termined by comparing the relative abundance of the *m/e* 81, 82, 110, and 111 peaks of the product 1-methylnorbornane with the relative abundance of the same peaks of authentic 1-methylnorbornane-d_0 (81/100%, 82/9.5%, 110/10%, 111/0.9%) and 1-methylnorbornane-d_1 (81/17.5%, 82/100%, 110/1.8%, 111/11%).[50]

The measured isotopic composition of neopentane and 1-methylnorbornane did not depend on the history of the injection port liner. Several solutions derived from the decomposition of $\mathrm{L^{D}{}_{2}PtNp^{D}Cl}$ in cyclohexane which contained mixtures of neopentane-d_{11} and neopentane-d_{12} were analyzed by GC/MS using an injection port liner which had been in use for ca. 3 months without cleaning and by GC/MS using a new injection port liner. The mass spectra obtained under these two conditions were very similar.

Error Analysis. Standard deviations from least-squares analyses of kinetic plots were adjusted to 95% confidence levels (*t* values for *N* − 2 degrees of freedom). When several values were averaged (e.g., kinetic isotope effects, rate constants), *t* values for *N* − 1 degrees of freedom were used. When error bars (95% confidence limits) were used, the error in slope and intercept were determined by drawing two lines through the error bars having the largest and smallest reasonable slopes. This method produced error limits which were comparable with those determined by least-squares analysis.

Acknowledgment. We thank Marifaith Hackett and Chris Roberts for allowing us to use their vacuum lines and Professor Joseph San Filippo, Jr., for helpful discussions. The NMR spectrometers used at Harvard were purchased in part through NSF CHE 8008891 and through NIH BRS Shared Instrument Grant Program 1 S10 RR01748-01A1.

Registry No. **1**, 102307-54-0; **1**-d_2, 102307-61-9; **5**, 102307-55-1; **6**, 102307-56-2; **11**, 75110-84-8; $\mathrm{(CD_3)_3CCD_2OH}$, 75160-19-9; $\mathrm{PCl_3}$, 7719-12-2; $\mathrm{(COD)PtNp_2}$, 75101-19-8; $\mathrm{(COD)PtCl_2}$, 12080-32-9; $\mathrm{(COD)PtNp^{D}{}_{2}}$, 102307-57-3; (COD)PtNpCl, 102307-58-4; $\mathrm{(COD)PtNp^{D}Cl}$, 102307-59-5; $\mathrm{L_2PtNp^{D}Cl}$, 102342-12-1; $\mathrm{L^{D}{}_{2}PtNpCl}$, 102307-60-8; $\mathrm{L^{D}{}_{2}PtNp^{D}Cl}$, 97921-41-0; $\mathrm{(COD)Pt(CH_2Nb)_2}$, 102307-62-0; $\mathrm{(COD)Pt(CH_2Nb)Cl}$, 102307-63-1; $\mathrm{L^{D}{}_{2}Pt(CH_2Nb)Cl}$, 102307-64-2; *trans*-$\mathrm{L_2PtEtCl}$, 102307-65-3; *trans*-$\mathrm{L_2PtMeCl}$, 102307-66-4; *trans*-$\mathrm{L_2Pt(CH_2Ad)Cl}$, 102307-67-5; tricyclopentylphosphine-d_{27}, 102307-68-6; (cyclopentyl-d_9)magnesium bromide, 102307-69-7; tricyclopentylphosphine, 7650-88-6; cyclopentylmagnesium bromide, 33240-34-5; pivalic-d_9 acid, 42983-07-3; neopentyl-d_{11} bromide, 75160-21-3; neopentyl-d_{11} tosylate, 102307-70-0; (neopentyl-d_{11})magnesium bromide, 102307-71-1; neopentylmagnesium bromide, 33974-41-3; neopentane-d_1, 4741-94-0; neopentane-d_{11}, 102307-72-2; neopentant-d_{12}, 5152-54-5; 1-methylnorbornane-d_1, 102307-73-3; dueterium, 7782-39-0.

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(50) A reference sample of 1-methylnorbornane-d_1 was made by allowing a cyclohexane solution of $\mathrm{CODPt(CH_2Nb)_2}$ to react with DCl in $\mathrm{D_2O}$ (99 atom %). Similarly, 1-methylnorbornane-d_0 was made by allowing a solution of $\mathrm{CODPt(CH_2Nb)_2}$ to react with HCl in $\mathrm{H_2O}$.

Preparation and NMR Studies of Pentacoordinated Silicon Anions

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The 18-crown-6 potassium salts of trifluorodiphenylsiliconate (**1**), trifluoromethylphenylsiliconate (**8**), tetrafluorophenylsiliconate (**2A**), and difluorotriphenylsiliconate (**9**) have been prepared. These are found to be remarkably stable, particularly as they are nonhygroscopic. Each has been studied by variable-temperature ^{1}H and ^{19}F NMR spectroscopy. Their dynamic behavior is discussed in detail.

Introduction

Pioneering work on the chemistry of pentacoordinate silicon was carried out in the 1960s by Frye,[1] Müller,[2] and Muetterties,[3] who not only provided well-substantiated proof of the preparation of pentacoordinate silicon species but also began systematic studies of their physical and chemical properties. Since those early days a great variety of pentacoordinate silicon species have been prepared and studied by a number of techniques.[4-9] One impetus for these studies has come from a desire to understand the intermediacy of five-coordinate silicon in nucleophilic displacements.[10] Equally important has been the desire to understand silicon pentacoordination in the general context of pentacoordinate species. The extensive chemistry of pentacoordinate species has recently been reviewed by Holmes,[11] where considerable emphasis has been placed

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on the structural relationships among pentacoordinate species (trigonal bipyramidal vs. square pyramidal), on the factors favoring axiophilicity in trigonal-bipyramidal structures, and on the similarities between five-coordinate phosphorus and silicon.

At the same time, a number of synthetic methods have been reported which involve the intermediacy of pentacoordinate silicon. In particular, the activation of Si–H, Si–O, and Si–N bonds by pentacoordination has recently been reviewed by Corriu.[12] Klanberg and Muetterties' (K–M) classic paper on several pentacoordinate silicon anions (**1**–**3**) (as either their tetraethyl-, tetrapropyl-, or

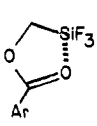
$Ph_2\bar{Si}F_3$ **1**

$Y\bar{Si}F_4$ **2** A Y=Ph, B Y=Me, C Y=Bu

$\bar{Si}F_5$ **3**

tetrabutylammonium salts) was the first example of a temperature-dependent NMR study of pentacoordinate silicon.[3] In this paper, K–M discussed the considerable difficulties arising from extraneous exchange processes that resulted from the hygroscopic nature of the their compounds. Even though efforts were made to eliminate these difficulties, they could only be minimized and, thus, only a qualitative description of the dynamic behavior of these simple pentacoordinate anions resulted. For example, K–M suggested that trifluorodiphenylsiliconate (**1**) underwent fluorine exchange by an intramolecular process at low temperature and a dissociative one at room temperature. Later work by Janzen and co-workers[13] on similar anions pointed out similar difficulties; although measures were taken to slow the extraneous exchange processes, these workers concentrated their efforts on studying the nature of such extraneous exchanges.

More recent NMR studies of the dynamic behavior of pentacoordinate silicon have concentrated on cyclic species; in particular, compounds like **4**–**6** have been studied in detail.[4-7] Activation parameters for the exchange processes have been measured, and arguments have been made that extraneous exchange processes do not interfere and that the exchange is an intramolecular process (probably pseudorotational). Activation barriers range between about 9 and 30 kcal/mol[4-7] and are generally similar to those of analogous phosphorus species.[11]



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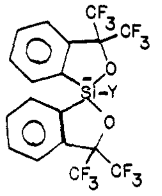
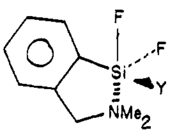
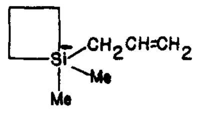


5 Y=aryl, alkyl, F, and OPh



6 A Y=Me B Y=F

Our interest in pentacoordinate silicon derived from two sources. In recent studies, we proposed the intermediacy of pentacoordinate silicon anions when chloromethyl-substituted silanes rearranged on reaction with KF solubilized by 18-crown-6.[14] These reactions were surprisingly insensitive to the presence of water. Thus, we thought that stoichiometric quantities of KF might be used to prepare nonhygroscopic pentacoordinate species of **1**–**3** (with a potassium-18-crown-6 counterion). We were also interested in the extent to which silicon could be carbon-substituted given that when this work began only two carbon substituents had been reported on pentacoordinate silicon in solution.[3,5,7] In our gas-phase studies, we have made a variety of pentacoordinate species with **7** being full carbon-substituted with five.[15]



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In this paper we combine these interests and address several questions of general interest: (1) can acyclic, pentacoordinate silicon species of **1**–**3** be prepared which are insensitive to extraneous exchange processes, (2) do such species really undergo F exchange with different mechanisms at different temperatures, (3) can activation barriers be obtained for the dynamic process(es), and (4) how do such barriers compare with those already measured in cyclic silicon species and in analogous phosphorus compounds?

Experimental Section

General Remarks. The reactions studied were carried out under atmospheric conditions after discovering that the 18-crown-6 potassium salts are not sensitive to air or moisture. Most reactions have been done in serum cap vials fitted with a magnetic stirring bar. NMR analyses were carried out on an IBM NR-80/B spectrometer; all ^1H, ^{13}C, and ^{29}Si shifts are reported relative to Me_4Si; ^{19}F shifts are reported relative to $CFCl_3$. All ^{13}C NMR were run with proton decoupling; hence, any splittings reported are between C and F. Variable-temperature experiments were carried out in several solvent systems; the most useful of these was an acetone-d_6/vinyl chloride mixture (approximately 50/50 by volume). This mixture allowed low-temperature experimentation with a minimal amount of viscosity broadening, at least in the temperature ranges we required. Temperature calibration was accomplished by inserting a thermocouple in a full NMR tube while varying the temperature settings of the variable-temperature unit. Calibration was done on a regular basis before and after important temperature runs. The accuracy of the calibration is probably no better than ±2 °C.

Unless otherwise noted, all organic reagents were obtained from either Petrarch Systems or Aldrich Chemical and used without purification. Anhydrous KF was obtained from MCB Chemicals. It has been stored at 120 °C and used without purification.

Preparation of Methylphenyldifluorosilane. To a 250-mL flask equipped with a magnetic stirring bar and condenser was added finely divided SbF_3 (58.4 g, 0.33 mol) under a blanket of Ar. This was cooled to −78 °C, and methylphenyldichlorosilane (80.0 g, 0.42 mol) was rapidly added by syringe. This mixture quickly froze and was allowed to slowly come to room temperature. Near room temperature a highly exothermic reaction occurred. The mixture was filtered and distilled (bp 135–137 °C), yielding 66.2 g (85.5%) of methylphenyldifluorosilane.[16]

Preparation of the 18-Crown-6 Potassium Salt of Trifluorodiphenylsiliconate (1). Diphenyldifluorosilane (1.20 g, 5.00 mmol), KF (0.291 g, 5.00 mmol), and 18-crown-6 (1.32 g, 5.00 mmol) were reacted in toluene (10 mL) in a serum cap vial fitted with a magnetic stirring bar. After the mixture was stirred for

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about 1 h, a precipitate formed which was generally collected the next day. Filtration and washing with ether yielded a white crystalline material (2.54 g, 94%), which after two recrystalizations from THF/ether gave analytically pure 1 with a melting point of 130–131 °C. Compound 1 was characterized as follows: ^{1}H NMR: δ 3.62 (s, 24 H), 7.00–7.22 (m, 3 H), 7.93–8.13 (m, 2 H); ^{13}C NMR δ 70.77 (s), 126.95 (br s), 127.77 (s), 138.58 (q). Anal. Calcd for $C_{24}H_{34}SiO_6F_3K$: C, 53.12; H, 6.31. Found: C, 52.76; H, 6.35.

Preparation of the 18-Crown-6 Potassium Salt of Trifluoromethylphenylsiliconate (8). Phenylmethyldifluorosilane (0.791 g, 5.00 mmol), KF (0.291 g, 5.00 mmol), and 18-crown-6 (1.32 g, 5.00 mmol) were reacted in toluene (10 mL) in a serum cap vial fitted with a magnetic stirring bar. After the mixture was stirred for about 1 h, a precipitate formed which was generally collected the next day. Filtration and washing with ether yielded a white crystalline material (2.05 g, 85%), which after two recrystalizations from THF gave analytically pure **8** with a melting point of 133–133.5 °C. Compound **3** was characterized as follows: ^{1}H NMR δ 0.70 (s, 3 H), 3.62 (s, 24 H), 7.02–7.09 (m, 3 H), 7.80–8.10 (m, 2 H); ^{13}C NMR δ at room temperature 70.80 (s), 126.80 (s), 127.47 (s), 138.12 (s), at −77 °C 4.84 (d of t), 70.85 (s), 127.55 (s), 128.70 (s), 129.64 (s), 139.08 (t). Anal. Calcd for $C_{19}H_{32}SiO_6F_3K$: C, 47.48; H, 6.71. Found: C, 47.45; H, 6.67.

Preparation of the 18-Crown-6 Potassium Salt of Tetrafluorophenylsiliconate (2A). Phenyltrifluorosilane (0.203 g, 1.25 mmol), KF (0.73 g, 1.25 mmol), and 18-crown-6 (0.330 g, 1.25 mmol) were reacted in toluene (2.5 mL) in a serum capped vial fitted with a magnetic stirring bar. After about an hour, a precipitate formed. It was collected and washed with ether (0.56 g, 90%). Its NMR behavior was shown to be identical with the tetrabutylammonium salt of **2A** prepared by K–M. We have been unable to find a suitable recrystallization medium for the crown salt. Thus, our sample is slightly impure.

Preparation of the 18-Crown-6 Potassium Salt of Difluorotriphenylsiliconate (9). Triphenylfluorosilane (1.39 g, 5.00 mmol), KF (0.291 g, 5.00 mmol), and 18-crown-6 (1.32 g, 5.00 mmol) were reacted in toluene (10 mL) in a serum cap vial fitted with a magnetic stirring bar. After the mixture was stirred for 6 days, the precipitate was collected. Filtration and washing with ether yielded a white crystalline material (2.73 g, 90%), which could not be recrystallized. Analytical data are reported for this material. ^{1}H NMR: δ 3.63 (s, 24 H), 7.05–7.70 (m, 3 H), 7.94–8.24 (m, 2 H). ^{13}C NMR: δ 71.0 (s) and 10 peaks from 128 to 139 (all s). Anal. Calcd for $C_{30}H_{39}SiO_6F_2K$: C, 59.97; H, 6.54. Found: C, 59.39; H, 6.39.

Comments on the Low-Temperature NMR Studies. Low-temperature studies were carried in two solvent systems: (1) pure acetone-d_6 or (2) acetone-d_6 to which about 50 volume % of vinyl chloride was added. The latter system was required for temperatures approaching −100 °C, its great virtue being that low temperatures were attained with less viscosity broadening.

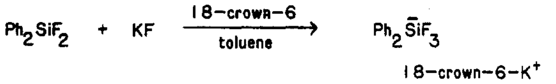
The solutions of 1 and 8 studied were not particularly sensitive to water or the addition of hexamethyldisilazane, which has been used by others to remove water.[13] Thus, neither chemical shifts nor the temperatures where various dynamic processes occurred were much affected by water or hexamethyldisilazane. In fact, quite commonly our solutions had a small peak due to water. This seemed to have no effect and could not be decreased by adding the hexamethyldisilazane or other drying agents.

Complete line-shape analysis was carried out by using the EXC2 program[17] in which spin–spin coupling is ignored, since it so small compared to the huge differences in chemical shift. Indeed, we were only able to measure F–F couplings at low temperatures where line widths had narrowed considerably. The activation parameters obtained are reported in Table II.

Results and Discussion

Klanberg and Muetterties (K–M) reported the preparation of anions **1–3** (as variously substituted ammonium cations) and studied their dynamic properties by temperature-dependent ^{1}H and ^{19}F NMR.[3] Attempts to prepare other pentacoordinate silicon species, particularly trialkyl- and triaryl-substituted ones, failed. The ready hydrolysis of these ammonium salts made both their analysis and subsequent NMR study difficult. Protic impurities as well as hydrolysis product contamination affected this work. Nevertheless, when extreme care was taken, NMR studies could be carried out and, indeed, gave important structural information about these ions. Compounds of the type F_5Si^- and RF_4Si^- were shown to have fluorine spectroscopic equivalence throughout a wide temperature range, while $Ph_2F_3Si^-$ could be shown to have two different fluorine signals at low temperatures. These were ascribed to equatorial and axial environments in a trigonal-bipyramidal structure with the Ph's occupying the equatorial position. As the low-temperature limit was approached, coupling between Si and F indicated that exchange was occurring by an intramolecular process. On the other hand, the mechanism by which equivalence occurred at higher temperature was suggested to be a dissociative one.

We have prepared pentacoordinate silicon species **1**, **2A**, **8**, and **9** as their 18-crown-6 potassium salts by reaction between their respective fluorosilane and a stoichiometric amount of both KF and 18-crown-6 in toluene (eq 1).



$$Ph_2SiF_2 + KF \xrightarrow[\text{toluene}]{\text{18-crown-6}} \underset{\text{18-crown-6-K}^+}{Ph_2\bar{Si}F_3} \qquad (1)$$

After a few hours of vigorous stirring a precipitate forms; upon collection and washing, samples suitable for NMR study are obtained. These salts are not hygroscopic, and their NMR study is not fraught with the difficulties that others have noted. They do not change appearance when stored in air for longer than 6 months. The method fails in attempts to prepare trifluorodimethyl- and difluorotrimethylsiliconates.

^{1}H, ^{13}C, ^{29}Si, and ^{19}F NMR have been used to characterize and study these salts. ^{1}H spectra are dominated by a 24 hydrogen singlet of the crown moity; in addition, a characteristic splitting of the aromatic proton region occurs upon pentacoordination. Generally, the parent fluorosilane has a complex aromatic region centered at about δ 7.5. Its pentacoordinate counterpart has this region split into the complex resonances, one usually centered around δ 7 and the other, around δ 8. The ^{19}F spectra of 1 and 8 are characterized by broad singlets at ambient temperature; these typically broaden further as the temperature is decreased, essentially disappear, and reappear as two signals in a 2:1 ratio at still lower temperature. At low temperature ^{29}Si–^{19}F coupling is evident in the ^{19}F NMR. The ^{19}F NMR spectra of **2A** and **9** are, however, different. The F singlet does not change through a wide temperature range. Some of the details of these experiments are collected in Table I. The discussion which follows highlights the dynamic characteristics of these compounds separately.

Trifluorodiphenylsiliconate (1). This anion, although previously studied by K–M, has yielded several new results in our hands. Acetone-d_6/vinyl chloride solutions show ^{29}Si–^{19}F coupling (^{19}F spectra) at much higher temperatures (approximately 30 °C) than K–M saw.[3] The loss of coupling at higher temperatures led Klanberg and Muetterties to suggest that 1 undergoes a dissociative process to exchange fluorines at temperatures above −100 °C (eq 2).

$$Ph_2\bar{Si}F_3 \rightleftharpoons Ph_2SiF_2 + F^- \qquad (2)$$

We, having seen coupling at temperatures far above −100 °C, believe that dissociative processes are not occurring. To further assess this we have undertaken a complete line-spape analysis (CLS) of 1. We find not only that $\Delta G^{\ddagger}$

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Table I. Temperature-Dependent NMR Description of 1 and 8

	Compound 1-Diphenyl
38 °C	^{19}F shows a broad singlet at δ −110.7 (55 Hz at half height)
38 to −10 °C	signal broadens
−12 °C	coalescence temperature
−22 °C	two broad signals in approximate 2:1 ratio
−33 to −54 °C	two signals sharpen δ −100.5 (2 F) and −133.9 (1 F)]
−62 °C	definite Si–F coupling (J's of 252.7 and 204.6 Hz, respectively)
−77 °C	peaks split into doublet and triplet, respectively F–F coupling is also seen [J of 2.58 Hz] lines are between 6 and 7 Hz at half-height
	Compound 8—Methylphenyl
38 °C	^{19}F shows broad singlet at δ −99.8 (129.8 Hz at half-height) ^{1}H shows a singlet in the methyl region
38 to 2 °C	^{19}F signal broadens ^{1}H signal broadens
2 °C	coalescence temperature for F analysis
−12 °C	^{19}F shows two broad signals ^{1}H is a quartet
−12 to −53 °C	two ^{19}F signals sharpen [δ −83.5 (2 F) and −133.33 (1 F)] methyl ^{1}H signal remains quartet (J of 6.63 Hz)
−62 °C	definite Si–F coupling (J's of 251 and 210 Hz, respectively)
−68 °C	^{19}F signal at δ-83.5 is split into quartet (J_{FSiCH} is 9 Hz) this signal is also coupled to F with J of 2.6 Hz ^{19}F signal at δ −133.3 remains a singlet
−77 °C	^{19}F signals somewhat sharper methyl ^{1}H signal split into triplet (J of 9.3 Hz)

Table II. Activation Parameters[a] for ^{19}F Exchange in 1 and 8

compd	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
diphenyl (1)	11.7	11.2	2.5
methylphenyl (8)	9.9	9.4	−4.4

[a] $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are given in kcal/mol; $\Delta S^{\ddagger}$ is given in cal/(deg mol).

is 11.7 kcal/mol (Table II) but also that a plot of log (k/T) vs. $1/T$ is linear throughout the 110 °C temperature range studied. This suggests that no change of exchange mechanism occurs in this temperature range. Thus, since we see coupling at the low-temperature end and have linearity throughout the temperature range, it seems highly likely that Si and F are coupled throughout. We are unable to see the coupling at higher temperature not because of dissociation but because the lines are simply too broad. Additional confirmation of this has been obtained by using ^{29}Si NMR, where we observed ^{29}Si–^{19}F coupling at room temperature.

K–M indicated that no F–F couplings in 1 could be observed at −100 °C. We have been able to measure such couplings at −53.7 °C in our solvent system. As predicted by K–M, the F–F coupling constant is <5 Hz. Indeed, we measured a F–F coupling constant of 2.6 Hz for 1. This observation indicates once again that two magnetically distinct fluorines exist at low temperature and that they can be distinguished not only by their integral differences but also by their mutual coupling (the F with integral = 1 is split into a triplet; its counterpart is split into a doublet).

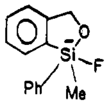
These data indicate that 1 is undergoing an intramolecular exchange at ambient temperature, that at intermediate exchange rates the ^{19}F signal is virtually completely broadened, and that at low temperature fluorine is found in two separate environments as exchange becomes extremely slow. The data are consistent with a trigonal-bipyramidal geometry at the low-temperature limit although one cannot rule out the possibility of some slight geometric distortions. Indeed, X-ray structural analysis of the tetramethylammonium salt of 1 has revealed a slightly distorted trigonal-bipyramidal structure.[8a] The intramolecular exchange is easily accommodated by a pseudorotation process, although the data do not eliminate the possibility of other intramolecular exchange processes. Thus, we confirm the main observations of K–M but see some different behavior for 1. It is hard to imagine that the solvent systems could account for such differences, however. Ours would have a dielectric constant much greater than that of K–M (where the solvent is dichloromethane) and would be a better system for a dissociative process.

Trifluoromethylphenylsiliconate (8). Alkyl substitution on a pentacoordinate silicon occurs in a number of environments as seen in structures **2B**, **2C**, **5**, **6A**, and **10–12**.[3,5,6,8] In these compounds, the alkyl substitution is either on a silicon which otherwise is part of a cyclic ligand system (**5**, **6A**, and **10–12**) or is part of an acyclic substitution pattern which has not been responsive to dynamic NMR study (**2B**). We prepared **8** hoping that its similarity to **1** would allow its dynamic NMR study, on the one hand, and an assessment of the effect of alkyl substitution on pentacoordinate silicon, on the other. To our knowledge **8** is the only acylic, alkyl, dicarbon-substituted siliconate to be reported. Its preparation and properties are quite similar to those of **1**. It is stable to air and moisture. Its NMR behavior also is similar to **1**. At ambient temperature it exhibits a broad ^{19}F signal, as the temperature is lowered that signal greatly broadens, and at low temperature two signals split out in a 2:1 ratio. These are more complicated than in the diphenyl (**1**) case, since coupling between Me and F occurs. We see Me–F coupling between the F's in the axial positions, but not the F in the equatorial position. Thus, the F signal with double intensity is split into a quartet (the quartet lines are doubled by very small F–F coupling), but the single intensity F line is unsplit. These data indicate that both the methyl and phenyl substituents are equatorially oriented with Me coupling to F greater to the axial F's. This is consistent with several samples in pentacoordinate phosphorus, where Me to F(axial) coupling exceeds that of Me to F(equatorial).[3] CLS analysis of **8** gives a $\Delta G^{\ddagger}$ = 9.9 kcal/mol with a linear log (k/T) vs. $1/T$ plot throughout the 110 °C range studied.

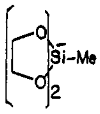
$PhMe\overset{-}{Si}F_3$

8

10



11



12

Thus, **8** is very similar to **1** both in terms of its low-temperature limit structure (with two carbon substituents equatorial) and its dynamic properties. The replacement of a phenyl by methyl lowers the free energy activation barrier by about 2 kcal/mol. We believe that it is premature to speculate on the origin of this difference although it is real. The linearity of the kinetic plot over such a wide temperature range again indicates that a single exchange mechanism is operating, and, again, these data are consistent with a pseudorotational dynamic process. As this work is ongoing, we will reserve additional comment until other work designed to further assess substituent effects is completed, although we would draw attention to the recent work of Martin, Farnham, and co-workers[5] on **5**. They have demonstrated a linear free energy correlation between the rate of ligand permutation and the electronegativity of Y.

The ^{13}C NMR spectrum of **8** at room temperature deserves special comment since it shows no methyl carbon, probably because of line broadening. However, at −77 °C, the methyl carbon is seen as a doublet of triplets due to the unequal coupling of this carbon to one equatorial F and two axial F's.

Tetrafluorophenylsiliconate (2A) and Difluorotriphenylsiliconate (9). These ions are prepared by the method outlined in eq 1. Compound **2A** was prepared both to further test the synthetic method and to determine whether our monosubstituted pentacoordiante 18-crown-6 derivative would behave differently than that of K–M. We find no differences, with PhSiF$_4^-$ giving only one ^{19}F signal through a wide temperature range although our sample is slightly impure (see Experimental Section). Such behavior is consistent with a rapidly exchanging ion whose exchange cannot be slowed for NMR analysis. K–M reached a similar conclusion while drawing attention to the similar behavior of analogous phosphorus compounds.[3]

Ph$_3$SiF$_2^-$ (**9**) is the first acyclic, tricarbon-substituted siliconate reported, although a related bipyridyl ion was reported some years ago by Corey and West.[18,19] It has physical properties like its counterparts but shows no temperature-dependent NMR behavior. Over a wide temperature range, only a single ^{19}F signal is observed. These observations suggest that three phenyls occupy equatorial positions and do not exchange.

The 18-crown-6 pentacoordinate silicon compounds described herein have properties which have allowed detailed temperature-dependent NMR study. In compounds **1** and **8** activation free energy barriers of 11.7 and 9.9 kcal/mol were obtained. Although these barriers are quite a bit lower than that for Ph$_2$PF$_3$ (18.7 kcal/mol),[20] the qualitative NMR behavior of our pentacoordinate silicon compounds is similar to that of analogous phosphorus compounds, a conclusion similar to that reached by Holmes.[11] Since only a few pentacoordinate silicon compounds have yet been studied by dynamic NMR techniques, it is premature to generalize about the relationship between structure and activation barriers. Nevertheless and, perhaps, coincidentially, compounds **1** and **8** have $\Delta G^{\ddagger}$'s close to the other trifluoropentacoordinate species whose $\Delta G^{\ddagger}$'s have been reported: namely, **4** (7–9 kcal/mol) and **6B** (approximately 12 kcal/mol). Additional comment will await the completion of studies designed to probe these structural relationships in acyclic silicon compounds.

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Registry No. **1**·18-crown-6-K$^+$, 102307-90-4; **2A**·18-crown-6-K$^+$, 102307-91-5; **8**·18-crown-6-K$^+$, 102307-93-7; **9**·18-crown-6-K$^+$, 102418-62-2; PhMeSiF$_2$, 328-57-4; SbF$_3$, 7783-56-4; PhMeSiCl$_2$, 149-74-6; Ph$_2$SiF$_2$, 312-40-3; PhSiF$_3$, 368-47-8; Ph$_3$SiF, 379-50-0.

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MNDO Calculations for Compounds Containing Zinc[1]

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MNDO has been parametrized for zinc. Calculations are reported for a number of compounds of zinc. The results are comparable with those for other metals.

Introduction

The MNDO method[3,4] is now established[5] as a practical procedure for studying chemical behavior, giving results comparable[6,7] with those from good ab initio models (e.g., 6-31G*) while requiring less than one-thousandth as much computer time. Parameters have been reported for hydrogen,[3] for the second period elements beryllium,[9] boron,[10] carbon,[3] nitrogen,[3] oxygen,[3] and fluorine,[11] for the third-

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(1) Part 84 of the series "Ground States of Molecules". For Part 83 see: Dewar, M. J. S.; Dieter, K. M., in progress.

(2) Welch Predoctoral Fellow 1985.

(3) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(4) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(5) For example, CA SEARCH list 148 citations of MNDO in the period since January, 1982, to be compared with 1073 for ab initio.

(6) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**; *101*, 5558. Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898. These comparisons were restricted to a relatively small number of molecules composed only of second period elements by the availability of geometry-optimized 6-31G* calculations. Extension of such tests to additional molecules would clearly be very useful, allowing further comparisons with the very extensive tests we have carried out, and published, of our own procedures. Such systematic tests of ab initio methods should indeed have been carried out many years ago by those using them. It should not have been left to us to do this.

(7) Wiberg[8] has shown that good estimates of heats of formation can be derived from 6-31G* energies by applying empirical corrections based on group additivity relationships. Similar improvements could no doubt be effected in the same way in the case of MNDO. Such a treatment is, however, inherently limited to stable molecules. It cannot be used to study reactions because there is no way to apply such corrections to intervening segments of potential energy surfaces in general or to transition states in particular. Since the potentially most important application of theoretical calculations to chemistry lies in the study of reactions and reaction mechanisms and since our procedures have been developed primarily for such use, the only relevant way to compare ours with ab initio ones is to compare the corresponding uncorrected energies. The only comparisons of this kind hitherto reported are those of Dewar and Storch.[6]

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