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Monomeric Organolithium Compounds in Tetrahydrofuran: *tert*-Butyllithium, *sec*-Butyllithium, "Supermesityllithium", Mesityllithium, and Phenyllithium. Carbon–Lithium Coupling Constants and the Nature of Carbon–Lithium Bonding

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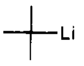
While *tert*-butyllithium is tetrameric in hydrocarbon solvents and in the gas phase, it is now established to be a dimer in diethyl ether and a monomer in tetrahydrofuran (THF) by cryoscopy at −108 °C and by NMR (signal multiplicities and the magnitude of the Li–C coupling constants). *sec*-Butyllithium is a monomer–dimer equilibrium in THF (88:12 by cryoscopy at −108 °C, 78:22 by ^{13}C NMR at −96 °C). Addition of the η^3 ligand *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA) converts all dimers to monomers. (2,4,6-Tri-*tert*-butylphenyl)lithium ("supermesityllithium") and mesityllithium also are monomers. Phenyllithium at −103 °C in dilute (260 m*m*) THF solution is found to be a monomer–dimer equilibrium (35:65) as was established earlier by cryoscopy. However, in the presence of PMDTA, phenyllithium, even in concentrated THF solutions, consists exclusively of monomers. The magnitude of C–Li coupling constants depends on the state of aggregation, but only to a limited extent on other factors, e.g. carbon hybridization. This suggests the C–Li bond to be largely ionic but to have minor covalent character.

Aggregation is a nearly ubiquitous characteristic of organolithium compounds.[1-3] Tetramers and even hexamers are common in the gas phase and in solution in hydrocarbons.[1] Electron donor solvents (tetrahydrofuran is more effective than diethyl ether) and chelating ligands (e.g. tetramethylethylenediamine, TMEDA) tend to favor tetramers or dimers, but monomers of simple organolithium compounds almost never are found.[2] The distribution of aggregates in solution generally varies with temperature, and quite different species might prevail at different temperatures.[2] A few crystal structures revealing monomeric organolithium compounds are known, but these are rare and generally involve highly stabilized carbanion moieties, bulky substituents, tridentate ligands, or some combination of these.[3] One compound, $LiCH(SiMe_3)_2$, is monomeric in the gas phase.[3d] We now report NMR and cryoscopic measurements that show both *tert*-butyllithium (**1**) and (2,4,6-tri-*tert*-butylphenyl)lithium (supermesityllithium) (**2**) to be monomeric in tetrahydrofuran (THF) solution. The latter result is not especially surprising in view of the bulk of the alkyl substituents, but the unaggregated nature of $(CH_3)_3CLi$ in THF is quite unexpected and requires table entries in the review literature[1a,b] to be corrected. Furthermore, we find mesityllithium (**3**) to be a monomer and even phenyllithium (**4**) and 2-butyllithium exhibit monomer–dimer equilibria in THF solution.



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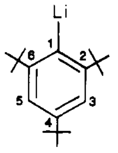

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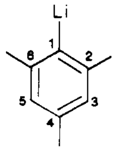

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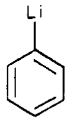

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Results and Discussion

***tert*-Butyllithium (1).** The literature on the nature of *tert*-butyllithium (first synthesized by Bartlett et al.[4a]) is quite extensive but does *not* suggest that monomers may be present.[4] Over rather wide concentration ranges in benzene, hexane, and cyclohexane, *tert*-butyllithium has been found to be tetrameric by both cryoscopic and ebullioscopic measurements,[1,4] as well as by Raman spectroscopy.[4b,5] ^{7}Li NMR studies in cyclohexane and toluene established the tetrameric nature of *t*-BuLi. However, the coupling pattern in ^{13}C-enriched samples allowed no differentiation between slow or fast intramolecular exchange.[6] ^{13}C NMR spectra from natural abundance samples in C_6D_6 at room temperature indicated a rapid exchange due to coupling of ^{13}C with *four* equivalent ^{7}Li atoms.[7] A recent paper[8] describes the observation, but with ^{6}Li-enriched

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Table I. NMR Spectroscopic Data for *tert*-Butyllithium[s]

nucleus	solv	temp, °C	δ	coupling const[a] (multiplicity)	ref
^{13}C	C_5H_{10}	rt	32.6		8
			10.7	4.1 (9)[b]	
		−22	10.7	5.4 (7)[b]	
	C_6D_6	rt	33.3		7
			10.5	... (13)[c]	
	C_6H_{12}	rt	10.8[d]	...	6b
	THF-d_8	−90	40.4[e]		this work
			17.1	31.5 (4)[c]; 11.9 (3)[b]	
	Et_2O	−64	36.2[q]		this work
			14.2	20.0 (7)[c]	
^1H	C_6H_6	rt	0.99	...	4b
	THF-d_8	−100	0.74[f]	...	this work
	Et_2O	−85	0.86[r]	...	
^6Li	C_5H_{10}	+35	1.07[g]	4.10[b] (2) [h]	8
		−85	0.86[g]	5.44[b] (2)[h]	
^7Li	C_5H_{10}	rt	0.65[k]	...	15
	C_6H_6	rt	0.54[k]	...	15
	Et_2O	rt	0.26[k,l]	...	15
			0.37[k,m]	...	
	C_6H_{12}	rt	0.96[n]	11[c] (9)[o]	6b
	toluene	rt	0.26[n]	~10	6b
	toluene	rt	0.40[p]	...	9b
	C_5H_{10}	rt	0.89[p]	...	9b
	Et_3N	rt	0.89[p]	...	9b
	THF-d_8	−95	0.26[i]	...	this work
	Et_2O	−85	0.85	...	this work

[a] In Hz. [b] $J_{^{13}C,^6Li}$. [c] $J_{^{13}C,^7Li}$. [d] δ_{TMS} (ppm), calculated from a value relative to δ_{CS_2} 192.8. [e] Relative to a solvent signal, 67.4 ppm. [f] δ (ppm) relative to a residual solvent proton signal, 3.58 ppm. [g] δ (ppm) relative to external 1 M $LiClO_4$ in acetone-d_6. [h] Sample enriched with ^6Li, natural abundance ^{13}C. [i] δ (ppm) relative to external 1 M LiBr in THF/THF-d_8 (1:1). [k] δ (ppm) relative to aqueous LiBr (0.7 g/mL) with internal proton lock. [l] Prepared from $(t\text{-}Bu)_2Hg$. [m] Commercial sample. [n] δ (ppm) relative to external 0.5 M LiBr in THF. [o] Sample with 57% enriched α-^{13}C, natural ^7Li abundance. [p] δ (ppm) relative to 3 M external LiBr in H_2O. [q] Relative to Et_2O, 66.9 ppm. [r] Relative to Et_2O, 1.16 ppm. [s] δ (ppm) values with positive numbers for high-frequency shifts.

samples, of species that undergo both rapid and slow exchange in cyclopentane solution at various temperatures. Below −22 °C a seven-line multiplet appears in the ^{13}C spectrum (coupling of ^{13}C with *three* ^6Li atoms, $J_{^{13}C,^6Li}$ = 5.4 Hz); this coalesces on warming above −5 °C to a nine-line multiplet (coupling of ^{13}C with *four* ^6Li atoms, $J_{^{13}C,^6Li}$ = 4.1 Hz). The rates of dissociation of the tetramer into the dimer in cyclopentane were measured as well as the rates of intermolecular exchange with (lithiomethyl)trimethylsilane.[9] While these processes were accelerated by the addition of trimethylamine to the cyclopentane solutions, there was no indication in these studies that the base caused dissociation of the lithium tetramer.[4c,10] Instead, the strong accelerating effect of triethylamine on the exchange reactions of *tert*-butyllithium in cycloalkane solvents was attributed "to interaction of the base with the transition state in the (presumably) dissociative process".[11]

In agreement with these observations, but in contrast to the behavior of other alkyllithiums, the addition of triethylamine up to equimolar ratios failed to give any evidence for dissociation as indicated by changes of ^7Li chemical shifts or colligative properties, nor was any heat evolved. A reasonable explanation was put forth that the bulk of the alkyl substituents in the tetramer precluded interaction with the amine. That $(t\text{-}BuLi)_4$ also is the predominant species in the gas phase is shown by mass spectrometric measurements.[9a,12] Probably as a consequence of the implications of all these findings, tables in reviews[1a,b] list *t*-BuLi as being tetrameric in THF and in diethyl ether. However, to our knowledge, actual measurements in those solvents have *not* been reported. Such experiments have been frustrated by the extreme reactivity of *tert*-butyllithium. Diethyl ether is attacked at temperatures above −40 °C and THF even more readily.[1c,13,14]

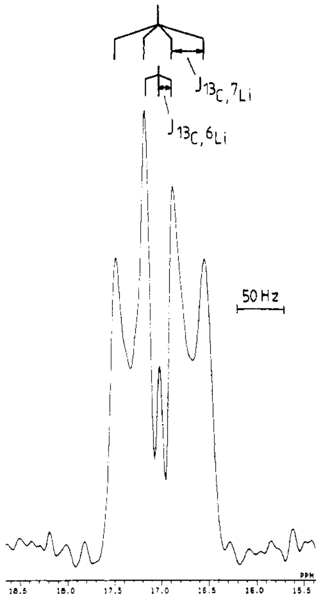

Figure 1. ^{13}C NMR spectrum of *tert*-butyllithium in THF-d_8, natural isotope abundance. C1 signal with slight resolution enhancement (1.4 M, −90 °C).

By working carefully at low temperatures, we have now overcome these difficulties and have obtained samples of

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Table II. ^1H **Chemical Shifts**[a] **of Supermesityllithium (2), Supermesitylene (5), Mesityllithium (3), and Mesitylene (7)**

	2		5		3	7
proton at carbon no.[f]	THF-d_8[b,c]	C_6D_6[b,d]	THF-d_8[b,c]	C_6D_6[b,d]	(THF-d_8)[c,e]	(THF-d_8)[c,e]
1			7.24	7.40		6.74
3,5	6.79	7.58	7.24	7.40	6.44	6.74
o-CH_3	1.29	1.61	1.32	1.33	2.33	2.22
p-CH_3	1.25	1.56	1.32	1.33	2.07	2.22
TMEDA CH_2	2.31	1.78			2.30	
TMEDA CH_3	2.15	2.04			2.16	

[a] In presence of TMEDA (1 equiv). [b] δ (ppm) at room temperature. [c] Relative to residual proton signal, 3.58 ppm. [d] Relative to residual proton signal, 7.15 ppm. [e] δ (ppm) at −10 °C. [f] Numbering, see formula in the text.

t-BuLi in diethyl ether and in THF/THF-d_8 suitable for cryoscopy and for NMR analysis with only a very small amount of contamination due to solvent decomposition. The ^7Li and ^1H NMR spectra of ca. 1.6 M t-BuLi in THF-d_8 each show only a singlet, indicative of only one species (Table I). In the ^{13}C NMR spectrum the C1 signal is split into a quartet, $J = 31.5$ Hz, superimposed by a minor triplet, $J = 11.9$ Hz (Figure 1). This results from $^{13}C,^7Li$ and $^{13}C,^6Li$ couplings, respectively, and indicates that carbon is coupled only to *one* lithium atom. The magnitude of the $^{13}C,^6Li$ and $^{13}C,^7Li$ coupling constants lies within the range typical of monomers (see below and Table VI).[15] Hence the results contrast with those found in aliphatic or aromatic hydrocarbon solvents. Cyroscopic measurements in THF[1e] corroborate these findings: the mean value of aggregation (n) equals 1.1 ± 0.1 in a (formal) 0.172 m t-BuLi/THF solution at −108 °C. t-BuLi thus follows the general tendency of organolithium compounds to be less strongly aggregated in THF than in aliphatic or aromatic hydrocarbon solvents, or the crystalline state.

Interestingly, addition of 1 equiv of TMEDA to the t-BuLi/THF cryoscopy solution shows TMEDA to be largely free (ca. 79%) by feezing point depression determination. Hence, TMEDA does not compete effectively with THF as a complexing agent for *tert*-butyllithium in THF solution.

In diethyl ether, the ^7Li, ^1H, and ^{13}C NMR signals similarly indicate the presence of only a single species. However, in contrast to the results in THF-d_8, the ^{13}C NMR signal of the quaternary carbon atom is split into seven lines, $J = 20.0$ Hz (Figure 2), which arise from coupling to *two* ^7Li isotopes in dimeric t-BuLi. This signal is superimposed by weaker lines, which are caused by ^7Li, ^6Li, and ^6Li, ^6Li isotopomers. As expected from this observation, the $^{13}C,^7Li$ coupling constant is typical for organolithium dimers. Thus, t-BuLi is a nice example of a metal organic compound being tetrameric in nonpolar solvents (aliphatic and aromatic hydrocarbons), dimeric in a more bulky donating solvent (diethyl ether), and monomeric in a less crowded donating solvent (THF).

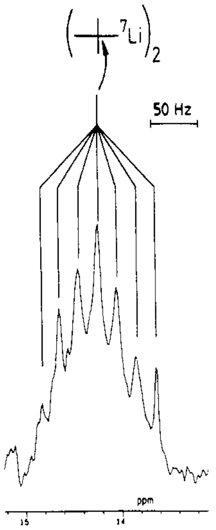

Figure 2. ^{13}C NMR spectrum of *tert*-butyllithium in diethyl ether, natural isotope abundance. C1 signal with slight resolution enhancement (1.4 M, −64 °C).

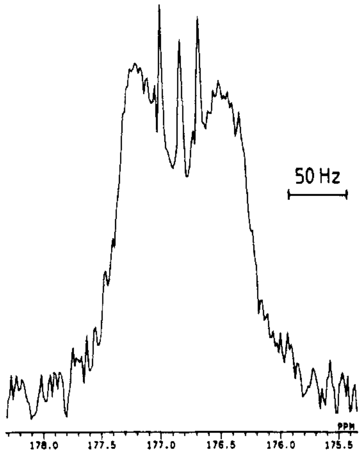

Figure 3. The ^{13}C NMR signal of the lithiated carbon of **2** (THF-d_8, −79 °C).

(Tri-*tert*-butylphenyl)lithium (2). Supermesityllithium (2) was obtained by reaction of 1-bromo-2,4,6-tri-*tert*-butylbenzene with excess n-BuLi in the presence of TMEDA as a crystalline compound containing 1 equiv of TMEDA. The ^{13}C NMR spectrum demonstrates the monomeric nature of **2** in THF-d_8 solution at −81 °C: the resonance of C1 (176.8 ppm) consists of a sharp triplet due to coupling from ^{13}C to *one* ^6Li isotope ($J_{^{13}C,^6Li} = 16.1$ Hz), overlayed by a broad "doublet" shaped signal which arises from coupling of ^{13}C to *one* ^7Li nucleus (Figure 3). This unusual signal shape closely resembles the ^{13}C NMR signal found by Seebach et al.[16a] for 7-iodo-7-lithiobicyclo[4.1.0]heptane (probably a monomeric carbenoid) in THF at −100 °C. The four lines of the 1:1:1:1 quartet from $^{13}C,^7Li$ splitting "coalesce" pairwise on cooling to give a "doublet". The reasons for this phenomenon are not clear. Presumably, this effect arises from lengthening of the molecular correlation time, τ_c, on cooling. Partial orientation of the lithioorganic species and the large quadrupole

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(15) Scherr, P. A.; Hogan, R. J.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 6055.

(16) (a) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1980**, *63*, 2046. (b) We are currently discussing the unusual line shapes of supermesityllithium (Figure 3) and *sec*-butyllithium (Figure 9) with several interested groups. Prof. Fraenkel has pointed out that an alternative explanation for these phenomena might include ^7Li relaxation by chemical shift anisotropy that would broaden only the central lines of the ^{13}C quartet. We thank Prof. Fraenkel for this private communication.

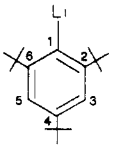
Table III. ^{13}C **Chemical Shifts of Supermesityllithium (2), Supermesitylene (5), Mesityllithium (3), and Mesitylene (7)**

	2		5		3		7
carbon no.[g]	THF-d_8[a,b]	C_6D_6[c]	THF-d_8[a,b]	C_6D_6[c,d]	THF-d_8[b,e]	THF-d_8[f]	(THF-d_8)[b,e]
1	177.0/176.8	174.7	120.0/120.1	119.6	181.3/187.8	190.7	127.5/127.6
2,6	160.0/159.4	160.0	150.6/150.2	150.3	149.7/148.6	147.8 146.8	137.9/138.0
3,5	115.7/116.0	116.1	120.0/120.1	119.6	123.2/122.5	122.3	127.5/127.6
4	143.0/142.5	144.0	150.6/150.2	150.3	131.6/129.5	128.8	137.9/138.0
o-$C(CH_3)_3$	39.0/39.1	38.7	35.5/35.6	35.1			
p-$C(CH_3)_3$	34.9/34.9	34.2	35.5/35.6	35.1			
o-CH_3	34.0/33.8	34.4	31.9/31.9	31.8	28.9/29.2	31.5 30.3	21.3/21.4
p-CH_3	32.5/32.5	32.5	31.9/31.9	31.8	21.7/21.9	22.2	21.3/21.4
TMEDA-CH_2	58.9/58.9	56.8					
TMEDA-CH_3	46.2/46.5	46.6					

[a] δ (ppm) at room temperature/−80 °C in the presence of TMEDA (1 equiv). [b] Relative to solvent α-C, 67.4 ppm. [c] At room temperature in the presence of TMEDA (1 equiv). [d] Relative to solvent, 128.0 ppm. [e] At −15 °C/−80 °C without amine ligand. [f] At −100 °C in the presence of 1 equiv of PMDTA. [g] Numbering, see formula in the text.

moment of ^7Li as compared to that of ^6Li might give rise to the observed line shapes.[16b]

Tables II and III compare ^1H and ^{13}C NMR data for supermesityllithium (**2**) and its parent hydrocarbon, tri-*tert*-butylbenzene (**5**) at different temperatures and in different solvents. Consistent with the presence of a singly monomeric species, the ^{13}C chemical shifts are practically identical in THF-d_8 at room temperature and at −81 °C. As is usual for aryllithiums, C1 in **2** resonates at very low field (176.8 ppm; cf. dimeric phenyllithium, 188.9 ppm[2c]). This downfield shift as compared to that in **5** has been ascribed to reduced π-electron density and increased σ-electron density at the metalated carbon.[2c] That is, the π density is polarized away from the ipso carbon. A striking effect is observed in the ^1H NMR spectrum: the ortho *tert*-butyl protons resonate at a lower field than their para analogues. We ascribe this to spacial proximity of these protons to the lithium substituent which causes deshielding of nearby protons due to the electrical field produced by lithium.[17] As this effect is averaged out over 18 protons, the relative shift differences of 0.04 and 0.05 ppm in THF-d_8 and C_6D_6, respectively, are comparatively high. This interpretation is corroborated by the NMR chemical shift behavior of the TMEDA protons: in a benzene-d_6 solution of **2**·TMEDA (dissolved crystals) the methyl groups of TMEDA appear at a *lower* field than the CH_2 groups, a consequence of close Li–H_3C contacts due to strong Li chelation by TMEDA.[18] These interactions have been demonstrated experimentally in our group by ^6Li–^1H 2D-heteronuclear Overhauser spectroscopy (^6Li–^1H 2D-HOESY).[19a,b] However, in a THF-d_8 solution of **2**·TMEDA the shift order of the TMEDA CH_3 and CH_2 protons is "normal" with the CH_3 signal at a higher field.



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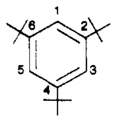

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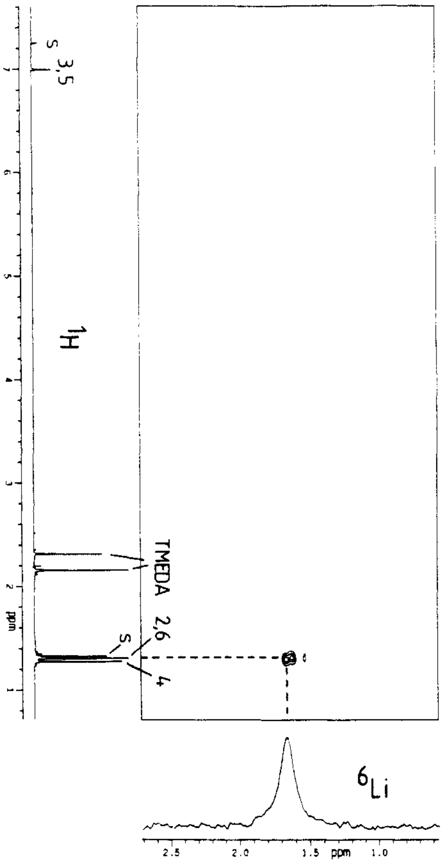

Figure 4. ^6Li–^1H 2D-heteronuclear Overhauser spectroscopy (HOESY) contour plot of **2**·TMEDA in THF-d_8, 0 °C (s = supermesitylene (1,3,5-tri-*tert*-butylbenzene)), natural abundance ^6Li (mixing time τ = 1.5 s).

Thus, TMEDA apparently is largely replaced by the more abundant THF-d_8 ligand. This conclusion is consistent with the cryoscopic findings on *t*-BuLi where TMEDA is largely free in a *t*-BuLi/THF mixture (see above).

The ^6Li–^1H 2D-HOESY spectrum of a THF-d_8 solution of dissolved crystals of **2**·TMEDA exhibits a cross peak between ^6Li and the hydrogen atoms of the ortho *tert*-butyl groups (Figure 4).[19c] This reflects the close contacts between these groups in the molecule. In accordance with ^1H chemical shift assignments for TMEDA, a cross peak in Figure 4 between ^6Li and the TMEDA CH_3 groups is missing in THF-d_8 solution.

MNDO Calculations. MNDO calculations on unsolvated **2** indicate the eclipsed structure (the CH_3 of the ortho *tert*-butyl group eclipses lithium) to be the lowest

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(17) Musher, J. I. *J. Chem. Phys.* **1962**, *37*, 34.

(18) In a benzene/TMEDA mixture the CH_3 protons appear *upfield* from CH_2.

(19) (a) Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970. (b) Bauer, W.; Müller, G.; Pi, R.; Schleyer, P. v. R. *Angew. Chem.* **1986**, *98*, 1130; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1103. (c) The intensive cross peak in Figure 4 on rigorous insepction appears as two contours in close proximity. However, this reflects the relatively poor resolution in the $f_1(^1H)$ dimension rather than spectral significance. The tiny cross peak at f_1 = 1.3 ppm and f_2 = 1.55 ppm which is seen in Figure 4 arises from noise due to signal tailing of the intensive cross peak. We avoided applying "cosmetic white wash".

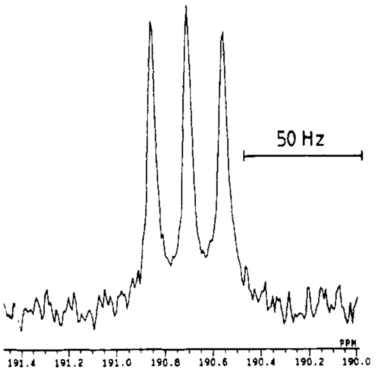
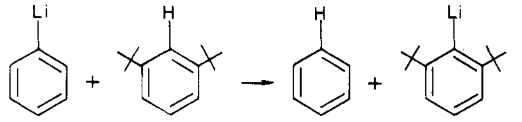


Figure 5. ^{13}C NMR spectrum of **3**, 96% enriched with ^{6}Li, lithiated carbon, 0.5 M, THF-d_8, −100 °C, with 1 equiv of PMDTA.

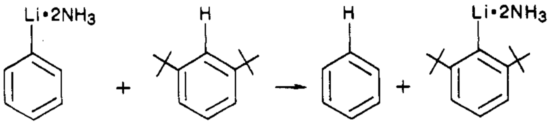
in energy, because of the interaction of the CH bond with lithium. Indeed, the isodesmic reaction 1 is exothermic



(1)

4 **6a** **8** **6b**

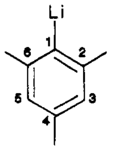
by 16 kcal/mol. This surprisingly large difference is due, at least in part, to the known overestimation of CH...Li interaction energies by the present MNDO parametrization. However, the results are quite different when solvation is included in the calculations. Thus, reaction 2 is *endothermic* by 1.1 kcal/mol. This indicates the net effect of the two *tert*-butyl groups to be quite small.



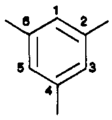
(2)

4•2NH3 **6a** **8** **6b•2NH3**

Mesityllithium (3). The ^{6}Li-labeled precipitate of **3** obtained by metal–halogen exchange from the bromine compound[20] dissolves readily in THF at 0 °C with or without the presence of TMEDA. At temperatures below ca. −20 °C the solubility decreases rapidly. Low-temperature ^{13}C NMR spectra (<−80 °C) of these suspensions give broadened signals for the lithium compound. No ^{13}C,^{6}Li coupling can be observed under these conditions. As no splitting of the carbon signals is observed even at −100 °C, an equilibrium between different aggregated species is unlikely and the broadened lines must arise from poor solubility. In contrast to supermesityllithium, (**2**) under similar conditions, the ^{13}C chemical shifts of **3** are temperature-dependent (cf. Table III). Presumably, this also is due to solubility differences at different temperatures.



3



7

However, in presence of 1 equiv of the η^3 ligand *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA), **3** is completely soluble in THF at −100 °C. NMR spectroscopy shows a single species to be present. The ^{13}C NMR signal for C1 is split into a 1:1:1 triplet (190.7 ppm); the coupling constant, $J_{^{13}\mathrm{C},^{6}\mathrm{Li}}$ = 15.3 Hz, is indicative of a monomer (Figure 5). In this PMDTA–THF solution at −100 °C, both the signals for the ortho methyl carbons and those for C2,6 are split (Δδ = 1.0 and 1.2 ppm, respectively) due to chemical nonequivalence of these carbons whereas the signals of the inherently anisochronous meta carbons C3,5 should be nearly identical and coalesce under these conditions (Table III). The signal splitting must arise from a low barrier to rotation around the C–Li bond and from geometries in solution like **9a** or **9b** (coordinatively unsaturated lithium); i.e., the ligand (PMDTA) is tightly bound to Li, even in presence of the donor solvent THF-d_8. The ortho CH$_3$ protons in **3** are shifted downfield in the ^{1}H NMR spectrum as compared to their para analogues (Δδ = 0.24 ppm). Again, we ascribe this effect to spatial proximity of these protons to the lithium substituent. As with supermesityllithium, close contacts between lithium and the hydrogen atoms on the ortho methyl groups can be demonstrated by ^{6}Li–^{1}H HOESY (Figure 6). Moreover, this serves as an independent confirmation of the assignments of the ^{1}H NMR spectrum (Table II).

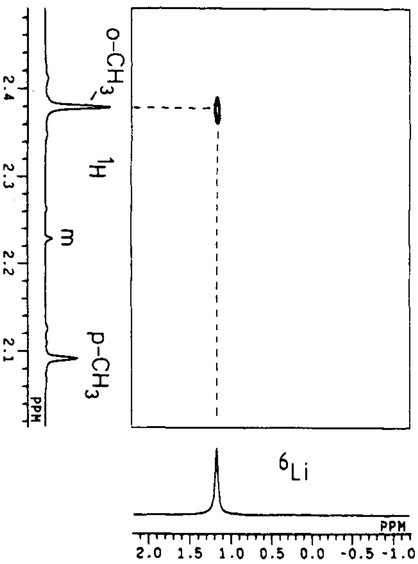
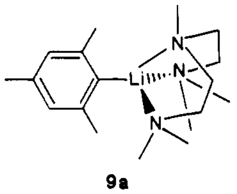
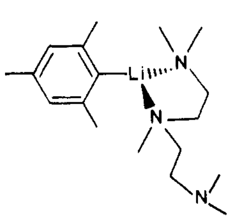


Figure 6. ^{6}Li–^{1}H HOESY of **3**, contour plot, THF-d_8, −15 °C, without amine ligands, 96% enriched with ^{6}Li (mixing time τ = 2.0 s; m = mesitylene).

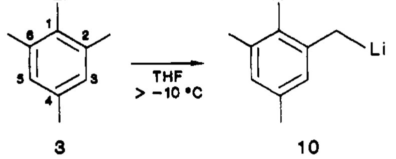


9a



9b

In contrast to supermesityllithium (**2**)/THF solutions, which are stable over long periods even at room temperature, the colorless mesityllithium (**3**)/THF solution slowly turns deep red at temperatures higher than ca. −10 °C. This is most likely due to the transmetalation reaction (3): such π-stabilized benzyl anions (e.g. **10**) cannot be formed from supermesityllithium (**2**).



(3)

3 **10**

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(20) Pearson, D. E.; Frazer, M. G.; Frazer, V. S.; Washburn, L. C. *Synthesis* **1976**, 621.

(21) Fraenkel, G.; Dayagi, S.; Kobayashi, S. *J. Phys. Chem.* **1968**, *72*, 953.

Table IV. ^{13}C NMR Data for Phenyllithium (4), in Different Aggregation States[a]

Ph^{6}Li, 4	C1	C2,6	C3,5	C4	lit.
monomer[b]	196.7	143.4	124.8	120.9	this work
dimer[b]	188.5	144.6	124.8	123.2	this work
tetramer[c]	176.2	142.9	127.9	127.3	25a

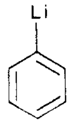
[a] δ (ppm). [b] 0.26 *m* (overall concentration) in THF/THF-d_8, −103 °C, relative to THF-d_8, 67.4 ppm. [c] 6 M in ether.

Table V. ^{13}C NMR Data for *sec*-Butyllithium (13) in Different Aggregation States[a]

sec-BuLi (13)	C1	C2	C3	C4	solv, temp	lit.
hexamer	19.09 18.85 18.75	20.91	31.45 31.31 31.22 31.11	15.81	C_5H_{10}, −41 °C	28a
tetramer	19.27	16.89	31.69	15.98	C_5H_{10}, −41 °C	28a
dimer	ca.24[b]	ca.24[b]	36.4	18.9[c]	THF-d_8, −96 °C	this work
monomer	28.8	26.7	39.4	20.2	THF-d_8 and PMDTA, −96 °C	this work

[a] δ (ppm). [b] Hidden under solvent peak. [c] Appears as coalesced signal together with C4 of the monomer.

Phenyllithium (4). In the crystalline state, phenyllithium (4) is a tetramer with Et_2O,[22] a dimer with TMEDA,[23] or a monomer with PMDTA[24] as ligands. With ^{13}C NMR, Seebach et al.[2c] found a dimer in THF-d_8 solution due to splitting of the signal of the ^{6}Li-bearing carbon into a quintet (188.9 ppm ($J_{^{13}C,^6Li}$ = 8 Hz)). In diethyl ether solution and in presence of TMEDA, Fraenkel et al.[2d] noted an additional signal at 184.2 ppm, which was assigned to the tetramer. However, ^{13}C,^{6}Li coupling was not observed at −75 °C. In contrast, Jackman and Scarmoutzos[25a] found different chemical shifts for the tetramer in concentrated diethyl ether solutions (Table IV) with the resonance of C1 at 176.2 ppm. Van Koten[25b] et al. found a value of 175.9 ppm for phenyllithium in toluene-d_8 with one added equivalent of THF, consistent with Jackman's value for the tetramer. In presence of excess THF, a chemical shift value of 188.7 ppm was found, corresponding to the dimer. Our own experiments[25c] are consistent with Jackman's and van Koten's findings. In relatively dilute solution (c_{formal} = 0.259 *m*) 4 was established to be a monomer–dimer equilibrium (39:61) by cryoscopy in THF.[1e] This finding is now corroborated by ^{13}C NMR: a 0.26 *m* THF/THF-d_8 solution of phenyl-^{6}Li reveals two sets of signals for the aromatic ring, with one being identical with that of the already known dimer.[25] At 196.7 ppm, a signal assigned to the monomer appears (Figure 7).



4

Neither the monomer nor the dimer signal for the ^{6}Li-substituted carbon shows ^{13}C,^{6}Li splitting under these conditions. Integration of corresponding ^{13}C NMR signal pairs of the monomer and the dimer established a 35% monomer–65% dimer equilibrium mixture. Taking into account an increased amount of the monomer at the melting point of THF (−108 °C) as compared to the ^{13}C NMR conditions,[2c] this value is in excellent agreement with the ratio determined by cryoscopy. The ^{13}C NMR chemical shifts of monomeric, dimeric, and tetrameric 4, respectively, are summarized in Table IV.

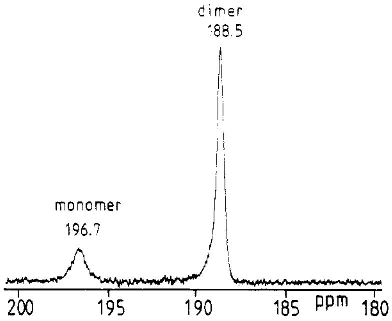


Figure 7. ^{13}C NMR spectrum (ipso carbon atoms) of 0.26 *m* Ph^{6}Li, 4 in THF/THF-d_8 (5:1), −103 °C.

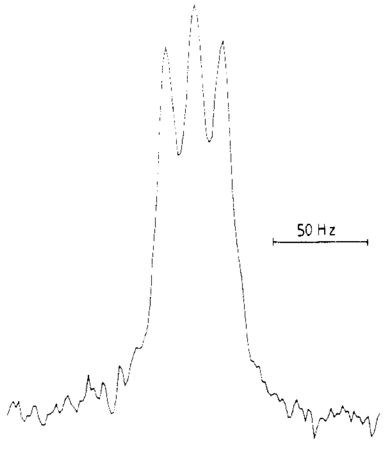


Figure 8. ^{13}C NMR of Ph^{6}Li (1.6 M) in THF-d_8, −103 °C, ipso carbon, in the presence of 1 equiv of PMDTA.

As in the alkyllithium series (cf. *t*-BuLi, above, and dimeric/tetrameric *n*-BuLi[2c]) the chemical shift order for the lithiated carbon in 4 is monomer > dimer > tetramer. If this behavior is due to decreased mean excitation energy, ΔE, in the paramagnetic shielding term, σ_i^{para}, which contributes to the shielding constant σ,[26] a hypsochromic shift can be predicted for the ultraviolet spectra in going to higher aggregation from the monomer.

In contrast to the ^{13}C NMR results, the signals of monomeric and dimeric phenyllithium could not be resolved in the ^{1}H NMR spectrum. A 0.26 M THF/THF-d_8 solution of 4 at −90 °C showed only broad resonances at 7.75

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[24] Schümann, U.; Kopf, J.; Weiss, E. *Angew. Chem.* **1985**, *97*, 222; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 215.

[25] (a) Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1984**, *106*, 4627. (b) Van Koten, G.; Jastrzebski, J. T. B. H.; Stam, C. H.; Brevard, C. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Ademine: 1985; p 267 FF. (c) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R., to be submitted for publication.

[26] Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.

Table VI. Summary of ^{13}C–$^{6,7}Li$ Coupling Constants[a,b] for $(RLi)_n$

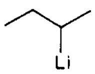
species	$J_{^{13}C,^{6}Li}$	$J_{^{13}C,^{7}Li}$	solv	temp, °C	lit.
$(RLi)_9$					
11 $CH_3CH_2CH_2Li$	2.22[c]	(5.86)	C_5H_{10}	−56	2e
$(RLi)_8$					
11 $CH_3CH_2CH_2Li$	2.48[c]	(6.55)	C_5H_{10}	−56	2e
$(RLi)_6$					
13	3.25[c]	(8.58)	C_5H_{10}	−41	28a
11 $CH_3CH_2CH_2Li$	3.35[c]	(8.85)	C_5H_{10}	−56	2e
$(RLi)_4$					
1 $(CH_3)_3CLi$	5.4[d]	(14.3)	C_5H_{10}	−88	8
	4.1[c]	(10.8)		+26	
12 $CH_3CH_2CH_2CH_2Li$	(5.5)	14.6	THF	−96	6b, 19a
13	6.1	(16.1)	C_5H_{10}	−41	28a
14	(5.8)	15.4	Et_2O	−60	2d
15 CH_3Li	(5.5)	14.5	THF	−80	29
16	6	16	THF	−90	28b
$(RLi)_2$					
1 $(CH_3)_3CLi$	(7.6)	20.0	Et_2O	−64	this work
4 PhLi	8	20	Et_2O/TMEDA	−75	2c,d
12 $CH_3CH_2CH_2CH_2Li$	7.8	(20.6)	THF	−100	2c
17	9.7	(25.6)	THF	−100	2c
18	8.5	(22.4)	THF	−100	2c
19	10.3	(27.2)	THF	−100	2c
20	9.0	(23.8)	2-MeTHF	−115	2c
21 Ph—C≡C—Li	8.2	(21.7)	THF	−95	30
RLi					
13	14.0	36.6	THF/PMDTA	−96	this work
4	15.6	(41.2)	THF/PMDTA	−103	this work
3	15.3	(40.3)	THF/PMDTA	−100	this work
2	16.1	(42.5)	THF/TMEDA	−80	this work
1 $(CH_3)_3CLi$	11.9	31.5	THF	−90	this work
22 HalRR′CLi[e]	16.3 to 17.2	(40.0 to 45.4)	THF	ca. −100	2c
23	15.3	(40.4)	THF	−100	31
24	12.0	(31.7)	THF	−106	32
25	11.0	(29.1)	THF	−113	32
26	12.0	(31.7)	THF	−127	32
27	10.7	(28.3)	THF	−93	32
28	10.0	(26.4)	THF	−100	32

[a] In Hz. [b] Calculated values (in parentheses) from $J_{^{13}C,^{7}Li} = (\gamma(^7Li)/\gamma(^6Li))J_{^{13}C,^{6}Li}$; $\gamma(^7Li)/\gamma(^6Li) = 2.641$. [c] Fluxional. [d] Static. [e] 12 examples.

(H2,6), 6.76 (H3,5), and 6.64 (H4) ppm, respectively.

Addition of the η^3 ligand PMDTA to a THF-d_8 solution of phenyllithium (**4**) results in exclusive formation of monomers: the ^{13}C NMR spectrum shows only one species to be present. The ^6Li-metalated carbon resonates at 196.5 ppm (Figure 8). At low temperatures a 1:1:1 splitting (J = 15.6 Hz) is observed, thus proving the monomeric nature of **4** under these conditions. Therefore, besides *t*-BuLi (see above), phenyllithium is another example of an organolithium compound occurring in solution in three different states of aggregation (monomer, dimer, and tetramer) depending on the solvent, the ligand, and the temperature.

***sec*-Butyllithium (13)** was found by Fraenkel to be a mixture of a tetramer and several diastereomeric hexamers in 2 M cyclopentane at −41 °C.[28a] However, a 1.2 M THF solution of this compound at −96 °C does not show this behavior. Instead, two sets of signals consistent with a *monomer* and a *dimer* are found (Table V).



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Integration of the corresponding ^{13}C signals gives a 78:22 monomer:dimer ratio. Cryoscopic measurements are quite consistent with this finding: a THF solution of *sec*-BuLi (c_{formal} = 0.158 *m*) reveals an aggregation number (n) equal to 1.12 ± 0.05, corresponding to 88% monomer and 12% dimer. As the cryoscopy conditions favor the disaggregated species (lower concentration and temperature as compared to the NMR conditions), the two methods essentially give identical results. Under comparable conditions (c_{formal} = 0.430 *m*) a 39:61 tetramer:dimer ratio was found for *n*-BuLi in THF by cryoscopy.[1e] Thus, there is a strong tendency in the series *n*-BuLi to *sec*-BuLi to *t*-BuLi to become less strongly aggregated in THF. As was found for phenyllithium (see above), the chemical shift order of the lithiated carbon atom C2 in **13** increases in going from the tetramer to the monomer (Table V). However, C2 of the hexamer does not follow this tendency and appears downfield from the corresponding signal of the tetramer.

Addition of 1.4 equiv of PMDTA to an 1.2 M *sec*-BuLi/THF solution completely converts all dimers into monomers: only the ^{13}C signals of the monomer (Table V) appear at −96 °C. Most interestingly, the ^{13}C signal of C2 of the monomer under these conditions again reveals the line-shape anomalies already observed for supermesityllithium (**2**), (Figure 3): at −60 °C, the expected 1:1:1:1 quartet (J = 36.6 Hz) due to ^{13}C, ^7Li coupling appears, overlayed by the minor 1:1:1 triplet of the ^6Li isotopomer and some noise due to the short measuring time (Figure 9a). However, on cooling the solution to −96 °C, the "inverse coalescence" phenomenon, i.e. pairwise averaging of the quartet lines, takes place, leading to a broad doublet, the maxima of which are in between the lines of the resolved quartet (Figure 9b). A well-resolved 1:1:1 triplet, J = 14.0 Hz, due to ^{13}C,^6Li in the minor isotopomer, is seen in addition. The magnitude of the ^{13}C,$^{6,7}Li$ coupling constant of the *sec*-BuLi monomer is larger than that of *t*-BuLi; however, it is smaller than that of the aryllithium compounds in Table VI.

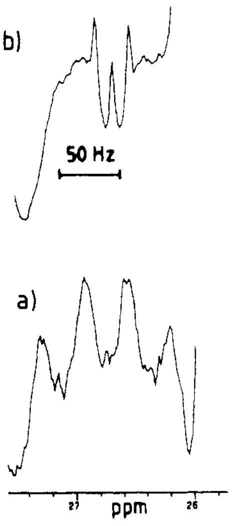
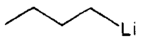


Figure 9. ^{13}C NMR of *sec*-BuLi (1.2 M) in THF-d_8, C2 signal, in the presence of 1.4 equiv of PMDTA: (a) at −60 °C; (b) at −96 °C.

***n*-Butyllithium (12).** *n*-BuLi (12) is known to exist as a dimer–tetramer equilibrium in THF.[2a,c,g,19a] Experiments to explore the possible existence of monomers employed an *n*-Bu^{6}Li/THF-d_8/PMDTA (1 equiv) solution.



12

At −100 °C the signals of the tetramer and the dimer are still present in the ^{13}C NMR spectrum. An additional minor set of signals is observed. However, as neither these nor any of the signals of the aggregates show $^{13}C,^6Li$ splitting under these conditions, no umambiguous assignment of the new resonances to an *n*-BuLi monomer can be made. It is clear that PMDTA does not form monomers exclusively as was the case with phenyllithium or with *sec*-butyllithium.

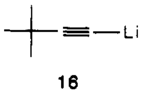
Addition of the lithium-selective[27] crown ether 12-crown-4 to a *n*-BuLi/THF-d_8 solution at ca. −90 °C in order to disaggregate dimer and tetramer results in immediate deprotonation of the ligand even at this low temperature. Large amounts of butane were detected in both the ^1H and the ^{13}C NMR spectra.

$^{13}C,^{6,7}Li$ Coupling Constants. The number of lines of a ^{13}C NMR signal split due to coupling to ^6Li or ^7Li is indicative for the aggregation state of an organolithium compound. Surprisingly, within relatively narrow limits the $^{13}C,^{6,7}Li$ coupling constants depend only on the state of aggregation. Table VI summarizes several values of $J_{^{13}C,^{6,7}Li}$. Even chemically completely different compounds such as *tert*-butyllithium (1), vinyllithium (14), and lithio-3,3-dimethylbutyne (16) show nearly identical $^{13}C,^{6,7}Li$ coupling constants when tetrameric. Hybridization of the lithiated carbon atom obviously does not influence the magnitude of $J_{^{13}C,^{6,7}Li}$. Although chemical shift differences of the metalated carbon atoms can be extremely large (e.g. $(CH_3Li)_4$, −12.3 ppm, vs $(H_2C{=}CHLi)_4$, 186.3 ppm), the corresponding differences in the $^{13}C,^{6,7}Li$ constants are minimal ($\Delta J_{^{13}C,^6Li}$ = 0.2 Hz for these two examples, cf. Table VI).

14

CH_3Li

15



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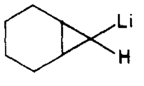

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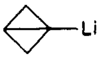

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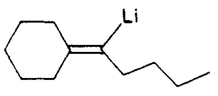

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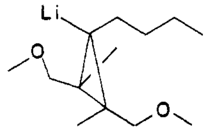
Ph—≡—Li

21



23

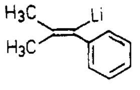
Considering different aggregated species in Table VI, the magnitude of the $^{13}C,^{6,7}Li$ coupling constant roughly follows eq 4 and 5, where n equals the number of lithium

$$J_{^{13}C,^6Li} = 1/n\ (17 \pm 2)\ \mathrm{Hz} \tag{4}$$

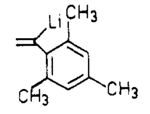
$$J_{^{13}C,^7Li} = 1/n\ (45 \pm 5)\ \mathrm{Hz} \tag{5}$$

atoms *directly* bonded to carbon in terms of the NMR time scale, i.e., n = 1 (monomer), 2 (dimer), 3 (static tetramer), 4, 6, 8, or 9 (fluxional tetramer, hexamer, octamer, or nonamer, respectively).

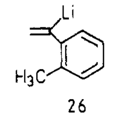
We suggest the ionic character of the C–Li bond to be responsible for the insensitivity of $J_{^{13}C,^{6,7}Li}$ to hybridization of ^{13}C. This can be contrasted with the $J_{^{13}C,^1H}$ coupling constants, which vary from 125 (sp^3) to 160 (sp^2) to 250 Hz (sp). Significant deviations from the generalizations given in eq 4 and 5 are the $^{13}C,^{6,7}Li$ coupling constants of the *t*-BuLi and *sec*-BuLi monomers and the monomeric vinyllithium derivatives 24–28,[32] which are lower than the expected values (Table VI). This might indicate that the nature of the carbon–lithium bond is constant in different *aggregates*, whereas in *monomers* there exists a variation from a nearly ionic to a completely ionic bond. This is corroborated by the finding that benzyllithium compounds which are monomeric in THF show no carbon–lithium coupling even at very low temperatures.[2c] Theoretical studies carried out in our group[33] and by others[34] show the carbon–lithium bond to be essentially (80–90%) ionic. This contradicts our earlier conclusions,[35] which were based



24



25



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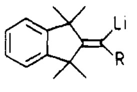

27 R = Ph
28 R = CN

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on INDO calculations of ^{13}C–^7Li coupling constants and suggested a more covalent C–Li bond. The predicted values have proven to be much too large for CH_3Li monomers and too small for the tetramer as compared with the experimental values that are now available. Both the minor covalent character of the C–Li bond and, as has been pointed out by Streitwieser,[34] spin polarization could be responsible for the observed coupling. It will be of interest to examine the behavior of additional monomeric organolithium compounds in this regard.

Experimental Section

Solvents and reagents were purified and dried by using standard techniques: THF, distillation from potassium/benzoylbiphenyl; THF-d_8 and C_6D_6, storage over Na/Pb alloy; diethyl ether and hexane, storage over sodium wire; TMEDA and PMDTA, distillation from CaH_2 with storage over CaH_2. *n*-Bu^{6}Li in hexane was prepared as described.[2c]

NMR spectra were recorded on a JEOL JNM-GX400 spectrometer (^{1}H, 400 MHz). A 5-mm ^{1}H/^{13}C dual probe and a broad-band 10-mm probe were used, respectively. The recording conditions and pulse sequences are as described elsewhere.[19]

Selected spectral parameters are as follows. One-dimensional ^{13}C NMR: 32K data points; spectral width, 25 000 Hz; exponential line broadening, BF 0.8...1.6 Hz; zero filling for extraction of ^{13}C,Li coupling constants. ^{1}H NMR: 32K data points, spectral width 3000...5000 Hz; exponential line broadening, BF 0.08 Hz. ^{6}Li–^{1}H 2D-HOESY (Figure 4): spectral width, 2755 Hz (f_1) and 200 Hz (f_2); data matrix, 256 (f_1) × 512 (f_2) points; 60 recorded increments in f_1 with zero filling to 256; mixing time, 2.0 s; 32 scans per increment in f_1; calculation with Lorentzian to Gaussian transformation in f_1, CBF −40 Hz and CGF 50 Hz; exponential line broadening in f_2, BF 1.0. ^{6}Li–^{1}H–2D–HOESY (Figure 6): spectral width, 191 Hz (f_1) and 200 Hz (f_2); data matrix, 64 (f_1) × 512 (f_2) points; 32 recorded increments in f_1 with zero filling to 64 and with 16 scans per increment; calculation in f_1 Gaussian filter, CFB −5 Hz and CGF 7 Hz; f_2 exponential filter, BF 0.8 Hz.

Preparation of *t*-BuLi. Commercial *t*-BuLi (0.4 mL, 1.8 M in pentane) was placed into a flame-dried 5-mm NMR tube under argon. After evaporation of the solvent, the residual white powder was dissolved very carefully in 0.5 mL of THF-d_8 at −100 °C. Slight solvent decomposition (ca. 3% by NMR) was indicated by the light yellow color of the sample. The NMR tube was placed into the precooled NMR probe as quickly as possible: the temperature was never allowed to rise above ca. −40 °C. Samples for cryoscopy in THF were prepared analogously.[1e] *t*-BuLi in undeuteriated diethyl ether was prepared in a similar way with comparable amounts of reagents and solvents. In order to have an NMR lock, the 5-mm sample tube was placed concentrically in a 10-mm tube containing acetone-d_6.

(Tri-*tert*-butylphenyl)lithium (2; Supermesityllithium). 1-Bromo-2,4,6-tri-*tert*-butylbenzene[20] (2.0 g, 6.1 mmol) was dissolved in diethyl ether under nitrogen and cooled to 0 °C. *n*-BuLi (5 mL, 1.6 M solution in hexane) was added and the mixture stirred for 2 h. The ether was removed under vacuum (10^{-1} mm), and then hexane (20 mL) was added. After the solution was cooled to −100 °C and TMEDA (1.5 mL) added, a complex was observed to precipitate. This powder, separated by filtration at −50 °C, was washed with hexane and then dissolved in hexane/ether (10 mL/5 mL). After the solution was filtered, cooling the solution led to crystals suitable for X-ray crystallographic analysis (to be reported later). These crystals also were shown to be pure by NMR. For NMR analysis, ca. 30 mg of the dry crystals were dissolved in 0.5 mL of THF-d_8 or 0.5 mL of benzene-d_6, respectively, in a 5-mm NMR tube under argon.

Mesityllithium was prepared as described,[21] using a 1.22 M Bu^{6}Li/hexane solution. The hexane-washed precipitate was employed directly for NMR analysis.

Phenyllithium was prepared as described,[1e] using a 1.22 M Bu^{6}Li/hexane solution. The crystals were powdered under vacuum by means of a magnetic stirring bar to remove the ligand (diethyl ether). For NMR measurements, 69 mg (0.83 mmol) of the finely ground Ph^{6}Li was transferred into a dry 10-mm NMR tube in a glovebox and dissolved in 3.0 mL of THF and 0.62 mL of THF-d_8 at low temperature by using standard syringe/septum techniques. Alternatively, 67 mg (0.81 mmol) of Ph^{6}Li in a 5-mm tube was dissolved in 0.3 mL of THF-d_8, followed by addition of 0.18 mL (0.84 mmol) of PMDTA.

Preparation of *sec*-BuLi. Commercial *sec*-BuLi (0.5 mL, 1.2 M in cyclohexane) was placed into a flame-dried 5-mm NMR tube under argon. After the solvent was stripped off in vacuo, 0.5 mL of THF-d_8 was added very carefully at −70 °C. After the NMR spectra was recorded, 0.18 mL (0.84 mmol) of PMDTA was added at the same temperature. Samples for cryoscopy in THF were prepared in an analogous manner.[1e]

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Registry No. 1, 594-19-4; **1** dimer, 110095-20-0; **2**, 35383-91-6; **2**·TMEDA, 110095-21-1; **3**, 5806-59-7; ^{6}Li-**3**, 110095-25-5; ^{6}Li-**3**·PMDTA, 110095-26-6; **4**, 591-51-5; ^{6}Li-**4**, 92382-42-8; ^{6}Li-**4** dimer, 110095-16-4; **4**·2NH$_3$, 110095-23-3; ^{6}Li-**4**·PMDTA, 110095-19-7; **6a**, 1014-60-4; **6b**, 110095-22-2; **6b**·2NH$_3$, 110095-24-4; **7**, 108-67-8; **8**, 71-43-2; **12**, 109-72-8; ^{6}Li-**12**, 20535-67-5; **13**, 598-30-1; **13** dimer, 110095-18-6; **13**·PMDTA, 110095-17-5; **23**, 110116-26-2; **24**, 66050-73-5; **25**, 110095-27-7; **26**, 110095-28-8; **27**, 66050-71-3; **28**, 110095-29-9; PMDTA, 3030-47-5; ^{7}Li, 13982-05-3; ^{6}Li, 14258-72-1; TMEDA, 110-18-9; THF, 109-99-9; Et$_2$O, 60-29-7; 12-crown-4, 294-93-9; 1-bromo-2,4,6-tri-*tert*-butylbenzene, 3975-77-7.

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