Structure Effects of Ion Pair Separation: Planar and Pyramidal Sulfur- and Silicon-Substituted Carbanions[1]

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The conversion of a lithium reagent to a free carbanion (contact to separated ion pairs) is expected to cause structural changes such as decreased pyramidalization,[2a] decreased inversion barriers at carbon, and increased charge delocalization to substituent groups.[2b] Meaningful comparisons have not been possible since many well-studied lithium reagents, such as those substituted by strong electron-attracting groups (α-phosphoryl-,[3] α-sulfinyl-, and α-sulfonylalkyllithiums[4] and lithium enolates[5]) coordinate through oxygen and not carbon and others are so delocalized (benzhydryl, trityl, fluorenyl, etc.) that C–Li association is weak.[2a,6] We know of only one system for which X-ray data are available for both a contact and solvent-separated ion pair: Ph$_3$CLi(TMEDA)[7a] and Ph$_3$CLi(12-crown-4)$_2$.[7b] The contact ion is slightly pyramidalized, the separated ion planar. Although the effects of THF and more strongly coordinating media (crown ethers, HMPA) on reactivity[8] and solution structure of many organolithium reagents have been studied, the extent of ion separation is usually unknown.[4a,3b,8c,9]

The discovery[1a,b,10] that solvation and ion pair status of many lithium reagents in THF/HMPA can be reliably determined by NMR spectroscopy has made it possible to make a detailed correlation between lithium coordination and carbanion geometry.

(1) For previous papers, see: (a) Reich, H. J.; Green, D. P. *J. Am. Chem. Soc.* 1989, *111*, 8729. (b) Reich, H. J.; Borst, J. P. *J. Am. Chem. Soc.* 1991, *113*, 1835. Reich, H. J.; Borst, J. P.; Dykstra, R. R.; Green, D. P. *J. Am. Chem. Soc.*, in press. (c) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* 1989, *111*, 3444. (d) Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* 1985, *107*, 4101. (e) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* 1986, *108*, 2102.

(2) (a) Sygula, A.; Rabideau, P. W. *J. Org. Chem.* 1987, *52*, 3521. (b) Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* 1980, *102*, 4709.

(3) (a) Denmark, S. E.; Miller, P. C.; Wilson, S. R. *J. Am. Chem. Soc.* 1991, *113*, 1468. (b) Bottin-Strzalko, T.; Seyden-Penne, J.; Pouet, M.-J.; Simonnin, M.-P. *J. Org. Chem.* 1978, *43*, 4346. (c) Zarges, W.; Marsch, M.; Harms, K.; Haller, F.; Frenking, G.; Boche, G. *Chem. Ber.* 1991, *124*, 861.

(4) (a) Chassaing, G.; Marquet, A. *Tetrahedron* 1978, *34*, 1399. (b) Gais, H.-J.; Vollhardt, J.; Hellmann, G.; Paulus, H.; Lindner, H. J. *Tetrahedron Lett.* 1988, *29*, 1259. (c) Boche, G.; Marsch, M.; Harms, K.; Sheldrick, G. M. *Angew. Chem.* 1985, *97*, 577. Boche, G. *Angew. Chem.* 1989, *101*, 286. Boche, G. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 277.

(5) Seebach, D. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 1624.

(6) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Chem. Ber.* 1989, *122*, 2303. Becker, B.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 458. Vanermen, G.; Toppet, S.; Van Beylen, M.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* 1986, 707. Becker, B.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 458.

(7) (a) Brooks, J. J.; Stucky, G. D. *J. Am. Chem. Soc.* 1972, *94*, 7333. (b) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* 1985, *107*, 2174.

(8) (a) Normant, H. *Angew. Chem., Int. Ed. Engl.* 1967, *6*, 1046. Richey, H. G., Jr.; Farkas, J., Jr. *J. Org. Chem.* 1987, *52*, 479. (b) 1,2- vs 1,4-addition: Dolak, T. M.; Bryson, T. A. *Tetrahedron Lett.* 1977, 1961. Wartski, L.; El Bouz, M.; Seyden-Penne, J.; Dumont, W.; Krief, A. *Tetrahedron Lett.* 1979, 1543. Cohen, T.; Abraham, W. D.; Myers, M. *J. Am. Chem. Soc.* 1987, *109*, 7923. (c) Enolates: Seebach, D.; Amstutz, R.; Dunitz, J. D. *Helv. Chim. Acta* 1981, *64*, 2622. Jackman, L. M.; Lange, B. C. *J. Am. Chem. Soc.* 1981, *103*, 4494. Liotta, C. L.; Caruso, T. C. *Tetrahedron Lett.* 1985, *26*, 1599. (d) Stereochemistry: Panek, E. J.; Rodgers, T. J. *J. Am. Chem. Soc.* 1974, *96*, 6921.

(9) Abatjoglou, A. G.; Eliel, E. L.; Kuyper, L. F. *J. Am. Chem. Soc.* 1977, *99*, 8262.

(10) Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* 1989, 318. Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* 1991, *30*, 1011. Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* 1991, *113*, 5751. Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* 1992, *114*, 2112. Jackman, L. M.; Chen, X. *J. Am. Chem. Soc.* 1992, *114*, 403.

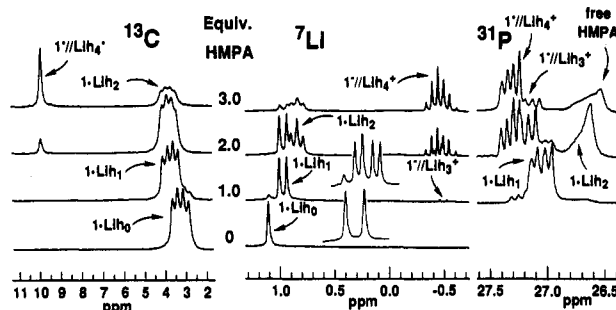**Figure 1.** HMPA titration of 0.13 M 1-Li in 3:2 THF/ether at –132 °C. The ^{7}Li and ^{31}P spectra are at natural isotopic abundance. Insets in the ^{7}Li spectra at 0 and 1 equiv and the ^{13}C signals of C-2 are from ^{13}C· enriched samples of 1. ^{7}Li shifts were referenced to external 0.3 M LiCl in methanol.
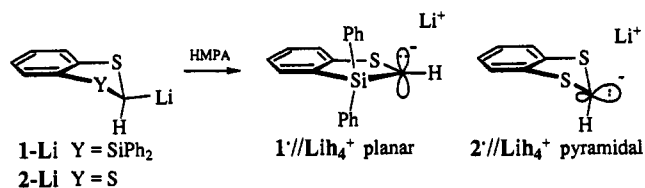
Scheme I

1-Li Y = SiPh$_2$
2-Li Y = S

1'//Lih$_4^+$ planar   2'//Lih$_4^+$ pyramidal

Table I. ^{13}C δ and J_{CH} Values in THF/Ether at –100 °C

reagent	CX	δ_{ipso} S	δ_{ipso} Si	δ_{para} S	δ_{para} Si	δ_{CX}	$^1J_{CH}$
2	CH	139.2		126.2		35.9	156
	C–Li	150.2		122.9		27.8	123
	C$^-$//Li$^+$	152.0		120.8		27.8	123
4	CH	136.0		126.5		35.9	154
	C–Li	150.2		121.9		20.3	141
	C$^-$//Li$^+$	158.6		120.4		4.3	183
3	CH	141.1	133.9	124.6	130.7	13.7	135
	C–Li	151.8	143.3	120.7	127.7	–1.8	131
	C$^-$//Li$^+$	160.5	146.6	119.6	126.6	–1.4	151

We report the results of a low-temperature ^{13}C, ^{7}Li, ^{31}P, and ^{29}Si NMR study of the sulfur- and silicon-substituted organolithium reagents 1–4[11] in which we show that ion separation may give either planar or pyramidal carbanions. We will abbreviate Li-(HMPA)$_n$ as Lih$_n$ and use the symbol // to indicate separated ions (Scheme I).

The ^{7}Li, ^{31}P, and ^{13}C NMR spectra obtained during an HMPA titration of 1-Li[12] in THF/ether (Figure 1) identify 1-Lih$_0$, 1-Lih$_1$, and 1-Lih$_2$ as contact ions (s, d, and t in the ^{7}Li NMR due to $^2J_{LiP}$, observation of $^1J_{CLi}$ of 24.3, 21.4, and 18.8 Hz in the ^{7}Li and ^{13}C NMR spectra of ^{13}C-enriched compound). Above 2 equiv of HMPA, separated ions 1$^-$//Lih$_3^+$ and 1$^-$//Lih$_4^+$ predominate, and the $^1J_{CLi}$ coupling disappears.[1b] Similar HMPA titrations were performed for 2-Li, the acyclic models 3 and 4 (Table I), and a series of related compounds.[11] All are contact ion pairs in THF; addition of HMPA forms separated ion pairs.

Examination of the ^{13}C NMR spectra of 1-Li (Figure 2) shows that 1-Lih$_0$ (Figure 2B) and 1-Lih$_1$ (Figure 2C) have diastereotopic Si(Ph)$_2$ signals. A coalescence temperature of –40 °C for 1-Lih$_0$ (ΔG^* for inversion 10.8 kcal/mol) and –100 °C for 1-Lih$_1$ (ΔG^* = 9.3 kcal/mol) was found. These data, together with the decrease

(11) For spectroscopic data on PhS(PhSe)CHLi, (PhSe)$_2$CHLi, PhS·(PhMe$_2$Si)CHLi, PhSe(PhMe$_2$Si)CHLi, and Ph(PhSe)CHLi, see supplementary material.

(12) Preparation of 1·H: Cabiddu, S.; Floris, C.; Melis, S. *Tetrahedron Lett.* 1986, *27*, 4625. Cabiddu, S.; Fattuoni, C.; Floris, C.; Gelli, G. *Heterocycles* 1988, *27*, 1679.

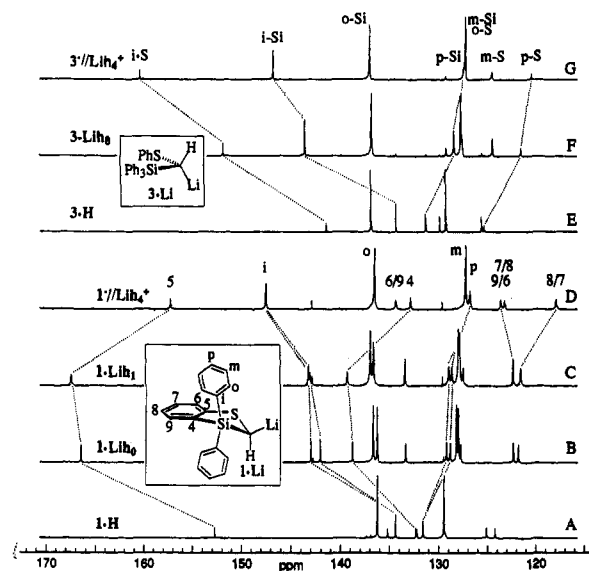**Figure 2.** ^{13}C NMR spectra at -100 °C of **1** and **3** in 3:2 THF/ether. A, **1-H**; B, **1-Li(THF)**; C, **1-Lih$_1$**; D, **1$^-$//Lih$_4^+$** (6 equiv HMPA); E, **3-H**; F, **3-Li(THF)**; G, **3$^-$//Lih$_4$** (6 equiv HMPA).

in $^1J_{CH}$[13] and $^1J_{CSi}$[13a] on going from **1-H** (135 and 51 Hz) to **1-Li** (114 and 49 Hz), indicate that the contact ions are pyramidal. The solvent-separated ion **1$^-$//Lih$_4^+$** (Figure 2D) shows a loss of Si(Ph)$_2$ diastereotopicity and large $^1J_{CH}$ (154 Hz) and $^1J_{CSi}$ (95 Hz) values, which define the carbanion as having a planar or near planar structure. The acyclic models **3**, **4**, and others[11] also show a decrease in J_{CH} on going from C–H to C–Li, signaling a small *increase* in pyramidality and an increase on ion separation, indicating that substantial *flattening* occurs when the C–Li contact is lost. In sharp contrast, $^1J_{CH}$ for the bis-thio lithium reagent **2-Li** does not change on ion separation (123 Hz for **2$^-$//Lih$_4^+$** vs 183 Hz for the model **4$^-$//Lih$_4^+$**), and the free carbanion **2$^-$** is, therefore, pyramidal.

A rationalization for the different behavior of **1-Li** and **2-Li** on ion separation is suggested by an analysis of the ^{13}C chemical shifts of the aromatic carbons (Table I, Figure 2). In compound **2-Li** and the model systems **3-Li** and **4-Li**, the ipso carbons of the S-Ph and Si-Ph groups move downfield on going from C–H to C–Li and the separated ion C$^-$//Li$^+$ (Figures 2E–G). The para carbons move upfield. Other S-, Se-, and Si-substituted carbanions show similar behavior.[11] Carbon chemical shift effects near anionic centers are complex. In benzyl anions, charge polarization effects are thought to account for the nearly equal

downfield shifts for the ipso and upfield shifts for the para carbons between C–H and C–Li.[2b,14] In compounds **1-Li** to **4-Li**, the charge is not directly conjugated with the benzene ring, and the small upfield para shifts reflect a correspondingly small degree of charge polarization. We feel that the large ipso shifts cannot be solely due to charge polarization and propose that they are a consequence of $n \to \sigma^*$ hyperconjugative interactions (R_2C^-—S—Ph $\leftrightarrow$ R_2C=S$^-$-Ph).[15] Such interactions represent an important carbanion-stabilizing mechanism.[16]

The ring quaternary carbons C-4 and C-5 of **1** shift *downfield*, just as do related carbons in **3** on going from C–H to contact C–Li. However, an *upfield* shift of these carbons was observed on going to the solvent-separated species **1$^-$//Lih$_4^+$** (Figure 2D). We interpret this upfield shift in terms of a reduction of hyperconjugative interaction into the ring. The Si-Ph groups show significantly higher than normal ipso carbon downfield and para carbon upfield shifts on ion separation, and this may signal an increase in the interaction of the carbanion center within the exocyclic silyl phenyls.

The divergent behavior of **1** and **2** can be rationalized by considering two limiting structures. The first has a pyramidal carbon and a puckered ring; carbanion–lithium interaction and $n_C \to \sigma^*$ overlap with endocyclic C–S and C–Si (for **1-Li**) bonds is maximized and n_C-n_S repulsion minimized. Both **1-Li** and **2-Li** adopt this geometry in the contact ion. For **1-Li**, removal of lithium tips the balance to a second structure with a planar carbon and perhaps a less strained flat ring in which the major $n_C \to \sigma^*$ interactions are with the exocyclic Si-Ph groups, as shown in Scheme I. In contrast, **2-Li** remains pyramidal in the separated ion and the ring nonplanar, since a planar ring and planar carbanion places the lone pair orthogonal to the C–S bonds and in a position to interact in a destabilizing fashion with sulfur lone pairs.

Supplementary Material Available: ^{13}C chemical shifts and coupling constants for PhS(PhSe)CHLi, (PhSe)$_2$CHLi, PhS-(PhMe$_2$Si)CHLi, PhSe(PhMe$_2$Si)CHLi, and Ph(PhSe)CHLi; HMPA titration of **2** (2 pages). Ordering information is given on any current masthead page.

(13) (a) Gais, H.-J.; Vollhardt, J.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1092. (b) Waack, R.; Doran, M. A.; Baker, E. B.; Olah, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 1272. Brown, T. L.; Gerteis, R. L.; Bafus, D. A.; Ladd, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 2135.

(14) Browne, S. E.; Asher, S. E.; Cornwall, E. H.; Frisoli, J. K.; Harris, L. J.; Salot, E. A.; Sauter, E. A.; Trecoske, M. A.; Veale, P. S., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1432.

(15) The 1-carbon of PhLi is strongly downfield shifted:[1c] Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. *J. Phys. Chem.* **1969**, *73*, 1624.

(16) Wolfe, S.; LaJohn, L. A.; Bernardi, F.; Mangini, A.; Tonachini, G. *Tetrahedron Lett.* **1983**, *24*, 3789. Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 1397. Bernardi, F.; Bottoni, A.; Valli, G. S.; Venturini, A. *Gazz. Chim. Ital.* **1990**, *120*, 301. Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1976**, *98*, 7498. Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arod, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.