J|A|C|S
ARTICLES
Published on Web 10/02/2008

Microsolvation and ^{13}C−Li NMR Coupling†

Rudolf Knorr,* Thomas Menke, Kathrin Ferchland, Johann Mehlstäubl, and
David S. Stephenson

Department of Chemistry and Biochemistry, Ludwig-Maximilians-Universität,
Butenandtstrasse 5-13, 81377 München, Germany

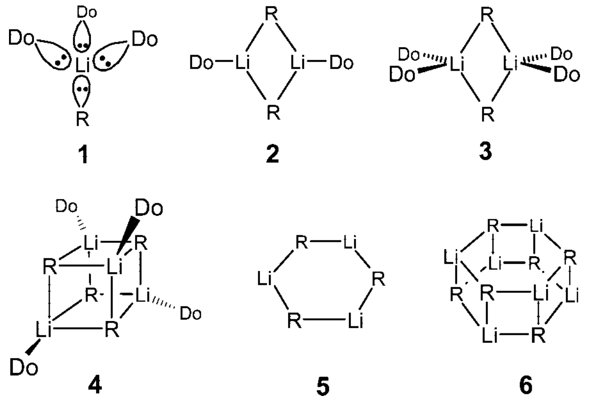
Received April 17, 2008; E-mail: rhk@cup.uni-muenchen.de

Abstract: The empirical expression $^1J_{\mathrm{CLi}} = L[n(a + d)]^{-1}$ is proposed; it claims a reciprocal dependence of the NMR coupling constant $^1J(^{13}\mathrm{C}, \mathrm{Li})$ in a C−Li compound on two factors: (i) the number n of lithium nuclei in bonding contact with the observed carbanion center and (ii) the sum $(a + d)$ of the numbers a of anions and d of donor ligands coordinated at the Li nucleus that generates the observed $^1J_{\mathrm{CLi}}$ value. The expression was derived from integrations of separate NMR resonances of coordinated and free monodentate donor ligands (*t*-BuOMe, Et$_2$O, or THF) in toluene solutions of dimeric and monomeric 2-(α-aryl-α-lithiomethylidene)-1,1,3,3-tetramethylindan at moderately low temperatures. This unusually slow ligand interchange is ascribed to steric congestion in these compounds, which is further characterized by measurements of nuclear Overhauser correlations and by solid-state structures of the dimers bearing only one donor per lithium atom ($d = 1$). Increasing microsolvation numbers d are also accompanied by typical changes of the NMR chemical shifts δ (positive for the carbanionic ^{13}C$^{\alpha}$, negative for C^{para} and *p*-H). The aforementioned empirical expression for $^1J_{\mathrm{CLi}}$ appears to be applicable to other cases of solvated monomeric, dimeric, or tetrameric C−Li compounds (alkyl, alkenyl, alkynyl, and aryl) and even to unsolvated ($d \approx 0$) trimeric, tetrameric, or hexameric organolithium aggregates, indicating that $^1J_{\mathrm{CLi}}$ might serve as a tool for assessing unknown microsolvation numbers. The importance of obtaining evidence about the ^{13}C NMR C−Li multiplet splitting of both the nonfluxional and fluxional aggregates is emphasized.

Introduction

Microsolvation of organolithium compounds (R$_m$Li$_m$) by coordinating electron-pair-donating ligands ("explicit Do") is essential[1] for the interpretation of reactivity. As shown in Chart 1, C−Li compounds may be monomeric (**1**) or aggregated in dimers (**2** and **3**), tetramers (**4**), trimers (**5**), hexamers (**6**), or other types[2] of clusters.[3] Because three and four are the usual coordination numbers of lithium cations in RLi, it may be guessed how many donor ligands (Do) would *probably* be required to satisfy the coordination sphere of lithium: usually three (and only occasionally two[4] or four[5,6]) Do per Li in monomers R$_1$Li$_1$ (**1**) and not more than one Do per Li in tetramers R$_4$Li$_4$ (**4**). On the other hand, hexamers R$_6$Li$_6$ (**6**) and one[7] of the very rare trimers R$_3$Li$_3$ of type **5**, namely, the trimer of **8** in Chart 2, are the stable forms in noncoordinating solvents.

Chart 1



Predictions[4] of one or two Do per Li in the dimers R$_2$Li$_2$Do$_2$ (**2**) and R$_2$Li$_2$Do$_4$ (**3**) are less straightforward. Unfortunately, all of the Li−Do bonds in solution can be labile, with ligand-interchange processes that are fast on the NMR time scales. Therefore, it is usually not possible to differentiate between coordinated (nonchelating) and noncoordinated (free) monodentate ligands by NMR spectroscopy, because only averaged spectra can be observed at all accessible temperatures. The very strong donor ligand hexamethylphosphoramide (HMPA) is an exception[8] to this rule, as are monodentate ethereal ligands such as tetrahydrofuran (THF) when coordinating to the more polar

---

† Sterically Congested Molecules, 20. For Part 19, see ref 64.

(1) Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1997**, *119*, 5573–5582 (specifically p 5581).

(2) (a) Setzer, W. N.; Schleyer, P. von R. *Adv. Organomet. Chem.* **1985**, *24*, 353–451. (b) Weiss, E. *Angew. Chem.* **1993**, *105*, 1565–1587 and Table 2 therein. (c) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501–1523.

(3) It should be noted that the lines drawn between Li and R in Chart 1 symbolize connectivities rather than the usual two-electron bonds.

(4) Pratt, L. M.; Truhlar, D. G.; Cramer, C. J.; Kass, S. R.; Thompson, J. D.; Xidos, J. D. *J. Org. Chem.* **2007**, *72*, 2962–2966.

(5) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1995**, *117*, 9863–9874 and references therein.

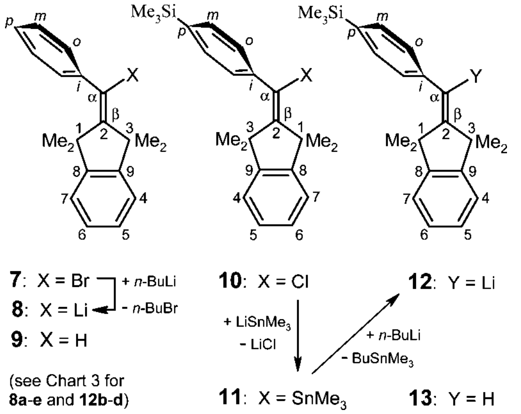
(6) Jantzi, K. L.; Guzei, I. A.; Reich, H. J. *Organometallics* **2006**, *25*, 5390–5395.

(7) Knorr, R.; Hoang, T.-P.; Nöth, H.; Linti, G. *Organometallics* **1992**, *11*, 2669–2673.

(8) Reich, H. J.; Kulicke, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 273–274 and references therein.

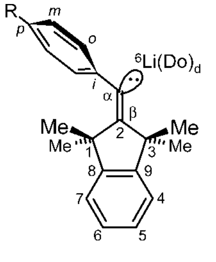
10.1021/ja8026828 CCC: $40.75 © 2008 American Chemical Society

Chart 2



7: X = Br
8: X = Li
9: X = H
(see Chart 3 for **8a-e** and **12b-d**)
10: X = Cl
11: X = SnMe$_3$
12: Y = Li
13: Y = H

Chart 3



8a-e: R = H
12b-d: R = SiMe$_3$

8, 12	donor Do
8a	none
8b, 12b	*t*-BuOMe
8c, 12c	Et$_2$O
8d, 12d	THF
8e	TMEDA

lithium amides[5,9−11] or to the endocyclic Li of dimeric Me$_2$CuLi·LiCN.[12] By use of ^{31}P NMR integrations at temperatures below −140 °C, the first[8] detection and quantification of monodentate ether solvates in C−Li compounds became possible using a monomeric alkyllithium compound bearing one HMPA ligand, an intramolecularly chelating tertiary amine, and dimethyl ether or oxetane as the third ligand. The present article reports on alkenyllithium compounds (**8** and **12**) for which the interchange processes of some monodentate ligands are slowed down to an unusual degree, probably as a result of steric congestion, enabling microsolvation numbers *d* to be measured at moderately low temperatures by direct ^{1}H and ^{13}C NMR integrations of the separated resonances of free and coordinated Do. Despite steric congestion, the monomers of **8** and **12** can aggregate to disolvated dimers of type **2** in both liquid and solid phases.

At low temperatures, where the C−Li exchange is slow on the ^{13}C NMR time scale, the resonance of a carbanionic center in R of **1**−**6** may split into a $(2nI + 1)$ multiplet caused by direct bonding contact between the carbanion and *n* equivalent lithium nuclei. When the ^{6}Li isotope (nuclear spin quantum number $I = 1$) is chosen for the preparation of RLi, as was done in the majority of our experiments, one expects $(2n + 1)$ multiplet components: a monomer **1** ($n = 1$) should exhibit a 1:1:1 triplet (see Figure 1 in section 2 of the Results and Discussion), while a dimer **2** or **3** and also a trimer **5** should show quintet splitting with the intensity ratio 1:2:3:2:1 (because of $n = 2$ equivalent neighboring ^{6}Li nuclei). For tetramers **4** and hexamers **6**, splitting into a septet by $n = 3$ nearest Li neighbors is to be expected. The spacings (frequency intervals) of these multiplets equal the one-bond coupling constants $^1J(^{13}\text{C}, ^6\text{Li})$, whose magnitudes were proposed[13−15] to obey the very simple "17/*n*" relation $^1J_{\text{CLi}} = (17 \pm 2\ \text{Hz})/n$ irrespective of the structure and hybridization of the carbanion. However, this relation does not agree with the $^1J_{\text{CLi}}$ values observed in this work (Table 1) or with the $^1J_{\text{CLi}}$ value of 11.9 Hz measured in ref 13 for monomeric *tert*-butyllithium (*t*-BuLi) in THF, as was already noticed by those authors.[13,14,16] Further cases of disagreement have been reported,[17] pointing to an omission of at least one important factor in the 17/*n* relation. Subsequent computational studies confirmed[18] the inverse dependence of $^1J_{\text{CLi}}$ on *n* but also revealed that coordination of electron-pair donors at monomeric methyllithium[18,19] (MeLi) and at monomeric *t*-BuLi[18] led to strongly reduced $^1J_{\text{CLi}}$ values, whereas a continuum solvation model[19] produced smaller reductions. Thus, microsolvation by individual ("explicit") particles appears to be the most important missing factor, while the computed $^1J_{\text{CLi}}$ values depend less strongly on the nature of the ligands[18,19] and carbanions.[18] We have developed an *experimental* verification and quantification of these computational hints in a novel expression for $^1J_{\text{CLi}}$ that appears to provide a new tool for assessing unknown microsolvation numbers.

Results and Discussion

1. Characterization of the Donor-Free Cyclotrimer (8a)$_3$ in Solution. The unsolvated 2-(α-lithiobenzylidene)-1,1,3,3-tetramethylindan (**8a**, shown in Chart 3) was prepared from 2-(α-bromobenzylidene)-1,1,3,3-tetramethylindan (**7**) with *n*-butyllithium (*n*-BuLi) in pentane (Chart 2) by a slightly improved version[20] of the published[7] procedure. This Br/Li interchange reaction is remarkable because it proceeds in the absence of donor ligands; it is also convenient because of its reliable tendency to produce single crystals that are free from side products when properly rinsed with pentane. According to the published[7] X-ray diffraction analysis, the crystals consist of trimeric aggregates of type **5**, but the constitution of (**8a**)$_3$ in solution had not yet been established and will now be deduced. When dissolved in [D$_8$]toluene at −84 °C, (**8a**)$_3$ displays a single set of quaternary ^{13}C NMR resonances, among them a quintet absorption of C$^\alpha$ (at $\delta = 172.2$ ppm) with $^1J(^{13}\text{C}, ^6\text{Li}) = 8.5$ Hz (Table 1, entry 15). This quintet establishes the presence of two C−Li connections ($n = 2$), which is compatible with a dimer but also with a "nonfluxional" (static) trimer **5**, the latter without contact of ^{13}C$^\alpha$ to the third, more remote ^{6}Li nucleus ($^3J \approx 0$ over three bonds). Positive evidence of the trimeric aggregation was achieved simply by warming the sample to a temperature (−21 °C) at which *intra*aggregate scrambling of the three Li cations became sufficiently fast for observation of

---

(9) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 6009–6010.
(10) Hilmersson, G.; Davidsson, Ö. *J. Org. Chem.* **1995**, *60*, 7660–7669.
(11) Hilmersson, G.; Ahlberg, P.; Davidsson, Ö. *J. Am. Chem. Soc.* **1996**, *118*, 3539–3540.
(12) Henze, W.; Vyater, A.; Krause, N.; Gschwind, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 17335–17342 and Figure 8 therein.
(13) Bauer, W.; Winchester, W. R.; Schleyer, P. von R. *Organometallics* **1987**, *6*, 2371–2379.
(14) Bauer, W.; Schleyer, P. von R. *Adv. Carbanion Chem.* **1992**, *1*, 89–175 (specifically pp 94 and 98).
(15) (a) Lambert, C.; Schleyer, P. von R. *Angew. Chem.* **1994**, *106*, 1187–1199. (b) Lambert, C.; Schleyer, P. von R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129–1140.
(16) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1988**, *110*, 6033–6046 (specifically p 6036).
(17) For instance, see note 21 in the following: Reich, H. J.; Holladay, J. E.; Mason, J. D.; Sikorski, W. H. *J. Am. Chem. Soc.* **1995**, *117*, 12137–12150.
(18) Koizumi, T.; Kikuchi, O. *Organometallics* **1995**, *14*, 987–991.

Table 1. Aggregation States, NMR Parameters ($\Delta\delta$, $^1J_{\mathrm{CLi}}$) with Pertinent Conditions, Experimental Contact Numbers (n, a, d), and Sensitivity Factors (L) for Alkenyllithium Compounds **8** and **12**

					$\Delta\delta(^{13}\mathrm{C})^a$			contact numbers^b				
entry	RLi	solvent	Do (equiv/anion)	T (°C)	C$^\alpha$	C^{para}	$^1J_{\mathrm{CLi}}$ (Hz) ^{c}	n	a	d ^{d}	T_{coll} (°C)^e	L (Hz)
1	**(8b)**$_1$	*t*-BuOMe	*t*-BuOMe	−70	+61.3	−11.8	13.5	1	1	(2)	−60(5)	40.5
2	**(8b)**$_1$	toluene	*t*-BuOMe (5.0)	−57	+61.7	−11.3	13.5	1	1	2	−35(8)	40.5
3	**(8b)**$_1$ ^{f}	toluene	*t*-BuOMe (∼1.5)	−82	+61.6	−11.5	13.5	1	1	2	−18(3)	40.5
4	**(8b)**$_2$ ^{f}	toluene	*t*-BuOMe (∼1.5)	−82	+53.3	−7.3	7.0 ^{g}	2	2	1	−	42.0
5	**(12b)**$_1$	toluene	*t*-BuOMe (3.0)	−51	+61.6	−16.1	12.5	1	1	2	−43(5)	37.5
6	**(8c)**$_1$	Et$_2$O	Et$_2$O	−105	+61.7	−11.8	14.0	1	1	(2)	−80(5)	42.0
7	**(8c)**$_2$	toluene	Et$_2$O (1.3)	−32	+52.4	−7.4	7.3	2	2	1	−1(2)	43.8
8	**(8d)**$_1$	THF	THF	−37	+66.5	−13.0	10.7	1	1	(3)	−23(5)	42.8
9	**(8d)**$_1$	toluene	THF (∼50.0)	−66	+65.6	−12.4	10.8	1	1	(3)	−30(5)	43.6
10	**(8d)**$_1$	toluene	THF (4.0)	−90	+65.8	−12.6	10.8	1	1	(3)	−25(5)	43.2
11	**(8d)**$_2$	toluene	THF (1.0)	−63	+52.2	−7.6	7.3	2	2	1	−40(5)	43.8
12	**(12d)**$_1$	THF	THF	−72	+66.0	−18.5	10.0	1	1	(3)	−28(5)	40.0
13	**(12d)**$_2$	toluene	THF (1.8)	−60	+51.8	−	∼6.9	2	2	1	−40(10)	∼41.4
14	**(8e)**$_1$	TMEDA	TMEDA	−42	+59.7	−11.1	14.2	1	1	(2)	−15(10)	42.6
15	**(8a)**$_3$	toluene	none	−84	+48.8	−5.5	8.5	2	2	0.5^h	−10(5)	42.5

^{a} $\Delta\delta = \delta(\mathrm{RLi}) - \delta(\mathrm{RH})$, i.e., it is the δ value relative to that for the protolysis product RH (**9** or **13**) present in situ (Tables S6 and S7).[20] ^{b} n = no. of Li cations bound directly to ^{13}C$^\alpha$; a = no. of anionic centers bound directly to Li; d = no. of Do ligands in contact with Li, determined through ^{1}H and/or ^{13}C NMR integration as illustrated in Figures 2−10. ^{c} ^{13}C−^{6}Li NMR coupling constants. ^{d} The d values in parentheses could not be measured for the monomers but were inferred from the characteristic lithiation shifts $\Delta\delta$ of C$^\alpha$ and C^{para}. ^{e} T_{coll} is the *minimum* temperature of collapse of the ^{13}C$^\alpha$ multiplet splitting; values in parentheses are the errors in the measured values. ^{f} Monomer/dimer ratio = 55:45. ^{g} Measured at −52 °C. ^{h} $d \approx$ "0.5" for π plus C−H coordination?[20]

an averaged $^1J_{\mathrm{CLi}}$ value while the *inter*aggregate Li-interchange reaction was still slow on the ^{13}C NMR time scale;[21] the experimentally determined splitting of 5.9 Hz agrees well with the expected average $(2\,^1J + \,^3J)/3 = (2 \times 8.5 + 0)/3 = 5.7$ Hz calculated for the "fluxional" trimer. This agreement excludes a dimer, which would not exhibit such a change, and all higher oligomers R$_m$Li$_m$, because these would have significantly smaller averaged coupling constants, $(2 \times 8.5 + 0)/m$, through scrambling of $m \geq 4$ ^{6}Li cations.

The following observations indicate that **(8a)**$_3$ in [D$_8$]toluene solution retains essential traits of the pseudothreefold axial symmetry of its solid-state structure,[7] in which each of the three **8** units is devoid of symmetry because of single Li−C^{ortho} and Li−CH$_3$ interactions: The only nonequivalences observed for **(8a)**$_3$ in toluene from −60 to −96 °C were diastereotopic splittings (1:1) of the twin types of nuclei, namely, *o*-H, *m*-H, 3-C*H*$_3$, 1-C*H*$_3$, C^{ortho}, C^{meta}, 3-*C*H$_3$, and 1-*C*H$_3$, whose chemical shifts are listed in Tables S10 and S11.[20] The large shift nonequivalences[20] of C^{ortho}, 3-*C*H$_3$, and *o*-H are compatible with an accumulation of negative electric charge at the ortho and 3 positions, which are close to the Li cation (as in the crystal[7]). As the sample is warmed, the interchange within both the C^{ortho} and 3-*C*H$_3$ diastereotopic pairs becomes fast on the ^{13}C NMR time scale at comparable coalescence temperatures ($T_c \approx -40$ °C; Table S11)[20] and hence involves similar energy barriers at these positions. This rules out a simple phenyl rotation but is compatible with switching of Li between the diastereotopic ortho and 3-methyl groups. Both 3-C*H*$_3$ and *o*-H remain sufficiently close to ^{6}Li to produce ^{1}H−^{6}Li HOESY[22−25] cross peaks at 25 °C. The considerably broadened, coalesced *o*-H resonance at δ = 5.94 ppm is characteristic of **(8a)**$_3$ at room temperature; it exhibits the expected doublet splitting ($^3J_{\mathrm{HH}}$ = 7.5 Hz) only at ≥25 and 105 °C when measured at 80 and 400 MHz, respectively. During prolonged measurements at 105 °C, **(8a)**$_3$ in [D$_8$]toluene slowly decomposed with formation of [α-D]-**9** (X = D for **9** in Chart 2), which suggests that **(8a)**$_3$ was deuterated by the solvent and may be a stronger base than benzyllithium in toluene.[26]

Because **(8a)**$_3$ is only sparingly soluble in cyclopentane, the ^{6}Li coupling with ^{13}C$^\alpha$ in natural abundance could not be measured in this solvent. Most of the ^{13}C chemical shifts of **(8a)**$_3$ in cyclopentane (except for C^2 in Table S9)[20] are sufficiently similar to those in [D$_8$]toluene,[27] including the diastereotopic splittings at −84 °C, to allow the conclusion that only **(8a)**$_3$ exists and significant amounts of other aggregates are excluded in cyclopentane solution.

2. Dimeric Aggregates (8b−d)$_2$ and (12b−d)$_2$ are Disolvated. The Br/Li interchange reaction (Chart 2) of the bromoalkene **7** with *n*-BuLi in cyclopentane[20] and diethyl ether (Et$_2$O, 3 equiv) furnished another kind of single crystals of **8**. X-ray diffraction analysis (Figure S1)[20] revealed a dimeric structure **(8c)**$_2$ of type **2**, disolvated by Do = Et$_2$O (one per Li) as sketched in Chart 4. The corresponding THF disolvate **(8d)**$_2$ crystallized with a similar structure (Figure S2)[20] from a saturated toluene solution of **8** in the presence of Do = THF (1.5 equiv per Li). The *p*-trimethylsilyl derivatives **10−13** were prepared by a different

---

(19) Parisel, O.; Fressigné, C.; Maddaluno, J.; Giessner-Prettre, C. *J. Org. Chem.* **2003**, *68*, 1290–1294.

(20) Details are reported in the Supporting Information.

(21) For similar identifications of trimers, see the following: (a) Bauer, W. *J. Am. Chem. Soc.* **1996**, *118*, 5450–5455. (b) Harder, S.; Ekhart, P. F.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; Schleyer, P. von R. *Organometallics* **1992**, *11*, 2623–2627.

(22) (a) Bauer, W.; Müller, G.; Pi, R.; Schleyer, P. von R. *Angew. Chem.* **1986**, *98*, 1130–1132. (b) Bauer, W.; Müller, G.; Pi, R.; Schleyer, P. von R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1103.

(23) Bauer, W.; Clark, T.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1987**, *109*, 970–977.

(24) Bauer, W.; Schleyer, P. von R. *Magn. Reson. Chem.* **1988**, *26*, 827–833.

(25) Bauer, W. In *Lithium Chemistry*; Sapse, A.-M., Schleyer, P. von R., Eds.; Wiley: New York, 1995; pp 125−172.

(26) Acidity of toluene in THF: (a) pK_a = 40.9: Streitwieser, A.; Ciula, J. C.; Krom, J. A.; Thiele, G. *J. Org. Chem.* **1991**, *56*, 1074–1076. (b) pK_a = 40.7: Ahlbrecht, H.; Schneider, G. *Tetrahedron* **1986**, *42*, 4729–4741.

(27) This contrasts with the interaction of toluene with monomeric LiN(SiMe$_3$)$_2$ as reported by: Lucht, B. L.; Collum, D. *J. Am. Chem. Soc.* **1996**, *118*, 2217–2225 (specifically p 2224) and references therein.

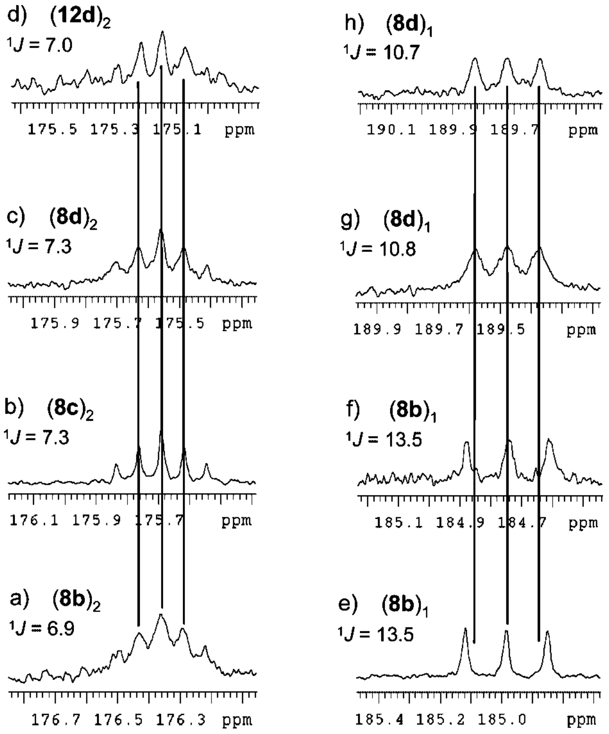
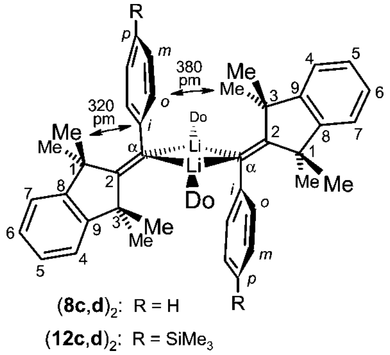


Figure 1. C^{α} quintets (of [^{6}Li] dimers) and triplets (of [^{6}Li] monomers). (a) $(\mathbf{8b})_2$ with *t*-BuOMe (1.5 equiv) in [D$_8$]toluene at −52 °C: $^1J_{CLi} = 6.9$ Hz. (b) $(\mathbf{8c})_2$ with Et$_2$O (1.3 equiv) in [D$_8$]toluene at −32 °C: $^1J_{CLi} = 7.3$ Hz. (c) $(\mathbf{8d})_2$ with THF (0.85 equiv) in [D$_8$]toluene at −72 °C: $^1J_{CLi} = 7.3$ Hz. (d) $(\mathbf{12d})_2$ with THF (1.8 equiv) in [D$_8$]toluene at −60 °C: $^1J_{CLi} = 7.0$ Hz. (e) $(\mathbf{8b})_1$ with *t*-BuOMe (5 equiv) in [D$_8$]toluene at −57 °C: $^1J_{CLi} = 13.5$ Hz. (f) $(\mathbf{8b})_1$ in *t*-BuOMe at −70 °C: $^1J_{CLi} = 13.5$ Hz. (g) $(\mathbf{8d})_1$ with THF (4 equiv) in [D$_8$]toluene at −90 °C: $^1J_{CLi} = 10.8$ Hz. (h) $(\mathbf{8d})_1$ in THF at −37 °C: $^1J_{CLi} = 10.7$ Hz.

Chart 4. Generalized Solid-State Structures of the Disolvated Dimers $(\mathbf{8c})_2$ and $(\mathbf{12c})_2$, Both with Do = Et$_2$O, and of $(\mathbf{8d})_2$ and $(\mathbf{12d})_2$, Both with Do = THF



route, as indicated in Chart 2: the known[28] α-chloroalkene **10** reacted with LiSnMe$_3$ in THF to yield the α-(trimethylstannyl)alkene **11** (62%), which was used in place of **10** for preparing the alkenyllithium compound **12** uncontaminated by LiCl. This Sn/^{6}Li interchange reaction of **11** in pentane was carried out with *n*-BuLi in the presence of either *tert*-butyl methyl ether (*t*-BuOMe, 2.5 equiv, very slow) or Et$_2$O (2.1 equiv) and caused crystals of the dimers $(\mathbf{12b})_2$ or $(\mathbf{12c})_2$, respectively, to precipitate as formed. The X-ray diffraction structure of $(\mathbf{12c})_2$ (Figure S3)[20] reveals disolvation with two Et$_2$O ligands in the same double-gauche conformation as in $(\mathbf{8c})_2$ (Figure S1).[20] In accord with Chart 4, the architecture of $(\mathbf{12d})_2$ (shown in Figure S4)[20] is similar to that of $(\mathbf{8d})_2$ in Figure S2, inclusive of the coordinated THF.

In view of the different crystal systems, the amassed evidence of architectural similarity (Table S4)[20] suggests that this arrangement is not dominated by crystal effects but should be characteristic of molecular energetic minima and thus that this structure may be expected to carry over to the solutions. The close packing in those dimers, as quantified in Chart 4 through the short carbon−carbon distances of the α-aryl group from both 1-Me (320 pm) and 3-Me (380 pm), is confirmed by NOESY experiments in solution.[20] Moreover, the contacts of Li to the $C^{\alpha}-C^{ipso}$ bond (the C14−C15 bond in Figures S1−S4),[20] one of the two $C^{ortho}-H$ bonds (C16−H16A), and two of the six C−H bonds of 3-Me are in accord with the results of ^{6}Li−^{1}H HOESY measurements[20] on $(\mathbf{8d})_2$ in toluene solution. Furthermore, the almost orthogonal orientation of the α-aryl group with respect to the double bond $C^2{=}C^{\alpha}$ (common to all four of these crystalline dimers) allows an efficient delocalization of negative charge from the C^{α}−Li bonds into the π-system of the α-aryl group ("quasi-benzyllithium" conjugation), with the consequence of significant upfield NMR shifts $\Delta\delta$ (see below) for C^{para} (and of R = H in **8a−e**) in solution.

The following ^{13}C NMR parameters were found to provide reliable evidence for the dimeric aggregation of the alkenyllithium compounds **8b−d** and **12b−d** in those solutions that frustrate molecular mass determinations: (i) When labeled with ^{6}Li, these compounds present the ^{13}C resonances of their carbanionic centers C^{α} as 1:2:3:2:1 quintets with $^1J_{CLi} \approx 7$ Hz at low temperatures, as exemplified in Table 1 (entries 4, 7, 11, and 13) and displayed in Figure 1a−d. These quintets establish contacts of a C^{α} nucleus with two ^{6}Li nuclei (i.e., $n = 2$) and persist on warming of the sample [up to at least −1 °C in the case of $(\mathbf{8c})_2$ (entry 7)] until they collapse through the accelerated interaggregate Li interchange. Therefore, at least $(\mathbf{8c})_2$ and presumably also the other dimers do not (and should not) exhibit the $^1J_{CLi}$ averaging expected from fluxional higher oligomers, as described above for $(\mathbf{8a})_3$. (ii) In the presence of donor ligands in amounts suitably limited to avoid causing deaggregation, the chemical shifts of C^{α} and C^{para} are almost independent of temperature from the domain of frozen Li scrambling (C^{α} multiplets) up to the range above collapse of the multiplets. The latter two shift criteria for an unchanged species may be visualized more clearly (Chart S2)[20] in the form of lithiation shifts $\Delta\delta = \delta(\mathrm{RLi}) - \delta(\mathrm{RH})$, where RH (Tables S6 and S7)[20] is the protolysis product (**9** or **13**) inevitably present in situ. The dimers listed in Table 1 (entries 4, 7, 11, and 13) have $\Delta\delta(C^{\alpha}) \approx 52$ ppm (downfield) and $\Delta\delta(C^{para}) \approx -7.4$ ppm (upfield because of the delocalized negative charge), the magnitudes of which are significantly smaller than those of the monomers (treated in section 3) and larger than those of $(\mathbf{8a})_3$ (entry 15). With one or two of these criteria satisfied for $(\mathbf{8b{-}d})_2$, $(\mathbf{12c})_2$, and $(\mathbf{12d})_2$, a most unusual property was discovered close to the lower temperature limit of the liquidity range of the donor/toluene mixtures: separate (decoalesced) NMR resonances (^{1}H and ^{13}C) were observed for coordinated and free Do. This allowed the determination via NMR integrations that 1 equiv of Do per carbanion is coordinated in each of these cases, corresponding to the four crystal structures summarized in Chart 4.

Coordinated Et$_2$O displays separate resonances of the diastereotopic geminal OCH$_2$ protons that are shifted slightly

---

[28] Knorr, R.; Pires, C.; Behringer, C.; Menke, T.; Freudenreich, J.; Rossmann, E. C.; Böhrer, P. *J. Am. Chem. Soc.* **2006**, *128*, 14845–14853.

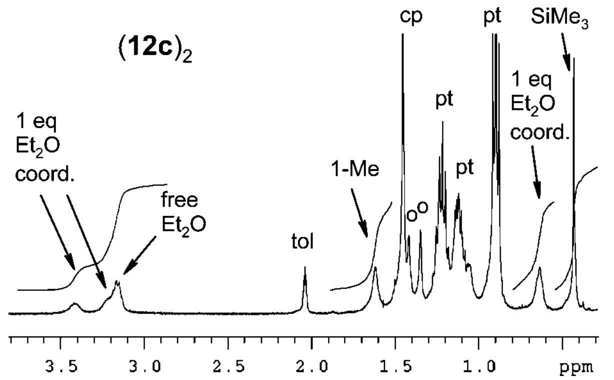


Figure 2. Partial ^1H NMR spectrum of $(\mathbf{12c})_2$ with 2.1 equiv of Et_2O in $[D_8]$toluene at −79 °C. o = alkene **13**, cp = cyclopentane, pt = pentane, tol = $[D_7]$toluene.

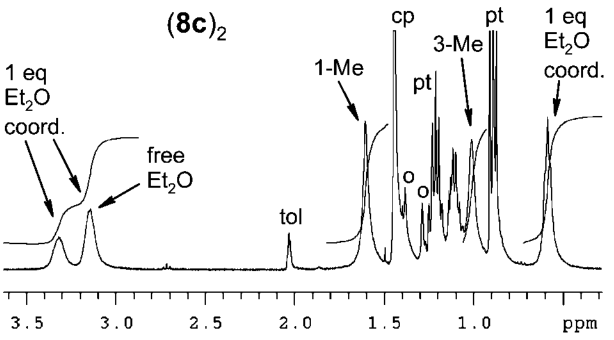


Figure 3. Partial ^1H NMR spectrum of $(\mathbf{8c})_2$ with 1.3 equiv of Et_2O in $[D_8]$toluene at −80 °C. o = alkene **9**, cp = cyclopentane, pt = pentane, tol = $[D_7]$toluene.

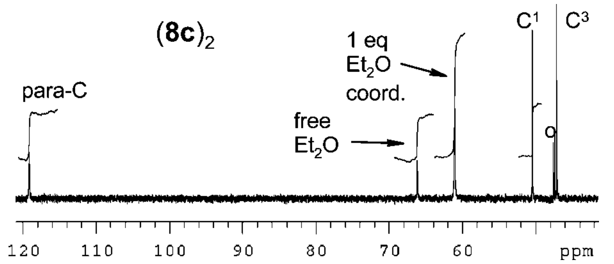


Figure 4. Partial ^{13}C NMR spectrum of $(\mathbf{8c})_2$ with 1.3 equiv of Et_2O in $[D_8]$toluene at −80 °C. o = alkene **9**.

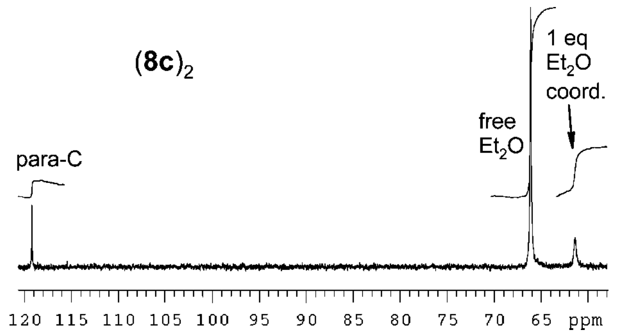


Figure 5. Partial ^{13}C NMR spectrum of $(\mathbf{8c})_2$ with 5.5 equiv of Et_2O in $[D_8]$toluene at −66 °C; the monomeric component (9%) is not shown.

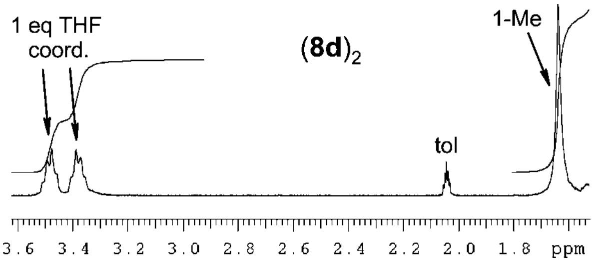


Figure 6. Partial ^1H NMR spectrum of $(\mathbf{8d})_2$ with 1.0 equiv of THF in $[D_8]$toluene at −63 °C. tol = $[D_7]$toluene.

downfield in the ^1H NMR spectra of $(\mathbf{12c})_2$ (Figure 2) and $(\mathbf{8c})_2$ (Figure 3), whereas the broadened triplets of the neighboring methyl protons appear upfield at $\delta \approx 0.65$ and 0.60 ppm, respectively. None of these phenomena are artifacts attributable to decay products or contaminants because they vanished on decomposition of $(\mathbf{8c})_2$ in the same sample. The diastereotopicity does not result from frozen Do rotation about the O−Li bond[20] because the ^{13}C nuclei of coordinated Et_2O remain equivalent in the presence of smaller (Figure 4) or greater (Figure 5) amounts of Et_2O.

Coordinated THF in $(\mathbf{8d})_2$ at −63 °C also exhibits diastereotopic OCH_2 protons (Figure 6) whose resonances integrate for 2 + 2 protons with respect to the six-proton singlet of the two $1\text{-}CH_3$ groups, indicating that this dimer is also disolvated.[29] The ^1H or ^{13}C resonances of free THF could be detected only when >1 equiv of THF was present. The CCH_2C protons of THF (not depicted) are shifted slightly upfield to $\delta \approx 1.0$ ppm. Neither $C^{2,5}$ nor $C^{3,4}$ of THF show diastereotopic splitting, indicating that THF rotation about the O−Li bond is probably not frozen on the ^{13}C NMR time scale at this temperature. The NOESY[30] measurement on $(\mathbf{8d})_2$ at 25 °C reveals cross-relaxation of *o*-H of the α-phenyl group with both $1\text{-}CH_3$ and $3\text{-}CH_3$ (the latter being weaker because the interaction occurs across the Li_2C_2 ring), confirming the closeness of the two half-dimers depicted in Chart 4 and hence the rather compact dimeric structure. The broadened proton resonances of both OCH_2 and CCH_2C of coordinated THF exhibit NOESY correlations with *o*-H, establishing the existence of a close confrontation of Do = THF with the α-phenyl group that accounts for the aforementioned upfield shift of the CCH_2C protons of THF and moreso of the methyl protons of Et_2O in $(\mathbf{8c})_2$ in Figure 3. Only the OCH_2 protons of $(\mathbf{8d})_2$ correlate with $3\text{-}CH_3$ (very broad) and less strongly with $1\text{-}CH_3$ (broadened). The $3\text{-}CH_3$ resonance was assigned through the HOESY[22−25] correlations of ^6Li with *o*-H, OCH_2, and $3\text{-}CH_3$ (but not $1\text{-}CH_3$) at 25 °C.

Coordinated Do = *t*-BuOMe provides simpler ^1H NMR spectra because its OMe protons are not prone to diastereotopic splitting. A toluene solution containing $(\mathbf{8b})_2$ and $(\mathbf{8b})_1$ in a 45:55 molar ratio (62:38 in monomeric units) at −82 °C[20] together with only ~1.5 equiv of Do per carbanion (entry 4) displayed no ^1H or ^{13}C NMR absorptions of free Do (Figure 7); instead, well-separated OCH_3 resonances were observed in a 43:57 ratio (45:55 expected) for the Do fractions coordinated at dimeric and monomeric **8b**, respectively. Small amounts of THF are able to displace Et_2O from $(\mathbf{8c})_2$ and *t*-BuOMe from $(\mathbf{8b})_2$, forming $(\mathbf{8d})_2$ and generating the well-resolved resonances of free Et_2O and *t*-BuOMe, respectively.

---

[29] A minor component, believed to be the monosolvated dimer $(\mathbf{8a})_2 \cdot$THF, was observed[20] when a substoichiometric amount of THF was added to the cyclotrimer $(\mathbf{8a})_3$ in $[D_8]$toluene.

[30] Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546–4553.

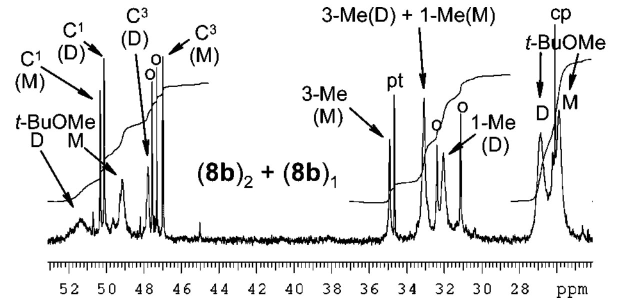


Figure 7. Partial ^{13}C NMR spectrum of (**8b**)$_2$ and (**8b**)$_1$ (62:38 in monomeric units) with 1.5 equiv of *t*-BuOMe in [D$_8$]toluene at −82 °C. D = dimer, M = monomer, o = alkene **9**, cp = cyclopentane, pt = pentane.

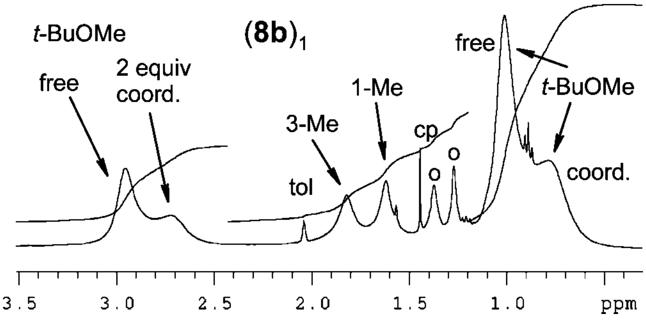


Figure 8. Partial ^{1}H NMR spectrum of (**8b**)$_1$ with 5 equiv of *t*-BuOMe in [D$_8$]toluene at −94 °C. o = alkene **9**, cp = cyclopentane, tol = [D$_7$]toluene.

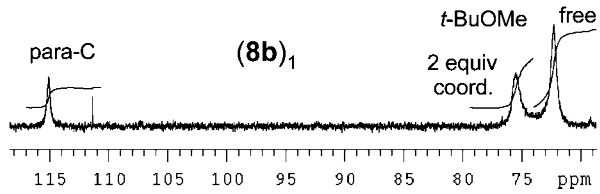


Figure 9. Partial ^{13}C NMR spectrum of (**8b**)$_1$ with 5 equiv of *t*-BuOMe in [D$_8$]toluene at −94 °C.

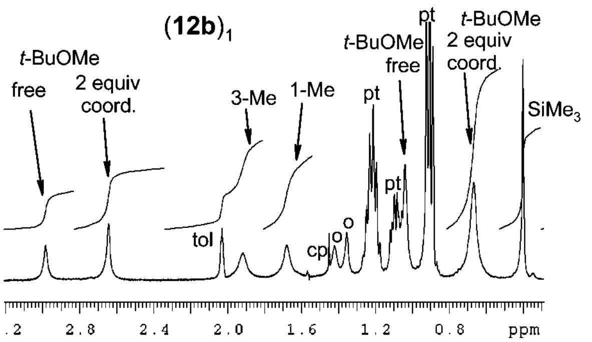


Figure 10. Partial ^{1}H NMR spectrum of (**12b**)$_1$ with 3 equiv of *t*-BuOMe in [D$_8$]toluene at −96 °C. o = alkene **13**, cp = cyclopentane, pt = pentane, tol = [D$_7$]toluene.

3. Monomers (8b−e)$_1$, (12b)$_1$, and (12d)$_1$ Provide a Novel View of $^1J_{\mathrm{CLi}}$. The ligand Do = *t*-BuOMe promotes formation of the monomers (**8b**)$_1$ and (**12b**)$_1$, presumably because the dimers are less efficiently stabilized by this bulkier donor. In the presence of only 3 equiv of *t*-BuOMe, (**12b**)$_1$ coexists with a small portion of the dimer (entry 5 of Table 1). The toluene solution of **8b** with merely ~1.5 equiv of Do per carbanion at −82 °C (entries 3 and 4) contained (**8b**)$_2$ and (**8b**)$_1$ in the above-mentioned 45:55 molar ratio (Figure 7), whereas only (**8b**)$_1$ could be detected with 5 Do equiv per carbanion at −57 °C (entry 2) and −94 °C (Figures 8 and 9). The 1:1:1 triplets of the C$^\alpha$ resonances shown in Figure 1e,f indicate one contact of C$^\alpha$ with ^{6}Li (i.e., $n = 1$) in (**8b**)$_1$, and the concomitant values of $^1J_{\mathrm{CLi}}$ (13.5 Hz) are equal in the solvents toluene (entries 2 and 3) and neat *t*-BuOMe (entry 1). The quotient of the $^1J_{\mathrm{CLi}}$ values for (**8b**)$_1$ (entries 1−3) and (**8b**)$_2$ (entry 4), 13.5/7.0 = 1.93, leads to the relation $^1J_{\mathrm{CLi}}$ = (13.6 Hz)/n, which confirms the 17/n relation[13−15] in its functional form but not numerically. Similarly, the Et$_2$O complexes (**8c**)$_1$ and (**8c**)$_2$ (entries 6 and 7) can be characterized by $^1J_{\mathrm{CLi}} \approx$ (14.3 Hz)/n, again falling short of the 17/n relation. Fortunately, it was possible to observe and integrate separate ^{1}H and ^{13}C NMR resonances of free and coordinated Do in these spectra. Both (**8b**)$_1$ and (**12b**)$_1$ are microsolvated by *only two* *t*-BuOMe donors per carbanion (entries 2, 3, and 5), as illustrated in Figures 8−10. These disolvated monomers can also be characterized by their lithiation shifts Δδ (Table 1): +62 ppm for C$^\alpha$ of (**8b**)$_1$ and (**12b**)$_1$, −11 ppm for C^{para} of (**8b**)$_1$, and −16 ppm for C^{para} of (**12b**)$_1$. On the basis of these Δδ values, a value of 2 for the microsolvation number *d* (in parentheses in Table 1) was inferred for those cases where NMR resonance separation was not achieved: (**8b**)$_1$ in neat *t*-BuOMe, (**8c**)$_1$ with Do = Et$_2$O, and (**8e**)$_1$ with Do = *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (TMEDA) (entries 1, 6, and 14, respectively). This tricoordination (C,O,O or C,N,N) of the lithium cations in the disolvated monomers (**8b**)$_1$, (**8c**)$_1$, and (**8e**)$_1$ can be ascribed to steric congestion, which limits the space available for the donors *t*-BuOMe, Et$_2$O, and TMEDA. In accord with such overcrowding, (**8b**)$_1$ does not react with di-*tert*-butyl ketone at ambient temperature to produce the expected alcoholate. But what about the remaining monomers in Table 1, (**8d**)$_1$ and (**12d**)$_1$, which are coordinated to the smaller donor THF?

The 1:1:1 triplets of (**8d**)$_1$ with the surprisingly diminished $^1J_{\mathrm{CLi}}$ magnitude of 10.8 Hz (Figure 1g,h) are also independent of changes of the solvent from neat THF to toluene (entries 8−10 of Table 1). However, the quotient of the $^1J_{\mathrm{CLi}}$ values for (**8d**)$_1$ and (**8d**)$_2$ (entries 10 and 11, respectively) is only 10.8/7.3 = 1.48, in clear violation of the expected 2:1 relationship. A correspondingly low $^1J_{\mathrm{CLi}}$ quotient of 10.0/6.9 = 1.45 for (**12d**)$_1$ and (**12d**)$_2$ (entries 12 and 13, respectively) is obtained. Since all of the dimers in Table 1 have practically equal values of $^1J_{\mathrm{CLi}}$ (6.9−7.3 Hz), it seems that (**8d**)$_1$ and (**12d**)$_1$ alone (but not the **b** and **c** monomers) are responsible for this apparent breaking of the 1/n relationship. Why is this the case?

Likewise surprisingly, the magnitudes of lithiation shifts Δδ of these two THF-coordinated monomers are distinctly larger than those of the other monomers (Table 1): +66 ppm for C$^\alpha$ of (**8d**)$_1$ and (**12d**)$_1$ versus +61.5 ppm for the others, −13 ppm for C^{para} of (**8d**)$_1$ versus −11.5 ppm for (**8b**)$_1$ and (**8c**)$_1$, and −18.5 ppm for C^{para} of (**12d**)$_1$ versus −16.1 ppm for (**12b**)$_1$. Since the corresponding lithiation shifts are almost equal for the disolvated dimers (entries 4, 7, 11, and 13) irrespective of the nature of the donor, it can be concluded that only the smallest donor, THF, endows the monomers with magnetic properties (Δδ and $^1J_{\mathrm{CLi}}$) that differ significantly from those induced by the other electronically but not sterically similar ethereal donors. On this basis, we reasoned that *d*, the number of Do ligands coordinated at Li, might determine the magnitude of $^1J_{\mathrm{CLi}}$ and that a reciprocal relation as expressed in eq 1 should obtain, in

Table 2. Aggregation States of Four Other Organolithium Compounds, with Donor Ligands (Do), NMR Coupling Constants ($^1J_{CLi}$) and Pertinent Conditions, Contact Numbers (n, a, d), and Sensitivity Factors (L) Computed Using Equation 2

								contact numbers[a]			
entry	RLi	agg. state[b]	solvent[c]	Do[c]	T (°C)	$^1J_{CLi}$ (Hz)[d]	refs	n	a	d	L (Hz)
16	*t*-BuLi	M	THF	THF	−90	11.9	13	1	1	3	47.6
17	*t*-BuLi	M	THF	TMTAN	−108	14.3	39	1	1	"2.3"	47.5[e]
18	*t*-BuLi	M	THF	TDMAEA	−108	13.0	39	1	1	"2.7"	47.5[e]
19	*t*-BuLi	D	Et_2O	Et_2O	≤−64	7.6	13	2	2	1	45.6
20	*t*-BuLi	D	C_5H_{10}	Et_2O	−80	7.8	36	2	2	1	46.8
21	*t*-BuLi	T	C_5H_{10}	Et_2O	−80	5.4	36	3	3	0	48.6
22	*t*-BuLi	T	C_5H_{10}	none	≤−10	5.44	34, 35	3	3	0	49.0
23	*s*-BuLi	M	THF	PMDTA	−96	14.0	13	1	1	3	56
24	*s*-BuLi	T	C_5H_{10}	none	−41	6.1	40	3	3	0	55
25	*s*-BuLi	H	C_5H_{10}	none	−41	6.1	41	3	3	0	55
26	*n*-BuLi	D	toluene	TMEDA[f]	−78	8.1	43	2	2	2	64.8
27	*n*-BuLi	D	THF[g]	THF	≤−90	8.0(2)[e]	44−46	2	2	2	64
28	*n*-BuLi	T	THF[g]	THF	≤−96	5.5(2)[e]	23, 44, 46	3	3	1	66.0
29	*n*-BuLi	T	$(MeO)_2CH_2$	$(MeO)_2CH_2$	−73	5.5	47	3	3	1	66.0
30	*n*-BuLi	T	Et_2O	Et_2O	−70	5.3	33	3	3	1	63.6
31	*n*-BuLi	T	Et_2O	Et_2O	−90	5.4(1)	47	3	3	1	64.8
32	$H_2C{=}CHLi$	D	THF	THF	−100	8.3	49	2	2	2	66.4
33	$H_2C{=}CHLi$	T	THF	THF	−90	5.9	49	3	3	1	70.8
34	$H_2C{=}CHLi$	T	Et_2O	Et_2O	−60	5.8	41	3	3	1	69.6

[a] n = no. of Li cations bound directly to $^{13}C^{\alpha}$; a = no. of anionic centers bound directly to Li; d = no. of Do ligands in contact with Li, chosen for the individual cases as explained in section 4 in the text. [b] M = monomer; D = dimer; T = tetramer; H = hexamer. [c] TMTAN = 1,4,7-trimethyl-1,4,7-triazacyclononane; TDMAEA = $(Me_2NCH_2CH_2)_3N$; C_5H_{10} = cyclopentane; PMDTA = $MeN(CH_2CH_2NMe_2)_2$; TMEDA = $Me_2NCH_2CH_2NMe_2$. [d] ^{13}C−^{6}Li NMR coupling constants.[32] [e] Mean value. [f] Labeled with ^{15}N. [g] Or 1:5 THF/pentane.[44]

qualitative accord with the computational hints[18,19] mentioned in the Introduction:

$$^1J_{CLi} = L[n(a+d)]^{-1} \tag{1}$$

In this expression, a is the number of anions connected with the Li cation under consideration, so $a + d$ is the total number of atoms in the coordination sphere of that lithium; the sensitivity factor L (in Hz) controls the magnitude of $^1J_{CLi}$.[31] For the ^{7}Li isotope, which has nuclear spin $I = {}^3/_2$ and hence $2nI + 1 = 3n + 1$ multiplet components of the $^{13}C^{\alpha}$ resonance, L would be larger by a factor of 2.641. The values of L for ^{6}Li are listed in the last column of Table 1 and depend hardly at all on the nature of Do: the averaged factor $L = 42 \pm 2$ Hz is seen to apply to **8** and **12** (entries 1−4 and 6−14 of Table 1) with Do = *t*-BuOMe, Et_2O, THF, and TMEDA. A single striking deviation [by −6% compared with the value for $(\mathbf{12d})_1$ in entry 12] is provided by the combination of the weak donor *t*-BuOMe with the para substituent $SiMe_3$ in $(\mathbf{12b})_1$ (entry 5).

4. Other Applications of Equation 1. Although it was conceived for the solvated monomers and dimers of **8** and **12**, eq 1 is also applicable to the monomers and aggregates of several other organolithium species whose coupling constants $^1J_{CLi}$ and C−Li contact numbers n have been determined from their $^{13}C^{\alpha}$ multiplets but whose microsolvation numbers d in solution remained unknown. Because the number a of anion contacts to a Li nucleus under consideration most often equals n, as may be seen from the model structures **1**−**6** shown in Chart 1, the unknowns in eq 2 (obtained by rearranging eq 1) are the sensitivity factor L and the number d of electrically neutral donors Do coordinating to the lithium cation:

$$L = n(a+d)^1J_{CLi} \tag{2}$$

Values of L characterizing the four RLi compounds in Table 2 were unambiguously established through a special property of one aggregate of each compound.[32] This property was either ^{15}N NMR coupling of Do = TMEDA with ^{6}Li (revealing $d = 2$ in the case of known $n = a$ in entry 26 of Table 2) or unequivocal evidence of a nonfluxional type-**4** tetramer ($n = 3$) carrying $d = 0$ or 1 donor per Li (entry 22 or 33, respectively), as outlined below. Equation 2 would be verified if it is possible to describe various aggregation states of a certain organolithium compound by a common, reasonably sized sensitivity factor L within acceptable limits. The best (averaged) L value can then be used to calculate d values for other donors or other RLi compounds of the same type (i.e., with a comparable substituent pattern at the carbanionic center).

In the first RLi series in Table 2, unsolvated *t*-Bu^{6}Li is a tetramer of type **4** (but without Do) in the solvents cyclohexane,[33] cyclopentane (entry 22),[34,35] cyclopentane with excess Do = Et_2O (entry 21),[36] and THF (by computation)[4] as well as in the solid state.[37] The tetrameric structure in cyclopentane solution follows from the fact that the fluxional nonet-splitting (4.1 Hz)[34] of $^{13}C^{\alpha}$ above −10 °C equals $^3/_4$ of the nonfluxional (septet-splitting) coupling constant $^1J_{CLi} = 5.44$ Hz (entry 22); this rules out a hexameric structure (for which a fluxional multiplet splitting of $^1J_{CLi}/2 = 2.72$ Hz would have been

---

(31) In simple terms, $L/4 = {}^1J_{CLi}$ for a trisolvated ($a + d = 4$) monomer ($n = 1$); $L = 68$ Hz would be consistent with the 17/n relation.

(32) Reported coupling constants $^1J(^{13}C, ^7Li)$ were converted to $^1J(^{13}C, ^6Li)$ values by multiplication with the quotient of the gyromagnetic ratios, $\gamma(^6Li)/\gamma(^7Li) = 1/2.641$. Because of the small nuclear quadrupole moment of ^{6}Li, this isotope provides much better conditions than the isotope ^{7}Li for observing the $^1J_{CLi}$ splitting of the $^{13}C^{\alpha}$ resonance, as demonstrated by: Fraenkel, G.; Fraenkel, A. M.; Geckle, M. J.; Schloss, F. *J. Am. Chem. Soc.* **1979**, *101*, 4745–4747.

(33) McKeever, L. D.; Waack, R. *J. Chem. Soc., Chem. Commun.* **1969**, 750–751.

(34) Thomas, R. D.; Clarke, M. T.; Jensen, R. M.; Young, T. C. *Organometallics* **1986**, *5*, 1851–1857.

(35) Thomas, R. D.; Jensen, R. M.; Young, T. C. *Organometallics* **1987**, *6*, 565–571.

(36) Bates, T. F.; Clarke, M. T.; Thomas, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5109–5112.

(37) (a) Kottke, T.; Stalke, D. *Angew. Chem.* **1993**, *105*, 619–621. (b) Kottke, T.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 580–582.

expected). The resulting L value of 49.0 Hz (eq 2) imposes $d = 1$ (disolvation by Et_2O) on dimeric t-BuLi in Et_2O (entry 19)[13] or in Et_2O/cyclopentane (entry 20)[36] in order to reproduce their common $^1J_{CLi}$ value of 7.7(1) Hz, in accord with the X-ray analysis of the dietherate.[37] With $L = 49.0$ Hz, the earlier assumption[36] of a tetrasolvated t-BuLi dimer ($d = 2$ Et_2O ligands per Li) would demand $^1J_{CLi} = 6.1$ Hz rather than 7.7 Hz. With the average L value of 47.5 Hz,[38] which fits the trisolvation of monomeric t-BuLi ($^1J_{CLi} = 11.9$ Hz in entry 16), the coupling constant value of 14.3 Hz observed[39] for monomeric t-BuLi in the presence of the tridentate donor TMTAN (entry 17) leads to $d =$ "2.3", which might be explained by a mobile equilibrium between the trisolvated and disolvated monomers. ^{15}N labeling might be helpful in checking this allegation and also the 2- to 3-fold coordination of the tetradentate donor $(Me_2NCH_2CH_2)_3N$ (TDMAEA), for which $d =$ "2.7" in entry 18.

A higher L value of 55 Hz for one of the aggregates of unsolvated 2-butyllithium (s-BuLi) (entry 24) is obtained as follows: This species is clearly a nonfluxional tetramer of type **4** (without Do) on account of coupling ($^1J_{CLi} = 6.1$ Hz) to three ^6Li nuclei ($n = 3$) in combination with the reduced splitting of 4.6 Hz ($= {}^3/_4$ of 6.1 Hz) observed[40] for the fluxional state attained at −1 °C. A second aggregate (entry 25) had been considered to be a fluxional type-**6** hexamer mainly on the basis of the size of its multiplet splitting (3.05 Hz).[41] Indeed, the doubling required in this case (apparent $n = 6$) to arrive at the nonfluxional hexamer (correct $n = 3$) afforded $^1J_{CLi} = 6.1$ Hz with the resulting L value of 55 Hz, in excellent agreement with the published[41] suggestion.[42] This L value demands trisolvation by PMDTA and THF in THF[13] for monomeric s-BuLi (entry 23).

Fluxional and nonfluxional states are spectroscopically identical for a dimeric aggregate of type **2** or **3**, such as $(n\text{-BuLi})_2\cdot(\text{TMEDA})_2$ (entry 26). With this chelating Do, the microsolvation number $d = 2$ (from 1 TMEDA) was established[43] by detecting the $^{15}N{-}^6Li{-}^{15}N$ arrangement through the NMR coupling patterns (^6Li, triplet 1:2:1; ^{15}N, triplet 1:1:1). The resulting L value of 65 Hz sets the stage for the other n-BuLi aggregates (entries 27−31),[23,33,44−47] in agreement with the corresponding solid-state structures.[48] However, it should be noted that this L value does not conform to the mixed cubic aggregates[44] $(n\text{-BuLi})_3\cdot(\text{ROLi})_1$ and $(n\text{-BuLi})_2\cdot(\text{ROLi})_2$, which have distinctly smaller $^1J_{CLi}$ values.

The tetrameric type-**4** aggregate of vinyllithium ($H_2C{=}CH{-}Li$) in THF solution ($d = 1$) is unambiguously established through its $^1J_{CLi}$ value of 5.9 Hz for the nonfluxional state ($n = 3$, entry 33) in combination with a fluxional multiplet splitting of 4.4 Hz ($= {}^3/_4$ of 5.9 Hz) at −60 °C and additional careful investigations.[49] The resulting value $L = 70.8$ Hz compares well with that of the Et_2O-solvated tetramer (entry 34)[41] and implies tetrasolvation ($d = 2$, entry 32) for the dimer[49] in THF. Results of further applications of eq 2 to methyllithium ($L = 68$ Hz), 1-propyllithium ($L \approx 60$ Hz), 2-propyllithium ($L \approx 57$ Hz), neopentyllithium ($L = 60$ Hz), phenyllithium ($L = 61$ Hz), lithium acetylides ($L \approx 69$ Hz), and other species are summarized in Table S1,[20] and a summarizing overview (Table S2)[20] lists the established or provisionally recommended L values.

Conclusions

2-(α-Lithiobenzylidene)-1,1,3,3-tetramethylindan (**8**) and its p-$SiMe_3$ derivative (**12**) are wholly (>95%) monomeric in electron-pair-donor solvents at all temperatures investigated, whereas **8** dissolves with retention of its solid-state cyclotrimer structure in donor-free toluene.[50] The disolvated dimeric aggregates of **8** and **12**, as also characterized by X-ray analyses, become populated in toluene solutions when a shortage of ethereal donors (Do = t-BuOMe, Et_2O, and THF) disfavors the monomers. Steric congestion in these monomers and dimers has the surprising and valuable consequence of retarding the release of monodentate Do ligands from the Li cation, offering the unique chance of measuring microsolvation at Li directly by NMR integrations in toluene solution. This led to the proposal of an inverse dependence of $^1J_{CLi}$ on the sum ($a + d$) of the numbers of carbanion centers (a) and Do ligands (d) bound to the Li cation under consideration (eq 1). This dependence could be discovered here because monomeric **8** and **12** coordinate only two discrete Et_2O or t-BuOMe donor molecules at Li ($d = 2$) rather than the usual $d = 3$ (as inferred for Do = THF), and thus give rise to changes in $^1J_{CLi}$ even though the values $n = 1$ and $a = 1$ are common for these monomers. As an empirical expression, eq 1 may require some refinement.[51]

The applicability of eq 1 has been shown to extend to other RLi compounds whose ligand-exchange processes have not as yet been frozen on the NMR time scale. The possibility of determining unknown microsolvation numbers d from $^1J_{CLi}$ values via eq 2 (a rearranged form of eq 1) endows $^1J_{CLi}$ with a new dimension of analytical utility but requires knowledge of both the aggregation state (contact numbers n and a) and the sensitivity factor L (as exemplified in section 4). Reliable evidence for the presence of higher-than-dimeric aggregates can be obtained by comparing the frequency intervals in the $^{13}C^{\alpha}$ multiplets of the nonfluxional and fluxional states of the same RLi species. Some of the L factors may turn out to be much smaller than those given in Tables 1 and 2 and Tables S1 and S2 in the Supporting Information. For example, we did not

---

(38) The slightly lower L value of 44 Hz is obtained for the mixed type-**4** aggregate $(t\text{-Bu}^6\text{Li})_3\cdot(t\text{-BuO}^6\text{Li})_1$ in cyclopentane from its $^1J_{CLi}$ value of 4.9 Hz (as calculated from the fluxional multiplet splitting of 3.7 Hz).[34]

(39) Luitjes, H.; Schakel, M.; Aarndts, M. P.; Schmitz, R. F.; de Kanter, F. J. J.; Klumpp, G. W. *Tetrahedron* **1997**, *53*, 9977–9988.

(40) Fraenkel, G.; Henrichs, M.; Hewitt, M.; Su, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 255–256.

(41) Fraenkel, G.; Hsu, H.; Su, B. M. In *Lithium*; Bach, R. O., Ed.; Wiley: New York, 1985; pp 273−289.

(42) However, the putative dimers[40] with multiplet splittings of 4.9 Hz would need an unreasonably high d value of ~3.6 for $L \approx 55$ Hz and hence possibly require another assignment.

(43) Waldmüller, D.; Kotsatos, B. J.; Nichols, M. A.; Williard, P. G. *J. Am. Chem. Soc.* **1997**, *119*, 5479–5480.

(44) Sun, X.; Winemiller, M. D.; Xiang, B.; Collum, D. B. *J. Am. Chem. Soc.* **2001**, *123*, 8039–8046.

(45) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308–337.

(46) Eppers, O.; Günther, H. *Tetrahedron Lett.* **1989**, *30*, 6155–6158.

(47) Bergander, K.; He, R.; Chandrakumar, N.; Eppers, O.; Günther, H. *Tetrahedron* **1994**, *50*, 5861–5868.

(48) Nichols, M. A.; Williard, P. G. *J. Am. Chem. Soc.* **1993**, *115*, 1568–1572.

(49) Bauer, W.; Griesinger, C. *J. Am. Chem. Soc.* **1993**, *115*, 10871–10882.

(50) Only ~3 equiv of t-BuOMe in toluene suffices to deaggregate **8** or **12** almost completely; in contrast, two α-aryl-substituted enolates remained purely tetrameric in the "poorly coordinating" solvent t-BuOMe, according to: Streitwieser, A.; Juaristi, E.; Kim, Y.-J.; Pugh, J. K. *Org. Lett.* **2000**, *2*, 3739–3741.

(51) $^1J_{CLi}$ values are "much more sensitive to the degree of aggregation and number of solvent molecules in the first solvation shell than to thermal motions", according to computational results reported by: de la Lande, A.; Fressigné, C.; Gérard, H.; Maddaluno, J.; Parisel, O. *Chem.−Eur. J.* **2007**, *13*, 3459–3469.

analyze RLi species with more delocalized anionic charges and small $^1J(^{13}C, ^6Li)$ values,[32] such as benzyllithium compounds (2.6−3.8 Hz)[52−54] and allyllithium species (2.3−3.0 Hz).[55,56]

As a tempting extension,[57] a roughly inverse relationship between $^1J(^{15}N, ^6Li)$ and the number of coordinating donor ligands was noted recently,[58] in accord with earlier computational results;[59] however, it may be less straightforward to formulate a quantitative dependence because of the smaller magnitudes of many $^1J_{NLi}$ values and occasional overlaps of their ranges.[58] Nevertheless, disolvated monomeric and dimeric LiN(*i*-Pr)$_2$ coordinating to a series of donors in toluene/pentane solutions have been characterized[60] with $^1J_{NLi} \approx 9.9$ and 5.1 Hz, respectively, which would lead to $L \approx 30$ in an analogue of eq 1.

Experimental Section

General Remarks. Organolithium compounds were handled under a stream of dry argon cover gas. [^{6}Li]*n*-Butyllithium[45] (<8.9% ^{7}Li) in cyclopentane[20] or commercially available solutions of unlabeled *n*-butyllithium in hexanes were used in the preparation[20] of the 2-(α-aryl-α-lithiomethylidene)-1,1,3,3-tetramethylindans **8** and **12**. NMR tubes (5 mm) containing **8** or **12** either carried ground-glass joints with glass stoppers or were sealed with soft rubber stoppers that were then secured by wrapping with an airtight film of stretchable plastic foil. The ethereal solutions of **8** or **12** were stable for weeks at −18 °C in the sealed NMR tubes when kept in an inclined position (not less than 20 degrees above horizontal) in a tightly closed glass cylinder that was filled with argon gas and contained only tubes with the same solvent. The solvent [D$_8$]toluene destroyed **8** or **12** slowly[20] at 95 °C and above by deuteron transfer to C$^{\alpha}$.

NMR spectra were run on a Varian VXR-400S (^{1}H at 400 MHz, ^{13}C at 100.6 MHz, ^{6}Li at 58.9 MHz), a Varian HA-100 (^{13}C at 25.15 MHz), or a Bruker WP-80-DS (^{13}C at 20 MHz) spectrometer. Working temperatures were measured with the usual calibrated samples of methanol or ethylene glycol. Coupling constants J_{CH} were obtained through gated or selective decoupling and ^{13}C−H multiplicities through the DEPT method. A mixing time of 4 s was used for the ^{6}Li−^{1}H HOESY[22−25] experiments at 25 °C. The actual formal concentrations in mol/L per carbanion unit of **8**, **12**, or *n*-BuLi were estimated by in situ comparisons with the ^{1}H NMR integral of either a sealed, calibrated capillary filled with pure ClCH$_2$C≡N ($\delta_H \approx 3.9$ ppm) or the low-field ^{13}C satellites of the nondeuterated solvents. NMR data of some of the aggregates are reported below by way of example; they do not duplicate the full characterization or the preparative details given in the Supporting Information,[20] which also provides a short summary (Tables S5a and S5b) of the typical spectral sequences.

Monomers and Dimers of 8. NMR samples of monomers **8b**−**e** were obtained from the cyclotrimer[7,20] (**8a**)$_3$ (stored in 5 mm NMR tubes) by removal of the supernatant cyclopentane with a syringe, blowing with dry argon through a long pipet for 5 s, and addition of ∼0.7 mL of one of the following dry undeuterated solvents plus 5−10% of [D$_{12}$]cyclohexane or [D$_6$]benzene ("lock" substances) and a trace of tetramethylsilane (TMS) at room temperature: *t*-BuOMe, Et$_2$O, THF, or TMEDA. [D$_8$]Toluene solutions of the monomers (**8c**)$_1$ and (**8d**)$_1$ were prepared by the addition of a suitable amount of the donor ligands Et$_2$O or THF, respectively, and a trace of TMS.

The dimers of **8** could be generated in [D$_8$]toluene from (**8a**)$_3$ by treatment with smaller amounts[20] of the donors. In several cases, it was necessary to apply ultrasonic irradiation for a few minutes or heat the sample to 45 °C in order to dissolve the plates of (**8a**)$_3$ completely. Alternatively, the purified[20] crystals of (**8c**)$_2$ were prepared from **7** (Chart 2) and dissolved in [D$_8$]toluene.

Dimer (8b)$_2$. ^{1}H NMR ([D$_8$]toluene with 1 equiv of *t*-BuOMe, 400 MHz, −12 °C): δ 0.87 (s, *t*-Bu), 1.28 (broad s, 2 3-CH$_3$), 1.51 (broad s, 2 1-CH$_3$), 2.89 (s, *t*-BuO*Me*), 6.79 (very broad, 2 *o*-H), 6.82 (broad t, *p*-H). ^{13}C NMR ([D$_8$]toluene with 1 equiv of *t*-BuOMe, 100.6 MHz, −12 °C): δ 26.7 (*t*-Bu), 32.52 (2 1-CH$_3$), 33.62 (broad, 2 3-CH$_3$), 47.78 (broad, C^3), 50.3 (*t*-BuO*Me*), 50.41 (C^1), 75.8 (Me$_3$*C*OMe), 119.4 (broad, C^{para}), 122.7 (C^{7,4}), 122.8 (broad, 2 C^{ortho}), 126.5 (C^5), 127.0 (broad, C^6), C^{meta} hidden, 150.6 (broad, C^9), 152.6 (sharp, C^8), 156.9 (broad, C^{ipso}), ∼162.4 (very broad, C^2), 175.5 (very broad, C$^{\alpha}$), assigned in analogy with those of (**8d**)$_2$.[20]

Monomer (8b)$_1$. ^{1}H NMR (*t*-BuOMe, 400 MHz, −70 °C, 0.07 M): δ 1.11 (s, *t*-Bu), 1.27 (s, 2 1-CH$_3$), 1.31 (s, 2 3-CH$_3$), 3.10 (s, *t*-BuO*Me*), 6.29 (t, *p*-H), 6.54 (d, $^3J = 7.8$ Hz, 2 *o*-H), 6.83 (t, $^3J = 7.5$ Hz, 2 *m*-H), 6.98 (m, 7-H), 7.01 (m, 5-/6-H), 7.09 (m, 4-H). ^{13}C NMR (*t*-BuOMe, 100.6 MHz, −70 °C, 0.07 M): δ 27.1 (*t*-Bu), 32.8 (2 1-CH$_3$), 34.8 (2 3-CH$_3$), 46.9 (C^3), 49.1 (*t*-BuO*Me*), 50.1 (C^1), 72.2 (Me$_3$*C*OMe), 115.0 (C^{para}), 121.6 (2 C^{ortho}), 122.6 (C^7), 122.9 (C^4), 125.7 (C^5), 126.1 (C^6), 127.4 (2 C^{meta}), 148.4 (C^2), 152.1 (C^9), 154.0 (C^8), 160.1 (C^{ipso}), 184.8 (t, $^1J_{CLi} = 13.5$ Hz, C$^{\alpha}$). These δ_H and δ_C values (assignments established)[20] are almost equal to those at 25 °C,[20] indicating that the same species predominates in this temperature range. (**8b**)$_1$ is stable in the presence of di-*tert*-butyl ketone (2.5 equiv) for hours at ambient temperature.[20]

Monomer (8c)$_1$. ^{1}H NMR (0.18 M in Et$_2$O, 400 MHz, −70 °C): δ 1.12 (t, Et$_2$O), 1.30 (2 + 2 1-/3-CH$_3$), 3.36 (q, Et$_2$O), 6.30 (broad t, $^3J = 7$ Hz, *p*-H), 6.54 (d, $^3J = 7.5$ Hz, 2 *o*-H), 6.85 (t, $^3J = 7.5$ Hz, 2 *m*-H), 6.97 (m, 7-H), 7.02 (m, 5-/6-H), 7.10 (m, 4-H). ^{13}C NMR (in Et$_2$O, 25.15 MHz, −105 °C): δ 32.8 (2 1-CH$_3$), 34.6 (2 3-CH$_3$), 47.1 (C^3), 50.3 (C^1), 115.2 (C^{para}), 121.1 (2 C^{ortho}), 122.9 (C^7), 123.2 (C^4), 126.0 (C^5), 126.4 (C^6), 127.7 (2 C^{meta}), 147.8 (C^2), 152.1 (C^9), 153.9 (C^8), 160.3 (C^{ipso}), 185.4 (t, $^1J_{CLi} = 14.0$ Hz, C$^{\alpha}$). Values of δ_H and δ_C were assigned in analogy with those of (**8b**)$_1$.[20]

Monomer (8d)$_1$. ^{1}H NMR (THF, 400 MHz, −37 °C): δ 1.27 (broad, 2 1-CH$_3$), 1.30 (broad, 2 3-CH$_3$), 6.18 (t, $^3J = 7.2$ Hz, *p*-H), 6.49 (d, $^3J = 7.8$ Hz, 2 *o*-H), 6.74 (t, $^3J = 7.5$ Hz, 2 *m*-H), 6.94 (very broad, 7-H), 6.99 (m, 5-/6-H), 7.08 (very broad, 4-H). ^{13}C NMR (THF, 100.6 MHz, −37 °C): δ 33.2 (2 1-CH$_3$), 34.2 (2 3-CH$_3$), 47.0 (C^3), 50.5 (C^1), 114.0 (C^{para}), 121.7 (2 C^{ortho}), 122.6 (broad, C^7), 123.0 (broad, C^4), 125.7 (broad, C^5), 126.0 (broad, C^6), 126.9 (2 C^{meta}), 147.5 (C^2), 153.4 (C^9), 154.5 (C^8), 162.6 (C^{ipso}), 189.7 (t, $^1J_{CLi} = 10.7$ Hz, C$^{\alpha}$). Values of δ_H and δ_C were assigned in analogy with those of (**8b**)$_1$ in *t*-BuOMe.[20] This solution of (**8d**)$_1$ deteriorated over the course of 3−7 days at ambient temperature, forming H$_2$C═CH−OLi and ethylene.

2-(4-Trimethylsilyl-α-trimethylstannylbenzylidene)-1,1,3,3-tetramethylindan (11). Powdered 2-(α-chloro-4-trimethylsilylbenzylidene)-1,1,3,3-tetramethylindan (**10**)[28] (600 mg, 1.63 mmol) was

---

(52) Ruhland, T.; Hoffmann, R. W.; Schade, S.; Boche, G. *Chem. Ber.* **1995**, *128*, 551–556.

(53) Fraenkel, G.; Martin, K. V. *J. Am. Chem. Soc.* **1995**, *117*, 10336–10344.

(54) Böhler, B.; Hüls, D.; Günther, H. *Tetrahedron Lett.* **1996**, *37*, 8719–8722.

(55) Fraenkel, G.; Qiu, F. *J. Am. Chem. Soc.* **1997**, *119*, 3571–3579. Addition and Correction: Fraenkel, G.; Qiu, F. *J. Am. Chem. Soc.* **1998**, *120*, 6848.

(56) We cannot explain the physical basis of eq 1 at this time. For some reflections upon the 17/*n* relationship, see ref 53 and references therein.

(57) The relation $^1J(^{15}N, ^6Li) = (7\ Hz)/n$ was proposed on p 106 of ref 14 on the basis of the ^1J values of 7.5 Hz for monomeric PhNLiCHMe$_2$·(THF)$_3$ ($a + d = 4$) and 3.8 Hz for the disolvated dimer (PhNLiMe·Et$_2$O)$_2$ ($a + d = 3$) reported on p 5353 in: Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1987**, *109*, 5348–5355. In the spirit of eq 1, however, a tetrasolvated dimer ($a + d = 4$) would agree with a 7.5/*n* relation.

(58) Granander, J.; Sott, R.; Hilmersson, G. *Chem.—Eur. J.* **2006**, *12*, 4191–4197 and references therein.

(59) Koizumi, T.; Morihashi, K.; Kikuchi, O. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 305–309.

(60) Remenar, J. F.; Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1997**, *119*, 5567–5572 and Table 1 therein.

added at −70 °C under dry argon cover gas to a solution of $LiSnMe_3$ (∼3.3 mmol)[61−64] in THF (5.4 mL). As soon as **10** had completely dissolved (∼5 min without cooling), the mixture was placed in an ice bath for not more than 30 min and then diluted with distilled water and Et_2O. The aqueous layer was extracted (3×) with Et_2O, and the combined Et_2O phases were washed until neutral and then dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product (734 mg) containing **11** and the alkene **13**[28] (70:25) was crystallized from ethanol (5 mL), yielding spectroscopically pure **11** as colorless needles (504 mg, 62%) with mp 61−65.5 °C. The analytically pure sample had mp 73−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03 (s; ^{119}Sn satellites, $^2J = 51.7$ Hz; $SnMe_3$), 0.27 (s, $SiMe_3$), 1.20 (s, 2 3-CH_3), 1.52 (s; ^{119}Sn satellites, $^5J \approx 2.9$ Hz; 2 1-CH_3), 6.93 (dm, $^3J = 8.2$ Hz, 2 *o*-H), 7.04 (dm, 4-H), 7.15−7.24 (m, 5-/6-/7-H), 7.38 (dm, $^3J = 8.2$ Hz, 2 *m*-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −5.1 (qm, $^1J = 128.7$ Hz; ^{119}Sn satellites, $^1J = 339$ Hz; $SnMe_3$), −0.9 (qm, $^1J = 118.7$ Hz; $^3J = 2.0$ Hz; ^{29}Si satellites, $^1J = 52.3$ Hz; $SiMe_3$), 31.81 and 31.84 (2 qm, $^1J = 127$ Hz, 2 + 2 1-/3-CH_3), 48.4 (m; ^{119}Sn satellites, ^3J(cis) = 21.9 Hz; C^1), 50.6 (m; ^{119}Sn satellites, ^3J(trans) = 62.2 Hz; C^3), 122.2 and 122.3 (2 dm, $^1J = 156$ Hz, $C^{7,4}$), 126.7 and 126.9 (2 dd, $^1J = 159$ Hz, $^3J = 7.5$ Hz, $C^{5,6}$), 127.7 (dm, $^1J = 156$ Hz; ^{119}Sn satellites, $^3J = 18.7$ Hz; 2 C^{ortho}), 132.3 (dm, $^1J = 156$ Hz; ^{119}Sn satellites, $^4J = 9.5$ Hz; 2 C^{meta}), 135.9 (unresolved m; ^{119}Sn satellites, $^5J \approx 11.7$ Hz; C^{para}), 139.0 (unresolved t, $^3J \approx 3$ Hz; ^{119}Sn satellites not discernible; C^{α}), 145.9 (sharp t, $^3J = 7.5$ Hz; ^{119}Sn satellites, $^2J = 20.4$ Hz; C^{ipso}), 149.9 (m, C^8), 150.4 (m, C^9), 167.1 (m, C^2). Values of δ_H and δ_C were assigned through SCS[65] and in analogy with those of alkene **13**.[28] IR (KBr): 2955, 2916, 1612 (w), 1487, 1359, 1248, 1110, 1027, 861, 838, 751, 532, 527 cm^{-1}. Anal. Calcd for $C_{26}H_{38}SiSn$ (497.4): C, 62.79; H, 7.70. Found: C, 62.95; H, 7.75. **11** could also be formed from (**8d**)$_1$ in THF with $ClSnMe_3$ at room temperature within a few minutes.

Dimers and Monomers of 12. The Sn−^{6}Li interchange reaction of **11** in pentane (Chart 2) carried out with *n*-BuLi in the presence of *t*-BuOMe (2.5 equiv) proceeded very slowly to afford crystals of **12b**. A solution of these crystals in toluene contained (**12b**)$_1$ and (**12b**)$_2$, the latter being recognized through its $\Delta\delta$ values, which resemble those of (**12d**)$_2$ in entry 13 of Table 1. With diethyl ether (2.1 equiv) as the donor admixture, a faster Sn−^{6}Li interchange reaction provided single crystals of **12c** that were sufficiently stable for X-ray diffraction at 20 °C (Table S4).[20] The analyzed crystal (Figure S3)[20] consisted of dimeric aggregates (**12c**)$_2$ of type **2** solvated by one Et_2O molecule per carbanion, as in (**8c**)$_2$. Purified crystals of **12c** or **12d** were dissolved in [D_8]toluene to yield (**12c**)$_2$ alone (poorly soluble) or (**12d**)$_2$ alone, respectively. (**12d**)$_2$ was also obtained by treating (**12c**)$_2$ in [D_8]toluene with THF, and (**12d**)$_1$ was generated by dissolving (**12b**)$_2$ in THF.

Acknowledgment. This work is dedicated to Professor Herbert Mayr. We thank Prof. H. Nöth and Drs. K. Polborn, M. Schmidt, and H. Schwenk-Kircher for performing X-ray analyses. Parts of these studies were sponsored by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Further applications of eq 1 (Tables S1 and S2); solid-state structural data (Tables S3 and S4 and Figures S1−S4); lithiation shifts and spectral sequences (Tables S5a and S5b); four typical total NMR spectra (Figures S5−S8); ^{1}H and ^{13}C NMR assignments (Tables S6 and S7); and full spectroscopic and preparative details of the observed monomers and aggregates (Tables S8−S20). This material is available free of charge via the Internet at http://pubs.acs.org.

JA8026828

---

(61) Tamborski, C.; Ford, F. E.; Soloski, J. E. *J. Org. Chem.* **1963**, *28*, 237–239.

(62) Kitching, W.; Olszowy, H.; Waugh, J.; Doddrell, D. *J. Org. Chem.* **1978**, *43*, 898–906.

(63) Reich, H. J.; Reich, I. L.; Yelm, K. E.; Holladay, J. E.; Gschneidner, D. *J. Am. Chem. Soc.* **1993**, *115*, 6625–6635 (specifically p 6632).

(64) Knorr, R.; Pires, C.; Freudenreich, J. *J. Org. Chem.* **2007**, *72*, 6084–6090.

(65) Knorr, R.; von Roman, T.; Freudenreich, J.; Hoang, T. P.; Mehlstäubl, J.; Böhrer, P.; Stephenson, D. S.; Huber, H.; Schubert, B. *Magn. Reson. Chem.* **1993**, *31*, 557–565.