

NMR Studies of Phenylsilyl Anions. Evaluation of Ion Pairing and Charge Distribution¹

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Abstract: The results of an NMR study (¹H, ¹³C, ⁷Li) of phenyl-substituted silyl anions are reported as a function of solvent, temperature, and the presence of crown ether complexing agents. Comparison of ¹³C chemical shifts for Ph₃SiLi, Ph₂MeSiLi, and PhMe₂SiLi, and for the corresponding silyl potassium compounds, with carbanion analogues is especially informative concerning the transmission of electronic effects in these systems. It is concluded that π -polarization of the phenyl rings (F_{π}) is the major cause of the observed phenyl carbon shifts in the silyl anions relative to the neutral chlorides, in contrast to the arylmethyl carbanions. The minor ¹³C chemical shift changes observed for the phenyl carbons by addition of crown ethers or by varying cation or solvent can be interpreted as a cation-induced modulation of this effect. The narrow range for the ⁷Li chemical shifts observed downfield of a LiCl reference supports a significant silicon-lithium interaction in these anion species in the ethereal solvents under investigation (Et₂O, THF, THF, DME).

There is considerable interest in ion-pair phenomena in carbanion systems, in part because of the consequences that these phenomena impart to reactivities, and due to their characteristic spectroscopic properties.³ The experimental findings gathered so far point toward equilibria of solvent-separated (SSIP) and contact ion pairs (CIP), where the relative proportions are determined by the choice of solvent, temperature, and counterion. UV,⁴ IR⁵, and more recently NMR⁶ have been the major spectroscopic techniques used to characterize these systems, which with a few exceptions have all been monocharged all-carbon systems, e.g., fluorenyl^{4a} and arylmethyl^{4b,c} carbanions.

Recently, however, several investigations have been directed toward defining the role of $p\pi-p\pi$ or $d\pi-p\pi$ conjugation in anions containing group 4 elements.⁷⁻¹⁰ The first report on the electronic spectrum of silyl anions showed that (triphenylsilyl)lithium in tetrahydrofuran (THF) has a low-wavelength absorption of 335 nm.⁷ By comparing this result with the UV absorption for (triphenylmethyl)lithium ($\lambda_{\max} \approx 500$ nm) the authors concluded that the much lower λ_{\max} of the silyl compound is indicative of negligible delocalization of negative charge to the phenyl rings. Experiments were also conducted in different solvents, and the main conclusion was that only one type of ion pair exists in the (triphenylsilyl)lithium system under the prevailing solvent con-

Table I. ¹³C Chemical Shifts of Silyl Anions and Related Species in THF Solvent^{a,b}

	ipso	ortho	meta	para	Me	C- α
Ph ₃ SiH	134.2	136.5	128.8	130.6		
Ph ₃ SiCl	133.8	135.9	128.9	131.5		
Ph ₂ MeSiCl ^b	134.4	134.0	128.1	130.5	0.9	
PhMe ₂ SiCl	137.0	133.8	128.8	131.0	2.3	
Ph ₃ SiLi	155.9	137.0	126.9	124.6		
Ph ₂ MeSiLi	160.1	135.4	126.7	123.9	4.8	
PhMe ₂ SiLi	166.0	133.8	126.5	122.7	7.5	
Ph ₃ SiK	158.6	136.9	126.7	123.8		
Ph ₂ MeSiK	163.2	135.1	126.5	123.0	5.8	
PhMe ₂ SiK	170.1	133.6	126.4	121.6	9.1	
Ph ₃ CH	145.0	128.9	130.2	126.9		57.7
Ph ₃ CCl ^c	145.3	129.7	127.7	127.7		81.3
Ph ₃ CLi	150.0	124.2	128.1	113.2		90.3
Ph ₃ CK	149.1	124.0	129.0	114.3		88.5

^a Cyclohexane used as reference (δ 27.7). Anion samples run in an unlocked mode. ^b Reference 20. ^c Reference 21.

ditions. It was also found that temperature change has no significant effect on the UV absorption of the silyllithium compound.

Using ¹H NMR, Cox et al. studied the lithium salts of the triphenyl group 4 species in THF.⁸ A variation in the shielding of the para hydrogens was observed, but definitive interpretation of the results was uncertain since the range for the para proton shifts was found to be quite small (<0.12 ppm), it thus being difficult to place undue emphasis on such subtle relative differences. Olah and Hunadi studied the ¹³C chemical shift data of the (phenylsilyl)lithium compounds in THF and concluded that delocalization of charge into the phenyl rings of Ph₃SiLi is reduced by an order of magnitude in comparison with the corresponding (triphenylmethyl)lithium analogue.⁹ This was accounted for by assuming a non-planar system and a reduced π -overlap between the metal and the phenyl carbons. Batchelor and Birchall¹⁰ reported recently the preparation of (phenylgermyl)sodium salts in NH₃ and concluded on the basis of the observed ¹³C chemical shifts that delocalization of negative charge in Ph₃GeNa is increased in comparison with Ph₃SiLi,⁹ but decreased relative to that found for the anions of the phenyl-substituted phosphines and arsines.¹⁰ This proposal was based on the assumption that the difference ($\delta_p - \delta_m$) is a good measure of the degree of resonance interaction with the anionic center. The magnitude of these effects was considered to be affected by solute-solvent interaction and ion-pairing or association phenomena.

It is evident from the earlier studies that there exist some remarkable differences between the silicon and carbon derivatives but also between the silyl and germyl anions. Moreover, if one

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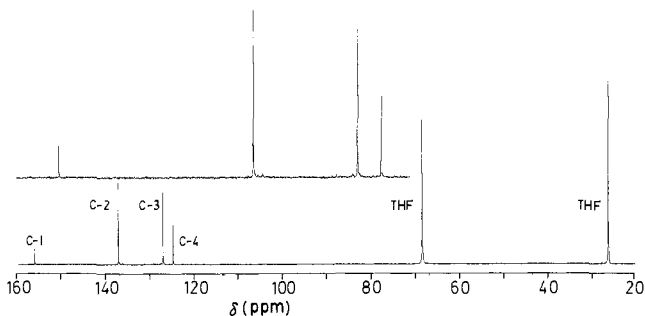


Figure 1. ^{13}C NMR spectrum of (triphenylsilyl)lithium, 0.32 M in tetrahydrofuran (inset, expanded scale).

compares the reported chemical shifts of the ipso and para carbons in Ph_2MeSiLi and PhMe_2SiLi , these were markedly different from that of Ph_3SiLi .⁹ This finding was unusual if conjugation were dramatically reduced for the silyl anions. As a continuation of our studies of ion-pairing phenomena in arylmethyl carbanions^{4,4,11} and in other anion systems,¹² we have carried out a systematic NMR study of the silyl anions by varying the cation, solvent, and temperature and in the presence of cation complexing agents and report our results herein.

Results and Discussion

Evidence from ^{13}C and ^1H Chemical Shifts in THF: Comparison with Literature Data. The major trends that are apparent in the results in Table I for the silyllithium and -potassium compounds relative to the corresponding chlorides or silanes are as follows. Formation of the silyl anions from the neutrals causes the ipso carbon to be strongly deshielded (22 to 40 ppm) and the para carbon to be shielded (6 to 8 ppm). The shift changes of the ortho and meta carbons are of a smaller magnitude (1 to 2 ppm), the ortho carbons being shifted downfield and the meta carbons upfield.

The ^{13}C chemical shifts obtained for Ph_3SiLi differ from the data previously reported:⁹ ipso 145.0, ortho 136.1, meta 127.5, para 128.4. The present results were reproduced when the Ph_3SiLi was prepared by an alternate method by using another starting material (see Experimental Section). The ^{13}C NMR spectrum of Ph_3SiLi is given in Figure 1. The possibility that Ph_3SiLi can undergo coupling reactions, as well as ring cleavage reactions of cyclic ethers, has been previously noted.^{13,14}

The carbon shifts that we have obtained for Ph_3SiLi are well in line with the data found for Ph_2MeSiLi and PhMe_2SiLi (Table I); the latter values are in excellent agreement with the previously reported data.⁹ The present shifts for Ph_3SiLi are also similar, especially for the ortho, meta, and para carbons, to those reported for Ph_3GeNa .¹⁰

The new data that we have obtained for Ph_3SiLi lead to a re-examination of its electronic structure. It has been considered that para-carbon chemical shifts provide a good measure of charge density at this position.^{9,15} The change in $\delta(\text{para})$ chemical shift for Ph_3CLi vs. Ph_3CCl of -14.5 ppm, and Ph_3CLi vs. Ph_3CH of -13.7 ppm, is thus in accord with extensive charge delocalization onto the phenyl rings. On this basis the $\delta(\text{para})$ values for Ph_3SiLi vs. Ph_3SiCl and Ph_3SiLi vs. Ph_3SiH , i.e., -1.5 and -1.7 ppm, respectively, were interpreted as indicative of reduction of charge delocalization in Ph_3SiLi relative to Ph_3CLi by a factor of 9–10.⁹ It was hence concluded that resonance involving charge delo-

Table II. ^1H NMR Chemical Shifts of Silyl Anions and Related Carbanions in THF^a

	H2	H3	H4
Ph_3SiLi	7.33	6.98	6.88
Ph_2MeSiLi	7.41	6.98	6.84
PhMe_2SiLi	7.31	6.93	6.74
Ph_3SiK	7.31	6.90	6.78
Ph_2MeSiK	7.36	6.91	6.74
PhMe_2SiK	7.38	6.98	6.75
Ph_3CLi	7.25	6.46	5.90
Ph_3CK	7.23	6.58	6.02

^a Cyclohexane used as reference (δ 1.43). Samples run in an unlocked mode.

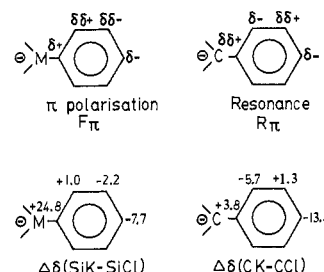
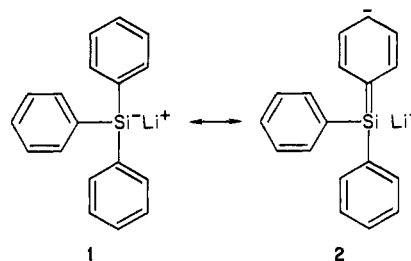


Figure 2. ^{13}C chemical shift changes on going from triphenyl chloride derivatives to the corresponding potassium salts.

calization onto the phenyl rings as represented by structure 2 was negligible.



Treatment of the present results in similar fashion gives $\Delta\delta(\text{para})$ for Ph_3SiLi vs. Ph_3SiCl as -6.9 ppm and $\Delta\delta(\text{para})$ for Ph_3SiLi vs. Ph_3SiH as -6.0 ppm, i.e., a diminution by ca. 2.2 relative to Ph_3CLi vs. Ph_3CCl . Hence, when this argument is used, it may not be possible to discount appreciable resonance delocalization of the type shown in structure 2. This point will be discussed further subsequently.

The ^1H NMR data for the silyllithium and -potassium compounds in THF are presented in Table II. The results for Ph_3SiLi are in excellent agreement with those reported earlier by Cox et al.⁸ (average deviation 0.02 ppm). There is a small but significant upfield shift in $\delta(\text{para})$ on going from Ph_3SiLi to Ph_3SiK (0.10 ppm), in accord with a greater charge density in this position in the latter species. Ph_3CLi and Ph_3CK exhibit significant upfield shifts in $\delta(\text{para})$ relative to Ph_3SiLi and Ph_3SiK (0.98 and 0.76 ppm, respectively). This result parallels closely the ^{13}C shift data and further confirms the previously drawn conclusions concerning the decreased charge development on the phenyl ring in the phenylsilyl anions as compared to the phenylmethyl carbanions.

Transmission of Electronic Effects: Resonance vs. π -Polarization. Two major mechanisms of substituent electronic effects must be considered when generating a negative charge on the metal in the phenyl-substituted group 4 metal derivatives:¹⁶ (a) a resonance interaction involving suitable orbitals of the metal and the carbon π -system to which it is attached (R_π); (b) a π -inductive effect including direct π -polarization (F_π) of the phenyl rings, orbital repulsion effects (O_π), and possibly inductomesomeric effects ($X_{\sigma/\pi}$).

From the ^{13}C NMR chemical shift data of the para carbons observed for Ph_3SiLi and Ph_3SiK it is apparent that, whatever

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Table III. Solvent Effect on ^{13}C Chemical Shifts of Silyl Anions and Related Carbanions Relative to THF^a

		ipso	ortho	meta	para	Me	C- α
Ph ₃ CLi	Et ₂ O	-1.3	+0.2	+0.8	+3.7		
	MTHF	-0.1	-0.1	0	0		+0.2
Ph ₃ CK	MTHF	-0.5	-0.4	+0.2	+0.5		-0.9
Ph ₃ SiLi	Et ₂ O	-0.5	+0.2	+0.3	+0.4		
	MTHF	-0.2	0	+0.1	+0.1		
	DME	0	+0.2	+0.2	+0.3		
Ph ₂ MeSiLi	Et ₂ O	-0.3	+0.3	+0.5	+0.6	-0.1	
	MTHF	-0.3	0	0	0	0	
	DME	-0.3	+0.1	+0.2	+0.3	0	
PhMe ₂ SiLi	MTHF	-0.1	-0.1	0	0	-0.1	
	DME	-0.3	+0.3	+0.3	+0.3	+0.2	
Ph ₃ SiK	MTHF	-0.8	-0.1	+0.2	+0.2		
Ph ₂ MeSiK	MTHF	-0.8	0	+0.3	+0.3	-0.2	
PhMe ₂ SiK	MTHF	-0.8	0	+0.5	+0.6	-0.5	

^a $\Delta\delta$ values (solvent - THF). A positive value indicates a downfield shift.

the operative mechanism of substituent transmission, more charge is located on silicon in these anions than on the C- α carbon in Ph₃CLi(K). This will at identical temperature/solvent/counterion conditions favor contact ion pairing in the triphenylsilyl species compared with the ion-pair situation for the triphenylmethyl anion.^{4c,6h} On the basis of knowledge of the factors that control ion-pair structure, one could then reasonably assume that the potassium salts will exist as the contact ion pairs in THF and particularly in the less polar 2-methyltetrahydrofuran (MTHF).

In the silyl anions the principal origin of the charge distribution in the phenyl rings is probably π -inductive effects, such as electric field-induced π -polarization (F_π) of the phenyl rings. As seen in Figure 2, the charge pattern is typical for such a polarization effect and quite different from the pattern expected if conjugative effects were important.¹⁶ Moreover, in these anion systems one would expect that π -polarization caused by the negative charge on the silicon atom is to some extent modulated by the cationic field. In the triphenylmethyl anion, both conjugative and π -inductive effects will be important for the remote carbon shifts, though the former mechanism is expected to be dominant (Figure 2).

A successive substituent change, Ph \rightarrow Me, would thus cause the para carbons to be more shielded as one goes along the series Ph₃CLi \rightarrow Ph₂CHLi \rightarrow PhCH₂Li. This trend is in fact observed in the $\delta(\text{para})$ values:^{6f} 113.3 \rightarrow 107.2 \rightarrow 104.7. However, as seen in Table I, in the silyl series this shielding tendency upon decreased phenyl substitution is strongly suppressed for the lithium as well as the potassium silyl anions (Ph₃SiLi \rightarrow Ph₂MeSiLi \rightarrow PhMe₂SiLi: $\delta(\text{para})$ 124.6 \rightarrow 123.9 \rightarrow 122.7). Hence this observation provides additional evidence that the mesomeric effect is strongly suppressed in the phenyl-substituted silyl anions.

Ion-Pairing Phenomena: Solvent, Crown Ether, and Temperature Effects. In the case of carbanion-alkali metal compounds, considerable evidence has been adduced for the formation of equilibria involving contact and solvent-separated ion pairs in different systems,⁴⁻⁶ as mentioned earlier. An analogous situation will presumably arise with the silyl anion systems, though in this case the degree of covalent interaction between silicon and the alkali metal could perhaps be greater, especially in the case of the lithium compounds.

The preliminary conclusion was reached above that the silyl-potassium compounds exist in THF at room temperature largely in the form of CIP. Changing the solvent from THF to the less solvating MTHF would then mainly decrease the external solvation of the CIP, thus inducing a more effective cationic field. One would hence expect the overall π -polarization to be less important in MTHF, which should be revealed as an upfield shift of the ipso, ortho positions and a downfield shift of the meta, para positions relative to the THF data. This is also observed (Table III) both for Ph₃CK and the phenyl-substituted silylpotassium anions. It should be noted, however, that the ^1H and ^{13}C NMR chemical

Table IV. Crown Ether Induced ^{13}C Chemical Shifts of Silyl Anions

	solvent	crown	ipso	ortho	meta	para
Ph ₃ SiLi	THF	12-C-4	+2.8	0	-0.3	-0.9
Ph ₃ SiK	MTHF	18-C-6	+2.1	+0.3	-0.4	-0.7

^a Equimolar amounts of Ph₃SiLi(K) and crown ether. ^b $\Delta\delta$ values (THF/MTHF/crown - THF/MTHF). A positive value indicates a downfield shift.

shifts are not expected to be especially sensitive to cation solvation for the relatively large potassium cation.^{6h}

Addition of the cation complexing agent 18-C-6 to Ph₃SiK in MTHF results in an upfield shift in the para-carbon resonance of 0.7 ppm (Table IV). In accordance with the results of the solvent study, we would expect the influence of the cationic field to be diminished upon crown ether complexation. Consequently, the π -polarization caused by the negative charge will be more effective in the presence of 18-C-6, yielding upfield shifts for the meta, para positions. The magnitudes should be larger than those obtained in the THF-MTHF comparison. This is clearly seen in Table IV, and the resulting charge pattern on the phenyl ring is similar to that obtained when generating the anions from the neutral precursors but reduced in magnitude. A comparison between Table I and IV reveals such a correspondence, and the induced differentials are roughly decreased by an order of magnitude. Corresponding results are observed on addition of 12-C-4 to Ph₃SiLi in THF (Table IV).

The results for the silyllithium compounds on changing the solvent reveal a considerable contrast compared to the carbon analogues. Thus for Ph₃CLi there is a 3.7-ppm upfield shift on going from Et₂O to MTHF, but no further change occurs on going to the still more polar THF. These results indicate that in Et₂O the equilibrium favors largely the CIP, while in MTHF and THF SSIP predominate.^{6h} The tendency toward SSIP formation in arylmethyl anions on changing the cation from potassium to lithium was noted previously.^{6c,h,11} In the case of Ph₃SiLi there are only minor, random shift changes on going from Et₂O to DME; in fact the para-carbon-shift values are the same within experimental error in Et₂O and DME. This is certainly not consistent with a change from CIP to SSIP, which is expected to afford a significant upfield shift for these positions. Even assuming exclusively CIP in these solvents, one would expect the (meta)para carbons to be more shielded in DME. It is known that the chemical-shift changes experienced by the CIP anion upon solvation should increase as the size of the cation decreases.^{6h} Hence one would expect that the shift trends observed for the silylpotassium species should also be observed for the lithium salts but enhanced in magnitude. The results for Ph₂MeSiLi and PhMe₂SiLi follow a similar trend. This lack of a consistent trend in the charge pattern for the silyllithium compounds as compared

Table V. Effect of Temperature on ^{13}C Chemical Shifts of Ph_3SiLi in THF

temp, °C	ipso	ortho	meta	para
25	155.9	137.0	126.9	124.6
-14	155.8	137.0	127.0	124.7
-48	155.7	137.0	127.0	124.7
-80	155.7	137.0	127.1	124.9

Table VI. ^7Li Chemical Shift Data of (Phenylsilyl)lithiums and (Triphenylmethyl)lithium as a Function of Solvent^a

	Et_2O	MTHF	THF	DME
Ph_3CLi	+1.35	-0.57	-0.35	
Ph_3SiLi	+1.00	+0.49	+0.66	+0.43
Ph_2MeSiLi		+0.58	+0.61	+0.23
PhMe_2SiLi			+0.53	+0.32

^a External reference: 1 M $\text{LiCl}/\text{H}_2\text{O}$ (see Experimental Section). A positive value indicates a downfield shift.

to the silylpotassium compounds, or the carbon analogues, suggests a stronger Si-Li interaction (covalent character) in these compounds. The virtual lack of a temperature effect on the carbon chemical shifts of Ph_3SiLi in THF over the temperature range 25–80 °C (Table V) is probably also indicative of this bonding situation.

Evidence from ^7Li Chemical Shifts. As additional evidence of the ion-pair state of silyl anions, ^7Li NMR studies were conducted and the resulting chemical shifts are recorded in Table VI. Direct measurement of the cation resonance has been shown to provide significant information of the ion pairing of the metal anion systems which cannot be obtained readily by other methods.¹⁷

The shielding of the Li nucleus in these systems should reflect the structure of the first cation solvation shell. Hence, the chemical shift should be dependent on the nature of anion, solvent, and ion-pair structure. Shift changes will then arise from ring currents of the phenyl rings, electrostatic polarization of the lithium nucleus, and orbital overlap between lithium and anion/solvent. Electrostatic polarization and orbital overlap will cause downfield shifts. All these influences will be modulated by the interionic distances. Ring-current effects on the cation resonance will in addition be controlled by the actual position of the cation relative to the anion.^{8,18}

On going from a CIP to a SSIP, the electrostatic polarization and ring-current effects will decrease and solvent molecules will replace an anion in the first solvation shell, thus changing the contribution due to orbital overlap. Hence, for a SSIP, the main contribution to a variable shielding will be caused by changes in orbital overlap between the lithium cation and, for instance, the heteroatoms of the solvent molecules.

The ^7Li chemical shifts of the silyllithium compounds are given in Table VI for several solvents with data for Ph_3CLi being recorded for comparison. A single sharp signal, $\nu_{1/2} = 1.5\text{--}6$ Hz, was obtained. In any given solvent, the ^7Li shifts of the silyllithiums change only very slightly as the degree of phenyl substitution is varied. This indicates that the interaction between lithium and solvent molecules, and between lithium and silicon, remains largely unchanged in this series. This corresponds to our conclusions drawn from ^{13}C chemical shifts.

In contrast to the results obtained for the silyllithiums, the data for Ph_3CLi reveal a marked dependence of the ^7Li chemical shift as a function of solvent. Since other spectroscopic evidence has shown that in Et_2O at room temperature Ph_3CLi exists largely as the CIP and in THF as the SSIP,^{6c,h,11} the change in chemical shift to more negative values gives a measure of the decreased carbanion-Li interaction and an increased interaction of Li with solvent molecules. Hence, for the silyllithium compounds, the much smaller change in chemical shift with increasing coordinating

ability of solvent, though in the same direction, suggests that there is not a drastic change in the type of bonding present. The ^7Li chemical shifts of the tight structures of carbanions and silyl anions are only qualitatively comparable, but combined with the solvent and temperature effects on the ^{13}C chemical shifts, it seems plausible to assume that the Si-Li interaction in the studied ethers is equal to or stronger than the association found for Ph_3CLi in Et_2O .

To conclude, it has been shown that the charge distribution in the phenyl rings of the silyl anions, as reflected by the ^1H and ^{13}C NMR chemical shifts, is mainly controlled by the π -polarizing effects of the negative silyl atom. The minor shift variation observed by varying solvent and cation can be explained by a cation-induced modulation of this effect.

Experimental Section

Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), 2-methyltetrahydrofuran (MTHF), and diethyl ether (Et_2O) were distilled over potassium metal and then stored over a sodium mirror. The crown ethers (Aldrich) were dried in vacuo before use.

The silyl anions were generated mostly by cleavage of the Si-Si bond in the hexasubstituted disilanes, $\text{Ph}_n(\text{Me}_{3-n})\text{Si-Si}(\text{Me}_{3-n})\text{Ph}_n$, by alkali metal. This reaction is preferred compared to halogen-metal exchange procedures, since the use of halides can give competing alkylation. 1,2-Diphenyl-1,1,2,2-tetramethyldisilane was prepared by the method of Gilman.¹⁹ The other disilanes (Organometallics or Petrarch) were purified by crystallization. Triphenylsilyl chloride (Aldrich) was also recrystallized before use.

A complementary experiment was performed in the study of (triphenylsilyl)lithium, where triphenylsilyl chloride was used as the starting material. (Triphenylmethyl)lithium and (triphenylmethyl)potassium were prepared by the action of *n*-BuLi and potassium metal, respectively, on triphenylmethane.

Cleavage of the Si-Si bond in the disilanes was performed at 0 °C in an ultrasonic bath by using lithium or potassium metal flakes under an argon atmosphere. The solutions were kept in septum-sealed reaction flasks in the ultrasonic bath for 3-4 h for reaction to be completed. Approximately 3 mL of the anion solution was transferred by means of a syringe into argon-flushed NMR tubes. The Et_2O samples were prepared by a solvent-exchange technique; the anions were initially prepared in THF, which was followed by solvent evaporation and transfer on a vacuum line. However, even by exchanging twice with Et_2O , traces of THF could be detected in the NMR spectra. Hence, the reported ^{13}C shifts for Et_2O solvent are subjected to some uncertainty.

NMR spectra were measured on a Bruker WM-250 or a Bruker CXP-200 multinuclear instrument. Selective decoupling was used to confirm the given assignments. Dry cyclohexane was used as internal standard (δ 27.7), since the cyclohexane chemical shift is less sensitive to medium effects than the tetramethylsilane (Me_4Si) carbon shift. Solutions were 0.2–0.3 M.

In the ^7Li NMR measurements $\text{LiCl}/\text{H}_2\text{O}$ was used as external reference. The LiCl capillary was held in a 10-mm tube filled with THF. For each of the samples the reference sample was run before and after the experiment to ensure a satisfactory field stability. No bulk susceptibility corrections were performed.⁸ A small upfield correction (ca. 0.5–0.6 ppm) should be applied to the present ^7Li chemical shifts in order to make these comparable to literature values. This is due to different magnetic field/NMR tube alignments. The accuracy of the ^7Li chemical shifts are within 2 Hz.

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Registry No. THF, 109-99-9; MTHF, 96-47-9; DME, 110-71-4; 12-C-4, 294-93-9; 18-C-6, 17455-13-9; Ph_3SiH , 789-25-3; Ph_3SiCl , 76-86-8; Ph_2MeSiCl , 144-79-6; PhMe_2SiCl , 768-33-2; Ph_3SiLi , 791-30-0; Ph_2MeSiLi , 3839-30-3; PhMe_2SiLi , 3839-31-4; Ph_3SiK , 15487-82-8; Ph_2MeSiK , 69634-43-1; PhMe_2SiK , 69634-44-2; Ph_3CH , 519-73-3; Ph_3CCl , 76-83-5; Ph_3CLi , 733-90-4; Ph_3CK , 1528-27-4; Et_2O , 60-29-7.

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