Appendix

The computations used the extended Hückel method with H_{ii}'s and other relevant parameters listed in Table II. The off-diagonal elements were evaluated with the weighted H_{ij} formula.[24]

The C-C, C-H, Ir-centroid, P-H, and Ir-P bond distances were set at 1.41, 1.1, 1.724, 1.42, and 2.42 Å, respectively. The H-Ir-C_α bond angle in the vinyl system was kept at 80.0°. The Ir-P-H angle were set at 123.1°.

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Fluxional Exchange of *tert*-Butyllithium Tetramers from Temperature-Dependent ^{13}C–^{6}Li Coupling[1]

Ruthanne D. Thomas,* Matthew T. Clarke, 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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^{13}C and ^{6}Li NMR studies have been carried out on *tert*-butyl- and *tert*-pentyllithium-^{6}Li in cyclopentane solution. The proton-decoupled ^{13}C resonance for the α-carbon of *tert*-butyllithium-^{6}Li varies from a sharp nine-line multiplet above -5 °C, $J(^{13}C-^{6}Li)$ = 4.1 Hz, to a sharp seven-line multiplet below -22 °C, $J(^{13}C-^{6}Li)$ = 5.4 Hz. This indicates slowing of the fluxional exchange of the *tert*-butyllithium tetramer at low temperatures. A line-shape analysis of the ^{13}C and ^{6}Li exchange-broadened spectra yields activation parameters for the fluxional exchange of $\Delta H^{\ddagger}$ = 25.0 ± 0.1 kcal/mol and $\Delta S^{\ddagger}$ = 44 ± 1 eu. In contrast, the α-carbon of *tert*-pentyllithium-^{6}Li is a temperature-independent nine-line multiplet with $J(^{13}C-^{6}Li)$ = 4.0 Hz. This is interpreted in terms of a similar fluxional process with $\Delta G^{\ddagger}$ (188 K) $\leq$ 7.9 kcal/mol. The possible mechanisms for fluxional exchange are discussed.

Introduction

It is well-known that alkyllithium compounds exist as aggregates, $(RLi)_n$, where n depends on the alkyl group, solvent, concentration, and temperature.[2] Aggregation states of alkyllithium compounds in hydrocarbon solvent range from dimers[3,4] to octamers and nonamers,[5] with the majority of compounds existing primarily as tetramers, I, and hexamers, II. These compounds undergo a variety
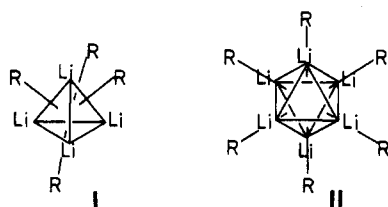
of exchange processes in solution including inversion at carbon bonded lithium, interaggregate carbon–lithium bond exchange, and intraaggregate carbon–lithium bond exchange. While NMR studies have revealed many details of inversion at carbon and interaggregate exchange,[6,7] much

less is known about the mechanism of intraaggregate exchange (fluxionality).

Lithium aggregates have been observed at both the fast and slow fluxional exchange limits in hydrocarbon solvent.[4-8] In general, the presence of fluxionality has been established on the basis of the multiplicity of the ^{13}C NMR resonance of the α-carbon due to carbon–lithium coupling[8,9] or, where the entire multiplet could not be seen, from the value of the observed coupling constant.[5] Evidence for the slowing of the fluxional character of *tert*-butyllithium has also come from the ^{7}Li NMR spectra of mixtures of *tert*-butyllithium and [(trimethylsilyl)methyl]lithium.[10] On the basis of these studies, hexamers are apparently fluxional under all conditions, while tetramers exchange more slowly. The presence of empty sites on the octahedral hexamer has been proposed as a possible explanation for the higher fluxional rate of hexamers relative to tetramers,[7] although details of the mechanism for fluxional exchange are unknown.

Information on the energetics and mechanism of fluxionality would be particularly useful in understanding the mechanistic details of the reactions of alkyllithium aggregates with other compounds. It is likely that the rate-determining step for some of the reactions of alkyllithium compounds with other substrates is related to the fluxional process. Brown very early suggested[10] that the

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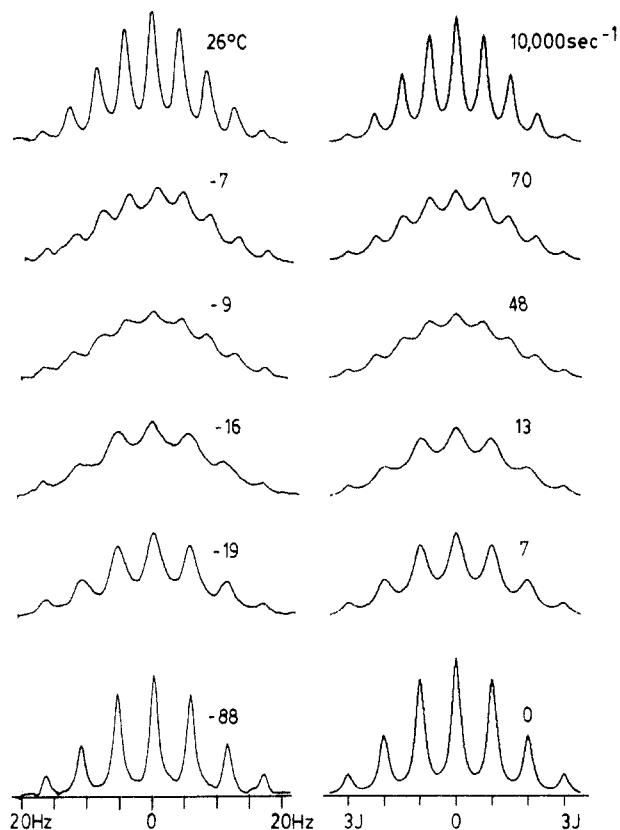(10) Hartwell, G. E.; Brown, T. L. *J. Am. Chem. Soc.* 1966, *88*, 4625-4629

Figure 1. Experimental (left) and calculated (right) ^{13}C NMR spectra of the α-carbon of *tert*-butyllithium-^6Li in cyclopentane.

rate-determining step for the initiation of diene polymerization might involve formation of a species similar to the transition state in the intraaggregate exchange of *tert*-butyllithium, since the rate of initiation was much faster than the rate of dimer formation. More recent work on the X-ray crystal structure of the 3-lithio-1-methoxybutane tetramer[11] further supports the role of the transition state as important in the reactions of organolithium compounds. Recent work in our laboratory[12] has shown that trimethylvinylsilane coordinates readily to *tert*-butyllithium in hydrocarbon solvent above the fluxional temperature of the *tert*-butyllithium tetramer but does not coordinate if added to the *tert*-butyllithium below the fluxional temperature. Prompted by these observations, we have undertaken a study of the fluxional exchange behavior of alkyllithium aggregates. We report here on the fluxional behavior of *tert*-butyl- and *tert*-pentyllithium in hydrocarbon solvent.

Results and Discussion

The proton-decoupled ^{13}C NMR spectrum of *tert*-butyllithium-^6Li in cyclopentane at room temperature consists of two resonances: a singlet at 32.6 ppm and a nonet at 10.7 ppm (peak separation of 4.1 Hz) assigned to the methyl and quaternary carbons, respectively. The nine peaks of the nonet are in the ratio of 1:4:10:16:19:16:10:4:1, which is the multiplet expected for a ^{13}C nucleus coupled to four equivalent ^{6}Li nuclei ($I = 1$). This is consistent with the known fluxional tetrahedral structure, I, of *tert*-butyllithium.[8,10]
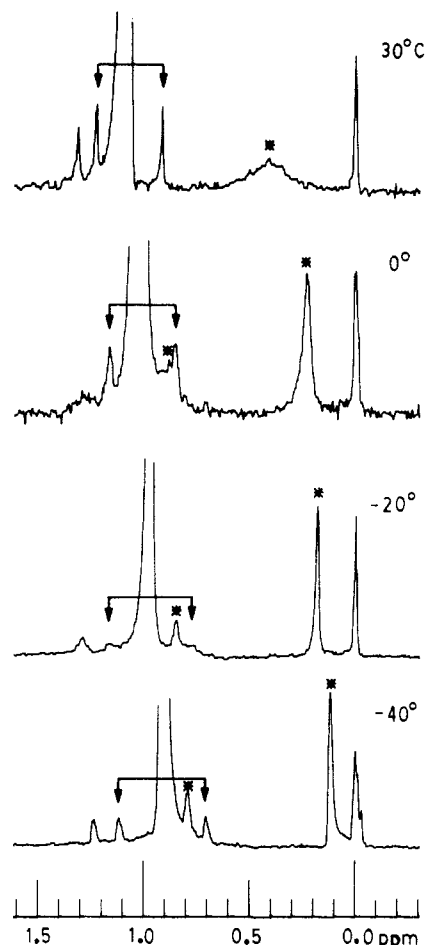
Figure 2. Enlarged base line of the ^{6}Li NMR spectra of 1 M *tert*-butyllithium-^6Li in cyclopentane containing 2.5% butoxide. Chemical shifts are relative to external 1 M LiClO$_4$ in acetone-d_6 at 0 ppm. Peaks marked with an asterisk are from butoxide-containing tetramers; see text. The bracketed peaks are ^{13}C satellites. The ^{13}C satellites are symmetric about the center of the large peak (to 0.01 Hz), but the large peak is distorted at the base line. The most downfield peak (1.3 ppm) is unidentified.

Upon cooling, the nonet peaks broaden, coalesce, and then reform below –10 °C into a seven-line multiplet with $J(^{13}\text{C}-^6\text{Li}) = 5.4$ Hz, left side of Figure 1. The process is completely reversible and is independent of prior heating or cooling of the sample. Such behavior has been observed earlier for *sec*-butyllithium tetramers[4] and is indicative of slowing of fluxional exchange of the tetramer at low temperatures. The seven-line multiplet represents coupling to the three nearest-neighbor lithium nuclei. Any coupling to the single remote ^{6}Li nucleus, which would be small,[13] is not resolved. The coupling of 4.1 Hz observed in the fast fluxional limit is the weighted average of three adjacent coupling interactions of 5.4 Hz and one remote coupling interaction of zero.

The ^{6}Li spectra are consistent with this interpretation. Over the temperature range +35 to –88 °C, the ^{6}Li spectrum is essentially one resonance with a chemical shift ranging from 1.07 ppm at +35 °C to 0.86 ppm at –85 °C. The ^{13}C satellites, however, show a change from $J = 4.10$ Hz above –5 °C to 5.44 Hz below –30 °C (Figure 2). The coupling of 5.44 Hz at low temperature corresponds to ^{13}C–^{6}Li nearest-neighbor coupling. The additional line (or lines, if the long-range ^{13}C–^{6}Li coupling is not zero) due to the single ^{6}Li nucleus remote to the ^{13}C nucleus is not observed because of overlap with the large central peak.

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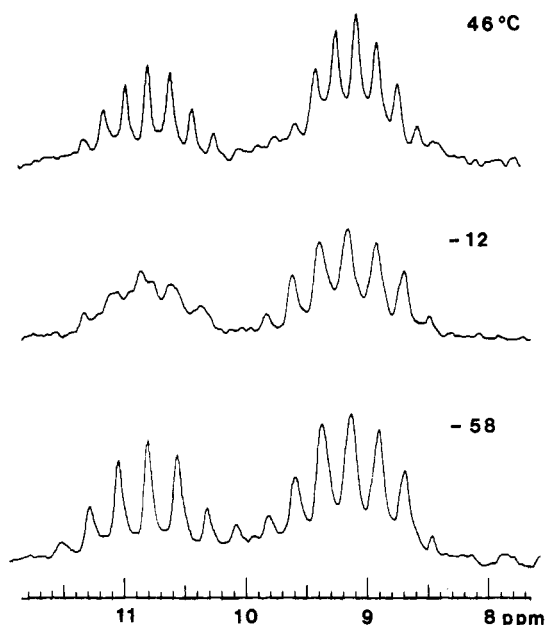
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46 °C

-12

-58

| 11 | 10 | 9 | 8 ppm |

Figure 3. ^{13}C NMR spectra of the α-carbons of *tert*-butyl-lithium-^6Li at 10.8 ppm and of $(t\text{-}OC_4H_9)(t\text{-}C_4H_9)_3^6Li_4$ at 9.1 ppm. The sample contains 17% alkoxide based on monomer, or 68% cross complex.

The smaller coupling at higher temperatures is due to signal averaging between the two lithium sites. The rapid exchange value is approximately $^3/_4$ of the slow-exchange value, as expected. The slight difference from that predicted could arise either from a temperature-dependent one-bond coupling or from an unresolved remote coupling of 0.1 Hz. Although this is of some importance in modeling the ^6Li exchange spectra, it is too small to be observed in the ^{13}C spectra.

At low temperatures there are two additional ^6Li peaks at 0.1 and 0.8 ppm due to $(t\text{-}OC_4H_9)(t\text{-}C_4H_9)_3Li_4$ formed from adventitious oxygen. This has been confirmed by adding *tert*-butyl alcohol to a *tert*-butyllithium solution. The 3:1 ratio of the peaks clearly shows the tetrahedral structure first suggested by Brown[10] and more recently found for solvated $(t\text{-}OC_4H_9)(n\text{-}C_4H_9)_3Li_4$.[14] Upon warming, the two peaks broaden and coalesce to a single broad resonance at 0.4 ppm, indicating an exchange process between the two sites. The observed fluxional exchange of *tert*-butyllithium tetramers was independent of the concentration of butoxide-containing tetramers (0.6–17% butoxide based on monomer).

To explore the nature of the process leading to the temperature-dependent $^{13}C\text{-}^6Li$ coupling for *tert*-butyllithium-^6Li, we have carried out a full line-shape analysis of the ^{13}C resonance of the α-carbon.

Fluxional Exchange Model. Since coupling is retained even in the fast-exchange limit, the exchange process producing the temperature-dependent coupling changes must be intramolecular. Furthermore, the C_{3v} symmetry of the spins in the tetrahedral structure (four ^6Li nuclei and one ^{13}C nucleus) results in no mechanistic information in the NMR line shape regardless of the type of lineshape analysis used.[15] We have therefore modeled the fluxional behavior assuming a random exchange of the single ^{13}C nucleus over the faces of an intact tetrahedron of ^6Li nuclei by using modified Bloch equations.

Table I. Unique Exchange Tetramers

$\sum m_1$ for each Li_3 face				degeneracy
Nonexchange				
-3	-3	-3	-3	1
0	0	0	0	1
3	3	3	3	1
Two-Site (3:1)				
$1/\tau_A = {}^1/_3k$, $1/\tau_B = k$; $p_A = 0.75$, $p_B = 0.25$				
-2	-2	-2	-3	4
-1	-1	-1	-3	4
-1	-1	-1	0	4
1	1	1	0	4
1	1	1	3	4
2	2	2	3	4
Two-Site (2:2)				
$1/\tau_A = 1/\tau_B = {}^2/_3k$; $p_A = p_B = 0.5$				
-1	-1	-2	-2	6
1	1	-1	-1	6
2	2	1	1	6
Three-Site (2:1:1)				
$1/\tau_{AB} = 1/\tau_{AC} = 1/\tau_{CB} = 1/\tau_{BC} = {}^1/_3k$, $1/\tau_{CA} = 1/\tau_{BA} = {}^2/_3k$; $p_A = 0.5$, $p_B = p_C = 0.25$				
0	0	-1	-2	12
0	0	-1	1	12
0	0	1	2	12

This exchange analysis is only valid if there is no exchange between *tert*-butyllithium tetramers and $(t\text{-}OC_4H_9)(t\text{-}C_4H_9)_3Li_4$. Figure 3 is the ^{13}C NMR spectrum at 46 °C for a sample of *tert*-butyllithium-^6Li in cyclopentane to which has been added *tert*-butyl alcohol (17% alkoxide based on monomer; 68% butoxide cross complex tetramer based on integration of the ^{13}C and ^6Li spectra). The downfield multiplet at 10.8 ppm is the nonet for rapidly fluxional *tert*-butyllithium tetramer with $J_{obsd} = 4.1$ Hz. The upfield multiplet at 9.1 ppm ($J_{obsd} = 3.7$ Hz) is the α-carbon of the three *tert*-butyl groups bound to lithium in $(t\text{-}OC_4H_9)(t\text{-}C_4H_9)_3^6Li_4$. This indicates that the exchange between the cross complex and the *tert*-butyllithium tetramers is in fact slow and can be ignored in the analysis of the fluxionality of the *tert*-butyllithium tetramer.

Also included in Figure 3 are ^{13}C spectra for the same high butoxide concentration sample at low temperatures. Lowering of the temperature leads to spectral changes of both the multiplets, but they appear to be independent of one another. In particular, the coalescence of the *tert*-butyllithium peak is qualitatively identical with that expected from the spectra in Figure 1 despite the 28-fold increase in the relative concentration of the cross complex. The additional features on the *tert*-butyllithium tetramer multiplet at -12 °C are characteristic of these peaks when there is low signal to noise and is not indicative of additional spectral features.

The magnetic environment of the ^{13}C nucleus is described by the sum of the ^6Li m_I values for the three ^6Li nuclei of a triangular face. Any change of the ^6Li m_I values due ^6Li T_1 relaxation was assumed to be minimal due to the very long ^6Li T_1 relaxation times for *tert*-butyllithium-^6Li in cyclopentane.[16] The 81 possible combinations of the ^6Li spin states were separated into 15 unique tetramers. These 15 tetramers were further divided into four types of exchange behavior, depending on the spin states present (Table I): nonexchange, two-site (population

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Table II. Fluxional Exchange Rates and Activation Parameters for *tert*-Butyllithium-^6Li in Cyclopentane

| temp[a] | sample 1 (3 M) | | sample 2 (5 M) |
	^{13}C NMR	^6Li NMR	^{13}C NMR
-5.0	85-100[b]		
-7.0			68-72
-8.0	50-62		
-9.0			45-50
-10.0	34-38		
-15.5	12-15		
-16.0			13
-16.2		10.6-15.5	
-17.0	8.5-9.5		
-18.0		7.8-8.8	
-19.0	6-8		7
-19.5		5.2-6.2	
-22.0	3-4		
-22.5		3.1-4.3	
$\Delta H^{\ddagger}$,[c] kcal/mol	25.1 ± 0.4	25.0 ± 2.6	25.0 ± 0.2
$\Delta S^{\ddagger}$,[c] eu	44.2 ± 1.7	43.8 ± 10	44.1 ± 0.9

$$\Delta H^{\ddagger}_{overall} = 25.0 \pm 0.1 \text{ kcal/mol}$$

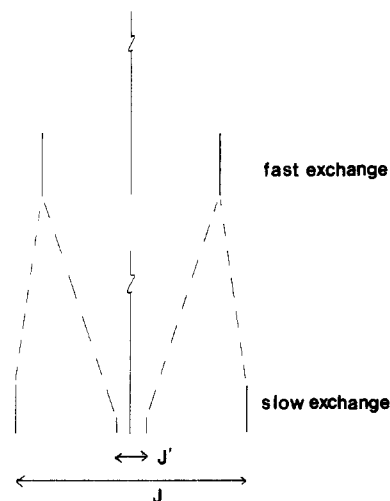$$\Delta S^{\ddagger}_{overall} = 44 \pm 1 \text{ eu}$$

[a] Temperature in °C (±0.2 °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. $1000/T$.

ratio of 2:2), two-site exchange (3:1), and three-site exchange (2:1:1). Each of the unique tetramers was treated separately by modified Bloch equations,[17] with the exchange lifetimes assigned relative to a common exchange rate, k, as shown in Table I. The actual equations used are given in the Appendix. The 15 different exchange tetramers were then combined with the appropriate degeneracies to yield the exchange-broadened spectra, right side of Figure 1.

The ^{13}C exchange-broadened spectra were very sensitive to the choice of both the nonexchange spin–spin relaxation time, T_2, and to the nonexchange one-bond $^{13}C-^6Li$ coupling. The line width of all of the ^{13}C peaks of the α-carbon multiplet at both the fast- and slow-exchange limits (26 and -45 °C) were identical and equal to 1.65 Hz. This was therefore used as the nonexchange line width for all the theoretical specta. The spin–spin relaxation time was then taken to be the reciprocal of π times the width at half-height. Differential broadening of the different ^{13}C peaks of the multiplet due to coupling to the spin 1 nucleus[18] was ignored since at the exchange limits all of the peaks of the multiplets had the same line width.

The line width of the methyl peak was originally considered as a possible internal line width standard; however, it increased monotonically with a decrease in temperature and was greater than the observed line width of the α-carbon peaks at and below -60 °C, suggesting an additional unidentified exchange interaction. In any case, the line width of the methyl peak was not a reliable source of line width information for the α-carbon peaks.

Representative experimental and calculated ^{13}C spectra of the α-carbon are shown in Figure 1. The results for samples at 3 and 5.0 M concentrations (containing 2.5% and 0.6% alkoxide, respectively, based on monomer) are summarized in Table II. It is clear that there is no concentration dependence on the exchange rates. Additional samples with concentrations as low as 0.8 M gave identical

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Figure 4. Idealized ^6Li spectra showing coupling to natural abundance ^{13}C. J is the observed nonexchange one-bond $^{13}C-^6Li$ coupling (5.44 Hz). J', the long-range $^{13}C-^6Li$ coupling, is calculated from J (at fast exchange) = $(3J + J')/4$.

qualitative results, but no quantitative analysis of these spectra was attempted due to the poor signal to noise of the ^{13}C NMR spectra.

The exchange rates were also estimated from the ^{13}C satellites of the ^6Li resonance. Idealized ^6Li spectra showing ^{13}C coupling are shown in Figure 4. The slow-exchange limit ^6Li spectrum can be thought of as the superposition of three ^6Li spectra: (1) a single peak for tetramers containing only ^{12}C at the α-position (95.7%); (2) peaks at $+^1/_2J$ and ~ 0 Hz due to the three ^6Li nuclei adjacent to and the one ^6Li nucleus remote to a ^{13}C nucleus in a spin state of $+^1/_2$ (2.1%); and (3) peaks at $-^1/_2J$ and ~ 0 Hz due to the ^6Li nuclei in a tetramer with ^{13}C nucleus in a spin state of $-^1/_2$ (2.1%). If the ^{13}C nucleus does not change spin states during the fluxional exchange, which is reasonable due to the long T_1 relaxation time of the quaternary carbon, then the change of the satellites with fluxional exchange can be treated as two separate two-site exchanges (Figure 4).
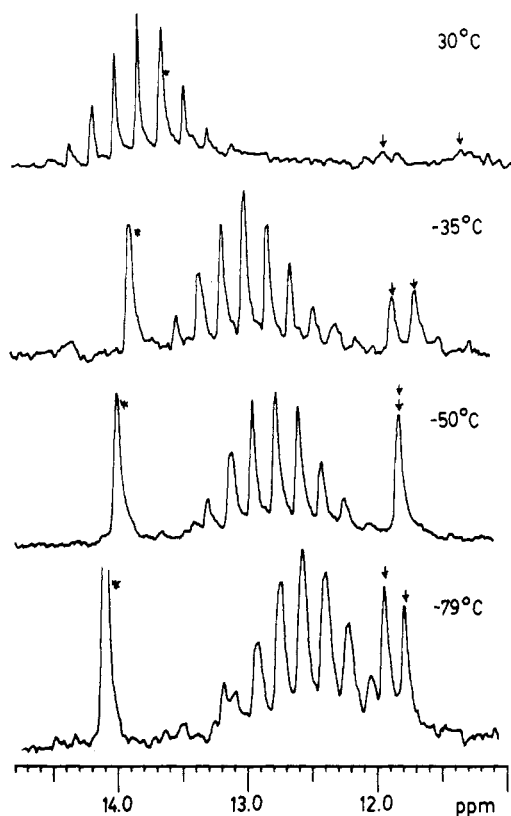
Each of the observed satellites at the slow-exchange limit was assumed to be the more abundant peak of a 3:1 two-site exchange. The inner, less abundant peaks of each pair were never definitely observed due to overlap with the large central peak. Therefore, the difference in chemical shift of the observed satellites as they broadened and moved toward the central peak with an increase in temperature was fit to the difference in chemical shift of the more abundant peaks in the two 3:1 two-site exchanges with $W_{1/2}$ = .098 Hz, J = 5.44 Hz, and J' = .1 Hz (nonexchange chemical shifts of ±2.72 and ±0.05 Hz). Although clearly not as accurate as a full line-shape analysis, the treatment of the ^6Li spectra served as a check of the analysis of the ^{13}C spectra. The results are consistent with the ^{13}C data and are also included in Table II.

An Eyring plot for the data is shown in Figure 5. A least-squares fit of the combined data from the three data sets yields $\Delta H^{\ddagger}$ = 25.0 ± 0.1 kcal/mol and $\Delta S^{\ddagger}$ = 44 ± 1 eu. The error bounds quoted likely underestimate the true error, especially due to the small temperature range possible using this technique. It is interesting to note, however, that the enthalpy of activation is identical with the enthalpy of activation for the exchange reaction of *tert*-butyllithium and [(trimethylsilyl)methyl]lithium.[19] The

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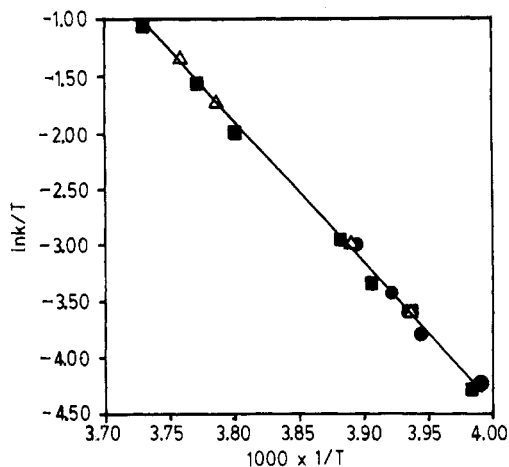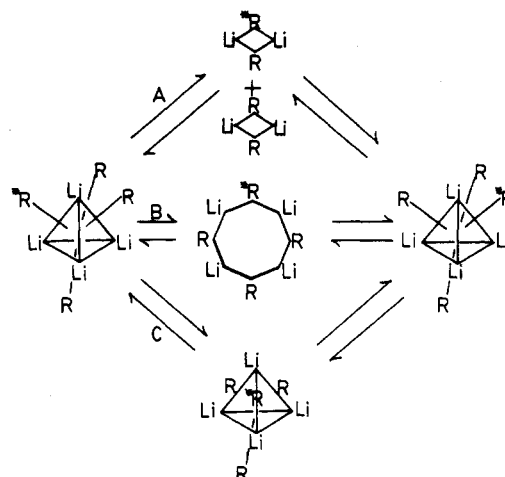
Figure 5. Eyring plot for fluxional exchange of *tert*-butyl-lithium-^6Li in cyclopentane: ■, from the ^{13}C NMR spectra of the α-carbon, 3 M solution; △ from ^{13}C NMR of α-carbon, 5 M solution; ● from ^{13}C satellites in the ^{6}Li NMR spectra, 3 M solution.

Figure 7. Fluxional exchange mechanisms: A, dissociation to dimers; B, dissociation to an eight-membered ring; C, concerted center to edge movement of three alkyl groups.

Figure 6. ^{13}C NMR spectra of the α-carbon of *tert*-pentyl-lithium-^6Li in cyclopentane. The peak marked with an asterisk is a solvent impurity. The peaks marked with arrows are degradation products. There is a greater than 24-h time lapse between the 30 °C spectrum and the other spectra, during which time significant decomposition of the *tert*-pentyllithium occurred.

rate-limiting step for this reaction was assumed to be the dissociation of the *tert*-butyllithium tetramers to dimers.

tert-Pentyllithium. While the fluxional exchange of *tert*-butyllithium could be readily stopped by lowering the temperature, *tert*-pentyllithium-^6Li (2-methyl-2-lithio-^6Li-butane) in cyclopentane is in the fast fluxional exchange limit even at –80 °C (Figure 6). The proton-decoupled ^{13}C NMR spectrum for *tert*-pentyllithium-^6Li in cyclopentane at +25 °C consists of four resonances: singlets at 36.9, 27.7, and 5.7 ppm, assigned to carbons 3, 1, and 4, respectively, and a nonet at 13.8 ppm (peak separation of 4.0 Hz) due to the carbon attached to lithium. As the temperature is lowered, the α-carbon peak shifts

upfield but is still a nine-line multiplet with the same ^{13}C–^{6}Li coupling. Below –85 °C all of the peaks of the ^{13}C spectrum broaden, apparently due to precipitation of the compound, but there is no suggestion of coalescence of the α-carbon multiplet. The ^{6}Li spectrum over the temperature range +25 to –85 °C is a sharp peak at 0.7 ppm with ^{13}C satellites indicating a constant $J(^{13}$C–^{6}Li) of 3.98 ± 0.1 Hz.

On the basis of the multiplicity and the relative intensities within the multiplet for the α-carbon, *tert*-pentyllithium is also a fluxional tetramer. On the basis of the similarity of the observed coupling to that for *tert*-butyllithium, it is very likely tetrahedral. Unlike the *tert*-butyllithium, however, it is rapidly fluxional over the entire temperature range studied.

On the basis of the observed coupling in the ^{6}Li spectrum of 3.98 ± 0.01 Hz, the nonfluxional ^{13}C–^{6}Li coupling would be 5.31 Hz. With use of this value for the nonexchange coupling and a line width of 1.65 Hz, the rate of fluxional exchange must be ≥2500 s^{-1}. This corresponds to a $\Delta G^{\ddagger}$ (188 K) of less than or equal to 7.9 kcal/mol. The comparable $\Delta G^{\ddagger}$ (188 K) for *tert*-butyllithium is 16.7 kcal/mol. The more sterically demanding *tert*-pentyl group has caused a marked increase in the rate of the exchange process even though the aggregation state and the geometry of the aggregate have not changed relative to *tert*-butyllithium.

Exchange Mechanisms. The concentration independence of the exchange rates indicates that the exchange is first order in *tert*-butyllithium tetramers. The very large positive $\Delta S^{\ddagger}$ and the rate acceleration upon going from *tert*-butyl to *tert*-pentyllithium both suggest a transition state which is less sterically crowded than the ground state. This observed exchange behavior is consistent with several mechanisms.

One possible mechanism is dissociation of the tetrameric aggregate to dimers, followed by rotation and recombination (Figure 7A). Such a mechanism would account for the large positive $\Delta S^{\ddagger}$ in a noncoordinating solvent and the rate acceleration for the more sterically demanding *tert*-pentyl group. As noted above, the enthalpy of activation for the fluxional exchange is identical with the 24 ± 6 kcal/mol found earlier for the exchange between *tert*-butyllithium and [(trimethylsilyl)methyl]lithium.[19] The rate-determining step for this reaction was assumed to be the dissociation of the *tert*-butyllithium to dimers. More recently, the activation parameters for exchange between dimers and tetramers of vinyllithium in hydro-

carbon were reported to be 23 kcal/mol and 46 eu,[7] again essentially identical with the results in this study.

Dixon, however, has argued[20] that 24 kcal/mol is much too low for the dissociation of alkyllithium tetramers to dimers. On the basis of PRDDO molecular orbital calculations, there is a difference of 43 kcal/mol between the methyllithium tetramer and dimers. He found, on the other hand, that there was very little difference in energy between tetrahedral and planar tetramers. This is support for the mechanism, first proposed by Brown,[21] of fluxional exchange via an eight-membered carbon–lithium ring (Figure 7B). Opening of the tetrahedral tetramer to the eight-membered ring is dissociative and leads to a transition state with increased degrees of freedom, both required by the exchange data. Planar ring structures are known for [(trimethylsily)methyl]copper[22] and for dimethyllithium cuprate,[23] although, to our knowledge, no such ground-state structures are known for simple alkyllithium compounds. In addition, this mechanism can account for the nearly 6 orders of magnitude difference[10] between the inter- and intraaggregate exchange rates for *tert*-butyllithium. It is difficult to rationalize the very slow interaggregate exchange based only on solvent cage effects if dissociation to dimers does in fact occur.

A third possible mechanism is the concerted center-to-edge rotation of three of the alkyl groups (Figure 7C). This mechanism was first proposed to explain the inversion at carbon for primary alkyllithium compounds.[24] In such a mechanism the carbon bonded to lithium undergoes a change to sp^2 hybridization. Such a transition state is restricted to methyl or primary alkyl groups and would be impossible for a tertiary alkyl group due to steric interactions with the lithium core. If, however, the tetramer (or at least the transition state) is primarily ionic in nature,[25] then three alkyl anions could rotate relative to the lithium core in a concerted center-to-edge fashion. It is not clear, however, that such a mechanism could lead to the large positive entropy of activation.

The precise nature of the transition state for *tert*-butyllithium fluxional exchange remains speculative. However, the unexpectedly rapid fluxional exchange of the *tert*-pentyllithium again demonstrates the dramatic effect of steric interactions on the properties of alkyllithium compounds. Work is currently in progress in our laboratory to identify the role of fluxional exchange in the reactions of alkyllithium compounds with other substrates.

Experimental Section

All laboratory manipulations involving the synthesis and sample preparation of air-sensitive compounds were performed in an argon-filled drybox with atmosphere recirculating 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. Di-*tert*-butylmercury was synthesized from *tert*-butyl Grignard reagent and mercuric chloride in ethyl ether.[26] Following normal workup, the *tert*-butylmercury was sublimed on the vacuum line without dynamic

pumping at 45 °C (lit. value 78–82 °C at 5 torr). The ^{13}C NMR spectrum in C$_6$D$_6$: 60.4 (s, $^1J(^{13}C-^{199}Hg) = 635$ Hz), 31.3 ppm (q, $^2J(^{13}C-^{199}Hg) = 29$ Hz). This is consistent with the ^{13}C data reported earlier.[27]

Di-*tert*-pentylmercury was synthesized in a similar manner from mercuric chloride and *tert*-pentyl Grignard in ethyl ether,[28] followed by normal workup and distillation (65–70 °C at 2 torr; lit. value 80–84 °C at 5 torr). The ^{13}C NMR spectrum in C$_6$D$_6$: 67.4 (s, $^1J(^{13}C-^{199}Hg) = 652$ Hz), 38.0 (t, $^2J(^{13}C-^{199}Hg) = 14.6$ Hz), 29.0 (q, $^2J(^{13}C-^{199}Hg) = 26.9$ Hz), 13.8 ppm (q, $^3J(^{13}C-^{199}Hg) = 73.2$ Hz).

tert-Butyllithium-^6Li was synthesized by direct reaction of an excess of ^{6}Li metal (94.5% isotopic abundance, Union Carbide Corp., Oak Ridge, TN) and di-*tert*-butylmercury in cyclopentane.[2] The lithium metal was freshly cut in the drybox and placed into a reaction vessel. The mercury compound was added and then the vessel evacuated on the vacuum line. Enough cyclopentane was distilled into the reaction vessel to produce a 2 M solution of *tert*-butyllithium (based on monomer) assuming complete reaction. The reaction was sealed and allowed to shake on a shaker table at room temperature for 2 weeks. Additional lithium metal was added and the reaction vessel allowed to react for an additional week. As monitored by ^{13}C NMR, no di-*tert*-butylmercury was present after the second addition of lithium metal. In general, the preparation with ^{6}Li metal all took considerably longer than the corresponding reactions with ^{7}Li metal, which were typically complete in a few days to a week. The cyclopentane solution was filtered through a fine glass frit. Either this solution was directly used for NMR studies, or the cyclopentane was removed on the vacuum line and the *tert*-butyllithium sublimed to yield white crystalline solid. There was no observable difference in the exchange behavior of samples by these two methods.

tert-Pentyllithium was synthesized in a similar manner from excess ^{6}Li metal and di-*tert*-pentylmercury. In all cases the cyclopentane solutions were used directly for NMR studies. Attempts to remove the cyclopentane solvent under vacuum resulted in a dark viscous oil that decomposed upon further pumping.

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, respectively.

All ^{6}Li chemical shifts as listed in the text are relative to external 1 M LiClO$_4$ in acetone-d_6 set to 0 ppm and contained 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 cannot be directly compared to chemical shift values measured with a superconducting magnet. To resolve the apparent large differences, ^{6}Li NMR spectra of one sample of *tert*-butyllithium-^6Li were run at 13.19 MHz with an iron core magnet (JEOL FX-90Q) and at 44.16 MHz with a superconducting magnet (Nicolet NT-300). The measured chemical shift values, downfield from external 1 M LiClO$_4$ in -acetone-d_6 are 1.0 and 0.4 ppm for the iron core and superconducting magnets, respectively. This corresponds to a corrected chemical shift of 0.8 ppm.[29]

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

^{13}C chemical shifts were assigned relative to Me$_4$Si 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, an exponential weighting factor of 34 (0.87-Hz broadening), and 8K transform.

Temperature control was achieved by using the standard JEOL temperature controller modified by adding fine adjustment to

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the temperature range scale in addition to the provided coarse adjustments. This enabled smaller temperature fluctuations near the ends of the original temperature ranges. 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 ±0.2 °C, the spectrum was rerun.

Line-Shape Calculations. The theoretical spectra were calculated by using in-house two-site and three-site exchange programs based on the modified Bloch equations.[17] Exchange rates were obtained by a visual comparison of calculated and observed spectra. The errors quoted for the activation parameters only include errors from the least-squares fit of the data.

Appendix

The modified Bloch equations used for calculating the line shapes are based on 2.14, 2.17, and 2.26 of ref 17. After substitution of the lifetime, $\tau_{M'}$ and relative populations from Table I, these become

nonexchange

$$iC_0 = -\alpha_A G_A$$

two-site (3:1)

$$\begin{bmatrix} i(0.75)C_0 \\ i(0.25)C_0 \end{bmatrix} = \begin{bmatrix} (-\alpha_A - (^1/_3)k) & k \\ ^1/_3 k & (-\alpha_B - k) \end{bmatrix} \begin{bmatrix} G_A \\ G_B \end{bmatrix}$$

two-site (2:2)

$$\begin{bmatrix} i(0.5)C_0 \\ i(0.5)C_0 \end{bmatrix} = \begin{bmatrix} (-\alpha_A - (^2/_3)k) & ^2/_3 k \\ ^2/_3 k & (-\alpha_B - (^2/_3)k) \end{bmatrix} \begin{bmatrix} G_A \\ G_B \end{bmatrix}$$

three-site (2:1:1)

$$\begin{bmatrix} i(0.5)C_0 \\ i(0.25)C_0 \\ i(0.25)C_0 \end{bmatrix} = \begin{bmatrix} (-\alpha_A - (^2/_3)k) & ^2/_3 k & ^2/_3 k \\ ^1/_3 k & (-\alpha_B - k) & ^1/_3 k \\ ^1/_3 k & ^1/_3 k & (-\alpha_C - k) \end{bmatrix} \begin{bmatrix} G_A \\ G_B \\ G_C \end{bmatrix}$$

where C_0 = scaling factor, $\alpha_M = 1/T_{2M} - 2\pi i (\nu_M - \nu)$, ν_M = resonance frequency of site M = $\sum m_1$ for each face in units of J (Hz), as given in Table I, k = exchange rate, as discussed in the text, and G_M = magnetization due to site M.

Gas-Phase Transition Metal Ion Chemistry: The Reactivity and Specificity of Atomic Iron(I), Chromium(I), and Molybdenum(I) Ions with Alcohols

Sunkwei Huang, Robert W. Holman, and Michael L. Gross*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

The reactions of gas-phase atomic transition-metal ions Fe$^+$, Cr$^+$ and Mo$^+$, generated by multiphoton dissociation ionization (MPD/MPI), with a series of aliphatic alcohols were studied by using Fourier transform mass spectrometry. The concepts of reactivity and specificity are used to correlate the different insertion reaction chemistry of each metal ion. These metal ions undergo three classes of bond insertion reactions: C–O insertion (dehydration), C–H or O–H insertion (dehydrogenation), and C–C insertion. The total reactivity of each metal ion is a function of its electronic configuration and the aliphatic chain length and degree of branching of the alcohols. For straight-chain alcohols containing three carbons or more, the order of reactivity is Fe$^+$ > Mo$^+$ > Cr$^+$. For shorter alcohols Mo$^+$ is the most reactive species while Cr$^+$ is unreactive with methanol and ethanol.

Introduction

In recent years the literature covering gas-phase metal ion reactions, particularly those of metal ions of catalytic interest, has grown steadily. The growing volume of experimental data dealing with transition-metal ions reacting with alkanes, cycloalkanes,[1a-c] bifunctional,[2] and multi-

functional,[3] organic substrates as well as studies of ligand effects at the metal center[3,4] and metal cluster reactions[5] reflects this trend.

Transition-metal ions are reactive toward many organic substrates because their valence electron configurations make it possible for the metal ion to insert into organic

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