7640 J. Am. Chem. Soc. 1986, 108, 7640–7645

which are assigned to the anion radical.[34] However, at longer time scales, cleavage of the Ir–C bond occurs for $[(OEP)Ir(C_8H_{13})]^-$, and the final reduction product is $[(OEP)Ir]^-$ which is identified by its characteristic UV–vis spectrum. A chemical reaction does not occur after reduction of $[(OEP)Ir(C_8H_{13})(CO)]$, and the one-electron reduction yields an anion radical that is stable on long time scales.

The exact sequence of steps in the transformation of $[(OEP)Ir(C_8H_{13})]^-$ to $[(OEP)Ir]^-$ is not clear. The overall reaction is given by eq 4 and involves the transformation of an Ir(III)

$$(OEP)Ir(C_8H_{13}) + 2e \rightleftarrows [(OEP)Ir]^- + C_8H_{13}^- \quad (4)$$

porphyrin to an Ir(I) porphyrin. A similar overall two-electron reduction with loss of the σ-bonded ligand has been shown for (TPP)Co(R), but in this case a Co(II) intermediate is proposed.[36]

The intermediate in reaction 4 is an Ir(II) anion radical, and hence an intramolecular charge transfer must occur. For the case of $[(TPP)Co(R)]^-$, loss of the R^- group generates (TPP)Co(II) which is then immediately reduced.[36] A similar sequence of steps is possible for $[(OEP)Ir(C_8H_{13})]^-$, but in this case either the loss of ligand or the addition of the second electron would be accompanied by the intramolecular charge transfer. However, an alternate series of steps involving the addition of a second electron and subsequent loss of $C_8H_{13}^-$ from $[(OEP)Ir(C_8H_{13})]^{2-}$ cannot be ruled out if one assumes the intramolecular charge transfer to be the rate-determining step in the chemical reaction following the initial reversible one-electron addition.

Finally, it is important to note that the reduced six-coordinate $[(OEP)Ir(C_8H_{13})(CO)]^-$ is more stable than the reduced five-coordinate $[(OEP)Ir(C_8H_{13})]^-$. This may reflect the π acid nature of CO, the geometry of the iridium atom, or both. In any event, the binding of CO by the anion radical prevents further reduction to form a square planar Ir(I) complex.

Acknowledgment. The support of the National Science Foundation (Grant No. CHE-8515411) is gratefully acknowledged.

Registry No. $(OEP)Ir(C_8H_{13})$, 104575-68-0; $(OEP)Ir(C_8H_{13})(CO)$, 104575-69-1.

Supplementary Material Available: The cell packing diagram and full tables of bond angles, bond distances, atomic positions for all atoms including calculated hydrogen positions, hydrogen thermal parameters, and least-squares planes for the structural determination of $(OEP)Ir(C_8H_{13})$ and table of anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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Anion Complexation and Migration in (8-Silyl-1-naphthyl)boranes. Participation of Hypervalent Silicon

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Abstract: Compounds **1–3**, of general structure 8-RMe_2Si-1-Me_2B-naphthalene, were prepared, and their complexes with F^- were examined. The structure of $\mathbf{1}\cdot F^-$ (R = Me) was determined by multinuclear NMR and X-ray crystallography, revealing an interaction between F^- and pentacoordinate Si. Syntheses of **2** (R = OEt) from dimethyl(8-iodo-1-naphthyl)silane and of **3** (R = F) from **2** proceeded via intramolecular anion migrations and hypervalent Si intermediates. Compound **2** is the only reported example of a silyl ether coordinated to a borane. The complex $\mathbf{3}\cdot F^-$ was more stable than $\mathbf{1}\cdot F^-$ because of increased participation of FMe_2Si in F^- bonding compared to Me_3Si. This work represents the first consideration of Si as a participant in bidentate anion complexation and the first exploration of bidentate Lewis acids in which the two active functional groups are different.

Multidentate effects in ionic complexation are of increasing interest and importance in enzyme modeling,[1] catalysis,[2] and ion transport.[3] While the complexation of cations may be accomplished with a variety of neutral *or* charged hosts, anion complexation has, until recently, been largely confined to the formation of inclusion compounds within positively charged cages.[4] In the past 2 years, bidentate coordination of anions by *neutral* organometallic compounds containing pairs of Lewis acidic functionalities has been achieved in the cases of mercury-,[5] tin-,[6] and boron-containing[7] hosts interacting with such guests as chloride, bromide, fluoride, hydride, and hydroxide. In all of these cases, the two Lewis acidic groups on a particular host were identical.

Among the many bidentate *cation* binders are compounds in which the two Lewis basic groups are not the same. For example, in the extremely simple case of aminoethers such as dimethyl(2-methoxyethyl)amine,[8] the nitrogen is clearly the more basic atom and is primarily responsible for coordination to cations and Lewis acids; however, the oxygen atom also contributes a bond

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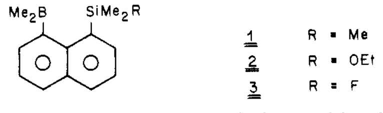
to the complexes, thereby influencing their structure and stability. In contrast to the cation binding case, there have been no studies to date of neutral, bidentate *anion* binders containing two different Lewis acidic atoms. It was therefore of interest to consider modifying the complexing properties of an anionophile by adding a second active functionality.

Among candidates for this second receptor group, we chose to explore organosilanes because of their slight Lewis acidity and considerable chemical stability. To our knowledge, the participation of silane groups in cooperative anion binding has not been previously contemplated, even though both gas-phase[9] and solution-phase[10] experiments have indicated that tetravalent Si is capable of binding anions by increasing its coordination number. Thus we thought it especially intriguing to consider the interaction of silylorganoboranes with anions.

This paper reports detailed studies of a series of (8-silyl-1-naphthyl)dimethylboranes and some of their anion complexes. Trimethylsilyl derivative **1**[11] forms a fluoride complex that is interesting from a structural point of view, while dimethylsilyl compounds **2** and **3** participate in unusual anion migration reactions. In this work, just as in previous work on proton,[12] anion,[7] and transition-metal[13] binders, the 1,8-naphthalenediyl framework rigidly holds the active functional groups at a comfortable distance for intramolecular interactions.



Experimental Section

General. All manipulations of air-sensitive liquids were performed with syringe and vacuum line techniques. Hexane and Et_2O were distilled from Na and Na–benzophenone, respectively; CD_2Cl_2, CH_2Cl_2, C_6H_6, and CD_3CN were vacuum transferred from P_2O_5; and tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF, Aldrich) was handled in an N_2-filled glovebag. Nuclear magnetic resonance spectra were recorded on a JEOL FX-90Q spectrometer containing a variable-temperature probe; samples were dissolved in CD_2Cl_2 unless otherwise noted. Solutions for ^{29}Si NMR were prepared in an alumina tube. Chemical shifts are in ppm downfield of Me_4Si (^1H, ^{13}C), BF_3OEt_2 (^{11}B), and $CFCl_3$ (^{19}F). Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN. The crystal structure was determined by C. S. Day of Crystalytics Corp., Lincoln, NE.

Tris(dimethylamino)sulfonium Fluorodimethyl((8-trimethylsilyl)-1-naphthyl)borate (1·F⁻·TAS). A sample of TASF (104 mg) was dissolved in 2 mL of CH_2Cl_2, and an aliquot of **1**[11] (114 mg) was added. The resulting solution was concentrated, and the residue was washed with hexane and redissolved in CH_2Cl_2. Sufficient C_6H_6 (2–5 mL) was added so that two layers formed. Well-defined rhomboidal crystals grew at the interface between the layers, and/or on the surface of the flask. Although ^1H NMR indicated complete complexation of **1**, it was not possible to obtain a high yield of solid product because the crystals began to redissolve before precipitation was complete. ^1H NMR δ −0.24 (br d, 6, J_{HF} = 13 Hz, MeB), 0.29 (br s, 9, MeSi), 2.71 (s, 18, MeN), 7.1–7.7 (m, 6, ArH); ^{11}B NMR δ 5; ^{19}F NMR δ −167 (br). Anal. Calcd for $C_{21}H_{39}N_3BFSiS$: C, 59.56; H, 9.28; N, 9.92; B, 2.55. Found: C, 59.74; H, 9.59, N, 9.80; B, 2.88. Exposure of **1·F⁻** to moisture caused decomposition to **1·OH⁻**, whose ^1H NMR was similar to that of **1·F⁻** except the Me peaks in **1·OH⁻** were sharp singlets.

Crystal Structure of 1·F⁻TAS. A colorless, rectangular parallelepiped crystal of dimensions 0.50 × 0.55 × 0.70 mm was employed. The crystal system was monoclinic, space group $P2_1/n$, lattice constants a = 9.920 (2) Å, b = 16.222 (4) Å, c = 15.750 (4) Å, $\alpha = \gamma = 90°$, β = 95.47 (2)°, V = 2523 (1) Å^3, and Z = 4. The structure was refined to R = 0.058 and R_w = 0.065 by using 3454 independent reflections of Cu Kα radiation, λ = 1.54184 Å, 2θ between 3.0° and 115.0°, and T = 20 °C.

The 28 non-hydrogen atoms were located with the SHELXTL Direct Methods programs. The 11 methyl groups were refined as rigid rotors with sp^3-hybridized geometry and a C–H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the hydrogen atoms. The final orientation of each methyl group was determined by three rotational parameters. The refined positions for the methyl groups gave B–C–H, Si–C–H, and N–C–H angles which ranged from 103.0° to 115.4°. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2-hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective atoms. The isotropic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded.

(8-(Ethoxydimethylsilyl)-1-naphthyl)dimethylborane (2). A solution of 1,8-diiodonaphthalene[14] (6.0 g, 16 mmol) in Et_2O (150 mL) was cooled to −30 °C and n-BuLi (16 mmol) was added. After 20 min of stirring at −30 °C, the mixture was further cooled to −80 °C and Me_2SiHCl (2.2 mL, 1.9 g, 18 mmol) was added. The solution was allowed to warm to room temperature overnight, washed with concentrated NaCl, dried with $MgSO_4$, filtered, and concentrated to 4.5 g of 88% pure **5a** [^1H NMR ($CDCl_3$) δ 0.43 (d, 6, J = 3. Hz, Me), 5.6 (sept, 1, J = 3 Hz, SiH), 7.0 (t, B of ABC, 1, J = 8 Hz, H-6); 7.3 (B′ of A′B′C′, 1, J = 7 Hz, H-3), 7.6–8.0 (3 d, 3, H-2,4,5), 8.2 (d of d, 1, J = 8 Hz, J' = 1 Hz, H-7)] with the remainder consisting mostly of **7**. Distillation did not improve the purity of **5a**.

The crude **5a** was dissolved in 180 mL of Et_2O and the solution treated with n-BuLi (17 mmol) at −80 °C for 20 min. The cold lithiate solution was added to a second −80 °C solution of Me_2BOEt[7] (2.2 mL, 21 mmol) and n-BuLi (1 mmol) in 25 mL of Et_2O. The combined solution was allowed to warm to 0 °C and then recooled to −80 °C. To this solution was added $MeSO_3H$ (0.92 mL, 1.36 g, 14 mmol), after which the mixture was kept at −80 °C for 1.5 h, allowed to warm to −20 °C, and partially concentrated. The concentrate was taken up in hexane and reconcentrated, the residue was extracted into 40 mL of additional hexane, and the extract was filtered, concentrated, and distilled at reduced pressure. The yield was 2.7 g of 85% pure **2**, the remainder consisting mostly of **7**. The yield of **2** from diiodonaphthalene was 50%: bp 155 °C (0.3 Torr); ^1H NMR δ 0.33 (s, 6, MeSi), 0.63 (s, 6, MeB), 1.42 (t, 3, J = 7 Hz; CH_3C), 4.29 (q, 2, J = 7 Hz, CH_2O), 7.3–8.0 (m, 6, ArH); ^{11}B NMR δ 19; ^{13}C NMR (toluene-d_8) δ 0.33 (MeSi), 11 (br, MeB), 16.9 (MeC), 62.3 (CH_2), 123.6, 126.2, 126.5, 129.8, 130.4, 132.0 (tertiary ArH); ^{29}Si NMR δ 20.3; MS, m/e (rel intensity) 255 ($M^+ - CH_3$, 35), 213 (28), 211 (46), 185 (100), 169 (55), 167 (30). HRMS calcd for $^{12}C_{15}{}^1H_{20}{}^{11}B^{16}O^{28}Si$ (M^+ − 15): 255.1376. Found: 255.1384.

(8-(Fluorodimethylsilyl)-1-naphthyl)dimethylborane (3). A sample of TASF (580 mg, 2.1 mmol) was dissolved in 10 mL of CH_2Cl_2, and **2** (310 mg, ~1 mmol) was added. The resulting solution was swirled at room temperature and then cooled to the freezing point, at which time BF_3OEt_2 (0.32 mL, 2.6 mmol) was added. The solution was allowed to warm to room temperature and left to stand for 2.5 h. It was then partially concentrated, diluted with hexane, and further concentrated. The residue was extracted with hexane, and the extract was concentrated and distilled. The yield was 150 mg (60%) of material, bp 135 °C (0.15 Torr, containing **3**, **8**, and **9** in a 20:1:4 molar ratio. A sample of **3** free of **8** and **9** was obtained by preparative GC. ^1H NMR δ 0.44 (d, 6, J_{HF} = 7 Hz, MeSi), 0.97 (d, 6, J_{HF} = 9 Hz, MeB), 7.3–8.0 (m, 6, ArH); ^{11}B NMR δ 72; ^{19}F NMR δ −151.3 (slightly br); ^{13}C NMR δ 1.1 (d, J_{CF} = 15 Hz, MeSi), 14 (br, MeB), 124.8 (d, J_{CF} = 2 Hz), 125.4 (s), 127.9 (d, J_{CF} = 2 Hz), 130.2 (s), 131.9 (s), 133.6 (d, J_{CF} = 7 Hz); ^{29}Si NMR δ 23 (d, J_{SiF} = 280 Hz); MS, m/e (rel intensity) 244 (M^+, 5), 229 (45), 169 (100), 77 (25). HRMS calcd for $^{12}C_{14}{}^1H_{18}{}^{11}B^{19}F^{28}Si$: 244.1255. Found: 244.1247.

Tris(dimethylamino)sulfonium Fluoro(8-(fluorodimethylsilyl)-1-naphthyl)dimethylborate (3·F⁻·TAS). Dichloromethane (2 mL) was vacuum transferred onto a sample of **3** (120 mg). A solution of TASF (115 mg) in 1 mL of CH_2Cl_2 was added. The mixture was partially concentrated, triturated with hexane, and further concentrated at 6 × 10^{-4} Torr to 110 mg of an amorphous white solid: ^1H NMR δ −0.05 (br d, 6, MeB), 0.4 (br d, 6, MeSi), 2.6 (s, 18, MeN), 7.3 (m, 4, ArH), 7.65 (d, 1, ArH), 8.0 (d, 1, ArH); ^{11}B NMR δ 15; ^{19}F NMR δ −98 (br, SiF), −130 (v br, BF). Anal. Calcd for $C_{20}H_{36}BF_2N_3SSi$: C, 56.19; H, 8.49; N, 9.83; B, 2.53. Found: C, 56.03; H, 8.74; N, 9.61; B, 2.10. Exposure of **3·F⁻** to moisture caused its decomposition to an oxy-bridged anion with loss of 2 equiv of HF.

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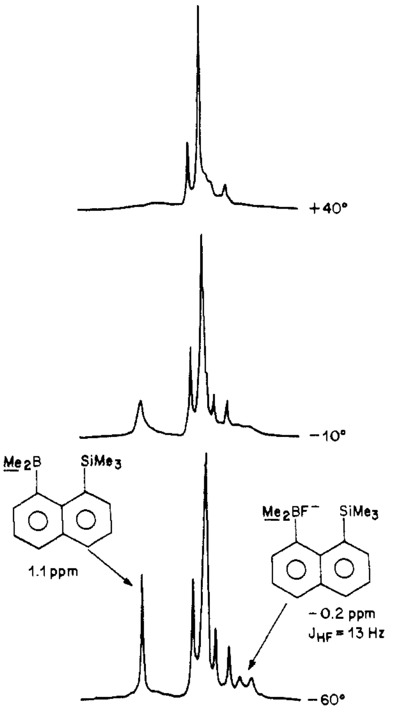


Figure 1. Upfield region of the ^1H NMR spectrum of **1**, 1 M in CD_2Cl_2, containing Me_4Si and 0.5 equiv of TASF, recorded at three different temperatures. Trimethylsilyl fluoride and 1-naphthyltrimethylsilane are present as nonparticipating impurities.

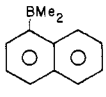
Table I. Rates of F^- Exchange among Molecules of **1**, 1 M in CD_2Cl_2, at Selected Temperatures

T (K) ± 2 K	k (s^{-1}) ± 5%
243	13
253	19
263	31
273	53
283	97
(323)	(480)

Results

Fluoride Complex of 1. The formation of a discrete complex upon treating **1** with TASF was first evidenced in the NMR spectrum by the marked upfield shift and splitting of the BMe proton signals. The SiMe protons were shifted, but less drastically. The chemical shifts of the ^{19}F and ^{11}B nuclei were consistent with the assigned structure. Of special interest was the ^{29}Si NMR signal, which was a doublet shifted 6.38 ppm upfield of the singlet observed for free **1**.

Exchange of F^- among molecules of **1** was slow on the NMR time scale. The BMe protons displayed line-broadening and coalescence as shown in Figure 1. Reversible coalescence was observed in both CD_2Cl_2 and CD_3CN, and the coalescence temperature was strongly concentration dependent. Line widths of noncoalesced signals were used to determine a series of rate constants at a set of temperatures (Table I). A plot of log (k/T) calculated from those rate constants vs. $1000/T$ is shown in Figure 2. From the slope of the line, we estimate $\Delta H^{\ddagger} \cong 6.4$ kcal/mol for the exchange reaction. Dimethyl(1-naphthyl)borane[7] (**4**) exchanged F^- at a rate too fast to estimate by NMR even at −60 °C. However, a >2:1 mixture of **4**·F^- and **4** did not donate *any* F^- to **1**.



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The structure of **1**·F^- was confirmed by X-ray crystallography. Lists of pertinent bond lengths and angles appear in Tables II and III, respectively, with a complete set of data deposited as supplementary material. Diagrams of the crystal structure comprise Figures 3–5.

Table II. Bond Lengths in the Anion of Crystalline **1**·F^-·TAS[a]

type	length, Å	type	length, Å
C_1–B	1.657 (8)	C_8–Si	1.891 (5)
B–C_{1m}	1.623 (8)	Si–C_{3m}	1.867 (6)
B–C_{2m}	1.617 (8)	Si–C_{4m}	1.886 (7)
F–B	1.475 (6)	Si–C_{5m}	1.860 (6)
F–Si	2.714 (7)	C_1–C_{8a}	1.449 (7)
C_1–C_2	1.378 (7)	C_2–C_3	1.402 (8)
C_3–C_4	1.342 (8)	C_4–C_{4a}	1.407 (7)
C_5–C_6	1.350 (9)	C_{4a}–C_5	1.400 (8)
C_6–C_7	1.411 (8)	C_{4a}–C_{8a}	1.446 (7)
C_7–C_8	1.382 (8)	C_8–C_{8a}	1.451 (6)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

Table III. Bond Angles in the Anion of Crystalline **1**·F^-·TAS[a]

type	angle, deg	type	angle, deg
C_1BF	110.0 (4)	C_8SiC_{3m}	115.0 (3)
C_1BC_{1m}	106.5 (4)	C_8SiC_{4m}	104.5 (3)
C_1BC_{2m}	114.7 (4)	C_8SiC_{5m}	112.5 (2)
FBC_{1m}	106.6 (4)	$C_{3m}SiC_{4m}$	103.7 (3)
FBC_{2m}	108.3 (4)	$C_{3m}SiC_{5m}$	115.7 (3)
$C_{1m}BC_{2m}$	110.5 (5)	$C_{4m}SiC_{5m}$	103.4 (3)
BC_1C_2	115.0 (4)	$C_{4a}C_5C_6$	121.9 (5)
BC_1C_{8a}	126.5 (4)	$C_5C_6C_7$	118.7 (5)
$C_2C_1C_{8a}$	116.3 (5)	$C_6C_7C_8$	123.2 (5)
$C_1C_2C_3$	124.3 (5)	C_7C_8Si	113.2 (4)
$C_2C_3C_4$	118.8 (5)	$C_{8a}C_8Si$	127.5 (4)
$C_3C_4C_{4a}$	121.5 (5)	$C_7C_8C_{8a}$	117.7 (4)
$C_4C_{4a}C_5$	121.1 (5)	$C_8C_{8a}C_1$	124.8 (4)
$C_4C_{4a}C_{8a}$	119.2 (5)	$C_8C_{8a}C_{4a}$	117.3 (4)
$C_5C_{4a}C_{8a}$	119.7 (5)	$C_1C_{8a}C_{4a}$	117.9 (4)
$BC_1C_{8a}C_8$	32.3[b]	$SiC_8C_{8a}C_1$	29.0[b]

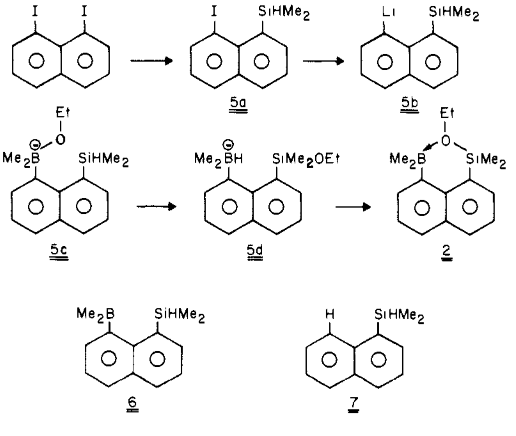
[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Dihedral angle.

Table IV. ^{11}B and ^{29}Si NMR Shifts of Aryl Boranes and Silanes

compd	$\delta(^{11}B)$	ref	(δ ^{29}Si)	ref
4	80[a]	7		
$PhSiMe_3$			−4.50	15
α-$C_{10}H_7SiMe_3$			−4.15	*b*
1	74.6	11	−3.48	*b*
1·F^-	5	*b*	−9.86[c]	*b*
$PhSiMe_2OEt$			5.1	15
2	19	*b*	20.3	*b*
$PhSiMe_2F$			19.8[d]	15, 16
3	72	*b*	23[e]	*b*
3·F^-	15	*b*	*f*	*b*

[a] In CD_2Cl_2. [b] This work. [c] J_{Si-F} = 13.2 Hz. [d] J_{Si-F} = 278 Hz. [e] J_{Si-F} = 280 Hz. [f] Not observable.

Scheme I



Formation and Reactions of 2 and 3. Iodosilane **5a**, prepared from 1,8-diiodonaphthalene,[14] was treated sequentially with BuLi

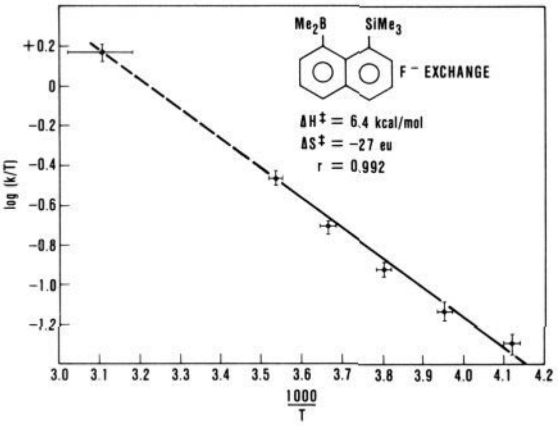


Figure 2. Plot of log (k/T) vs. $1000/T$ for data of Table I. The straight line was calculated by least squares, not including the point at 325 K which was obtained at the estimated coalescence temperature.

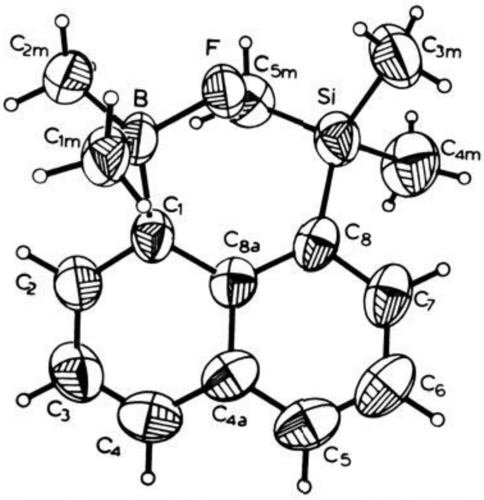


Figure 3. Perspective ORTEP drawing of $1{\cdot}F^-$ in crystalline $1{\cdot}F^-{\cdot}TAS$ with non-hydrogen atoms represented by thermal vibration ellipsoids encompassing 50% of their electron density.

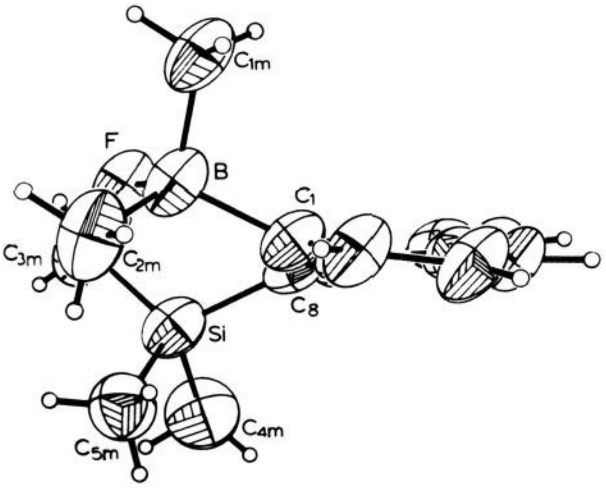


Figure 4. "Side view" ORTEP drawing of $1{\cdot}F^-$ in crystalline $1{\cdot}F^-{\cdot}TAS$.

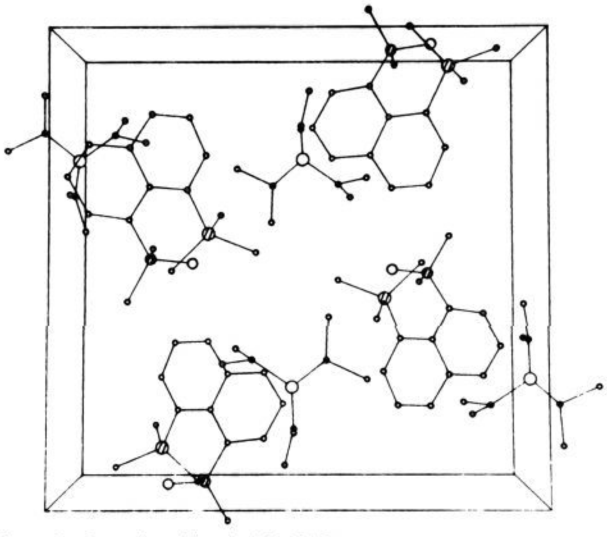


Figure 5. Crystal packing in $1{\cdot}F^-{\cdot}TAS$.

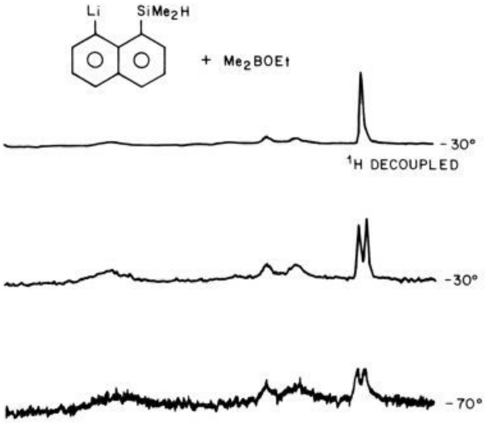
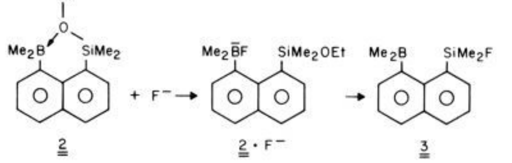


Figure 6. Boron-11 NMR spectra of **5b** + Me_2BOEt in Et_2O.

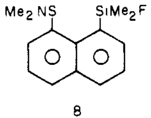
(to form **5b**), Me_2BOEt,[7] and $MeSO_3H$ with the intent of preparing **6** (Scheme I). Analysis of the product mixture by NMR revealed the unexpected lack of Me_2SiH groups in the major product, Me_2B signals considerably upfield and a ^{29}Si peak considerably downfield from predicted values for **6** (see Table IV), and the presence of low-field EtO multiplets. These data in conjunction with GC–MS enabled us to assign the structure **2** to the major product. The chief contaminant, ~15% of the mixture, was **7**. The peculiar positions of the Me_2B and SiOEt NMR peaks must be due to a bridging Si–O–B bond in **2**.

In order to possibly elucidate the mechanism of formation of **2**, the synthesis was monitored by low-temperature ^{11}B NMR. A mixture of **5b** and Me_2BOEt (1 equiv only) at −70 °C appeared to be reacting slowly, with broad signals for Me_2BOEt (~50 ppm) and various borate intermediates (~0 ppm) (Figure 6), presumably including **5c**. After warming the solution to −30 °C, the ^{11}B NMR spectrum was dominated by a well-resolved doublet at −20 ppm, which collapsed to a singlet upon broad-band ^1H irradiation. By analogy to $4{\cdot}H^-$ (δ $^{11}B = -19$ ppm, $J_{BH} = 29$ Hz),[7] the doublet may be attributed to borohydride **5d**, which would in turn lead to **2** on protonation.

Treatment of **2** with TASF gave a species, most likely $2{\cdot}F^-$, that features the now-familiar upfield Me_2B ^1H NMR doublet.



The EtO protons also were shifted markedly upfield, indicating the breaking of the SiOB bridge. Addition of $MeSO_3H$ or BF_3OEt_2 to a solution of $2{\cdot}F^-{\cdot}TAS^+$ gave **3**, rather than **2**. A slower but cleaner reaction resulted when BF_3OEt_2 was employed. Interestingly, the ^1H–^{19}F coupling constant in **3** is larger for the Me_2B group than for the Me_2Si group, and the ^{19}F peak is slightly broadened by the ^{11}B nucleus, even though the ^{11}B and ^{29}Si NMR shifts indicate an extremely weak interaction between F and B (Table IV), in contrast to the significant O–B bond in **2**. The TAS cation was not entirely innocent in this system, since a small amount (5%) of side product **8** was observed in the product mixture, in addition to contamination by **9**. The identities of the byproducts were confirmed by MS and HRMS, while **3** itself was characterized by elemental analysis as its F$^-$ complex.



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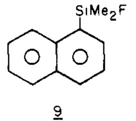

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The methyl signals of **3**·F$^-$ were extremely broad, possibly indicating slow interconversion of rotational isomers or pseudorotation at Si.[10,17] The F–Si ^{19}F signal was also unusually broad, but it sharpened to a doublet of multiplets below +10 °C. Irreversible F$^-$ abstraction by **3** from **1**·F$^-$ was observed, indicating greater participation by Me$_2$FSi than by Me$_3$Si in F$^-$ binding. However, **3**·F$^-$ was still less stable than **4**·F$^-$.

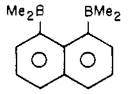
Discussion

Structure of Neutral Silylnaphthylboranes. Compound **1** belongs to the class of compounds known as 1,8-"permethylelement" naphthalenes.[18] Its structure appears to be influenced very little by polar effects, but it may involve some steric compression of the methyl groups. Molecular models indicate that this compression should be minor in view of the different bond lengths and angles at B and Si. However, peri-metalloidal groups on naphthalene and other annulenes[19] often cause geometric distortions at the ipso ring carbons in response to steric crowding. Small deviations of the NMR parameters of **1** from expected values most likely reflect these geometric changes.

Multinuclear NMR spectra of **2** differ substantially from **1** and other model compounds (Table IV). The ethoxy group of **2** is driven both sterically[20] and electronically to the space between the B and Si atoms. The result is an intramolecular Lewis acid–Lewis base interaction between O and B, making **2** the first example of complexation between a silyl ether and a borane. The O of a silyl ether is not an especially basic atom, less basic than the O of a dialkyl ether,[21] and it may be that geometric enforcement is necessary in order to observe strong Lewis donor-acceptor interactions between silyl ethers and triorganoboranes. In the case of **2**, the various NMR chemical shifts point to significant bonding between O and B. Indeed, if one of the Me groups on B were replaced by another organic substituent, the resulting compound would likely be chiral, since one would expect an almost complete absence of rotation about the Ar–B bond.

The F atom in **3** is even more sterically disposed[20] to be between B and Si than is the OEt group of **2**. Because of the extremely strong SiF bond,[22] there should be very little electron density on F available for donation to B in **3**. Nevertheless, the weak FB interaction does slightly perturb the NMR spectra of **3**.

Structure of F$^-$ Complexes of 1 and 3. Complexes **1**·F$^-$ and **3**·F$^-$ are the first anion complexes of bidentate Lewis acids in which one of the Lewis acid receptor groups is fractionally hypervalent. Evidence for participation by hypervalent Si in bonding to F$^-$ was obtained in solution by NMR spectroscopy and, in the case of **1**·F$^-$, in the solid state by X-ray crystallography. Proton signals arising from the Me groups of **1**·F$^-$ and **3**·F$^-$ are much broader than those of the corresponding neutral silylnaphthylboranes and also those of **10**·F$^-$.[7] Also, the F bound only to Si in **3**·F$^-$ gives a broader peak than does the F in neutral **3**. The ^{29}Si NMR spectrum of **1**·F$^-$ is a doublet, shifted 6.38-ppm upfield from the singlet exhibited by neutral **1**, indicative of fractional pentavalency[23] in **1**·F$^-$. The ^{29}Si nucleus in **3**·F$^-$, split by 2 nonequivalent ^{19}F nuclei and possibly existing in a mixture of isomers, was not observable. The positions and shapes of these NMR peaks are consistent with a bridging interaction of the boron-bound F$^-$ and Si.



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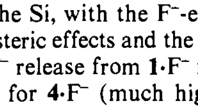
In addition, we calculate a $\Delta H^{\ddagger}$ for F-exchange among neutral **1** molecules of 6.4 kcal/mol. This is in marked contrast to F$^-$ exchange in simple boranes such as **4**,[7] BEt$_3$,[7] and BF$_3$,[24] which proceeds with no apparent $\Delta H^{\ddagger}$ or perhaps via stable intermediates. Examination of molecular models of **1**·F$^-$ with the F$^-$ oriented *away* from the Si reveals that such a conformer would suffer no steric barrier to the approach of a second molecule of **1** and subsequent F$^-$ transfer. It is therefore logical to surmise that the F$^-$ in **1**·F$^-$ is oriented *toward* the Si, with the F$^-$-exchange barrier caused by a combination of steric effects and the breaking of a weak F–Si bond. The rate of F$^-$ release from **1**·F$^-$ is intermediate between corresponding rates for **4**·F$^-$ (much higher) and **10**·F$^-$ (much lower).[7] Considering the importance of F$^-$ transfer reactions in various catalytic processes,[25] and the potential importance of anion transfer in ionic conductivity,[3] it is useful to establish criteria for achieving various rates of F$^-$ and other anion exchanges.

Confirmation of the F–Si interaction in **1**·F$^-$ was provided by X-ray crystallography. The F$^-$ is directed toward Si, and the F–Si distance of 2.714 Å is much less than the sum of the van der Waals radii of Si[26] and F[27] (3.4 Å). Distances and angles about Si are very similar to analogous parameters in the hypervalent aminosilane **11**;[28] in both cases the Si atom is distorted toward trigonal-bipyramidal geometry. The deviations of the C–B and C–Si bonds from planarity are not unexpected, since other crowded 1,8-disubstituted naphthalenes suffer distortions at the peri bonds as well.[18]



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Although NMR and crystallographic evidence establish the participation of Si in binding F$^-$ to **1**, the suitability of the Me$_3$Si substituent is far from ideal.[29] Replacing some or all of the Me substituents on Si with groups that form more polarizable bonds, increasing the electronegativity of the Si atom, and incorporating the Si into a 4- or 5-membered ring would all increase the affinity of the Si for an additional ligand. Repulsion of methyl groups on B and Si destabilizes **1**·F$^-$ as well. Indeed, replacement of one Me group on **1** with F, conceptually forming **3**, increases the electronegativity at Si (while exerting a minimal through-space inductive effect)[30] and also may relieve some of the steric crowding

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(26) VDW radius of Si: 2.0 Å. *Lange's Handbook of Chemistry*; Dean, J. A., Ed.; McGraw-Hill: New York, 1979.

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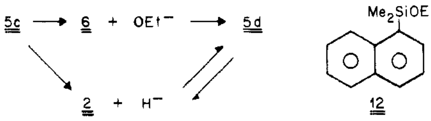
(30) ^{13}C NMR shifts for C-2 and C-3 of PhSiMe$_3$ are nearly identical with those of PhSiMe$_2$F.[16]

Scheme II



of the corresponding F$^-$ complex. We do in fact observe that **3**·F$^-$ is more stable than **1**·F$^-$. However, steric effects destabilize both **1**·F$^-$ and **3**·F$^-$ so that even the Si–F bonding does not fully compensate, as evidenced by the still greater stability of **4**·F$^-$.

Anion Rearrangement in 5c and 2. We initially set out to prepare **6** as an analogue of **1** because of the expected reduction in steric strain with one less Me group. We were intrigued to discover that our synthetic procedure led instead to **2**. It is clear from the low-temperature NMR data that the initially formed ate complex, **5c**, is extremely short-lived, rearranging rapidly to **5d** (Scheme I). By using the crystal structure of **1**·F$^-$ as a basis for constructing a model of **5c**, it is apparent that **5c** is poised to undergo an intramolecular, suprafacial S_N2 reaction at Si, and that minimal bond movement is necessary for this substitution to proceed. It has been previously observed that replacement reactions at Si involving H$^-$ and RO$^-$ do generally go with retention of configuration and via pentacoordinate intermediates.[29,31] The Si atom of **5c** may well be pentacoordinate, thereby resembling the Si that one might postulate in the transition-state structure for the conversion of **5c** to **5d**. By analogy, **1**·F$^-$ may be viewed as an image of a near-transition-state structure for S_N2 at Si.

The low-temperature ^{11}B NMR spectra do not rule out alternative intermolecular mechanisms for the transformation of **5c** to **5d** (Scheme II). However, other circumstantial evidence makes them unlikely. Any mechanism involving H$^-$ dissociation without participation by B would mean that **7**, present as an impurity, would have been converted to **12**; in fact, **7** does not react. Free H$^-$ in the solution would react with Me_2BOEt to form Me_2HBOEt^-, which would have given rise to a second borohydride signal. Reaction of dissociated EtO$^-$ with **13** would proceed via an S_N2-inversion transition state, a less favored process for EtO$^-$ and H$^-$ than retention,[31] and in any event, dissociation of EtO$^-$ from an R_3B species is not facile below −20 °C.[32]

The reaction of **2**·F$^-$ with an acid to form **3** also most likely proceeds via an intramolecular anion transfer. Coordination of EtO with the acid would render it a good leaving group, and F may be partially bound to Si (as in **1**·F$^-$) prior to the actual reaction. One can also imagine a reversion of **2**·F$^-$ to **2** on acid treatment, and this may actually occur to a small extent when $MeSO_3H$ is employed. However, the major products observed in the anion transfer of **2**·F$^-$ and also **5c** are the ones that one would predict based on the relative strengths of the various bonds to Si.[22]

Summary. We have presented an in-depth examination of the structure and dynamics of 8-silyl-1-naphthylborane anion complexes. In so doing, we have reported the first examples of participation of a neighboring silyl group in the complexation of anions to a borane and the first instance of silyl ether coordination to boron. We have also observed an extremely facile anion rearrangement between B and Si atoms (**5c** → **5d**) that is probably intramolecular. The results advance our understanding of cooperative anion coordination, anion transfer processes, and the chemistry of hypervalent Si. Further work on multidentate anion binding is in progress.

Acknowledgment. We are grateful to A. M. Mujsce for performing GC–MS analyses. The alumina sample tube for ^{29}Si NMR was a generous gift of Wilmad Glass Co. Inc. We also thank R. L. Cerny of the Midwest Center for Mass Spectroscopy, Lincoln, NE (a National Science Foundation Regional Instrument Facility, Grant No. CHE 8211164), for obtaining HRMS data. The synthesis of 1,8-diiodonaphthalene was performed by the Michigan State University Synthesis Laboratory.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, bond angles, dihedral angles, and nonbonded distances for crystalline **1**·F$^-$·TAS (14 pages). Ordering information is given on any current masthead page.

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