prepared by stirring TMTH (0.17 g, 1.00 mmol, 0.12 mL) with methyllithium (1.00 mmol) in 2 mL of diethyl ether for 20 min at room temperature. After the addition of hexamethylditin (0.33 g, 1.00 mmol) the slurry was cooled to 0 °C and 2 mL of THF was added. Some precipitate dissolved, and the reaction mixture turned slightly yellow. After the mixture was stirred for 1 h, 1-bromooctane (0.21 g, 1.10 mmol, 0.18 mL) was added. The reaction mixture was stirred for additional 20 min before quenching with 2 mL of water. GC analysis showed the presence of octyltrimethyltin (0.43 mmol, 43%) and hexamethylditin (0.41 mmol, 41%).

Reactions of Lithium Hydride Formed from TMTH/Alkyllithium with Weak Acids. Methyllithium (1.50 mmol) in 1.5 mL of diethyl ether or *n*-butyllithium (1.50 mmol) in 1.5 mL of hexanes was treated with TMTH (0.25 g, 1.50 mmol, 0.18 mL) at 0 °C. After being stirred for 20 min (MeLi) and 5 h (BuLi), respectively, at room temperature, the reaction mixture was cooled to 0 °C and quenched with an excess (1 mL) of the appropriate reagent. Yields of hydrogen obtained after 10 min are gathered in Table IX.

Reactions of Lithium Hydride Formed from TMTH/LDA with Weak Acids. LDA (1.00 mmol, 1.6 M in cyclohexane) and TMTH (0.33 g, 2.00 mmol, 0.24 mL) in 2 mL of an appropriate solvent (hexanes or diethyl ether) were stirred for 1 h at room temperature. The resulting slurry was cooled to 0 °C, connected to a gas measuring device, and quenched with 1 mL of the appropriate reagent. Yields of hydrogen obtained after 10 min are gathered in Table IX.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Society, and the National Science Foundation for their support of this research. We also thank Gregory Seymour for his valuable participation in this research.

Registry No. LDA, 4111-54-0; TMTH, 1631-73-8; $(\mathrm{Me_3Sn})_2$, 661-69-8; $\mathrm{Et_3SnH}$, 997-50-2; $(\mathrm{Et_3Sn})_2$, 993-63-5; $\mathrm{Bu_3SnH}$, 688-73-3; $(\mathrm{Bu_3Sn})_2$, 813-19-4; $\mathrm{Ph_3SnH}$, 892-20-6; $\mathrm{Ph_3SnMe}$, 1089-59-4; $\mathrm{Me_3SnN}$-*i*-$\mathrm{Pr_2}$, 1068-71-9; $\mathrm{Me_3SiCH_2SnMe_3}$, 18297-50-2; $\mathrm{Me_3SnLi}$, 17946-71-3; $\mathrm{Et_3SnSnMe_3}$, 2935-54-8; (n-$\mathrm{C_8H_{17}}$)$\mathrm{SnMe_3}$, 40218-16-4; (n-$\mathrm{C_7H_{15}}$)$\mathrm{SnMe_3}$, 59344-40-0; $\mathrm{Me_3SnBu}$, 1527-99-7; $\mathrm{Cy_3SnH}$, 6056-50-4; (chloromethyl)trimethylsilane, 2344-80-1; 1-chloroheptane, 629-06-1; octane, 111-65-9; heptane, 142-82-5; 1-bromoheptane, 629-04-9; 1-bromooctane, 111-83-1; 2-bromoheptane, 1974-04-5; 3-bromo-3-ethylpentane, 73908-04-0; 1-bromoadamantane, 768-90-1; 3-ethylpentane, 617-78-7; adamantane, 281-23-2; 1-iodoheptane, 4282-40-0; *o*-bromotoluene, 95-46-5; toluene, 108-88-3; 2-bromomesitylene, 576-83-0; mesitylene, 108-67-8; 6-bromo-1-hexene, 2695-47-8; methylcyclopentane, 96-37-7; 1-hexene, 592-41-6; lithium hydride, 7580-67-8.

Aggregation States and Exchange Properties of Alkyllithium Compounds in Hydrocarbon Solvent from ^{13}C–^{6}Li Coupling

Ruthanne D. Thomas,* Randy M. Jensen, and T. Corby Young

Center for Organometallic Research and Education, Department of Chemistry, North Texas State University, Denton, Texas 76203

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Variable-temperature ^{13}C and ^{6}Li NMR data are reported for 12 ^{6}Li-enriched alkyllithium compounds in cyclopentane solution (R = ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, isopentyl, isobutyl, 2-methylbutyl, 2-ethylbutyl, isopropyl, *sec*-pentyl, *tert*-butyl, *tert*-pentyl). ^{13}C–^{6}Li coupling was observed for the branched-chain compounds at low temperature except isopentyllithium-^{6}*Li*. Coupling was not observed for the straight-chain compounds except *n*-propyllithium-^{6}*Li*. The observed coupling ranges from 2.2 to 6.2 Hz. The value of the observed coupling and the coupling patterns have been used to assign the aggregation states and exchange properties of these compounds. Branching β to the lithium atom results in hexamers that are rapidly fluxional over all temperatures, but whose interaggregate exchange can be slowed at low temperatures. Branching α to the lithium atom produces either equilibrium mixtures of hexamers and tetramers for secondary compounds or tetramers for tertiary compounds. For the process $(\mathrm{RLi})_6 \rightleftharpoons {}^3/_2(\mathrm{RLi})_4$, ΔH was found to be 6.4 ± 0.4 and 2.7 ± 0.7 kcal/mol for isopropyllithium and *sec*-pentyllithium, respectively. Line-shape analysis of the fluxional exchange of the tetrameric aggregates suggests a different fluxional exchange mechanism for the secondary compounds than for the tertiary compounds.

Introduction

Recent years have seen a renewed interest in the reactivity, structure, and bonding of organolithium compounds. A large amount of structural and theoretical information is now available.[1,2] There has also been an increasing number of NMR solution studies, adding to the understanding of aggregation states and exchange properties of organolithium compounds in solution.[3-7] One of the major developments in the study of the solution behavior of these compounds has been the ability to observe ^{13}C–^{6}Li coupling. ^{13}C–^{7}Li coupling was very early used to establish the tetrahedral structure of methyllithium tetramers,[8] but the observation of such coupling was in general limited to coordinating solvents. ^{13}C–^{7}Li coupling was observed for only a few alkyllithium compounds in hydrocarbon solvent.[9] This was a disadvantage since ag-

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(1) For a review of lithium structures see: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985,** *24,* 353–451.

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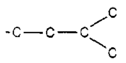
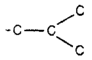
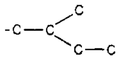
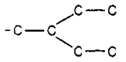
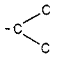
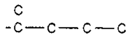
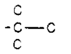
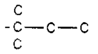
Table I. ^{13}C and ^{6}Li Chemical Shifts of Alkyllithium Compounds in Cyclopentane Solution[a]

		^{13}C δ^{c}						
R group	^{6}Li δ^{b}	C-1[c]	C-2	C-3	C-4	C-5	C-6	-CH_3
-C—C	1.90	0.3	10.7					
-C—C—C	1.94	16.1	22.4	22.3				
-C—C—C—C	2.06	11.7	30.9	31.5	13.0			
-C—C—C—C—C—C	2.00	12.3	29.1	37.9	31.6	22.8	13.8	
	2.01	8.2	34.7	38.8	21.5			
	1.92	27.4	29.3	29.3				
	1.91	23.5	35.9	36.6	11.8			25.4
	1.94	19.2	42.1	31.5	10.8			
	1.25	6.2[d] 10.3[e]	22.9					
	1.26	12.5[d] 16[e]	41.0	23.4	13.7			18.7
	1.07	10.7	32.6					
	0.70	13.8	36.9	5.7				27.7

[a] Solutions are 2 M at 30 °C. [b] From external 1 M $LiClO_4$ in acetone-d_6. [c] Numbering from lithium substitution. [d] Tetramer. [e] Hexamer.

gregation states larger than four are only observed in hydrocarbon solvent. In addition, coupling data from unsolvated molecules provides for a better comparison to theoretical data.

More recently it was recognized that the ^{6}Li nucleus ($I = 1$), even in the relatively low-symmetry environment of an alkyllithium aggregate, has a very long relaxation time, resulting in narrow lines for both the ^{13}C and ^{6}Li spectra.[10] This fact was used by Fraenkel to observe ^{13}C–^{6}Li coupling.[4-6] Seebach and co-workers have extended this approach to synthetically important systems in coordinating solvents.[3] More recently, Smith and co-workers have used ^{6}Li–^{1}H nuclear Overhauser enhancements to study molecular geometry.[11]

The observation of coupling is important because it (1) establishes the aggregation state for rapidly fluxional aggregates,[3-6] (2) provides a means of studying fluxional exchange,[12] (3) establishes an unambiguous correlation between the peaks in the ^{13}C and the ^{6}Li spectra, and (4) may enable the use of 2D NMR techniques to "filter-out" unwanted resonances in otherwise complex reaction mixtures. It is this latter application that we are now pursuing. However, at the beginning of this work, it was unclear for what compounds coupling could be observed in hydrocarbon solvent and how much the coupling would vary with alkyl group. Moreover, it was not yet established whether the larger aggregation states ($n > 6$) observed for n-propyllithium at low temperature in hydrocarbon solvent were a general result for all straight-chain alkyllithium compounds. We now present ^{13}C and ^{6}Li NMR data for a series of alkyllithium compounds in hydrocarbon solvent.

Results and Discussion

Straight-Chain Alkyl Groups. The ^{13}C NMR spectra for cyclopentane solutions of ethyl-, n-propyl, n-butyl-, and n-hexyllithium-^{6}Li are all qualitatively similar. The room-temperature chemical shifts (Table I) are consistent with those reported earlier for the corresponding compounds containing natural abundance lithium,[13] with the exception of n-hexyllithium. For n-hexyllithium we have reversed the assignment of carbons 4 and 5 to be consistent with the chemical shifts of the parent hydrocarbon.[14] In

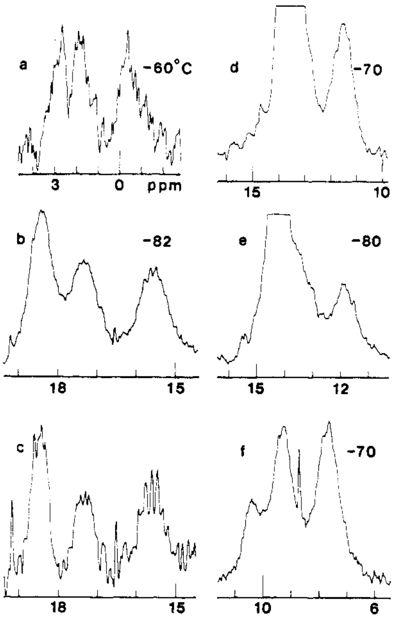


Figure 1. Low-temperature ^{13}C NMR spectra of the α-carbon of ^{6}Li-enriched alkyllithium compounds in cyclopentane solution: (A) ethyllithium-^{6}*Li* (0.3 M); (B) n-propyllithium-^{6}*Li* (2.0 M); (C) same spectrum as in B, but with resolution enhancement; (D) n-butyllithium-^{6}*Li* (2.0 M); (E) n-hexyllithium-^{6}*Li* (2.0 M); (F) isopentyllithium-^{6}*Li* (2.0 M).

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(11) Avent, A. G.; Eaborn, C.; El-Kheli, M. N. A.; Molla, M. E.; Smith, J. D.; Sullivan, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 3854–3855.

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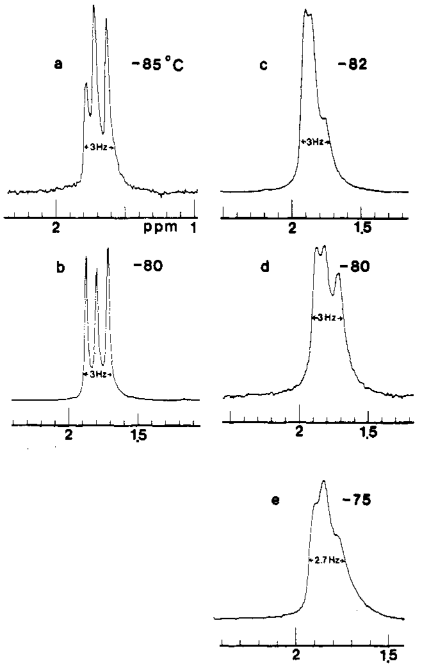


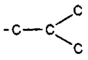
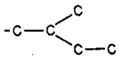
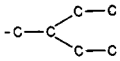
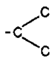
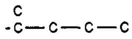
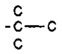
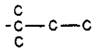
Figure 2. Low-temperature ^{6}Li NMR spectra of ^{6}Li-enriched alkyllithium compounds in cyclopentane (same samples as in Figure 1): (A) ethyllithium-^{6}*Li*; (B) *n*-propyllithium-^{6}*Li*; (C) *n*-butyllithium-^{6}*Li*; (D) *n*-hexyllithium-^{6}*Li*; (E) isopentyllithium-^{6}*Li*.

every case the α-carbon is a single sharp peak at 30 °C. With the ^{6}Li-enriched samples used in this study, lowering the temperature produces broadening until eventually three broad peaks are resolved. These are clearly defined in the spectra for *n*-propyl- and ethyllithium-^{6}*Li* but are obscured by overlap with the terminal methyl resonance in *n*-butyl- and *n*-hexyllithium (Figure 1). That these three peaks correspond to three different lithium species is more clearly apparent in the ^{6}Li spectra. In every case the ^{6}Li spectrum is one sharp resonance at 30 °C. Lowering the temperature produces broadening and splitting of the single resonance into three resonances (Figure 2).

Such behavior was first observed[6] for *n*-propyllithium-^{6}*Li*. In that study the different resonances were assumed to be different aggregates: hexamer, octamer, and nonamer (^{13}C, upfield to downfield; ^{6}Li, downfield to upfield). The assignment of the aggregation states was based on the ^{13}C–^{6}Li coupling observed in the ^{13}C spectrum.[6] In our hands, as observed earlier, the coupling for the *n*-propyllithium-^{6}*Li* is not well-resolved but can be observed with resolution enhancement (Figure 1C). Although the relatively poor signal to noise of this spectrum severely limits the resolution enhancement that can be used, the resolved peaks do have observed coupling constants of 3.3 and 2.5 Hz for the hexamer and octamer peaks (Table II). The three different nonamers are not resolved at this field strength, therefore not allowing resolution of coupling. We have not observed, even with resolution enhancement, coupling for any of the other straight-chain compounds. This is in marked contrast to the branched-chain compounds discussed below and to other branched-chain alkyllithium compounds in hydrocarbon solvent reported elsewhere.[4,5]

The inability to observe coupling for these compounds could be due to (a) rapid interaggregate exchange relative to the coupling, (b) smaller coupling constants, or (c) rapid relaxation of the ^{6}Li nuclei. Poor spectrometer shimming or problems with the particular samples have been ruled out on the basis of the relatively narrow lines observed in the ^{6}Li spectra (0.4–1.2 Hz for the straight-chain alkyllithiums but 0.3–0.6 Hz for external $LiClO_4$) and the narrow lines of the remaining carbon atoms in the ^{13}C spectra. Significantly smaller couplings seem unlikely due to the similarity of the compounds to *n*-propyllithium and to the similarity of the other NMR parameters for these compounds. The spin–lattice relaxation times for the ^{6}Li nuclei in straight-chain compounds vary from 15 to 20 s at room temperature to 1.5–3.0 s at −85 °C.[15] This would be insufficient to produce the unresolved peaks observed for these compounds, unless the coupling is significantly smaller. In any case, it would not explain the relatively unresolved ^{6}Li resonances (Figure 2) for *n*-butyl- and *n*-hexyllithium. The most likely explanation is rapid interaggregate exchange. This is further supported by the readily resolved coupling found for isobutyllithium and (2-ethylbutyl)lithium discussed below, which apparently exist only as hexamers and thus do not undergo interaggregate exchange between different chemically shifted species. Lower concentrations might lead to slower exchange and thus observation of coupling for the straight-chain compounds, although we have not observed such an effect with the relatively high concentrations (>0.3 M) required for sufficient signal to noise of the ^{13}C spectra.

Table II. ^{13}C–^{6}Li Coupling Constants

R group	k[a]	agg state	J_{obsd},[b] Hz	^1J(^{13}C–^{6}Li), Hz
–C—C—C	6	6	3.3	6.6
	8	8	2.5	6.7
	9	9	2.2[c]	6.7
	6	6	3.11	6.22
	6	6	3.4[d]	6.8[d]
	6	6	3.1	6.2
	3	4	6.1	6.1
	6	6	3.3	6.6
 $-\overset{C}{C}-C-C-C$	4	4	4.7	6.2
	3	4	6.2	6.2
	6	6	3.2	6.4
 $-\overset{C}{\underset{C}{C}}-C$	4	4	4.10	5.47
	3	4	5.44	5.44
 $-\overset{C}{\underset{C}{C}}-C-C$	4	4	3.98	5.31

[a] Number of equivalently coupled ^{6}Li nuclei. [b] Values cited to 0.1 Hz are accurate to ±0.3 Hz. Values cited to 0.01 Hz are accurate to better than ±0.06 Hz. [c] From ref 6a. [d] Approximate value from only part of the ^{13}C multiplet.

Although no attempt was made to determine the equilibrium constants for the equilibria among the hexamer, octamer, and nonamer aggregates due to overlapping peaks, there is an apparent shift in equilibrium toward smaller aggregates with increasing length of the alkyl chain. This is consistent with the lower steric requirements of the smaller aggregation states.

Branching γ to Lithium Substitution. Almost identical in behavior with the straight-chain compounds is that observed for isopentyllithium-^{6}*Li*, (3-methylbutyl)lithium-^{6}*Li*. The ^{13}C spectrum of the α-carbon and the ^{6}Li spectrum at −75 °C are shown in Figures 1f and 2e. Although there is a shift toward the smaller, hexameric aggregate, these spectra are qualitatively identical with

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[15] Thomas, R. D. Ph.D. Dissertation, 1981, Wayne State University, Detroit, MI.

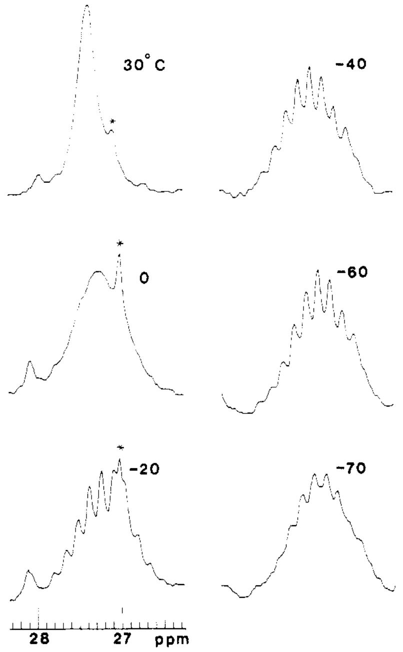

Figure 3. Variable-temperature ^{13}C NMR spectra of the α-carbon of 2 M isobutyllithium-^{6}*Li* in cyclopentane. The peak marked with an asterisk is a spinning sideband of cyclopentane.

those for the straight-chain compounds. As with most of the straight-chain compounds, no ^{13}C–^{6}Li coupling was observed.

Neohexyllithium-^{6}*Li*, (3,3-dimethyl-1-butyl)lithium-^{6}*Li*, was insufficiently soluble in either cyclopentane or toluene to observe a ^{13}C spectrum.

Branching β to Lithium Substitution. Unlike the compounds noted above, the ^{13}C NMR spectrum for the α-carbon of 2 M isobutyllithium-^{6}*Li*, (2-methylpropyl)lithium-^{6}*Li*, in cyclopentane is a broad singlet. Lowering the temperature to −20 °C causes the single broad peak to resolve into at least 10 lines, with an observed ^{13}C–^{6}Li coupling of 3.1 Hz (Figure 3). As the temperature is lowered further, this splitting persists and by −70 °C the lines again broaden. Below −70 °C the compound precipitated from solution. All spectral observations are completely reversible with changes in temperature.

The observation of more than 9 lines rules out both a nonfluxional aggregate (7 lines, assuming equivalent coupling to three ^{6}Li nuclei) and a rapidly fluxional tetramer (9 lines). On the basis of (a) the line intensities of the ^{13}C multiplet (Table III), (b) the approximate 3-Hz coupling as previously observed for *n*-propyllithium hexamer,[6] and (c) the similarity of the ^{6}Li chemical shifts (Table I) to the straight-chain alkyllithium compounds, which are known to be hexameric at room temperature, we assign this to a hexameric aggregation state. To our knowledge, the aggregation state of this compound had not been previously determined.

The possibility that the compound exists as a rapidly exchanging octamer or nonamer cannot be ruled out on the basis of line intensities, but it is highly unlikely given the near identity of the coupling with other hexameric aggregates and with the known preference of even less sterically strained alkyllithium compounds for hexameric aggregation. Even in compounds where higher aggregates have been observed, these higher aggregates are only present in significant amounts at low temperatures and are always in equilibrium with a hexamer.

The ^{6}Li spectra further suggest the existence of only a single aggregation state at this concentration. A single resonance is observed throughout the entire temperature range of +25 to −70 °C. The ^{13}C–^{6}Li coupling can also be observed as ^{13}C satellites at the base of the peak with a separation of 3.11 ± 0.06 Hz at −40 °C (Figure 4).

Table III. Predicted Line Intensites of ^{13}C Multiplets from Coupling to ^{6}Li Nuclei

RLi aggregate	no. of lines	relative intensities[a]						
dimer	5					0.33	0.67	1.00
nonfluxional aggregate ($n \geq 4$)[b]	7				0.14	0.43	0.86	1.00
fluxional tetramer	9			0.05	0.21	0.53	0.84	1.00
fluxional hexamer	13	0.007	0.04	0.15	0.36	0.64	0.89	1.00

[a] Only half of the multiplet shown, normalized to the center peak. [b] A nonfluxional aggregate, assuming coupling to three equivalent ^{6}Li nuclei.

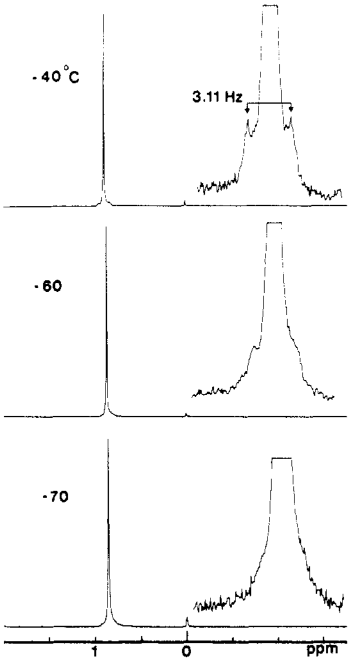

Figure 4. Variable-temperature ^{6}Li NMR spectrum of 2 M isobutyllithium-^{6}*Li* in cyclopentane.

The presence of the ^{13}C–^{6}Li coupling rules out the possibility of rapid interaggregate carbon lithium bond exchange among several aggregates. We saw no evidence for additional peaks at low temperature that could be additional higher aggregation states, as suggested by molecular weight determinations for the similar compound (2-methylbutyl)lithium at low temperature.[16] However, the coupling does broaden and disappear below −40 °C (Figure 4) that may suggest rapid interaggregate exchange between the hexamer and one or more additional aggregates. We could not clearly resolve ^{13}C–^{6}Li coupling for (2-methylbutyl)lithium-^{6}*Li*, apparently due to the overlap of signals from different optical isomers. However, a coupling of approximately 3.4 Hz was observed at −20 °C, which is consistent with the hexameric aggregation state of this compound.

Lengthening each of the alkyl-chain branches has little effect on the spectra. The α-carbon of (2-ethylbutyl)lithium-^{6}*Li* is a single broad resonance at 19.2 ppm at 27 °C. Lowering the temperature below 0 °C results in the resolution of an 11-line multiplet with an observed splitting

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[16] Fraenkel, G.; Beckenbaugh, W. E.; Yang, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 6878–85.

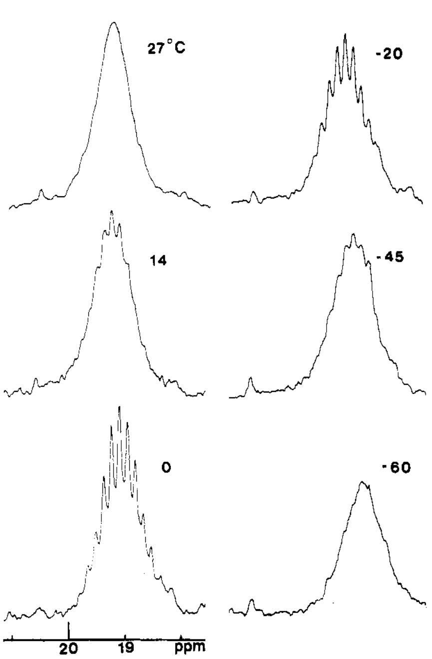

Figure 5. Variable-temperature ^{13}C NMR spectra of the α-carbon of 2 M 2-ethylbutyllithium-^{6}*Li* in cyclopentane.

of 3.1 Hz (Figure 5). As with the case of isobutyllithium, this is apparently a rapidly fluxional hexamer. The two outer peaks of the expected 13-line multiplet are too small to observe. Below −60 °C the peaks again broaden and the multiplet is no longer resolved.

The only major difference between the isobutyllithium and the (2-ethylbutyl)lithium is the temperature at which coupling is observed. The splitting observed for (2-ethylbutyl)lithium at approximately 14 °C is not observed for isobutyllithium until approximately −10 °C. This is indicative of a higher energy pathway for interaggregate exchange in (2-ethylbutyl)lithium and is likely the result of the increased steric bulk of the alkyl group. This is most easily explained in terms of a bimolecular exchange process.

Neopentyllithium-^{6}*Li* was insoluble in hydrocarbon solvent, and no spectrum was observed. [(Trimethylsilyl)methyl]lithium-^{6}*Li* is soluble at room temperature but precipitates from both cyclopentane and toluene solutions at lower temperatures. Coupling was not observed.

Branching α to Lithium Substitution—*sec*-Alkyllithium Compounds. The variable-temperature ^{13}C NMR spectra of the α-carbon of 2 M isopropyllithium-^{6}*Li* in cyclopentane are shown in Figure 6. Even at 30 °C two broad peaks are clearly resolved at 6.2 and 10.3 ppm. As the temperature is lowered, the downfield peak grows in intensity at the expense of the other and by 0 °C it has become the dominant peak. The relative areas of the peaks remain constant below −15 °C, which suggests that below this temperature interaggregate exchange is slow enough that equilibrium is not reached during the time required for the experiment (approximately 1 h).

Isopropyllithium is known to be primarily tetrameric below 0.02 m in hydrocarbon solution,[17] with equilibrium occurring between tetramers and hexamers at higher concentrations. The two resonances thus correspond to the hexamer and tetramer aggregation states.

The assignment of the peaks is based on the relative line intensities of the multiplets at low temperature. As the temperature is lowered, the downfield peak splits into a multiplet with 9–11 lines of equal spacing appearing above the noise, and the upfield peak splits into 7 lines. The upfield 7-line multiplet has relative peak intensities of 0.13:0.41:0.84:1.00 (half of the multiplet normalized to the center peak) with a coupling of 6.1 Hz. This is a nonfluxional aggregate, $(RLi)_n$, with $n \geq 4$, but it is impossible to assign the exact aggregation state (Table III). The downfield multiplet has intensities of 0.15:0.40:0.67:0.89:1.00 and observed coupling of 3.3 Hz. On the basis of both the ^{13}C multiplet and the magnitude of the observed coupling, this is a fluxional hexamer. Thus the upfield resonance, which predominates at high temperature, is assigned the tetramer. This assignment is consistent with the straight-chain compounds in which the smaller aggregates appear upfield in the ^{13}C NMR spectrum. No coupling consistent with a fluxional tetramer

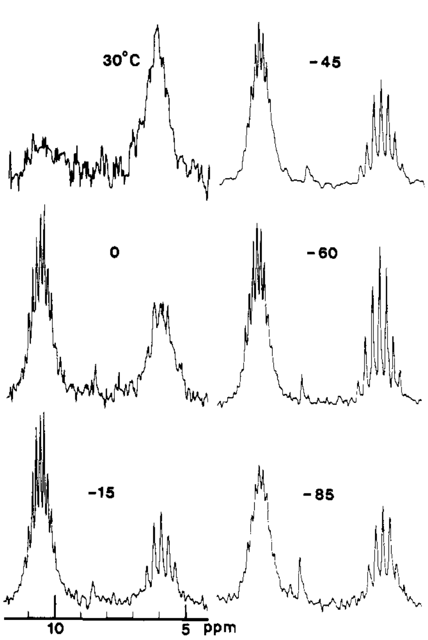

Figure 6. Variable-temperature ^{13}C NMR spectra of the α-carbon of 2 M isopropyllithium-^{6}*Li* in cyclopentane.

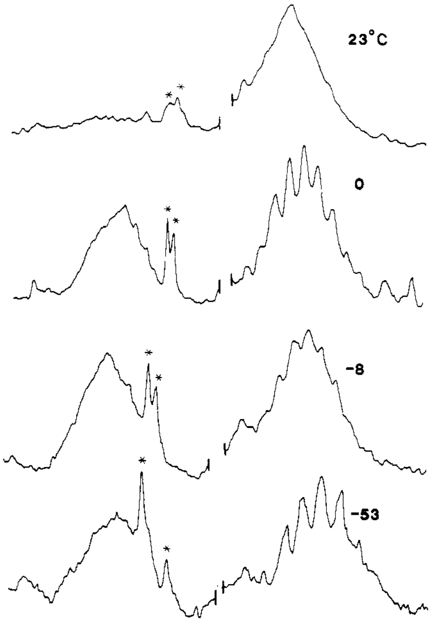

Figure 7. Variable-temperature ^{13}C NMR spectra of the α-carbon of 3 M sec-pentyllithium-^{6}*Li* in cyclopentane. Peaks marked by asterisks are degradation products.

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[17] Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664.

is observed, although there is broadening at higher temperatures.

The variable-temperature ^{6}Li spectra of isopropyllithium-^6Li confirm the existence of two lithium species. At room temperature there is one sharp peak. As the temperature is lowered, the exchange is slowed and two peaks are observed. The downfield peak has symmetrical satellites separated by 3.29 Hz, unambiguously indicating it is the hexamer. The upfield peak has broad satellites at 6.1 Hz. The broad satellite peaks for the tetramer sharpen somewhat at lower temperatures but never become as sharp as the hexamer satellites. The relative ^{6}Li chemical shifts of the two aggregates are opposite to the order observed in the straight-chain compounds for hexamer, octamer, and nonamer peaks as well as the hexamer and tetramer peaks reported for *sec*-butyllithium-^{6}Li[5] but are consistent with that found for the *sec*-pentyllithium-^{6}Li peaks discussed below.

The NMR spectra for *sec*-pentyllithium-^6Li are qualitatively similar to those for isopropyllithium-^6Li, except there is a shift in the equilibrium toward the tetrameric aggregate. At room temperature there are two broad resonances for the α-carbon at 12.4 and 16 ppm, assigned to the tetramer and hexamer, respectively. Unlike the isopropyllithium, lowering the temperature to approximately 5 °C first produces a sharpening of the tetramer multiplet to greater than seven lines with a peak separation of 4.3 Hz (Figure 7). The hexamer peak remains broad. Further lowering of the temperature causes broadening of the tetramer peak until below −25 °C it is a 7-line multiplet with J = 5.7 Hz. This behavior is indicative of a transition from a rapidly fluxional to a nonfluxional tetramer, as earlier observed for the known tetramer *tert*-butyllithium-^6Li.[12] As expected, the coupling for the fluxional tetramer is $^3/_4$ of the non-fluxional coupling. The hexamer peak is a broad, unresolved multiplet at low temperatures, presumably due to overlap of stereoisomers. Only fleetingly at approximately −20 °C does it appear to resolve into a multiplet with observed coupling of 3.2 Hz.

If hexamer–tetramer interaggregate exchange is ignored,[18] then the temperature-dependent ^{13}C line shapes of the exchange-broadened tetramers can be treated as described earlier for *tert*-butyllithium-^6Li[12] (Figure 8). This leads to activation parameters of $\Delta H^\ddagger = 9.1 \pm 0.9$ kcal/mol and $\Delta S^\ddagger = -16 \pm 4$ eu for the fluxional exchange (Table IV). A similar treatment of the data for isopropyllithium-^6Li yields $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 13 ± 2 kcal/mol and −3 ± 8 eu, respectively. Despite the large error bounds, it is clear that the fluxional exchange for these compounds does not have the large positive entropy of activation observed for the *tert*-butyllithium fluxional exchange. Either the fluxional exchange mechanism for the secondary compounds is different than for *tert*-butyllithium or the assumption ignoring the interaggregate exchange is incorrect, leading to large errors in the activation parameters. A more complete analysis of the fluxional exchange in these molecules is not possible due to unresolved coupling for the *sec*-pentyllithium hexamer and the inability to observe the rapidly fluxional isopropyllithium tetramer.

Above −20 °C for *sec*-pentyllithium or above −15 °C for isopropyllithium, the tetramer concentrates at the expense of the hexamer with an increase in temperature. From the relative peak areas of the α-carbons, ΔH and ΔS for the equilibrium

$$(\mathrm{RLi})_6 \rightleftharpoons {}^3/_2(\mathrm{RLi})_4$$

were found to be 2.7 ± 0.7 kcal/mol and 11.6 ± 2.5 eu, respectively. Similar treatment of the isopropyllithium data results in values of 6.4 ± 0.4 kcal/mol and 22.4 ± 1.3 eu. These values are consistent with the values of 3.5 kcal/mol and 14 eu reported for *sec*-butyllithium[5] in cyclopentane but are larger than the corrected ΔH value of 2.5 ± 0.6 kcal/mol measured for isopropyllithium in isooctane from infrared data.[19] Analogous enthalpies for straight-chain alkyllithium compounds, where there is essentially no tetrameric aggregation, have been estimated to be in the range of 14–36 kcal/mol.[20] The data for the three secondary alkyllithium compounds clearly show the increasing stability of the hexamer vs. the tetramer with decreasing steric bulk of the alkyl group.

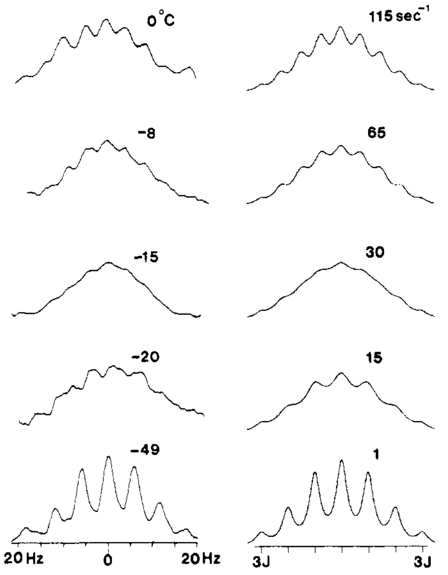

Figure 8. Experimental (left) and calculated (right) ^{13}C NMR spectra of the α-carbon of the *sec*-pentyllithium-^6Li tetramer in cyclopentane. Calculated spectra were generated by using $^1J(^{13}\mathrm{C}-^6\mathrm{Li})$ = 5.60 Hz and $w_{1/2}$ = 2.5 Hz.

Branching α to Lithium Substitution—*tert*-Alkyllithium Compounds. Three branches at the α-carbon further shifts the equilibrium toward the smaller aggregation states. As we have already found,[12] additional steric bulk also increases the rate of fluxional exchange. This is readily apparent from the observed coupling. The ^{13}C NMR spectrum for *tert*-butyllithium-^6Li consists of two peaks at 10.7 and 32.6 ppm. The upfield peak is a nonet with observed coupling of 4.1 Hz. Upon cooling, the nonet peaks broaden, coalesce, and then reform below −10 °C into a 7-line multiplet with J = 5.4 Hz. The temperature-dependent coupling indicates a change from a fast to a nonfluxional exchange tetramer with a decrease in temperature. The most striking feature of this spectrum relative to those discussed above is the observation of coupling even at high temperatures. This clearly indicates slow interaggregate exchange.

The α-carbon in the ^{13}C NMR spectrum of *tert*-pentyllithium-^6Li is a 9-line spectrum over the entire temperature range of +25 to −85 °C with an observed coupling of 4.0 Hz. This indicates a rapidly fluxional tetramer, even at low temperatures.

Summary and Conclusions

^{13}C–^{6}Li coupling can be observed for alkyllithium compounds in hydrocarbon solvent if there is sufficient steric

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[18] The interaggregate exchange must be at least slow based on the observation of coupling for the tetramer.

[19] Sergutin, V. M.; Antonov, N. G.; Zgonnik, V. N.; Kalninsh, K. K. *J. Organomet. Chem.* **1978**, *145*, 265–267.

[20] Guerink, P. J. A.; Klumpp, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 538–539.

Table IV. Fluxional Exchange Rates and Activation Parameters for Isopropyl- and *sec*-Pentyllithium-^{6}*Li* in Cyclopentane

temp^a	isopropyllithium (2 M)	*sec*-pentyllithium (3 M)
0	10–100	100–115
−8		60–70
−15	4–6	20–40
−20		13–18
−28	1–3	
−45	≤1	
−49		1–5
$\Delta H^{\ddagger}$,^{c} kcal/mol	13 ± 2	9.1 ± 0.9
$\Delta S^{\ddagger}$,^{c} eu	−3 ± 8	−16 ± 4

^{a}Temperature in °C (±1 °C). ^{b}Upper and lower limits of the fluxional exchange rate, k, in s^{-1}. ^{c}From a least-squares fit of ln (k/T) vs. 1000/T. The values for isopropyllithium are based only on the three highest temperatures in the table.

bulk of the alkyl groups to slow interaggregate exchange. Coupling is not readily observed for straight-chain alkyllithium compounds. The only exception is *n*-propyllithium-^{6}*Li*.

Of particular importance for the practical application of the ^{13}C–^{6}Li coupling is its relatively small variation with alkyl group. The total range of the one-bond coupling is only 5.3–6.8 Hz. All hexamers had coupling in the range 6.2–6.8 Hz (observed coupling of 3.1–3.4 Hz) while coupling for the tetramers ranged from 5.3 to 6.1 Hz (observed coupling of 4.0–6.1 Hz). The magnitude of the coupling thus seems to indicate the state of aggregation.

Given the same aggregation state, the coupling decreases with an increase in steric bulk. However, even for identical alkyl groups, the coupling appears to be slightly smaller for the tetramer than the hexamer. This is in contrast to the couplings for the hexamer, octamer, and nonamer that are essentially identical. This most likely reflects the increased charge separation of the tetramers vs. the hexamers, as earlier predicted by PRDDO molecular orbital calculations.[21] This is further supported by the decreased coupling of 4.8 Hz found for $(t\text{-}C_4H_9)_3(t\text{-}C_4H_9O)Li_4$,[22] where increased charge separation might be anticipated.

Experimental Section

All laboratory manipulations involving the synthesis and sample preparation of air-sensitive compounds were performed in an argon-filled drybox with recirculating atmosphere through an oxygen scavenger or in a high vacuum system. All solvents were dried over $LiAlH_4$ and degassed on the vacuum system prior to use.

Preparation of Compounds. Bis(alkyl)mercury compounds were prepared from mercuric chloride and an excess of the appropriate Grignard reagent in ethyl ether.[23] Following normal workup, the mercury compounds were characterized by ^{13}C NMR[24] and melting or boiling points.[25] The only bis(alkyl)mercury compound not previously reported was bis(2-ethylbutyl)mercury; ^{13}C NMR in benzene-d_6 ($J(^{13}\text{C}–^{199}\text{Hg})$): 50.6 ppm (671 Hz), 42.6 (34), 32.6 (73), 12.1. Anal. Calcd for $C_{12}H_{26}Hg$: C, 38.86; H, 7.07. Found: C, 37.00; H, 7.20.[26]

The halide-free organolithium compounds were synthesized by direct reaction of an excess of ^{6}Li metal (94.5% isotopic abundance, Union Carbide Corp., Oak Ridge, TN) and the corresponding bis(alkyl)mercury compound in cyclopentane as described earlier.[12]

In most cases the cyclopentane solution was filtered through a fine glass frit and used directly for NMR studies. For *tert*-butyllithium, the cyclopentane was removed on the vacuum line and *tert*-butyllithium sublimed to yield white crystalline solid. There was no observable difference in the NMR spectra for samples prepared by these two methods.

The ^{13}C NMR spectra for the straight-chain alkyllithium compounds were consistent with data reported earlier in hydrocarbon solvent,[13] with the exception of *n*-hexyllithium discussed above. The ^{13}C NMR spectra of the branched-chain compounds were assigned on the basis of off-resonance decoupling or INEPT experiments and by comparison with similar compounds.

NMR Parameters and Conditions. All spectra were obtained with proton decoupling on a JEOL FX-90Q spectrometer at 13.19 and 22.6 MHz for ^{6}Li and ^{13}C, respectively. The alkyllithium solution was contained in a sealed 8-mm NMR sample tube which was held coaxially within a 10-mm NMR tube. The outer tube contained 1 M $LiClO_4$ in acetone-d_6, used as the ^{6}Li chemical shift reference and lock solvent.

All ^{6}Li chemical shifts as listed in the text are relative to external 1 M $LiClO_4$ in acetone-d_6 defined as 0 ppm and contain no correction for the difference in bulk magnetic susceptibility between the sample and the reference. It should be noted, therefore, that these chemical shift values can not be directly compared to chemical shift values measured with a superconducting magnet.[27]

Typical conditions for ^{6}Li observation: a flip angle of 90°, 90-s repetition rate, 50–250-Hz spectral width, 4–32 transients, and 8K transform.

^{13}C chemical shifts were assigned relative to Me_4Si by setting cyclopentane to 25.8 ppm. Typical conditions for ^{13}C observation were a flip angle of 30°, 3-s repetition rate, 1400-Hz spectral width, 800–3000 transients, and 8K transform. The resolution enhancement used was subtraction of an exponentially weighted FID from a nonweighted FID.

Coupling constants cited to the nearest 0.1 Hz are from the ^{13}C spectra and are accurate to ±0.3 Hz. Values cited to the nearest 0.01 Hz are from the ^{13}C satellites observed in the ^{6}Li spectra and are accurate to better than ±0.06 Hz (usually ±0.02 Hz).

Temperature control was achieved by using the standard JEOL temperature controller. The temperature of the sample was determined before and after each run by replacing the sample with an identical tube containing a calibrated ethanol thermometer. If the two temperatures were not within ±1 °C, the spectrum was rerun.

Data Analysis. Error bounds reported for the equilibrium thermodynamic data are at the 95% confidence limit on the basis of the linear least-squares fit of ln K_{eq} vs. $(1/T) \times 1000$. The equilibrium constants were determined on the basis of 2 M monomer concentration of isopropyllithium-^{6}*Li* and a 3 M monomer concentration of *sec*-pentyllithium-^{6}*Li*. However, the values of the thermodynamic parameters are very insensitive to the concentration used. A factor of 2 change in the monomer concentration still leads to thermodynamic data within the error bounds quoted.

Temperature-dependent ^{13}C line shapes were calculated as described earlier[12] by using $^1J(^{13}\text{C}–^6\text{Li}) = 5.60$ Hz and $w_{1/2} = 2.5$ Hz. The errors quoted for the activation parameters only include errors from a least-squares fit of the Eyring equation.

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