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Ion Pair Carbon Acidities of Some Silanes in Tetrahydrofuran[1]

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The relative solvent-separated ion pair (SSIP) lithium acidity (p$K_{\mathrm{Li/THF}}$) and contact ion pair (CIP) cesium acidity (p$K_{\mathrm{Cs/THF}}$) were obtained for 9-fluorenyltrimethylsilane (**1**) (21.3, 21.6, respectively) and 9-fluorenyl-*tert*-butyldimethylsilane (**2**) (20.3, 20.6, respectively) in THF. Values for p$K_{\mathrm{Cs/THF}}$ were determined at 25 °C for (*p*-biphenylylmethyl)-*tert*-butyldimethylsilane (**3**), 35.4, benzyltrimethylsilane (**4**), 37.5, α,α-bis(trimethylsilyl)toluene (**5**), 34.1, 2-(trimethylsilyl)-1,3-dithiane (**6**), 33.5, (trimethylsilyl)acetonitrile (**7**), 28.8, and tris(trimethylsilyl)methane (**8**), 36.8. Some thermodynamic parameters were determined by measurements at other temperatures, and some ionic acidities (pK(FI)) were determined by conductivity studies. Carbanion stabilization by these silyl substituents varies from about 1 to over 3 pK units in different systems. 9,9-Bis(trimethylsilyl)fluorene (**9**) was found to undergo silyl transfer on treatment with various carbanions, but this reaction is slower than proton transfer.

Silicon-stabilized carbanions have become versatile intermediates in organic synthesis.[2] The earlier example of their use in the Peterson olefin synthesis[3] has recently been supplemented by many additional reactions using silicon-stabilized carbanions.[4] Several methods are available to generate these anions but proton abstraction by a lithium base provides a useful and common method. Kinetic and equilibrium acidity factors are important in the relative ease of deprotonation of such silanes. It has been well-documented that the trialkylsilyl group can behave as a weak electron acceptor when directly linked to a conjugated system. Examples are acidity measurements of trimethylsilyl-substituted anilinium ions and phenols,[5] infrared intensity studies of phenyltrimethylsilane,[6] and hydrogen isotope exchange rates of *m*- and *p*-(trimethylsilyl)toluenes with lithium cyclohexylamide in cyclohexylamine.[7]

In recent years, there has been increasing interest in the effect of silyl groups on carbon acidity. Ab initio MO calculations on silyl-substituted carbanions have been used to investigate the effect,[8,9] but the first experimental quantitative measurements of the silyl group stabilization effect on carbanions were done by Petrov et al., who reported the pK_a's of (trimethylsilyl)acetylene and (triethylsilyl)acetylene in DME with lithium as the gegenion to be 24.6 and 24.9,[10] respectively, on a scale in which the pK of *tert*-butylacetylene is 26.0; thus, the effect of the silicon group in this system is about 1 pK unit. More recently, Miah and Fraser reported equilibrium lithium ion pair acidities of benzyltrimethylsilane[11] and [(phenylthio)methyl]trimethylsilane[12] to be greater than that of toluene by NMR measurements with lithiated tetramethylpiperidine.

Eaborn et al. found that tris(trimethylsilyl)methane-*t* undergoes tritium exchange in DMSO/H_2O/KOH about 5–7 times faster than triphenylmethane.[13] From the experimental electron affinity of (trimethylsilyl)methyl radical. Wetzel and Brauman[14] have estimated that silicon stabilizes an alkyl anion by 20 kcal mol^{-1} in the gas phase. Bordwell has reported ionic pK's for several silyl-substituted carbon acids in DMSO:[15] 9-fluorenyltrimethylsilane, 21.7 (1.2 pK units per hydrogen more acidic than fluorene), (trimethylsilyl)malonic ester, 19.0 (2.3 pK units *less* acidic than malonic ester but 1.5 pK units more acidic than isopropylmalonic ester), and [(phenylsulfonyl)methyl]triphenylsilane, 21.3 (7.7 pK units lower than phenyl methyl sulfone). These results indicate that the carbanion-stabilizing effect of a silyl substituent is highly variable.

To provide further quantitative understanding of the effect of silyl substitution on carbon acidity and the effect of different metal counterions we determined the acidity in THF of the following compounds: 9-fluorenyltrimethylsilane (**1**), 9-fluorenyl-*tert*-butyldimethylsilane (**2**), (*p*-biphenylylmethyl)-*tert*-butyldimethylsilane (**3**), benzyltrimethylsilane (**4**) and α,α-bis(trimethylsilyl)toluene (**5**). The lithium salts (**1L** and **2L**) were shown to be solvent-separated ion pairs (SSIP), and the cesium salts are undoubtedly contact ion pairs (CIP). The results are

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Table I. Spectral Data for the Salts of 1-4 in THF at 25 °C

	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
1L	364	12 000
2L	363	12 000
1C	356	9760
2C	356	9760
3C	472	43 800
4C	372	19 210
5C	373	18 300

expressed relative to our ion pair acidity scales[16-19] as $pK_{Li/THF}$(SSIP) and $pK_{Cs/THF}$(CIP). Some ion pair dissociation constants were determined by conductivity measurements to give the corresponding relative free ion acidities, p*K*(FI). Concentration measurements and thermodynamic data further confirmed the p*K* assignments. In the course of these measurements we observed some silyl group transfer reactions. Silyl group transfer is slower than proton transfer and is much slower for *tert*-butyldimethylsilyl than for trimethylsilyl. Additional measurements were made on compounds expected to give more localized carbanions: 2-(trimethylsilyl)-1,3-dithiane (**6**), (trimethylsilyl)acetonitrile (**7**), and tris(trimethylsilyl)methane (**8**).

Results and Discussion

Ion Pair Acidities. The types of ion pairs involved were determined by spectroscopic analysis. 9-Lithio-9-(trimethylsilyl)fluorene (**1L**) and 9-lithio-9-(*tert*-butyldimethylsilyl)fluorene (**2L**) in THF have visible spectra similar to that of unsubstituted 9-lithiofluorene. The λ_{max}'s of **1L** and **2L** are at 364 and 363 nm, respectively. The shapes of the spectra do not depend on the concentrations of the salts, and λ_{max}'s do not change with decrease in temperature to −30 °C. Addition of 15-crown-5, a powerful coordinating agent for lithium cation, does not change the λ_{max}. The λ_{max}'s of the corresponding cesium salts (**1C** and **2C**) are both 356 nm, a decrease of 8 nm relative to the lithium salts. The spectra are similarly insensitive to changes in salt concentration and temperature. As has been observed generally for fluorenyl anions, solvent-separated ion pairs (SSIP) have longer λ_{max} than the corresponding contact ion pairs (CIP).[20] It is clear by analogy that the lithium salts **1L** and **2L** are SSIPs and the cesium salts **1C** and **2C** are CIPs. The cesium salts **3C** and **4C**[21] are also assumed to be CIP. Thermodynamic and conductivity measurements of the lithium and cesium salts provide further confirmation of these ion pair assignments and will be discussed later.

Spectral data for the study are presented in Table I. The accuracy of the extinction coefficient values for all compounds (direct titration) except **4** is estimated as ±5%. The extinction coefficient of **4** was measured by an alternative method (see Experimental Section), and the uncertainty is estimated to be 5–8%. The λ_{max}'s of the silicon-stabilized carbanions do not shift significantly relative to the anions of the parent hydrocarbons, and a change in substitution on the silicon from methyl to *tert*-butyl does not substantially change the spectra of the cesium and lithium salts.

Table II. Relative Ion Pair Acidities of 1-4 with Indicators in THF at 25 °C[a]

RH	M^+	InH[b]	$\Delta pK_{M/THF}$	$pK_{M/THF}$	$pK_{M/THF}$ av
1	Li^+	BA	1.18 ± 0.02	21.31	21.3
		BnMP	0.01 ± 0.03	21.36	
	Cs^+	9-MeFl	−0.75 ± 0.03	21.59	21.6
		4,5-MP	−1.22 ± 0.06	21.69	
2	Li^+	BA	0.11 ± 0.01	20.24	20.3
		BnMP	−1.03 ± 0.06	20.32	
	Cs^+	9-BnFl	−0.73 ± 0.02	20.57	20.6
		9-MeFl	−1.69 ± 0.10	20.63	
		4.5-MP	−2.31 ± 0.11	20.60	
3	Cs^+	DPM	2.13 ± 0.06	35.38	35.4
		DoTM	1.15 ± 0.01	35.37	
		DmXM	−0.62 ± 0.01	35.34	
4	Cs^+	p-MB	−1.3	37.5	37.5
		PpTS	0.4	37.6	
5	Cs^+	DPM	0.88	34.1	34.1
		DoTM	−0.06	34.2	
6	Cs^+	DPM	0.2	33.5	33.5
		DoTM	−0.7	33.5	
7	Cs^+	9-PSX	1.0	28.9	28.8
		DP3	0.8	28.7	
8	Cs^+	PpTS	−0.2	37.0	36.8
		DmXM	0.7	36.7	

[a] Per hydrogen. [b] Abbreviations and p*K*'s of indicators: lithium salts,[17] BA, benzanthrene, 20.13; BnMP, 9-benzylbenzo[*def*]fluorene, 21.35; cesium salts,[19] 9-BnFl, 9-benzylfluorene, 21.30; 9-MeFl, 9-methylfluorene, 22.32; 4,5-MP, 4,5-methylenephenanthrene, 22.91; DPM, diphenylmethane, 33.25; DoTM, di-*o*-tolylmethane, 34.22; DmXM, di-*m*-xylylmethane, 35.96; *p*-MB, *p*-methylbiphenyl, 38.73; PpTS; phenyl *p*-tolyl sulfide, 37.2, and PSX, 9-(phenylthio)xanthene, 27.88 (to be published).[37]

Table III. Aggregation Study of 1L in THF at 25 °C[a]

1L × 10^4 (M)	$pK_{Li/THF}$
13.2	21.38
6.56	21.36
3.05	21.36
0.759	21.32
0.568	21.30

[a] BnMP uased as indicator.

In recent papers, this laboratory has presented revised indicator scales of transmetalation potentials in THF with cesium and lithium as the gegenions.[16-19] The arbitrary reference point is that of fluorene at $pK_a = 22.90$ per hydrogen for the two scales. Employing the same technique as before, the ion pair acidity differences (ΔpK's) of these salts were determined by measuring the equilibrium (1) spectroscopically.

$$RH + In^-M^+ \rightleftarrows R^-M^+ + InH \qquad (1)$$

Table II lists the ion pair acidity results of the silicon compounds with different indicators. The concentrations used are in the range of 10^{-4} to 10^{-3} M, and the equilibrium constants do not change with concentration. An example is shown in Table III in which the pK_{Li} of **1** relative to 9-benzyl-9*H*-benzo[*def*]fluorene (BnMP, benzylmethylenephenanthrene) remains the same within experimental error over a 20-fold range in concentration. The apparent slight change with concentration corresponds to an average degree of aggregation of 1.05.[22] The carbanion solutions

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Table IV. Rates of Equilibration of Cesium Salts of Benzyltrimethylsilane and *p*-Methylbiphenyl in THF at 25 °C

[$PhCH_2TMS$] (M)	[$BiPhCH_2Cs$] (M)	10^5k_{obs} (s^{-1})	10^4k_2 (M^{-1} s^{-1})
4.60×10^{-2}	2.71×10^{-4}	61.6[a]	133
		67.4[b]	145
3.13×10^{-2}	4.32×10^{-5}	40.2[a]	128
		41.8[b]	134
		avg:	135

[PhCHCsTMS] (M)	[$BiPhCH_3$] (M)	10^5k_{obs} (s^{-1})	10^4k_{-2} (M^{-1} s^{-1})
5.25×10^{-5}	0.111	9.27[c]	8.35
		10.4[d]	9.38
4.37×10^{-5}	0.668	5.13[c]	7.69
		5.29[d]	7.95
		avg:	8.34

[a] From decrease in absorbance at 472 nm. [b] From increase in absorbance at 372 nm. [c] From decrease in absorbance at 372 nm. [d] From increase in absorbance at 472 nm.

were stable for several hours in the glovebox. The major source of error is most likely the extinction coefficient values used to convert absorbance readings to concentrations; unless noted, the accuracy of the pK values listed in Table II is about ±0.1 pK unit.

At high pK's the rates of proton transfer are slow. For **4** the equilibria required about 8 h and permitted kinetic measurements. These were made from both directions so that the equilibrium constant could be obtained from k_2/k_{-2}. The results for the equilibrium of **4** with the cesium salt of *p*-methylbiphenyl are summarized in Table IV. The rate ratio of 16 corresponds to $\Delta pK = -1.2$ from which the pK of **4** is 37.3, in good agreement with the equilibrium results. Less extensive study was made of **5**, but results with two indicators gave concordant results; the cesium salt of **5** showed spectral changes indicating decomposition on long standing (several hours).

The p$K_{Cs/THF}$ value obtained here for **4**, 37.5, does not agree well with the p$K_{Li/THF}$ value, 38.9, derived by Miah and Fraser.[11] The latter value comes from NMR measurements of equilibria with tetramethylpiperidine. The lithium pK, if anything, should be lower than the cesium value because the lithium salt has been shown to be a CIP.[21] It seems likely that the lithium amide pK's are in error because known aggregation effects were not taken into account.

The results show significant contrasts in the carbanion stabilization of silicon. The trimethylsilyl group stabilizes fluorenyl anion by only about 1 unit both for cesium and lithium ion pairs (p$K_{Li/THF}$ and p$K_{Cs/THF}$ = 22.90 for fluorene; p$K_{Li/THF}$ = 21.67, p$K_{Cs/THF}$ = 21.32 for **1**). Stabilization by the *tert*-butyldimethylsilyl group is somewhat greater, about 2 pK units. A similar comparison of the acidities of 4-methylbiphenyl (p$K_{Cs/THF}$ = 38.73) and **3** (p$K_{Cs/THF}$ = 35.36) demonstrates that the acidity-enhancing effect of the *tert*-butyldimethylsilyl group is now higher at 3.4 pK units. For toluene, p$K_{Cs/THF}$ has been shown to be 40.9.[19] The pK of 37.5 for **4** also shows stabilization by the TMS group of 3.4 pK units. Similarly, incorporation of a second TMS group into the methyl group of toluene results in a further decrease in pK by 3.4 units; these results show that the effect of TMS groups is approximately additive. The difference in the magnitude of the stabilization is probably associated with the relative degrees of delocalization of charge in the two cases. In the benzyl and biphenylylmethyl anion there is effectively greater charge at the site of substitution and the stabilization effect of the silyl group is greater.

Table V. Overlapping Thermodynamic Measurements[a]

M^+	R_1H[b]	R_2H	$\Delta H°$[c]	$\Delta S°$[d]
Li^+	**2**	BA	−0.6	−1.6
	BnMP	**2**	−1.5	0.2
	BnMP	BA	−2.1 (−2.9)[e]	−1.4 (−1.45)[e]
Cs^+	**2**	9-MeFl	2.7	1.1
	9-BnMP	**2**	−1.4	−1.3
	9-BnFl	9-MeFl	1.3 (1.7)[e]	−0.2 (−0.8)[e]

[a] For the reaction $R_1M + R_2H \rightleftarrows R_1H + R_2M$. [b] See Table II for abbreviations. [c] In kcal mol^{-1}. [d] In eu corrected for symmetry. [e] Direct measurement in parentheses.

This generalization was extended to other carbanions expected to be relatively localized. Measurements were made of the cesium ion pair acidities of **6**, **7**, and **8**. These measurements were done with the single indicator technique, but recent improvements in this technique have provided results of good precision.[23] The cesium salt of 1,3-dithiane has been shown to be monomeric in dilute THF solution.[23] It seems probable that the cesium salt of 2-(trimethylsilyl)-1,3-dithiane, **6C**, is also monomeric; the TMS group in **6** causes a decrease in pK by about 3 units. Possible aggregation of the cesium salts of **7** and **8** could not be determined. It seems likely by comparison with the dithianes that **8C** is monomeric but **7C** could well be aggregated. An incremental effect of 3–3.5 pK units per TMS group provides an extrapolation from **8C** to the p$K_{Cs/THF}$ of methane of about 47; this value compares with the recent estimate of 48–49 derived from dithianes.[23]

Note that the effect of a TMS group is significantly less than that of phenyl. Triphenylmethane (p$K_{Cs/THF}$ = 31.26) is substantially more acidic than **8** in contrast to the relative kinetic acidities.[13] This comparison emphasizes that Brønsted correlations are different for localized and delocalized carbon acids.

Thermodynamic Data. The pK's of **2** were determined at several temperatures over the range of 25 to −20 °C. $\Delta H°$ and $\Delta S°$ for the ion pair equilibria were then determined via Van't Hoff plots. The results recorded in Table V show satisfactory agreement and indicate that the p$K_{M/THF}$ values and the derived thermodynamic quantities have no important systematic errors. The values given are expected to be correct to about 0.5 kcal mol^{-1} and 1.0 eu for $\Delta H°$ and $\Delta S°$, respectively.[16] An alternative approach is to analyze the thermodynamic parameters on the basis of a scale anchored on a single indicator. For the cesium runs, fluorene is a convenient standard; however, fluorenyllithium is a mixture of contact- and solvent-separated ion pairs at room temperature[20] and 9-phenylfluorene serves as a more convenient reference.[17] In Table VI the relative enthalpy and entropy data for the salts of **2** are listed together with the values of some indicators. The enthalpy changes show the carbanion-stabilizing effect of the silyl group—1.5–2 kcal mol^{-1} relative to methyl or benzyl—but the entropy changes are comparable for the three substituents. The results also confirm the SSIP nature of **2L** and the CIP nature of **2C**.[24]

Conductivity and Free Ion Acidity. Although the alkali metal salts of the silyl-stabilized carbanions exist predominantly as ion pairs in THF, the free ions are

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Table VI. Comparison of Thermodynamic Data in THF

Li^{+a}			Cs^{+b}		
RH^c	$\Delta H^{\circ d}$	$\Delta S^{\circ e}$	RH^c	$\Delta H^{\circ d}$	$\Delta S^{\circ e}$
9-PhFl	(0.0)	(0.0)	Fl	(0.0)	(0.0)
BA	3.3	−0.3	9-MeFl	0.8	4.5
BnMP	6.2	4.2	9-BnFl	0.2	5.6
2	4.3	2.8	**2**	−1.5	4.4

[a] For the reaction RH + 9-PhFlLi ⇄ RLi + 9-PhFl. Data for the indicators are in ref 17. [b] For the reaction RH + FlCs ⇄ RCs + FlH. Data for the indicators are in ref 16. [c] See Table II for abbreviations. [d] In kcal mol^{-1}. [e] In eu corrected for symmetry.

Table VII. Dissociation Constants for Lithium and Cesium Salts of 1–3 and Free Ion Acidities in THF at 25 °C

compd	10^8K_d (M)	pK(FI)[a]
1L	1500	20.9
2L	2300	19.8
2C	7.8	19.8
3C	10.6	34.8

[a] On a per hydrogen basis. Defined as pK(FI) = pK(IP) − log K_d/K_{d° where K_{d° is the dissociation constant of the standard, fluorene. For the cesium salt, $K_{d^\circ} = 1.5 \times 10^{-8}$ M; for the lithium salt, $K_{d^\circ} = 0.69 \times 10^{-5}$ M.

important in the dilute solution reactions of delocalized carbanions because they are generally more reactive.[24] Moreover, it is useful to compare the silyl group stabilization effect with free carbanions. Thus we measured the dissociation equilibrium (2) for cesium and lithium ion pairs by the conductometric method described previously.[18]

$$RM \rightleftarrows R^- + M^+ \qquad (2)$$

The dissociation constant K_d was derived using the Fuoss equation[25] (3)

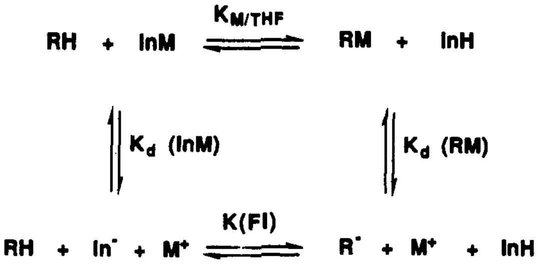
$$F/\Lambda_0 + f^2C\Lambda/FK_d{\Lambda_0}^2 \qquad (3)$$

where F is the Fuoss term, Λ is the equivalent conductance, f is the mean activity coefficient, and Λ_0 is the equivalent conductance at infinite dilution. As in the previous work,[18] F was calculated according to Fuoss and is equal to 0.91 to 0.96 for the lithium runs and unity in the cesium runs; f was obtained from the Debye–Hückel equation; it was close to unity for cesium and about 0.8–0.9 for lithium. Λ_0 values are often difficult to obtain with a high degree of precision. To be consistent with our previous work, it was assigned as 85 $cm^2\ \Omega^{-1}\ M^{-1}$ for lithium salts and 120 $cm^2\ \Omega^{-1}\ M^{-1}$ for cesium salts. From the conductivity data, plots of F/Λ versus $f^2C\Lambda/F$ showed good linearity with no curvature. These plots are shown as Figures S1–S3 in the supplementary material. K_d was obtained from least-squares analysis of the Fuoss plots.

The conductivity measurement results in Table VII indicate that the dissociation constants of lithium ion pairs are 10^3 times greater than those of the cesium salts and are comparable to the values found previously for the indicator hydrocarbons[18] and again confirm that the lithium salts are SSIP and the cesium salts are CIP.

Solov'yanov et al. have reported kinetic studies on carbanions including the 9-fluorenyltrimethylsilane system in dimethoxyethane (DME).[26] It is interesting to compare the properties of the silyl-stabilized carbanions in the different solvents. Two features are considered here. Their spectral results for **1L** in DME (λ_{max} 362.5 nm, ϵ = 12 400) are similar to ours in THF (λ_{max} 364 nm, ϵ = 12 000). Similarly, their value for K_d, 0.9×10^{-5} M, for **1L** in DME is close to that in THF, 1.5×10^{-5} M. That is, the properties of the SSIP are comparable in both solvents. There are significant differences, however, for the CIP cesium salts; for **1C**, ϵ is higher in DME, 12 400, compared to 9760 in THF, although λ_{max}'s are essentially the same, 357 and 356 nm, respectively. The Russian group reported $K_d = 2.6 \times 10^{-7}$ M for **1C** in DME. Although **1C** is stable in THF for several hours our conductivity studies of this compound were of limited precision; however, we estimate a K_d of less than 7×10^{-8} M, comparable to that for **2C** (Table VII). These results suggest that the bidentate nature of DME provides greater solvation for cesium cation and greater ion pair dissociation compared to THF.

Scheme I



The dissociation constants can be used to derive the relative free ion acidities of the silicon compounds. The dissociation constants of the silyl-substituted ion pairs are somewhat higher than those of the respective fluorene salts.[18] Thus, the relative ionic acidities of the silyl compounds are greater than those of the ion pairs. From the dissociation constants K_d the free ion acidities were derived from the ion pair pK assignments by the thermodynamic cycle shown in Scheme I. The pK(FI) is also referenced to fluorene at pK(FI) = 22.90 per hydrogen. The results are summarized in Table VII.

The pK(FI) values of **2** calculated from the lithium and cesium acidity scales are in agreement and indicate the absence of important systematic errors. The free ion pK of **1** derived from the lithium salt, 20.9, is in moderate agreement with the DMSO pK reported by Bordwell.[15]

From the free ion acidities, the intrinsic silyl group stabilization effect can be evaluated quantitatively: trimethylsilyl and *tert*-butyldimethylsilyl groups lower the pK(FI) of fluorene by 2 and 3 units, respectively. These values are somewhat lower than the 3–3.4 pK unit effect of the silyl group in the ion pair acidities of **3** and **4** and demonstrate further the moderate attenuating effect of silyl substitution with more delocalized carbanions.

We note that the $pK_{Li/THF}$ values of **1** and **2** are 0.3 unit lower than the corresponding $pK_{Cs/THF}$, values. That is, relative to the hydrocarbon indicator standards, these silicon-stabilized carbanions are 0.3 unit more stable as SSIP than as CIP. Moreover, from the free ion acidity data, we note that the relative pK(FI) for **2** is even lower than $pK_{Li/THF}$. The $pK_{Cs/THF}$ (CIP), $pK_{Li/THF}$ (SSIP), and pK(FI) for **1** are, respectively, 21.64, 21.33, 20.9, and for **2**, 20.60, 20.28, 19.8. The same trend is apparent for **3**; $pK_{Cs/THF}$ and pK(FI) are 35.62 and 34.8, respectively. Although the decreases in the three kinds of pK values are not large, the trends point to the conclusion that the relative stability of the silyl-stabilized carbanions are cation dependent; the silicon-stabilizing effect increases from CIP

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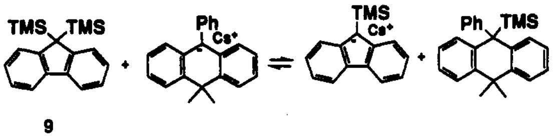
to SSIP to free ion. The effect may be determined by the size of the silyl group compared to the hydrocarbon standard. The larger group results in an increase in carbanion–cation distance and less ion pair stabilization. However, analysis is complicated by electrostatic interactions involving polarization at silicon and the highly polar nature of silicon–carbon bonds.[27] It is interesting that the same type of effect is seen in the ab initio calculations of Schleyer et al.[9] At the 3-21G(*) level, SiH_3 stabilizes methyl anion by 25 kcal mol^{-1}. In contrast, in methyllithium and methylsodium, SiH_3 substitution provides stabilization of only 9–11 kcal mol^{-1}. The calculations show the same trend for PH_2 and SH substitution and suggest that comparable results with related ion pair and ionic acidities would apply to such substituents.

Silyl Group Transfer. Many studies of substitution at silicon by nucleophiles have been carried out as summarized in an early monograph by Sommer[28] and more recently by Corriu.[29] It is well-known that oxygen and halogen bases and nucleophiles prefer to attack at silicon, whereas carbon and nitrogen bases and nucleophiles prefer to attack at hydrogen. However, because Si–C bonds are polarized with a high positive charge on the Si atom,[27] in some cases carbanions do attack at silicon as nucleophiles to substitute the silyl group and result in a new carbanion. For example, attempts to deprotonate (methoxymethyl)trimethylsilane, Me_3SiCH_2OMe, using *n*-butyllithium resulted in attack at silicon and subsequent cleavage of the Si–C bond.[30] Perozzi et al.[31] showed that PhLi can attack a neutral four-coordinate siliconate to result in five-coordinate siliconate. In our study, it was found that in some cases the substitution at silicon by the indicator carbanions competes with proton transfer. The silyl group functions as a "big" proton to transfer from one carbanion to another. This process depends on the basicity of the base and the leaving group, the metal gegenion and the substituent groups on silicon and is usually much slower than proton transfer; for example, the long equilibria involving 4 and the corresponding kinetic studies were not affected by silyl group transfer. Such transfer was demonstrated with the use of 9,9-bis(trimethylsilyl)fluorene, 9. 9-Methylfluorenylcesium ($pK_{Cs/THF}$ = 22.3) or 9-*tert*-butylfluorenylcesium ($pK_{Cs/THF}$ = 24.4) substitutes the trimethylsilyl group in 9 only very slowly. The cesium salt of 9-phenyl-10,10-dimethyldihydroanthracene (PDDA, $pK_{Cs/THF}$ = 28.1) attacks at the silicon in 9 at faster rate and reaches equilibrium, eq 4, with log *K* = 0.2–0.9.



eq. (4)

9

p-Biphenylylmethylcesium ($pK_{Cs/THF}$, = 38.7), on the other hand, reacts with 9 completely at a rapid rate.

The nature of the ion pairing plays a role in silyl group transfer. In contrast to the reactions with cesium bases discussed above, the lithium bases made from indicators with $pK_{Li/THF}$ in the range from 19 to 33 do not undergo the substitution reaction at silicon. Thus, silyl group transfer is more facile for CIPs than for SSIPs.

Steric hindrance to substitution at silicon is pronounced. This effect has been found in the substitution at silicon by oxygen and halogen nucleophiles.[2a] It was also found for the substitution by carbanions as nucleophiles in this study. When the substituents on silicon are changed from trimethyl to *tert*-butyldimethyl, the silyl group transfer is completely blocked even with cesium salts.

Conclusion

This study has led to a quantitative understanding of silyl stabilization in carbanions. Relative to hydrocarbons, the intrinsic stabilization (free ion stabilization) is about 2–3 p*K* units for delocalized carbon acids but is somewhat greater for localized carbanion systems. The stabilization decreases from free carbanions to organometallic ion pairs and is greater for SSIP than for CIP.

Experimental Section

General. Glassware was dried in an oven at 160 °C for at least 4 h prior to use. The measurements of transmetalation equilibrium constants were made in a glovebox filled with Argon. UV–vis spectra were recorded on an IBM 9431 UV–vis spectrophotometer or on a Shimadzu UV-2101PC spectrophotometer equipped with fiber optics cables connected to a thermostatted cell holder in the glovebox. Constant temperature was obtained by using a Neslab Model RTE-8DD temperature controller for room temperature and higher and by Neslab Model ULT-80DD for lower temperatures using 95% ethanol as the coolant. Proton nuclear magnetic resonance (^1H NMR) spectra were conducted on UCB-250 (a superconducting 250-MHz instrument), Bruker AM-400, and Bruker AM-500 (FT NMR) spectrometers operating in the FT mode. Gas–liquid chromatography (GLC) was performed on a Hewlett-Packard 5880 gas chromatograph using a 6-ft × 18-in. OV-101 column. Melting points (Pyrex capillary) were determined on a Buchi melting point apparatus and are uncorrected.

Materials. Commercial materials 4, 6, 7, and 8 were dried and distilled. Compounds 1,[32–34] 5,[35] and 9[34] are described in the literature. The indicators used were available from our previous studies. The purity of the compounds was monitored by combinations of ^1H NMR, GLC, mp, and elemental analysis.

9-Fluorenyl-*tert*-butyldimethylsilane, 2. To a 0 °C solution of 2.7 g (0.016 mol) of fluorene in 20 mL of THF was added over 30 min 8.7 mL of 2.3 M *n*-butyllithium (in hexane). The resulting red solution was added via a cannula to a flask containing magnesium bromide which was made from 0.5 g (0.020 mol) of magnesium turnings and 3.7 g (0.020 mol) of 1,2-dibromoethane in 25 mL of THF. After 1 h of stirring, to the fluorenylmagnesium bromide solution was added over 1 h 4.0 g (0.026 mol) of *tert*-butyldimethylchlorosilane in 10 mL of hexamethylphosphoric triamide (HMPA) and 10 mL of THF. The solution was stirred for an additional 8 h at 50 °C. The reaction mixture was extracted with 1 M HCl and 3 × H_2O to give a brown ether solution. The solution was dried over anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation under reduced pressure to give a brown oil. Fractional sublimation under vacuum produced white crystals as the second fraction: mp 78–79 °C; ^1H NMR ($CDCl_3$) δ 7.7–7.1 (m, 8 H), 3.8 (s, 1 H), 0.23 (s, 9 H), 0.18 (s, 6 H).

Anal. Calcd for $C_{19}H_{24}Si$: C, 81.40; H, 8.57. Found: C, 81.61; H, 8.62.

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(4-Biphenylylmethyl)-*tert*-butyldimethylsilane, 3. To a 0 °C solution of 2.7 g of 4-methylbiphenyl (0.016 mol) in 20 mL of THF was added over 20 min 8.7 mL of 2.3 M *n*-butyllithium in hexane. The 4-biphenylylmethyllithium solution was slowly added via a cannula to a flask containing magnesium bromide which was made from 0.5 g of magnesium turnings (0.020 mol) and 3.7 g of 1,2-dibromoethane (0.020 mol) in 25 mL of THF. After the solution was stirred for 1 h, 4.0 g of *tert*-butyldimethylchlorosilane (0.026 mol) in 10 mL of HMPA and 10 mL of THF was added to the solution. The solution was stirred for 5 h at room temperature and quenched with 0.5 M HCl. The mixture was extracted twice with diethyl ether, and the extracts were washed with 1 M HCl and water and then dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to give a yellow oil. Fractional sublimation under vacuum produced white crystals as the second fraction, mp 85.5–86.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.6–7.1 (m, 9 H), 2.1 (s, 2 H), 0.9 (s, 9 H), –0.1 (s, 6 H).

Anal. Calcd for $C_{19}H_{26}Si$: C, 80.83; H, 9.22. Found: C, 80.62; H, 9.22.

Purification of THF. Carefully dried THF is especially important in the single indicator studies. Fisher Scientific reagent grade THF was distilled from lithium aluminum hydride or from sodium–benzophenone into an oven-dried Schlenk flask containing a magnetic stirring bar. The flask was attached to a vacuum line and the content degassed by at least three freeze–pump–thaw cycles. It was then taken into the glovebox, and several drops of sodium–potassium alloy were added. The solution was stirred in the glovebox until a blue color persisted. The flask was then taken out of the glovebox and attached to the vacuum line, and the contents were degassed by three freeze–pump–thaw cycles. During the degassing process, the blue color of THF solvated electron might disappear due to freezing. In such cases, the solution was stirred after degassing until a blue color reappeared, and THF was vacuum transferred to a long neck receiving flask which had been oven- and flame-dried. The contents were again degassed and taken into the glovebox, and approximately 20 g of 3-Å molecule sieves was added for every 250 mL of THF solvent. The solvent was allowed to stand over sieves for at least 2 days in a quartz flask prior to use. We estimate the water content to be on the order of 10^{-6} M.

Acidity Measurements. General procedures of the double indicator method and single indicator method have been described previously.[23] The single indicator method was further improved by using quartz microbeakers. Earlier work with the double indicator method made use only of the λ_{max} of the substrate and indicator salts. In more recent determinations, the entire spectrum was used. To deconvolute the mixed spectra, we have used a linear least-squares computer program that calculates the absorbance of both anions at their corresponding λ_{max} based on the inputs of the standard spectrum of each individual anion. The details of the linear least-squares method will be described in a separate paper.[36] From our experience, this linear least-squares method is preferred to the general method of solving two linear equations for the absorbance at two wavelengths. An example is shown as Figure S4 in the supplementary material.

The extinction coefficients for most of the indicator and substrate anions were measured by titrating to the end point of a known amount of neutral in a known volume of solvent with a strong base (diphenylmethylcesium for titrating compounds with pK_a's lower than 30 and cumylcesium for those with pK_a's higher than 30). For anions whose spectra are not interfered with by the spectrum of the base, the end point was taken when further addition of the base caused no further increase in the absorbance of the anions. For those anions whose spectra overlap with the spectrum of the base, an excess amount of the base was added (overtitrated) and the mixed spectra of the anions and the base were then deconvoluted by the linear least-squares method used for the double indicator method to give the end point.

For compounds with pK_a's higher than 36, the deprotonation by cumylcesium becomes very slow. The measurement of extinction coefficients by titration methods described above involve experimental difficulties with greater uncertainty. In such cases, we have used an alternative method, which proved more reliable and internally consistent. The following method was used to determine the extinction coefficients of **4C**: 3–10 mg of neutral compound (so that the rate of deprotonation was convenient to follow) was placed in a microbeaker and added into a cell containing THF. A base-line correction was performed on the cell. An appropriate amount of cumylcesium solution was added so that the absorbance of cumylcesium at λ_{max} 346 nm reached about 1.0 absorbance units. Repeated scans were recorded every 3–5 min. The series of mixed spectra of cumylcesium and the substrate anion were then deconvoluted using the linear least-squares method, and the absorbance at 346 nm and at the λ_{max} of substrate anion was obtained. The ratio of the decrease in the absorbance at 346 nm to the increase in absorbance at λ_{max} of the substrate anion for each pair of successive spectra thus yields the ratio of the extinction coefficients of cumylcesium (ϵ = 17 000) to that of substrate anion. Several ratios were obtained and averaged. This method was found to give rapid and reliable extinction coefficients. Their internal consistency was checked, and the uncertainty of extinction coefficients was estimated to be 5–8%.

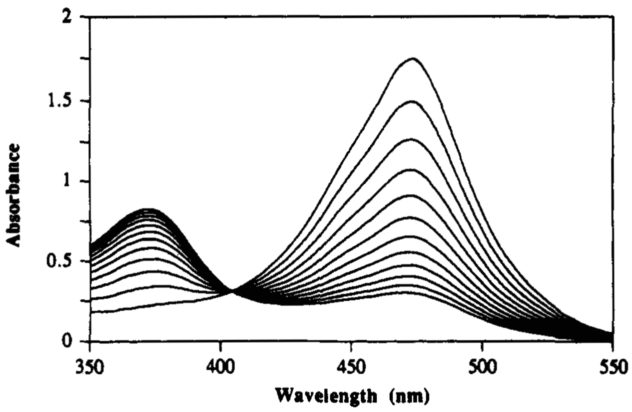

Figure 1. Repeated scans in a kinetic experiment of measuring the forward rate constant of 4 with the cesium salt of *p*-MB (λ_{max} = 472 nm) at 25 °C. The λ_{max} of 4C = 372 nm.

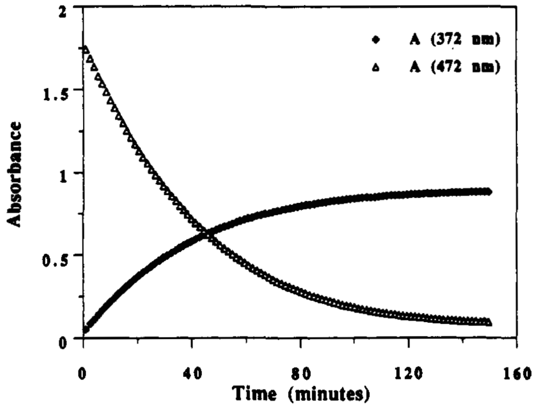

Figure 2. Absorbance of reactant anion and product anion as a function of time in the kinetic experiment of Figure 1.

Thermodynamic constants were obtained by determining the p*K*'s at 5–10 °C intervals over a temperature range of 25 to –20 °C. Linear least-squares plots of log *K* vs 1/*T* were obtained from which $\Delta H°$ and $\Delta S°$ were determined. The thermodynamic results are summarized in Tables V and VI.

Conductance measurements were done within the glovebox. Conductance was measured with an ESI Model 2110 Video Bridge operating in the parallel circuit mode using a procedure detailed previously.[18] Examples of the derived Fuoss plots are shown in Figures S1–S3 of the supplementary material. Derived dissociation constants are summarized in Table VII.

Kinetics. For benzyltrimethylsilane, 4, *p*-tolyl phenyl sulfide and *p*-methylbiphenyl were used as indicators. These transmetalation reactions were slow and required approximately 8 h

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before equilibrium was reached. For both the forward and reverse reactions, a large excess of neutral compounds (*p*-MB and 4) was used and the reactions were found to be pseudo-first-order in the cesium salt. The reactions were conveniently monitored by successive scans from 550 to 350 nm at a constant time interval (Figure 1). The cesium salt of *p*-MB has λ_{max} 472 nm; 4C has λ_{max} 372 nm. Note that the sharp isosbestic point indicates that silyl group transfer is not important on this time scale. The mixed spectra were deconvoluted using the linear least-squares method, and the absorbance at both λ_{max} were plotted against time. An example of such plots is shown in Figure 2 for the reaction in Figure 1. The data were then fitted against the usual equation for first-order kinetics using nonlinear least-squares. Division of the pseudo-first-order rate constant by the concentration yields the second-order rate constant. Since the absorbances of reactant anion and product anion were both followed at the same time, two rate constants were obtained for each run.

Silyl Group Transfer Studies. The UV–vis absorption spectrum was taken of the lithium or cesium salt of the appropriate indicator. A known amount of 9,9-bis(trimethylsilyl)fluorene, 9, was added and the extent of silyl group transfer was determined from the decrease in the indicator absorption and the appearance of the corresponding salt of 1. Only qualitative observations were made.

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Supplementary Material Available: Fuoss plots and an experimental spectrum (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.