties.

Experimental Section

Lewis acids and silanes were commercially available compounds of highest purity and were used without further purification. Preparation of solutions and formation of complexes was carried out in an efficient drybox under an atmosphere of dry argon by using methods previously described in connection with preparing stable ions. NMR spectra were recorded on either a Varian FT 80A spectrometer or a Varian XL200 spectrometer, and all chemical shifts were referenced to neat Me_4Si.

Acknowledgment. We are grateful to Professor L. H. Sommer (University of California at Davis) for a sample of 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane and to the National Science Foundation for financial support.

Registry No. **1** (X = C), 463-82-1; **1** (X = Si), 75-76-3; **2** (X = C), 75-28-5; **2** (X = Si), 993-07-7; **3** (X = C), 74-98-6; **3** (X = Si), 1111-74-6; **4** (X = C), 74-84-0; **4** (X = Si), 992-94-9; **5** (X = C), 74-82-8; **5** (X = Si), 7803-62-5; **6** (X = C), 507-20-0; **6** (X = Si), 75-77-4; **7** (X = C), 594-20-7; **7** (X = Si), 75-78-5; **8** (X = C), 71-55-6; **8** (X = Si), 75-79-6; **9** (X = C), 56-23-5; **9** (X = Si), 10026-04-7; **10** (X = C), 507-19-7; **10** (X = Si), 2857-97-8; **11** (X = C), 594-16-1; **11** (X = Si), 4095-10-7; **12** (X = C), 558-13-4; **12** (X = Si), 7789-66-4; **13** (X = C), 558-17-8; **13** (X = Si), 16029-98-4; **14** (X = C), 108-88-3; **14** (X = Si), 694-53-1; **15** (X = C), 101-81-5; **15** (X = Si), 775-12-2; **16** (X = C), 74-87-3; **16** (X = Si), 13465-78-6; **17** (X = C), 75-09-2; **17** (X = Si), 4109-96-0; **18** (X = C), 67-66-3; **18** (X = Si), 10025-78-2; **19** (X = C), 74-83-9; **19** (X = Si), 13465-73-1; **20** (X = C), 74-95-3; **20** (X = Si), 13768-94-0; **21** (X = C), 75-25-2; **21** (X = Si), 7789-57-3; **22** (X = C), 74-88-4; **22** (X = Si), 13598-42-0; **23** (X = C), 75-11-6; **23** (X = Si), 13760-02-6; **24** (X = C), 75-47-8; **24** (X = Si), 13465-72-0; **25** (X = C), 75-62-7; **25** (X = Si), 13465-74-2; **26** (X = C), 594-18-3; **26** (X = Si), 13465-75-3; **27** (X = C), 594-15-0; **27** (X = Si), 13465-76-4; **28** (X = C), 594-23-0; **28** (X = Si), 13977-54-3; **29** (X = C), 14349-82-7; **29** (X = Si), 13932-03-1; **30** (X = C), 14349-80-5; **30** (X = Si), 13536-76-0; **31**, 519-73-3; **31**, 789-25-3; **32**, 507-25-5; **32**, 13465-84-4; **33**, 593-53-3; **33**, 13537-33-2; **34**, 14059-90-6; **34**, 13550-39-5; **35**, 558-16-7; **35**, 13536-68-0; Me_3SiOMe, 1825-61-2; $Me_3SiOCOCH_3$, 2754-27-0; $Me_3SiOCOCF_3$, 400-53-3; $Me_3SiOSO_2(CF_3$, 27607-77-8; Me_3SiOSO_2F, 3167-56-4; BI_3, 13517-10-7; BBr_3, 10294-33-4; $TaBr_5$, 13451-11-1; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasilatricyclo[3.3.1.1^{37}]decane, 29954-89-0.