Multinuclear NMR Study of the Solution Structure and Reactivity of Tris(trimethylsilyl)methyllithium and its Iodine Ate Complex

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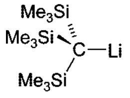
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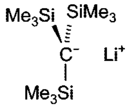
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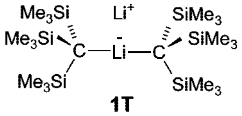
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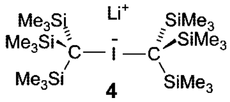
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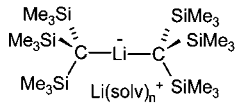
The extreme steric bulk of *tris*(trimethylsilyl)methyl derivatives (**1-X**) provides interesting structural and dynamic behavior for study. Dynamic NMR studies on **1-SePh** and **1-I** showed restricted rotation around the C−Si bonds of each trimethylsilyl groups. An extensive multinuclear NMR study of natural abundance and ^{6}Li and ^{13}C enriched **1-Li** revealed three species in THF-containing solvents, a dimer **1T**, and two monomers, the contact ion pair **1C**, and solvent separated ion pair **1S**. Observed barriers for interconversion of **1-Li** aggregates were unusually high ($\Delta G^{\ddagger}$ ca. 9 kcal/mol for exchange of **1S** and **1C**, $\Delta G^{\ddagger}_{41} = 16.4$ kcal/mol for exchange of **1T** with **1C** and **1S**), allowing for study of reactivity of each aggregate individually. We can show that **1S** is at least 50 times as reactive as **1C** and at least 5×10^{10} times as reactive as **1T** toward MeI. The large difference in reactivity allowed further study on the mechanism of the lithium−iodine exchange of **1-I** with **1-Li** and characterization of the intermediate iodine ate complex **4**. Additional calibrations are presented for the sensitive yet chemically inert ^{13}C NMR chemical shift thermometer **1-H**.

Introduction

The *tris*(trimethylsilyl)methyl group as a substituent in organometallic compounds imparts unusual chemical properties, largely as a result of extraordinary steric effects.[1,1b] Here we present our findings on the properties of *tris*(trimethylsilyl)-methyl lithium (**1-Li**), which was first studied by the Eaborn group.[1] In the solid state, when crystallized in the presence of THF,[1c] TMEDA[1d] or PMDTA[1d] it forms triple ions of type R_2Li^- Li^+ (**1T**), with counterions $Li(THF)_4^+$, $Li(TMEDA)_2^+$ and the very unusual inverse triple ion $Cl(Li^-PMDTA)_2^+$ (when formed in the presence of LiCl). Comparison of solid state MAS[2a] and solution NMR spectra suggested that the triple ion is also present in THF solution, in addition to a second species, which was assigned the structure **1C**, the contact ion pair.[1e] When prepared in the absence of donor solvents by Li/Hg exchange of $[(Me_3Si)_3C]_2Hg$ a four-center dimer with agostic Li−H interactions forms.[3]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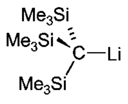
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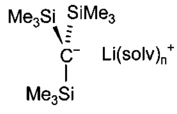
1S

We have encountered numerous triple ions in our NMR studies of the effects of HMPA on organolithium reagents.[4a−d]

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[1] (a) For example, *bis*(*tris*(trimethylsilyl)methyl)-zinc can be steam distilled and does not react with either bromine or boiling concentrated hydrochloric acid. Eaborn, C.; Retta, N.; Smith, J. D. *J. Organomet. Chem.* **1980**, *190*, 101–106. (b) Eaborn, C.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **2001**, 1541–1552. (c) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827–828. (d) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Stamper, J. G.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 969–970. (e) Avent, A. G.; Eaborn, C.; Hitchcock, P. B.; Lawless, G. A.; Lickiss, P. D.; Mallien, M.; Smith, J. D.; Webb, A. D.; Wrackmeyer, B. *J. Chem. Soc., Dalton Trans.* **1993**, 3259–3264. (f) Eaborn, C.; Clegg, W.; Hitchcock, P. B.; Hopman, M.; Izod, K.; O'Shaughnessy, P. N.; Smith, J. D. *Organometallics* **1997**, *16*, 4728–4736.

[2] (a) Pepels, A.; Günther, H.; Amoureux, J. P.; Fernandez, C. *J. Am. Chem. Soc.* **2000**, *122*, 9858–9859.

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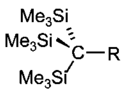
At the time we began this work,[5] **1T** was the only localized carbanion triple ion to be characterized (others have been found since[6a]), although triple ions formed by delocalized lithium π-complexes such as cyclopentadienyl lithiums (lithocenes),[6b] and pentadienyls[7a,8] as well as lithium amides,[9a,b,10,11] and β-keto[12] and lithium β-imino[9c] enolates were known. We undertook an NMR spectroscopic examination of **1-Li** to help better define the solution structure of this interesting system than was possible when earlier studies were performed.[1e,5] We found that the structural characteristics and dynamic behavior of the compound are even more unusual than previously reported.

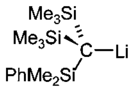
Results and Discussion

We have used three different THF-containing mixed solvents for the experiments on **1-Li**. This was necessary so that the full range of temperatures (from −135 °C to +60 °C) could be covered. Our workhorse solvent was 3:2 THF/ether, but 3:2:1 Me_2O/THF/ether and 1:3 THF/Me_2O were also used for very low-temperature work. The latter mixture was especially crucial for the rapid injection NMR (RINMR) work, since THF readily crystallized from the other mixtures below −130 °C when the sample was stirred (although unstirred samples gave long-lasting supersaturated solution appropriate for standard variable temperature work). We believe these three mixtures to have comparable solvation properties for lithium reagents. For example, the *n*-BuLi dimer/tetramer association constant was 66, 63, and 41 M^{-1} in the three solvents, and the monomer/dimer association constant of 2-ethylphenyllithium was 0.19 M^{-1} in both 3:2 THF/ether and 3:2:1 Me_2O/THF/ether at −140 °C.[4e] The ratio of **1S**, **1C** and **1T** to be discussed below are also very similar in these solvent mixtures. When direct rate comparisons were made, every effort was made to compare experiments in identical solvent mixtures, but occasionally comparisons between different solvents were useful. The lithium reagents were also briefly examined in diethyl ether, to determine the effects on structure of a lower dielectric constant solvent.

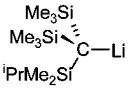
Solutions of **1-Li** could be prepared by the reported procedure of metalation of **1-H** with MeLi in THF at room temperature.[1c] Such solutions were suitable for some NMR spectroscopic work, and were used to prepare the selenide **1-SePh** by reaction with diphenyl diselenide and the iodide **1-I** by reaction with iodine. However, it was more convenient to prepare samples immediately before use by the Li/Se exchange[13a] of **1-SePh** with *n*-BuLi, *n*-Bu^6Li or Et^6Li (half-life of ca. 40 min at −130 °C). This technique produced clean solutions of **1-Li** which were adequate for careful spectroscopic or kinetic studies. The BuSePh formed did not interfere with the spectroscopic work. ^{13}C enriched **1-SePh** was prepared as previously described using [^{13}C]formaldehyde via [^{13}C]$(PhSe)_2CH_2$,[4b] or by a shorter synthesis in which [^{13}C]chloroform was reductively silylated to produce [^{13}C]**1-H**,[14] which was metalated by the literature procedure[1c] and quenched with Ph_2Se_2.



1-H R = H
1-SePh R = SePh
1-I R = I
1-Me R = Me
1-Bu R = Bu



2-Li



3-Li

The selenide precursors to the phenyl and isopropyl analogs **2-Li** and **3-Li** were prepared as shown in Scheme 1. This route could also serve to prepare ^{13}C labeled materials since [^{13}C]$CHBr_3$ is commercially available, but we did not find it necessary to do so.

Dynamic Properties of Tris(trimethylsilyl)methyl Derivatives. Some *tris*(trimethylsilyl)methyl derivatives show rotational DNMR effects in the temperature region of interest for many of the experiments reported here. Specifically, the trimethylsilyl ^{13}C signals of **1-SePh** decoalesced into a 2:1 ratio of signals around −130 °C (Figure 1a). Although we initially assigned this to restricted rotation around the C−SePh bond, which would render one of the trimethylsilyl signals different from the other two, we observed a very similar decoalescence

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(3) Hiller, W.; Layh, M.; Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 324–326.

(4) (a) Reich, H. J.; Sikorski, W. H.; Gudmundsson, B. Ö.; Dykstra, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4035–4036. (b) The sample temperature during NMR experiments was measured using the *tris*(trimethylsilyl)methane internal ^{13}C NMR chemical shift thermometer: Sikorski, W. H.; Sanders, A. W.; Reich, H. J. *Magn. Resonan. Chem.* **1998**, *36*, S118–S124. (c) Reich, H. J.; Goldenberg, W. S.; Gudmundsson, B. Ö.; Sanders, A. W.; Kulicke, K. J.; Simon, K.; Guzei, I. A. *J. Am. Chem. Soc.* **2001**, *123*, 8067–8079. (d) Jantzi, K. L.; Puckett, C. L.; Guzei, I. A.; Reich, H. J. *J. Org. Chem.* **2005**, *70*, 7520–7529. (e) Reich, H. J.; Holladay, J. E.; Mason, J. D.; Sikorski, W. H. *J. Am. Chem. Soc.* **1995**, *117*, 12137–12150. (f) Reich, H. J.; Goldenberg, W. S.; Sanders, A. W.; Jantzi, K. L.; Tzschucke, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 3509–3521. (g) Reich, H. J.; Borst, J. P.; Dykstra, R. R.; Green, D. P. *J. Am. Chem. Soc.* **1993**, *115*, 8728–8741. (h) Reich, H. J.; Borst, J. P.; Dykstra, R. R. *Tetrahedron* **1994**, *50*, 5869–5880. (i) Sikorski, W. H.; Reich, H. J. *J. Am. Chem. Soc.* **2001**, *123*, 6527–6535. (j) Reich, H. J.; Dykstra, R. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1469–1470. (k) Reich, H. J.; Dykstra, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 7041–7042. (l) Reich, H. J.; Green, D. P.; Medina, M. A.; Goldenberg, W. S.; Gudmundsson, B. Ö.; Dykstra, R. R.; Phillips, N. H. *J. Am. Chem. Soc.* **1998**, *120*, 7201–7210. (m) Reich, H. J.; Holladay, J. E.; Walker, T. G.; Thompson, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 9769–9780. (n) Jones, A. C.; Sanders, A. W.; Bevan, M. J.; Reich, H. J. *J. Am. Chem. Soc.* **2007**, *129*, 3492–3493. (o) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414–1416. (p) Reich, H. J.; Gudmundsson, B. Ö.; Green, D. P.; Bevan, M. J.; Reich, I. L. *Helv. Chim. Acta* **2002**, *85*, 3748–3772. (q) Reich, H. J.; Phillips, N. H. *Pure Appl. Chem.* **1987**, *59*, 1021–1026.

(5) (a) Reich, H. J.; Sikorski, W. H.; Thompson, J. L.; Sanders, A. W.; Jones, A. C. *Org. Lett.* **2006**, *8*, 4003–4006. (b) Jones, A. C.; Sanders, A. W.; Sikorski, W. H.; Jansen, K. L.; Reich, H. J. *J. Am. Chem. Soc.* **2008**, *130*, 6060–6061.

(6) (a) Bildmann, U. J.; Mueller, G. *Organometallics* **2001**, *20*, 1689–1691. (b) Eiermann, M.; Hafner, K. *J. Am. Chem. Soc.* **1992**, *114*, 135. (c) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744. (d) Zaegel, F.; Gallucci, J. C.; Meunier, P.; Gautheron, B.; Sivik, M. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1994**, *116*, 6466–6567.

(7) (a) Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657–5664. (b) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 6190–6198. (c) For an insightful discussion of dynamic processes involving C-Li multiplets in monomeric aryllithium reagents, see: Fraenkel, G.; Subramanian, S.; Chow, A. *J. Am. Chem. Soc.* **1995**, *117*, 6300–6307. (d) For many organolithium reagents, especially aggregated ones, quadrupolar broadening is severe enough with ^7Li (92.6% natural abundance) that C−Li coupling cannot be resolved. The ^6Li analogs show little or no quadrupolar broadening and thus couplings are more easily seen: Fraenkel, G.; Fraenkel, A. M.; Geckle, M. J.; Schloss, F. *J. Am. Chem. Soc.* **1979**, *101*, 4745–4747.

(8) Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 8480–8481.

(9) (a) Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751–5757. (b) Romesberg, F. E.; Bernstein, M. P.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 3475–3483. (c) Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 3546–3553. (d) Lucht, B. L.; Bernstein, M. P.; Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1996**, *118*, 10707–10718.

(10) (a) Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987**, *109*, 6524–6525. (b) Jackman, L. M.; Scarmoutzos, L. M.; Smith, B. D.; Williard, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 6058–6058.

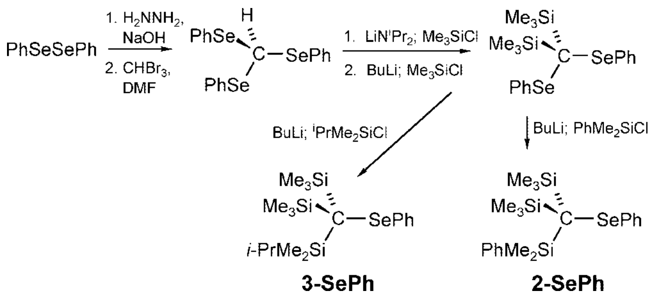
(11) Gornitzka, H.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 693–695.

(12) (a) Cambillau, C.; Bram, G.; Corset, J.; Riche, C. *Nouv. J. Chim.* **1979**, *3*, 9–11. (b) Cambillau, C.; Ourevitch, M. *J. Chem. Soc., Chem. Commun.* **1981**, 996–997. (c) Raban, M.; Haritos, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 5178–5182. (d) Teixidor, F.; Llobet, A.; Casabó, J.; Solans, X.; Font-Altaba, M.; Aguiló, M. *Inorg. Chem.* **1985**, *24*, 2315–2317.

(13) (a) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972–1988. (b) Seebach, D.; Hassig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308–337. (c) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta,* **1980**, *63*, 2046–2053.

(14) (a) Merker, R. L.; Scott, M. J. *J. Organomet. Chem.* **1965**, *4*, 98–100. (b) Guijarro, A.; Yus, M. *T etrahedron* **1996**, *52*, 1797–1810.

SCHEME 1. Synthesis of Selenide Precursors to 1-Li, 2-Li and 3-Li



for **1-I** (Figure 1b), for which this is not a tenable explanation. Rather, it must be restricted rotation around the C−Si bonds of each trimethylsilyl group that causes the observed dynamic effect, and this has been supported by a careful study reported for several other derivatives.[15]

Tris(trimethylsilyl)lithium in THF/Ether. Our extensive multinuclear NMR spectroscopic examination of **1-Li** both at natural abundance, as well as ^{6}Li and ^{13}C singly and doubly enriched showed that there were three species present in THF-containing solvents, the triple ion **1T**, the contact ion pair (CIP) **1C**, and the separated ion pair (SIP) **1S** (Figure 2). The NMR signals for **1C** and **1S** coalesced at ca. −70 °C, and the signals of **1T** coalesced with this averaged signal at >50 °C (we will discuss these experiments in more detail below). Thus all three species are structurally closely related. Variable concentration-experiments were complicated by this dynamic behavior, since under conditions where all three sets of signals were well resolved, **1T** was no longer in mobile equilibrium with the other two. We thus measured the concentration dependence of the three species at room temperature, where only the signals of **1T** and the average of **1C/1S** were seen. A plot of log[**1T**] vs log[**1C/1S**] showed a slope of 1.97, consistent with **1T** being a dimer, and **1C/1S** monomers (Figure 3). At −118 °C, where all three species could be quantitated, but where the triple ion equilibrates slowly with the monomers, there was a consistent deviation, such that comparison of **1T** and **1S** gave a slope of 1.6, whereas **1T** vs **1C** gave a slope of 2.3.[16] The deviations are in the direction that **1S** might be slightly aggregated at low temperature.

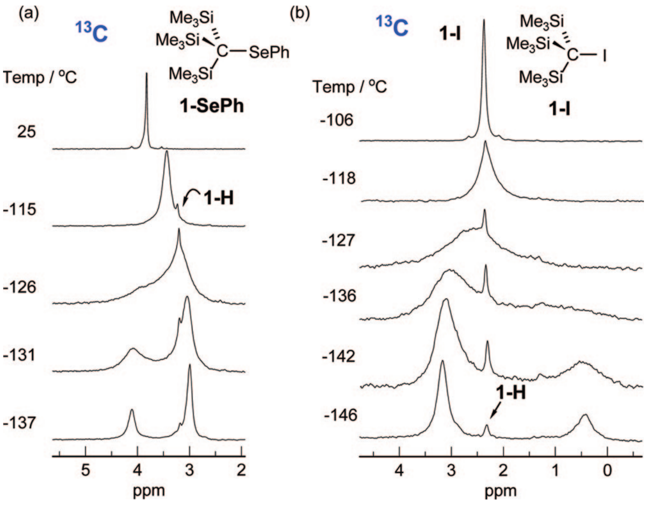


FIGURE 1. ^{13}C NMR spectra from a variable temperature study in 3:2 THF/Et$_2$O of: (a) 0.16 M *tris*(trimethylsilyl)methyl phenyl selenide (**1-SePh**); (b) 0.26 M *tris*(trimethylsilyl)methyl iodide (**1-I**).

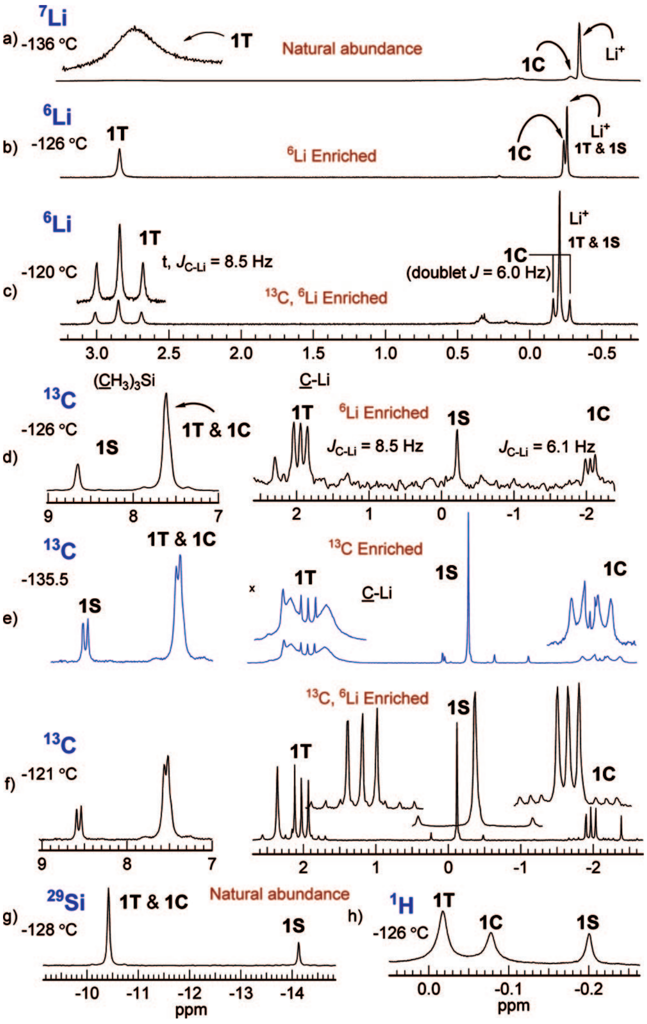


FIGURE 2. Multinuclear NMR study of **1-Li** in 3:2 THF/Et$_2$O. (a) ^{7}Li NMR spectra at natural abundance. (b) ^{6}Li NMR of ^{6}Li enriched **1-Li**. (c) ^{6}Li NMR of doubly enriched (^{13}C and ^{6}Li) **1-Li** (d−f) ^{13}C NMR of ^{6}Li enriched, ^{13}C enriched and doubly enriched **1-Li**. (g) ^{29}Si NMR spectrum and (h) ^{1}H NMR spectrum of **1-Li**.

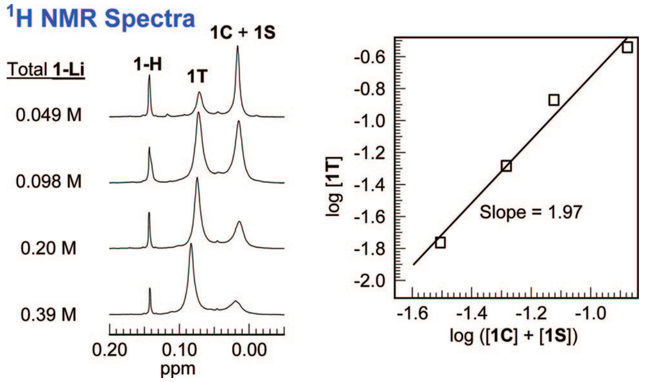


FIGURE 3. Variable concentration experiment of **1-Li** at 20 °C in 3:2 THF/ether.

The structure of the dimer **1T** could be firmly assigned as a triple ion from the appearance of two lithium NMR signals, one unusually downfield at δ 2.7, a shift effect seen for a number of other triple ions,[4a−d] and the other with a chemical shift characteristic of free solvated Li$^+$ at δ −0.2 (Figure 2c). The ^{13}C and ^{6}Li double isotopically enriched compound showed the expected coupling in the ^{13}C (1:1:1 t, $^1J_{\mathrm{C-Li}}$ = 8.5 Hz) and ^{6}Li

NMR spectra (1:2:1 t, ${}^1J_{\mathrm{Li-C}} = 8.5$ Hz) arising from coupling of one lithium to two carbons.

The assignment of **1C** as the contact ion pair (CIP) was based on the observation of coupling between ^{7}Li and carbon in the ^{13}C enriched material (Figure 2f), and in both the ^{13}C (1:1:1 triplet, ${}^1J_{\mathrm{C-Li}} = 6.0$ Hz) and ^{6}Li NMR spectra in the ^{6}Li/^{13}C doubly enriched compound (Figure 2c, 2f). The concentration-dependent experiments supported this assignment. The third component present in solutions of **1-Li** was assigned the separated ion pair (SIP) structure **1S**. We recognize that the observation of distinct NMR signals for CIP/SIP pairs in ethereal solvents is unprecedented, although such structures are well-known for [2.2.1]crypt[17,18] and HMPA[4f] solvated species, where the SIP and CIP have different levels of crypt/HMPA solvation and ligand exchange is slow on the NMR time scale. In such situations the exchange of CIP and SIP carbanions can be much faster than interchange of differently solvated lithium counterions.[4g] In other words, for these systems it is not the breaking of the C−Li bond, but rather cleavage of the Li-HMPA or Li-crypt association that provides the main barrier to ion pair interconversion.

The evidence for the assignment of **1S** can be summarized as follows. The signals for **1S**, **1C**, and **1T** grew in together when the metalation of **1-H** was followed by NMR spectroscopy, and their ratio was consistent throughout the metalation.[16] The signal(s) for **1S** were present in all samples prepared by several different methods (metalation, Li/Se exchange, Li/I exchange), and the appropriate signals of all of the nuclei of **1S** and **1C** coalesced above −80 °C. All these observations show that the signals for **1S** were not an adventitious impurity. The species is monomeric and shows no coupling between C and Li even at the lowest temperatures accessible. The addition of HMPA led to complete conversion to the separated ion pair **1S**, as is seen for many related lithium reagents (Figure 4).[4f−i] In the lithium NMR spectra, only one signal for separated Li^+ species of **1T** and **1S** was observed, as expected for a mobile free lithium cation. That **1S** was associated with a free lithium cation was shown by the preparation of nonequilibrium samples (see below) containing no **1T**, which still show a SIP-Li^+ at δ_{Li} −0.25 for **1S**. In less polar media (ether) the signals for **1S** disappear (Figure 5).

The ^{13}C NMR spectra of doubly enriched **1-Li** showed ^{29}Si satellites for the carbanion carbon, with ${}^1J_{\mathrm{C-Si}}$ of 41.0, 42.6 and 64.9 Hz for **1T**, **1C**, and **1S**, respectively. The substantially larger C−Si coupling for **1S** can be ascribed to a more planar environment at the carbanion carbon. Larger C−Si[4i] and C−H[4i,19,20] couplings for SIPs vs CIPs have been reported for related compounds.

Tris(trimethylsilyl)methyllithium in Diethyl Ether. Solutions of **1-Li** in $\mathrm{Et_2O}$ showed only a single species, which could be assigned the **1C** structure based on the observation of a 1:1:1 triplet (${}^1J_{\mathrm{C-Li}} = 8.0$ Hz) at δ 0.5 in the ^{13}C NMR spectrum and a single peak in the ^{6}Li NMR spectrum (Figure 5). The lower coordination strength and dielectric constant of ether vs THF results in suppression of the ionic species **1S** and **1T**. The HMPA titration showed a dramatic difference from the behavior in THF in that mono-HMPA (**1C**^{1}) and even some bis HMPA CIP (**1C**^{2}) species were formed, accompanied by conversion to some **1T** and eventually **1S**. Superscripts refer to the number of HMPA molecules coordinated to lithium.

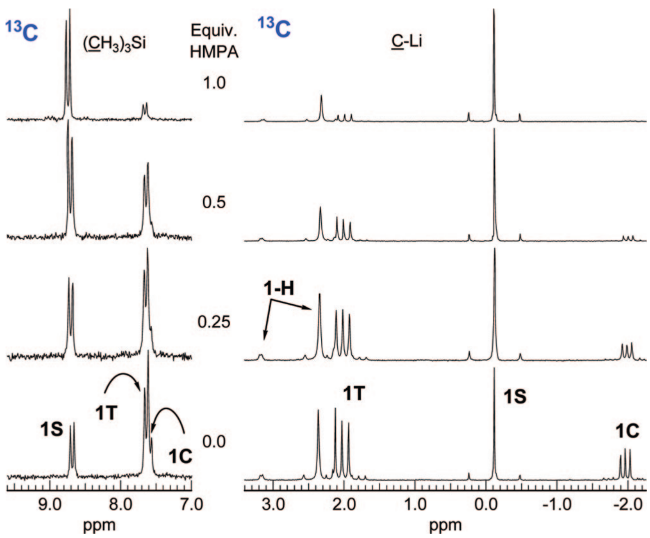


FIGURE 4. ^{13}C NMR spectra from an HMPA titration of ^{13}C- and ^{6}Li-enriched 0.12 M *tris*(trimethylsilyl)methyllithium (**1**{^{13}C}-^{6}Li) in 3:2 THF/$\mathrm{Et_2O}$ at −121 °C.

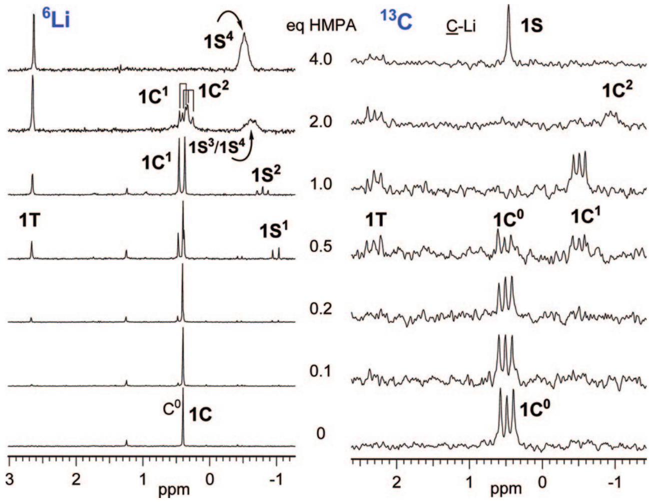


FIGURE 5. ^{6}Li and ^{13}C NMR spectra of an HMPA titration of a 0.09 M solution of **1-^{6}Li** in ether at −122 °C (**1C**^{1} indicates **1C** coordinated to one HMPA molecule).

Tris(trimethylsilyl)methyllithium and PMDTA. The tridentate cosolvent *N,N,N′,N″,N″*-pentamethylethylenetriamine (PMDTA) often (but not always[4c,e]) converts dimeric lithium reagents to monomers (e.g., neopentyllithium,[7b] PhLi,[4j,e,21,22] anisyllithium,[23] $\mathrm{LiN(SiMe_3)_2}$[9d]). Treatment of **1-Li** with PMDTA leads to a smooth conversion to the PMDTA-complexed **1S**.[16] Presumably steric factors prevent this tridendate ligand from coordinating to either **1C** or **1T**.

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(15) Casarini, D.; Foresti, E.; Lunazzi, L.; Mazzanti, A. *Chem.−Eur. J.* **1999**, *5*, 3501–3508.

(16) Spectra and additional data are shown in the Supporting Information.

(17) (a) Cahen, Y. M.; Dye, J. L.; Popov, A. I. *J. Chem. Phys.* **1975**, *79*, 1289–92. (b) Cahen, Y. M.; Dye, J. L.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 1292–1295. (c) Shamsipur, M.; Popov, A. I. *J. Phys. Chem.* **1986**, *90*, 5997–5999.

(18) Shamsipur, M.; Karkhaneei, E.; Afkhami, A. *Polyhedron* **1998**, *17*, 3809–3815.

(19) Schade, S.; Boche, G. *J. Organomet. Chem.* **1998**, *550*, 381–395.

(20) Rabideau, P. W.; Wetzel, D. M.; Husted, C. A.; Lawrence, J. R. *Tetrahedron Lett.* **1984**, *25*, 31–34.

(21) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371–2379.

(22) Schümann, U.; Kopf, J.; Weiss, E. *Angew. Chem.* **1985**, *97*, 222. Schümann, U.; Kopf, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 215–216.

(23) Harder, S.; Boersma, J.; Brandsma, L.; van Mier, G. P. M.; Kanters, J. A. *J. Organomet. Chem.* **1989**, *364*, 1–15.

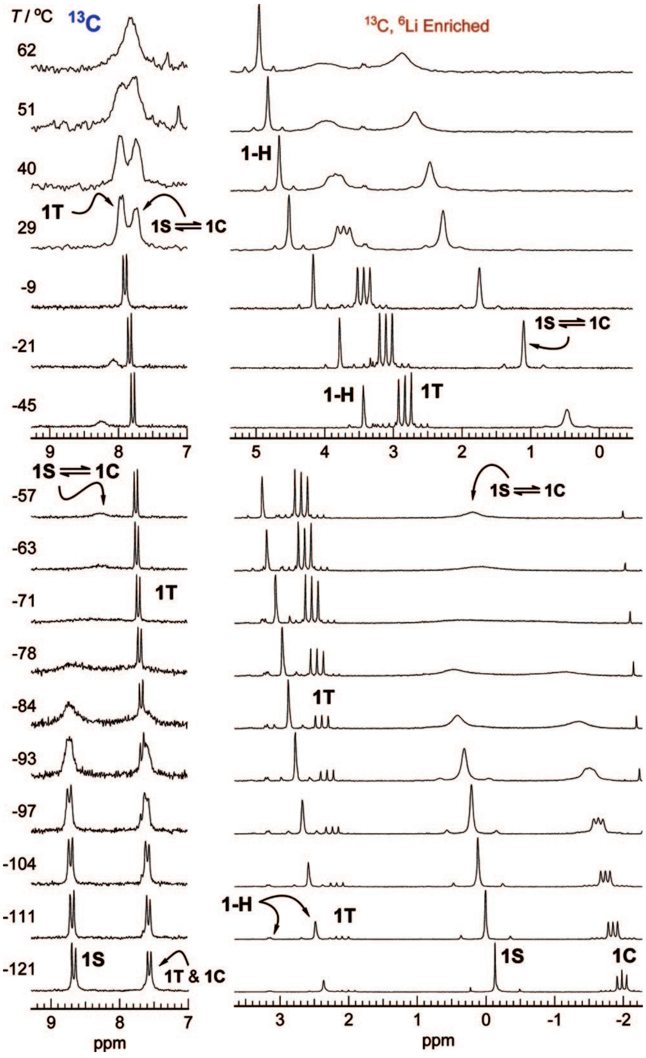

FIGURE 6. Variable temperature ^{13}C NMR study of ^{13}C- and ^{6}Li-labeled 0.12 M *tris*(trimethylsilyl)methyllithium (**1**{^{13}C}-^{6}Li) in 3:2 THF/Et$_2$O generated at low temperature under conditions where the triple ion does not form. Note that there is scale shift at −45 °C in the right panel.

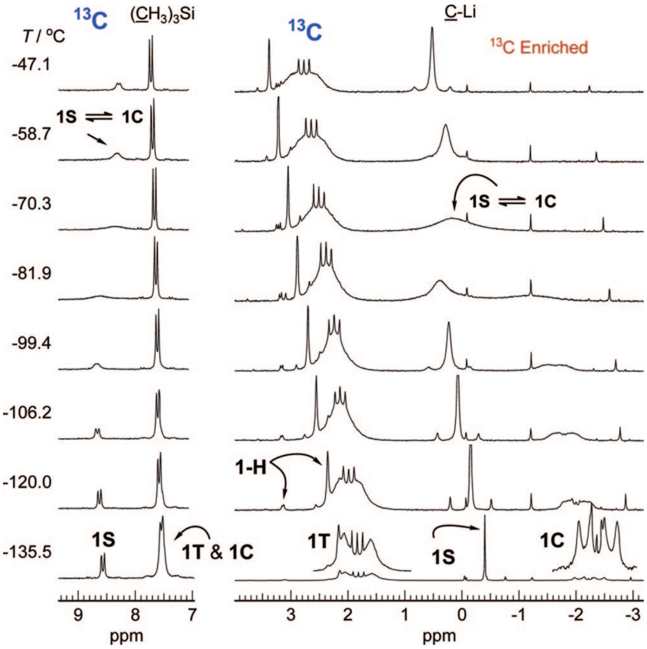

FIGURE 7. Variable temperature ^{13}C NMR study of [^{13}C]**1-Li** in 3:2 THF/Et$_2$O.

DNMR Studies of 1-Li. A number of variable temperature multinuclear NMR experiments were performed to establish the dynamic behavior of the species **1T**, **1S** and **1C**. Figure 6 gives an overview of this behavior using ^{13}C NMR spectroscopy with ^{13}C and ^{6}Li doubly enriched material. There are two coalescences: First the carbanion and methyl signals for **1C** and **1S** coalesce around −70 °C. The barrier is nearly identical in the two principal solvent mixtures used in this study ($\Delta G^{\ddagger}_{-80}$ = 9.6 kcal/mol in 3:2 THF/ether and 9.4 kcal/mol in 1:3 THF/Me$_2$O). Above 40 °C signals for the triple ion **1T** and the averaged **1C**/**1S** signals start to broaden, but coalescence can barely be reached even for the relatively close signals of the SiMe$_3$ carbons because of solvent limitations. Similar behavior was seen in variable temperature NMR experiments by observing the ^{1}H, ^{29}Si, ^{7}Li and ^{6}Li NMR signals.[16]

Figure 7 shows ^{13}C NMR spectra of the ^{13}C enriched compounds with Li at natural abundance between −135 and −47 °C. At low temperature the signal for **1C** is the expected 1:1:1:1 quartet from coupling to the spin 3/2 ^{7}Li nucleus ($^{1}J_{\mathrm{C-Li}}$ = 15.6 Hz). Careful examination reveals the natural abundance ^{6}Li coupled 1:1:1 triplet between the central two peaks of the quartet. The signal at δ 1.9 for the triple ion **1T** at −136 °C, on the other hand, is a broad doublet, characteristic of a nucleus coupled to a spin 3/2 ^{7}Li nucleus undergoing quadrupole induced T_1 relaxation at a rate comparable to J_{CLi}. T_1 is estimated at 11 ms at −135 °C from line-shape simulations using published equations.[7c,24] The sharp 1:1:1 triplet from the natural abundance of ^{6}Li is superimposed on the broad doublet (^{6}Li has a much smaller quadrupole moment, and hence longer T_1[7d]). Similar multiplets have been reported for other C−Li[13b,21] and P−Li signals.[4k] Triple ions generally show broad peaks in their ^{7}Li NMR spectra, thus leading to poor resolution of ^{7}Li−^{13}C coupling as seen here. It is usually necessary to observe ^{6}Li to detect them easily.[4a,i,7d] The larger size of the triple ion molecule results in longer correlation times, and the linear structure with two carbanions bonded to lithium[1c] presumably provides higher electric field gradients than the normal tetrahedral coordination of lithium. Both effects lead to more effective quadrupolar relaxation for **1T** compared to **1S** and **1C**.

As the temperature was raised, the methyl and carbanion signals of **1S** and **1C** coalesced between −70 and −80 °C (Figure 7). The signals for **1T** showed no signs of dynamic chemical exchange in this temperature range, since the peaks for the natural abundance C−^{6}Li signal remain sharp. However, they do show some interesting relaxation effects. As the temperature was raised, the underlying C−^{7}Li signal collapsed to a broad singlet; evidently the ^{7}Li T_1 is becoming shorter at higher temperatures (about 4 ms at −90 °C). This is the opposite trend to what is usually observed.[25] Interestingly, above −90 °C the signal broadens again, and becomes a broad doublet at −47 °C with a ^{7}Li T_1 of 10 ms.[16] Now T_1 is showing the normal increase with increasing temperature. A reasonable explanation for this behavior is that the average molecular correlation time for **1T** is close to the Larmor precession frequency at ca. −90 °C, leading to optimal quadrupole relaxation of ^{7}Li, with less effective T_1 relaxation at both higher and lower temperatures.[26]

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(24) Bacon, J.; Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1963**, *41*, 3063–3069.

(25) Hartwell, G. E.; Allerhand, A. *J. Am. Chem. Soc.* **1971**, *93*, 4415–4418.

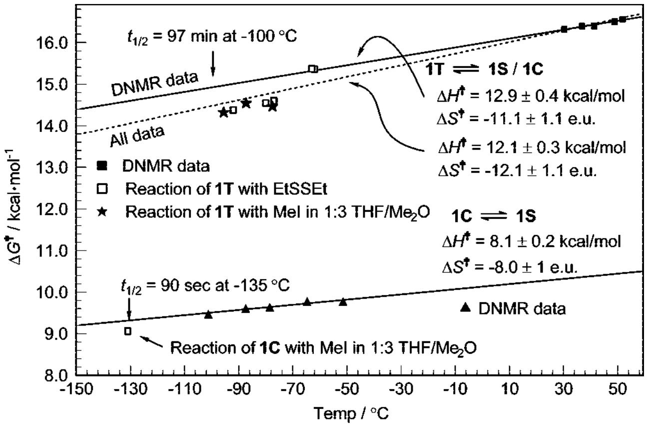

FIGURE 8. Rate data for the interconversion of **1T**, **1C** and **1S** in 3:2 THF/ether.

We performed DNMR line shape analysis of the Me_3Si signals in several variable temperature experiments analogous to the one in Figure 6, but with unlabeled material. As part of the simulation we determined the concentrations of **1S**, **1C** and **1T** as a function of temperature.[16] There is only a very slight increase in the fraction of **1T** at low temperature. Apparently, the opposing effects of increasing the number of particles upon dissociation of **1T** to monomers and reducing the number by additional solvation of **1S** and **1C** are nearly balanced for this system.

Figure 8 shows the Eyring plot and activation parameters found for the low temperature (interconversion of **1C** and **1S**) and high temperature (**1T** and **1S**/**1C**) processes. The barriers for interconversion of **1S** and **1C** ($\Delta G^{\ddagger}$ ca. 9 kcal/mol) are substantially higher than other barriers of this type. For comparison, barriers of 5.3 kcal/mol for a bis(arylthio)-methyllithium,[5b] and 2−4 kcal/mol for arene radical anions have been reported.[27] The much higher barriers for **1-Li** must have steric origins. We speculate that the lithium of **1C** may already be poorly solvated in THF solution for steric reasons, so that breaking of the lithium−carbon coordination of **1C** can not be effectively assisted by solvent, requiring separation of a severely undersolvated lithium cation. Conversely, in the conversion of **1S** to **1C** the normally tetrahedrally solvated free lithium cation may have to shed one or more of its associated solvents before close approach to the carbanion center is possible. The free energies of dissociation of THF from $Li(THF)_4^+$ and from $Li(THF)_3^+$ in the gas phase have been estimated at 14 and 24 kcal/mol.[28] Although gas phase dissociation energies of ionic species will always be higher than solution phase ones, these numbers provide some sense of the energetic cost of unassisted solvent dissociation from a lithium cation.

Conversion of **1T** to **1S** and **1C** likely encounters even more severe solvation problems, leading to the very high barriers observed ($\Delta G^{\ddagger}_{41} = 16.4$ kcal/mol). The central lithium is probably unsolvated, as judged from the crystal structure.[1c] Thus the C−Li bond must be broken with little or no stabilization of the C−Li fragment by solvation. Consistent with this is the observation that the powerful donor solvent HMPA has no effect on the rate of dissociation of **1T**, although a less sterically encumbered base such as an electron-rich benzaldehyde does accelerate it.[5b]

Extrapolation of the dissociation rate of the triple ion measured by DNMR to low temperatures (Figure 8) shows that one can expect laboratory scale lifetimes at −100 °C. Thus it should be possible to directly address the reactivity of the triple ion in such solutions using in situ NMR experiments. The DNMR data predict that even the interconversion of the two ion pairs **1C** and **1S** will become slow enough below −130 °C that reactivity experiments might be performed on them individually. We will address these issues below. This exciting possibility encouraged us to examine the analogs **2-Li** and **3-Li** to see whether these might have even higher barriers which would simplify the rapid injection NMR experiments.

Bis(trimethylsilyl)(phenyldimethylsilyl)methyllithium (2-Li). Smith and Eaborn examined the solid state structure of **2-Li** crystallized from ether.[1f] The structure was monomeric, with a single molecule of ether coordinated to lithium. The Si-Ph group was also coordinated to the lithium. We find that in 3:2 THF/ether solution **2-Li** is almost completely a SIP. Thus the ^{13}C NMR signals were essentially unchanged as HMPA was added, and the lithium signals went through the series of lithium-HMPA complexes characteristic of SIPs.[4f,16] In ether **2-Li** is entirely a CIP, as can be seen from the observation of C−Li coupling ($^1J_{C\text{-}(6)Li} = 7.3$ Hz) and the HMPA titration, which produces some triple ion, **2C**^{1} and **2C**^{2} CIP species, as well as the various HMPA-solvated SIP species.[16]

Bis(trimethylsilyl)(isopropyldimethylsilyl)methyllithium (3-Li). To test whether the increased formation of SIP in **2-Li** was a consequence of the inductive effect of the phenyl substituent we prepared the sterically similar isopropyl analog **3-Li**. This was also a SIP in THF/ether, and a CIP in ether, with behavior very similar to that observed for **2-Li**.[16] Thus the increased tendency of **2-Li** and **3-Li** to form SIPs compared to **1-Li** appears to be largely a steric effect (steric hindrance to solvation of the CIP). Neither **2-Li** nor **3-Li** allowed investigation of the triple ion, CIP and SIP reactivity in a single substrate like that possible for **1-Li**.

Reactivity of 1T, 1C, and 1S. Extrapolation of the DNMR data of Figure 8 to low temperatures suggests that Curtin-Hammett limitations should be easily avoidable for interconversion of **1T** with the monomers, and might be possible for the **1S**/**1C** interconversion. We report here several "proof-of-concept" experiments which demonstrate that the reactivity of different aggregates can be measured. For these experiments we used three techniques for low temperature mixing: (1) To the sample of the substrate in a 10 mm NMR at −138 °C tube was carefully added the reagent, the sample was frozen in liquid N_2, the NMR tube was placed in the spectrometer at the desired temperature (e.g −135 or −85 °C) and allowed to melt. This experiment provides only approximate temperature control, and a time resolution of several minutes. The experiment of Figure 6 was carried out this way (**1-SePh** as substrate and *n*-BuLi as reagent). (2) A sample containing **1-Li** was placed in the NMR probe cooled to the desired temperature, and an electrophile was carefully added by syringe using a long nylon needle. A long thin glass rod with a bent end was inserted into the tube, the solution was stirred and spectra were obtained. This

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(26) The observation of a minimum T_1 at−90 °C for **1T** in THF/ether ($(Me_3Si)_3CLiC(SiMe_3)_3$ $Li(THF)_4$, MW 470 or 765 (depending on whether the cation and anion move as a unit) and ^7Li Larmor frequency of 140 MHz) is qualitatively consistent with other observations. For example, $ReH_7(PPh_3)_2$ (MW 718 shows T_1 (min) at−73 °C for the hydride signals at 500 MHz in toluene-d_8: Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133.

(27) The barrier for interconversion of the SIP/CIP of lithium naphthalide in THF−ether is $G^{\ddagger} = 3.5$ kcal/mol at−50 °C: Hirota, N.; Carraway, R.; Schook, W. *J. Am. Chem. Soc.* **1968**, *90*, 3611–3618.

(28) Jarek, R. L.; Miles, T. D.; Trester, M. L.; Denson, S. C.; Shin, S. K. *J. Phys. Chem. A* **2000**, *104*, 2230–2237.

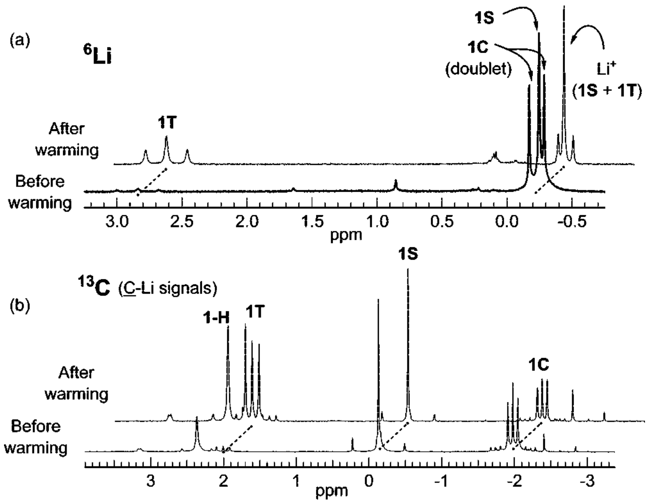


FIGURE 9. ^{6}Li (a) and ^{13}C (b) NMR spectra at −121 °C acquired before and after thermal equilibration of 0.12 M *tris*(trimethylsilyl)methyllithium ($\mathbf{1}\{^{13}C\}$-^{6}Li) in 3:2 THF/Et$_2$O generated by low-temperature Li−Se cleavage of $\mathbf{1}\{^{13}C\}$-**SePh** by *n*-Bu^{6}Li.

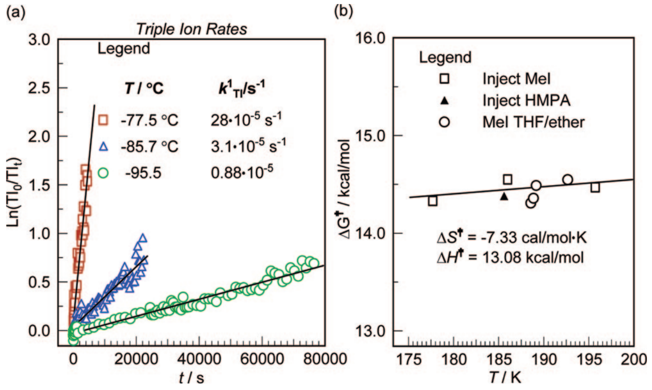


FIGURE 10. (a) RINMR kinetic study of the reaction of **1T** with MeI in 1:3 THF/Me$_2$O at 3 temperatures. (b) Activation parameters for the reaction compared with other trapping experiments.

experiment provides a time resolution of ca. 5−20 s; (3) The automated RINMR apparatus described recently[41] became available toward the end of this research, and was used for a few of the experiments. This apparatus provides excellent temperature control and a time resolution of 1 s or less at temperatures as low as −135 °C. The experiment in Figure 10 was performed this way.

Preparation of Nonequilibrium Ratios of 1C, 1S and 1T. When **1-SePh** was treated with *n*-BuLi below −130 °C, the sample showed mainly **1C**, **1S** and a trace of **1T**; the ratio of **1C**+**1S** to **1T** was 96:4 (Figures 6 and 9). Significant conversion to the equilibrium mixture did not occur until the temperature was raised above −90 °C. When the equilibrated sample was cooled back down to −121 °C, this ratio was 47:53. This experiment shows that laboratory time experiments can be performed on **1T** under non-Curtin-Hammett conditions. Several such experiments are described below.

Conversely, when any one of several electrophiles (MeI, Et$_2$S$_2$, Ph$_2$Se$_2$) was injected into solution of **1-Li** at temperatures below −100 °C, the **1C** and **1S** disappeared within seconds, leaving a solution containing only **1T**. This illustrates that the interconversion of **1T** with the monomers is slow at these temperatures, and that **1T** does not react with these electrophiles on a time scale of many minutes.

Reaction of 1T with Methyl Iodide. When methyl iodide was injected into a solution of **1-Li** in 3:2 THF/ether at −85 °C the NMR signals of **1S** and **1C** disappeared immediately (<1 s) to form (Me$_3$Si)$_3$CMe (**1-Me**), leaving only **1T** in solution. The latter reacted slowly over a period of 1−2 h following first order kinetics to form additional **1-Me**. In a series of such experiments where 1 to 8 equiv of MeI were added the rates were all identical within experimental error. Thus the reaction of **1T** with MeI is first order in **1T** and zero order in MeI. The triple ion does not react with MeI directly, but must first dissociate to the monomers, one or both of which then react quickly with MeI. The results of a variable temperature RINMR study in the 1:3 THF/Me$_2$O solvent mixture are reported in Figure 10. The rates are indistinguishable from those measured in 3:2 THF/ether. Extrapolation to −132 °C gave a value for the rate of dissociation of **1T** as $4 \cdot 10^{-10}$ s^{-1}. The pseudofirst order rate of reaction of MeI with **1T** must be slower than this.

Reaction of 1T with Diethyl Disulfide. The rate of reaction of **1-Li** with diethyl disulfide was examined between −62 and −92 °C. The behavior was nearly identical to that of MeI. The monomers **1S** and **1C** disappeared immediately to form (Me$_3$Si)$_3$CSEt, followed by a slow first-order reaction with **1T** whose rate was independent of disulfide concentration. The rate of the reaction of **1T** with the disulfide was identical to that with MeI (Figure 10b), confirming the same rate-limiting step for both, i.e. dissociation of **1T** to **1S** and **1C**.

There was a small discrepancy between the DNMR rates extrapolated from temperatures above 30 °C to the region of the RINMR rate experiments between −60 and −90 °C (Figure 8). One possible origin of this was suggested by a careful analysis of the ^{13}C chemical shifts of the C−Li and Me$_3$Si carbons of **1C/1S**. If the spectra of Figure 6 are aligned appropriately,[16] a dramatic chemical shift change in both the Me$_3$Si and C−Li carbon for **1C/1S** can be detected between −60 and 30 °C, suggesting that a change in structure of one or both of the component species (possibly loss of a solvent molecule from **1C**) occurred in this temperature range. This would mean the high-temperature DNMR rates for dissociation of **1T** and the low temperature RINMR rates were performed on solutions where one or more of the components are structurally different.

Reaction of 1T with Benzaldehydes. Of the electrophiles tried, only benzaldehydes reacted with **1T** at a rate faster or competitive with the dissociation to **1S** and **1C**. Even here, it turned out that the role of the aldehyde was to catalyze dissociation of **1T** to the monomers, and there was no indication of a chemical reaction with **1T**. These results have been reported in some detail, and will not be reiterated here.[5b]

Reactions of 1S and 1C with Electrophiles. Extrapolation of the DNMR data between −65 and −100 °C for interconversion of **1S** and **1C** (Figures 6 and 8) to −130 °C, the lowest practical temperature for RINMR experiments in this system, predicted a half-life of 22 s in 3:2 THF/ether. The measured half-life of 20 s using experiments described below in the similar solvent system 1:3 THF/Me$_2$O was very close this value, and is too fast to allow manual techniques for low-temperature mixing to address the question of the reactivity of **1S** and 1C. These experiments were handled using the automated RINMR apparatus.[41] Two 1-s interval RINMR experiments of the injection of MeI into solutions of **1-Li** at −131 °C in 3:1 Me$_2$O/THF are shown in Figure 11. In this experiment the ^{1}H NMR signals of **1S** disappeared during the 1 s mixing period ($k_{\text{obs.}} \geq$

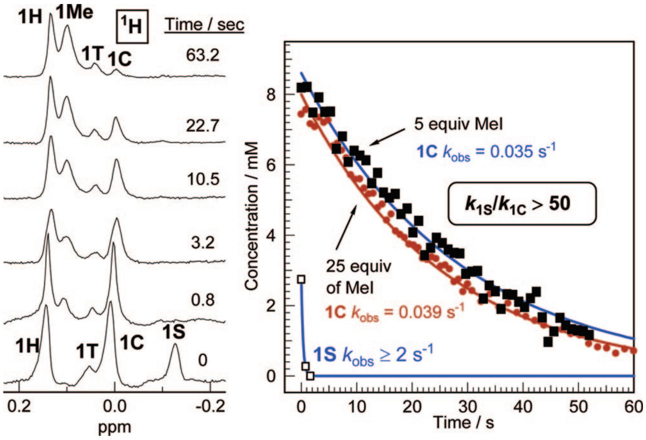
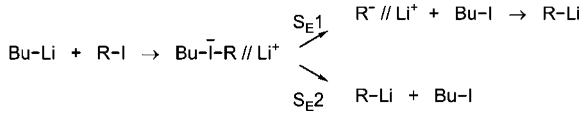


FIGURE 11. RINMR kinetic study of the reaction of **1C** with MeI at −131 °C in 1:3 THF/Me_2O at two concentrations of MeI.

SCHEME 2. Pathways for Conversion of Ate Complexes to Lithium Reagents



2 s^{-1}). The disappearance of **1C** had a half-life of ca. 20 s, and could be readily followed. The rate was independent of MeI concentration over a 5-fold range. Thus **1C** does not react with MeI, but first dissociates to **1S**.

From analysis of these data we can show that **1S** is at least 50 times as reactive as **1C**. Comparison with the extrapolated rate of reaction with **1T** gives lower limit of 5×10^{10} as the relative rate of reaction of **1S** versus **1T** toward MeI. However, since the **1S** rate could actually be much faster (2 s^{-1} is a lower limit) and the **1T** rate much slower (there is no indication that MeI reacts with **1T** in competition with its dissociation), the actual number is probably much larger that this.

Benzaldehyde behaved identically to MeI: **1S** reacted completely within the first second after injection at −131 °C, whereas **1C** disappeared at the known rate of its dissociation to **1S**.[5b]

The Lithium−Iodine Exchange. Reactions of Tris(trimethylsilyl)methyl Iodide (1-I). The ability to individually detect and measure the CIP and SIP structures of **1-Li** suggested that we could perform an experiment that might shed some light on the mechanism of the lithium−iodine exchange, in which we have had a long-term interest. There is substantial evidence that such reactions proceed through intermediate iodine ate complexes (R-I-R^- Li^+), as first suggested by Wittig,[29] and several such complexes have been spectroscopically characterized.[4m,30−33] An open question is the mechanism for conversion of the ate complex intermediate to the product lithium reagents. Spectroscopic studies have shown that iodine ate complexes, as well as those formed from ArLi and Ar_2Te[4m,n,30] and $ArSnR_3$[4o] are SIPs. Two limiting mechanisms can be envisioned for conversion to the lithium reagents (Scheme 2): (1) the ate complex dissociates to a SIP R^-//Li^+ and R-I (S_E1 mechanism) followed by ion combination to form RLi (CIP), or (2) the ate complex is attacked by the lithium cation to form the CIP RLi directly (S_E2 mechanism).

We reasoned that if a Li/I exchange were performed on **1-I** it might be possible to detect whether **1C** (S_E2 reaction) or **1S** (S_E1 reaction) was the primary product. In practice, the addition of **1-I** into a solution of *n*-Bu^6Li at −136 °C did lead to the immediate (10 s) disappearance of the *n*-BuLi dimer signal at δ 1.8 in the ^{6}Li NMR spectra (as with most other reactions of *n*-BuLi,[41] the tetramer was unreactive), and the appearance of a separated lithium species in the ^{6}Li and ^{7}Li NMR spectra. However, examination of the ^{13}C spectra in a similar RINMR experiment (Figure 12) performed on a 10 s time scale on ^{13}C enriched **1-I** revealed conversion of about 30% of the iodide to **1S** or **1C**, in what appeared to be their approx 1:3 equilibrium ratio. The major product was a new species, which we have identified as the iodine ate complex **4**. Apparently any **1-Li** initially formed reacts rapidly with **1-I** to form **4**, and it is the SIP lithium cation of **4** that was principally detected in the lithium NMR spectra, and not **1S**. At longer reaction times conversion of **4** to **1S** and **1C**, as well as formation of the butylation product **1-Bu** was detected. No **1T** was formed.

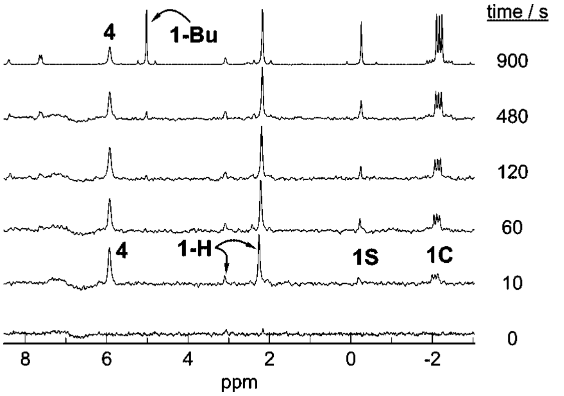
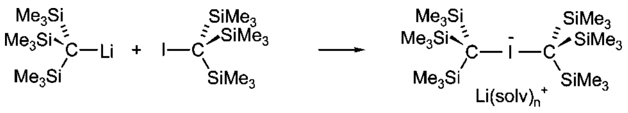


FIGURE 12. ^{13}C RINMR experiment of the addition of **1-I**-[^{13}C] (0.26 mmol) to 0.22 M *n*-Bu^6Li (0.8 mmol) in 3:2:1 Me_2O/THF/ether at −136 °C. All of the major signals are those of the C-X carbon.

Several experiments support the assignment of structure **4**. Addition of one equiv of **1-I** to a solution of **1-Li** at −78 °C led to almost complete disappearance of all four starting components (**1-I**, **1T**, **1S** and **1C**) with formation of a new species (**4**) (Figure 13c). This species had only a single peak in the ^{13}C NMR spectrum, but this was shown to be the result of a coincidence of the Me_3Si and C−I carbons at δ 6.1 by comparison of solutions of **4** prepared from natural abundance and ^{13}C enriched samples, each of which showed the major peak at δ 6.1.



1-Li **1-I** **4**

Injection of MeI into a solution of **4** at −125 °C led to the slow ($t_{1/2}$ ca. 20 min) disappearance of **4**, increase in the concentration of **1-Me**, and the reappearance of the signals for **1-I** (the latter complicated by a near coincidence of the Me_3Si carbon signal with those of **1-H**, and by dynamic broadening

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(29) Wittig, G.; Schollkopf, U. *Tetrahedron* **1958**, *3*, 91–93.

(30) The evidence for this statement for Ph_2ILi and Ph_3HgLi has not been fully published previously, and we include some NMR spectroscopic studies of HMPA titrations in Supporting Information.

(31) Farnham, W. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2449–2451.

(32) Schulze, V.; Brönstrup, M.; Böhm, V. P. W.; Schwerdtfeger, P.; Schimeczek, M.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 824–826.

(33) Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, *352*, 1–46.

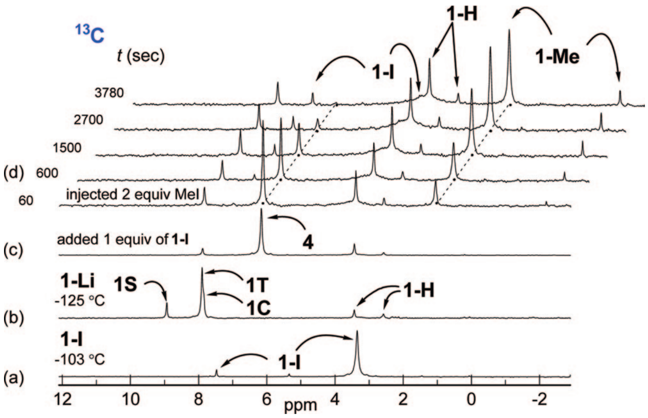

FIGURE 13. ^{13}C NMR spectra (Me_3Si signals) in 3:2 THF/ether. (a) **1-I** at −103 °C. (b) **1-Li** at −125 °C. (c) Addition of 1 equiv of **1-I** to **1-Li** - formation of **4**. (d) Injection of 2 equiv of MeI. The broad peak at δ 3.3 is the partially coalesced (see Figure 1) trimethylsilyl signal of **1-I**.

of the trimethylsilyl signals of **1-I** due to restricted rotation around the C−Si bond, see Figure 1[15]). The reaction is essentially first order in MeI (2.9 fold rate increase for 4 fold increase in concentration). Either the ate complex **4** is reacting directly with the MeI, or the ate complex is in rapid equilibrium with a small amount of **1S**, and this is the reactive species. We favor the latter explanation. The activation barrier obtained from the pseudofirst order rate constant for the experiment with 8 eq of MeI was $\Delta G^{\ddagger}_{-125} = 10.3$ kcal/mol. A ^{13}C DNMR coalescence experiment in 3:2 THF/ether on a solution of **4** containing excess **1-Li** showed that interconversion of **4** with **1-Li** had $\Delta G^{\ddagger}_{-69}$ of 10.3 kcal/mol. Similarly, ^{1}H and ^{13}C DNMR experiments of **4** with excess **1-I** coalesced in the same temperature range, and gave a similar $\Delta G^{\ddagger}_{-69}$ of 10.0 kcal/mol for coalescence of **4** and **1-I**.[16] Although these activation energies were measured at different temperatures, they suggest that dissociation of **4** to **1S** is at least comparable in rate to the reaction with MeI.

Two additional RINMR experiments with approximately 1-s sampling rates were performed in 1:3 THF/Me_2O at −130 °C. Solutions of the iodide **1-I** were injected into solutions of a sufficiently large excess of *n*-BuLi (5 equiv.) that there was more *n*-BuLi dimer than iodide present (BuLi tetramer is unreactive under these conditions). In the first experiment the reaction was followed by ^{7}Li, in the second by ^{1}H NMR spectroscopy. The ^{7}Li experiment confirmed that there was excess $(BuLi)_2$ present after the injection, and that during the first 20 s only a SIP Li signal was observed (the ^{7}Li NMR signals of **1S** and **4** cannot be distinguished). After this **1C** started to appear. In the ^{1}H experiment the signal corresponding to **4** was already present after 2 s, and there was no detectable starting iodide **1-I** left, and no detectable **1C**, **1S** or **1T** was initially formed. Small amounts of both **1S** and **1C** were detectable after 20 s in approximately their 1:1 equilibrium ratio, and these continued to increase over a period of several minutes, accompanied by the slow formation of the butylation product **1-Bu** from reaction of **1S** with BuI. Although these experiments are qualitative in nature and rate details are not fully interpretable, they are consistent with a reaction scheme in which **1S** and/or **1C** are formed in the first few seconds of the reaction (presumably via fast dissociation of the mixed ate complex $Me_3.Si)_3C{-}I{-}Bu^{-}\ Li^{+}$) and are then rapidly captured by remaining **1-I** to form **4** ($k > 2$ s^{-1}). The ate complex **4** then slowly dissociates to **1S**/**1C** and **1-I** ($k = 4.6 \cdot 10^{-4}$ sec^{-1}, $\Delta G^{\ddagger}_{-130} = 10.4$ kcal/mol), which is immediately converted to more **1S**/**1C** by the excess $(BuLi)_2$ present.

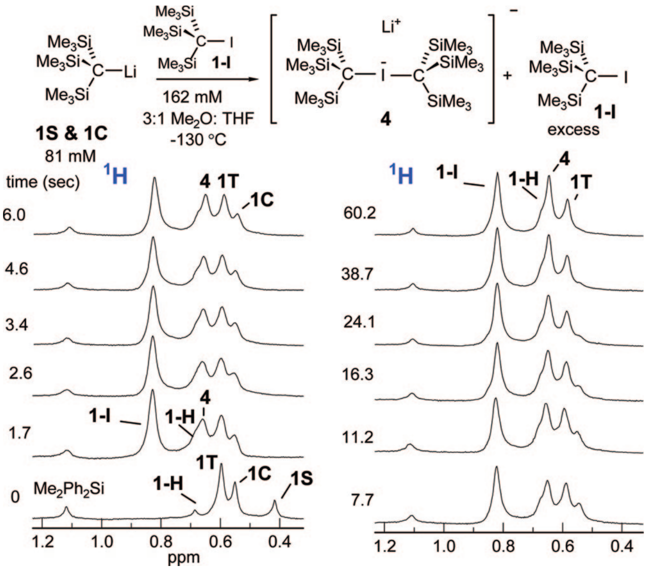

FIGURE 14. ^{1}H NMR spectra of a RINMR experiment in which 2 eq of **1-I** were injected into a 0.08 M solution of **1-Li** in 3:1 Me_2O/THF at −130 °C.

Since the interconversion of **1C** and **1S** ($k = 3.5 \cdot 10^{-2}$ sec^{-1} in 1:3 THF/ether at −131 °C, $\Delta G^{\ddagger}_{-130} = 9.1$ kcal/mol, Figure 8) is faster than the rate of dissociation of **4**, it is not possible to directly answer the question we posed on whether **1C**, **1S** or both are kinetic products of the ate complex dissociation. There is, however, an indirect approach. A RINMR ^{1}H experiment was performed in which an excess of **1-I** was injected into a solution of **1-Li** at −130 °C (Figure 14). In this experiment, **1S** disappeared in under 2 s, but **1C** disappeared at the same rate as the normal **1C** to **1S** conversion in the absence of **1-I** ($k = 0.04$ s^{-1}). In other words, **1-I** does not react with **1C** directly on a time scale of ca. 10 s. In the aforementioned injection of **1-I** into a solution of *n*-BuLi, no **1C** was detected in the first 10 s of the reaction. If **1C** were a kinetic product of the mixed ate complex dissociation (S_E2 mechanism in Scheme 2) it would have built up during the first 10 s of the experiment. That it does not suggests only **1S** is the kinetic product of the exchange.

There is one additional point of interest in the NMR spectra of **4**. Other derivatives of *tris*(trimethylsilyl)methane show decoalescence of trimethylsilyl ^{13}C NMR signals below −100 °C due to slow rotation around the C-$SiMe_3$ bond (Figure 1). Compound **4** shows no such behavior down to −135 °C. Of course it could simply be that the chemical shifts of the two types of methyls are accidentally coincident, but more likely the much longer bond length of the hypervalent C−I bond in **4** compared to that in **1-I** considerably reduces steric effects and lowers the barrier to trimethylsilyl rotation. For example, the C−I bond length in lithium bis(pentafluorophenyl)iodinate is 240 pm,[30] whereas a typical Ar−I bond length is 209 pm.[34]

^{13}C Chemical Shift Thermometer. In all of the $(Me_3Si)_3C$-X compounds the ^{13}C NMR signal of the C-X carbon undergoes a steady downfield drift of ca. 1 Hz/degree as the temperature was raised (see Figures 6 and 7). This effect is very pronounced for **1-H**, and we have performed appropriate calibrations which allow the difference between the ^{13}C chemical shifts of the C−H

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[34] Chaplot, S. L.; McIntyre, G. J.; Mierzejewski, A.; Pawley, G. S. *Acta Crystallogr., Sect. B* **1981**, *B37*, 2210–2214.

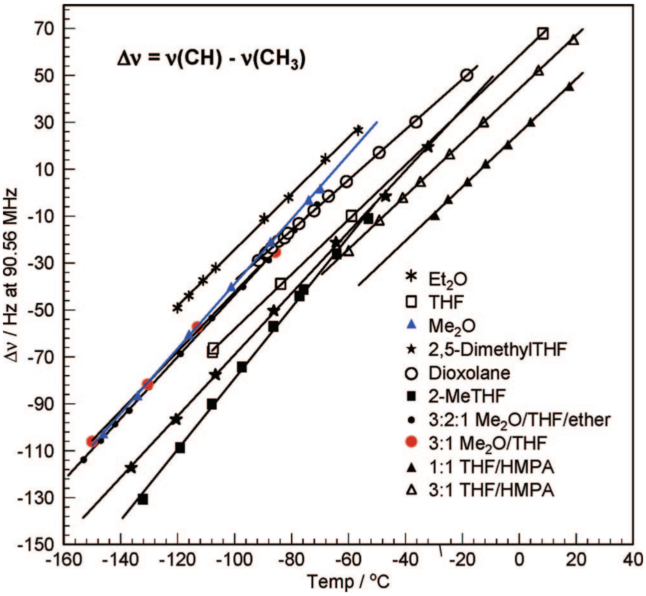

FIGURE 15. Temperature-chemical shift calibrations of **1-H** in various solvents. $\Delta\nu = \nu(CH) - \nu(CH_3)$.

TABLE 1. Chemical Shift Calibrations for the 1-H Chemical Shift Thermometer ($\Delta\delta = \delta(CH) - \delta(Si\text{-}CH_3)$)

Pentane	T (°C) = 83.231 (Δδ) − 86.6 (−124 to 26 °C)
C_6D_6	T (°C) = 82.249 (Δδ) − 19.9 (9 to 69 °C)
Toluene	T (°C) = 77.931 (Δδ) − 24.9 (−89 to 68 °C)
$CDCl_3$	T (°C) = 84.711 (Δδ) − 36.5 (−56 to 49 °C)
CH_2Cl_2	T (°C) = 81.729 (Δδ) − 44.5 (−89 to 33 °C)
3:2 THF/Et_2O	T (°C) = 78.675 (Δδ) − 58.1 (−139 to 60 °C)
MeOH	T (°C) = 83.925 (Δδ) − 83.9 (−80 to 42 °C)
Et_2O	T (°C) = 75.72 (Δδ) − 79.6 (−120 to −56 °C)
THF	T (°C) = 77.75 (Δδ) − 50.2 (−108 to 8 °C)
Me_2O	T (°C) = 65.66 (Δδ) − 71.8 (−146 to −70 °C)
2,5-Me_2THF	T (°C) = 69.28 (Δδ) − 47.2 (−136 to −32 °C)
1,3-Dioxolane	T (°C) = 84.31 (Δδ) − 65.05 (−92 to −18 °C)
2-MeTHF	T (°C) = 59.83 (Δδ) − 47.59 (−132 to −53 °C)
3:2:1 Me_2O/THF/Et_2O	T (°C) = 68.73 (Δδ) − 66.9 (−153 to −73 °C)
3:1 Me_2O/THF	T (°C) = 71.56 (Δδ) − 66.46 (−150 to −86 °C)
1:1 THF/HMPA	T (°C) = 78.66 (Δδ) − 22.12 (−30 to −18 °C)
3:1 THF/HMPA	T (°C) = 79.47 (Δδ) − 38.87 (−60 to −19 °C)
HMPA	T (°C) = 94.18 (Δδ) + 4.42

and Me_3Si carbons ($\Delta\delta = \delta(CH) - \delta(CH_3)$) to be used as an effective internal ^{13}C chemical shift thermometer with many advantages over conventional tube-substitution methods.[4b] We now routinely add approximately 0.1% by volume of 10% ^{13}C enriched **1-H** to NMR samples for convenient temperature measurement simply by running the ^{13}C NMR spectrum. The temperature dependence of the chemical shift (slope) varies only slightly with solvent, but the calibration line (intercept) is offset for each solvent. Since our initial report and in the course of this and related projects we have constructed additional calibration curves for a number of solvents of interest in organometallic chemistry. Figure 15 shows the new calibrations, and Table 1 shows the equations used to calculate chemical shifts, both for the original calibrations[4b] and the new data. The data for HMPA were not measured on a pure solvent, but were calculated from the calibrations for two HMPA/THF mixtures, by assuming additivity of effects.

It was shown that the calibration curves for mixed solvents can be estimated from a weighted average of those of the pure solvents,[4b] and we have made extensive use of this technique. However, such temperatures are likely to be less accurate because of deviations from ideal mixing behavior. Thus the calibration curve for 3:2 THF/ether produced temperatures approximately 2 degrees higher than when an equation calculated from a 3:2 combination of the two pure solvent equations was used. We estimate that for pure solvents or specifically calibrated solvent mixtures the temperatures are accurate to within 1 degree.

Conclusions

Tris(trimethylsilyl)methyllithium (**1-Li**) exists as a mixture of three species in solvents containing a significant fraction of THF—the separated ion pair **1S**, the contact ion pair **1C** and the triple ion **1T**. In diethyl ether solution only **1C** is detected, and addition of HMPA converts **1-Li** completely **1S**. Analogs in which one trimethylsilyl group was replaced by phenyldimethylsilyl (**2**) or isopropyldimethylsilyl (**3**) are all SIP in THF, and CIP in ether.

The triple ion **1S** interconverts with the two monomers slowly on the NMR time scale up to about 40 °C, and slowly on the laboratory time scale below −60 °C, with activation barriers from 14 to 16 kcal/mol. The monomers **1C** and **1S** interconvert slowly on the NMR time scale up to −100 °C, and laboratory time scale experiments on individual ion pair structures are possible below −130 °C using RINMR spectroscopy. Activation barriers are ca. 9 kcal/mol. These exceptionally high barriers for interconversion can be ascribed to steric effects which hinder solvent participation in ion pair interconversion process.

Nonequilibrium ratios of the **1-Li** species could be formed as follows: if **1-Li** was formed by Li/Se exchange of **1-SePh** below −100 °C then solutions of only **1S** and **1C** were formed, with only traces of **1T**. On the other hand, if equilibrated solutions of all three species were treated with MeI below −100 °C, the monomers could be selectively removed, leaving solutions containing only **1T**. Injection of MeI into solution of **1C** and **1S** at −130 °C removed **1S**, leaving only **1C** (and any **1T** that might have been present).

Reactivity experiments using RINMR spectroscopy showed that **1T** did not react directly with several electrophiles (MeI, EtSSEt), rates of reaction were identical to the dissociation rate of **1T** to the reactive monomeric species. We showed that **1T** is at least 10 orders of magnitude less reactive than **1S**. Reactivity comparisons of **1C** and **1S** had a much more limited dynamic range, since their interconversion had a half-life of ca. 20 s at −130 °C, but we were able to show that several electrophiles (MeI, benzaldehyde, and **1-I**) did not react with **1C**, but only with **1S**.

A RINMR study of the lithium−iodine exchange reaction of **1-I** at −130 °C showed that the main first detected product on treatment of **1-I** with *n*-BuLi was the iodine ate complex **4**, formed by reaction of **1-Li** with **1-I**. It could be shown that the primary product of the lithium−iodine exchange was **1S**, and not **1C**, so conversion of presumed intermediate ate complex $Li^+\ Bu\text{-}I\text{-}C(SiMe_3)_3^-$ to the lithium reagent proceeds by an S_E1 mechanism, and not by electrophilic attack of lithium cation on the ate complex (S_E2 mechanism), which would give **1C** as the primary product.

Experimental Section

General. All reactions requiring a dry atmosphere were performed in glassware flame-dried or dried overnight in a 110 °C oven, sealed with septa and flushed with dry N_2. Tetrahydrofuran (THF) and diethyl ether (ether) were freshly distilled from sodium benzophenone ketyl before use. Dimethyl ether (Me_2O) was distilled via cannula into the NMR tube from a graduated conical cylinder at −78 °C containing *n*-BuLi (for drying). Glassware was placed overnight in a 110 °C oven or flame-dried before purging with N_2 to remove moisture. Common lithium reagents were handled with septum and syringe-based techniques and were titrated using *n*-propanol in THF with 1,10-phenanthroline as an indicator.[35]

NMR Spectroscopy. Routine ^{1}H and ^{13}C NMR spectra were acquired on a 300 MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard.

All multinuclear NMR experiments were performed in 10 mm NMR tubes using a wide-bore AM-360 spectrometer at 360.15 MHz (^{1}H), 52.00 MHz (^{6}Li), 139.96 MHz (^{7}Li), 90.56 MHz (^{13}C), 71.54 MHz (^{29}Si), or 145.78 MHz (^{31}P). ^{13}C NMR spectra were referenced internally to the C−O carbon of THF (δ 67.96), Et_2O (δ 66.57) or Me_2O (δ 60.25), and Lorentzian multiplication (LB) of 2−3 Hz was applied. ^{6}Li and ^{7}Li spectra were referenced externally to 0.3 M LiCl in MeOH (δ 0.00) or internally to $Li^+(HMPA)_4$ (δ −0.40). ^{31}P NMR spectra were referenced externally to 1.0 M PPh_3 in THF (δ −6.00) or internally to free HMPA (δ 26.40). ^{7}Li and ^{31}P spectra were generally transformed with Gaussian multiplication, with the GB parameter set to the fractional duration of the FID and the LB parameter set to −(digital resolution)/GB.

The lithium reagent samples were prepared in 10 mm thin-walled NMR tubes which were oven-dried, fitted with a septum (9 mm i.d.), and N_2-flushed. Since nondeuterated solvents were used, the spectrometer was run unlocked, and shimming was performed on the ^{13}C FID of C-3 of THF or other solvent peak. Temperatures were measured using either a thermocouple submerged in a second NMR tube containing the same solvent mixture or the internal ^{13}C chemical shift thermometer $(Me_3Si)_3CH$.[4b]

RINMR Experiments. The apparatus and techniques for performing RINMR experiments have been described previously.[41] Low-temperature RINMR experiments were performed on a 360 MHz spectrometer with a 10 mm broadband probe. ^{1}H RINMR spectra were observed through the decoupler channel tuned to 360.132 MHz. Spectra were obtained in nondeuterated ether solvents with the spectrometer unlocked and were referenced internally to the trimethylsilyl peak of Me_3SiPh (δ 0.44). The temperature of the RINMR sample was checked at the beginning and the end of an experiment. For many experiments, the probe temperature was raised a few degrees ca. 10 s prior to the injection. This offsets the warming that results from the injection itself. The size of the offset has been determined in a number of control cases[41] and depends on the injection volume. There is approximately a 1 °C temperature jump for a 0.05 mL injection.

Tris(trimethylsilyl)methyllithium (1-^{6}Li) - Typical Procedure for Preparation of 1-^{6}Li from 1-SePh. To a dried, N_2-purged, 10 mm NMR tube fitted with a septum and maintained under positive N_2 pressure were added 0.204 g (0.526 mmol) of **1-SePh,** 7 μL of the ^{13}C chemical shift thermometer[4b] (1:10 ratio of ^{13}C-labeled and unlabeled **1-H**), 1.8 mL of THF, and 1.2 mL of Et_2O. The solution was cooled to −78 °C and 0.34 mL (0.524 mmol) of 1.54 M *n*-Bu^{6}Li in pentane were added. The sample was then ready for detailed, addition of cosolvents, or RINMR injections. Comprehensive details are provided in the Supporting Information.

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Supporting Information Available: Experimental procedures for the preparation of compounds and NMR samples, ^{1}H, ^{29}Si, ^{6}Li, ^{13}C and ^{31}P NMR spectra of NMR experiments not presented in the main body of this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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[35] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–168.