

## Decomposition of *tert*-Butyllithium/Lithium *tert*-Butoxide Mixed Aggregates: NMR Evidence for the Formation of Novel Mixed Lithium Hydride/Lithium *tert*-Butoxide Aggregates

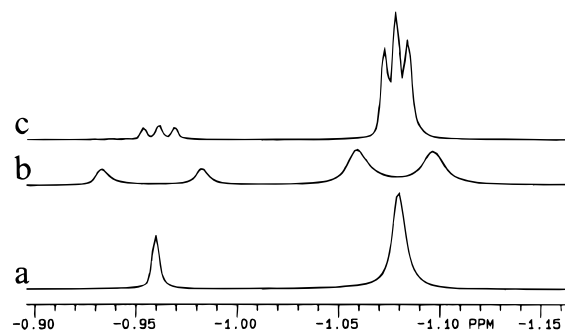
George T. DeLong, Daniele Hoffmann,  
Hanh D. Nguyen, and Ruthanne D. Thomas\*

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

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Mixed complexes of the general formula [RLi·LiOR] have long been known.<sup>1–3</sup> Such mixed aggregates are expected to form during nucleophilic addition reactions of organolithium compounds to aldehydes or ketones.<sup>1e,4</sup> The nature of mixed alkylolithium/lithium alkoxide systems has received considerable attention, as these mixtures may be considered models for the so-called “superbases” [RLi·MOR] with M = Na, K, Rb, Cs.<sup>5–8</sup> Several X-ray crystal structures of such mixed aggregates have recently appeared in the literature.<sup>3b,9</sup> The presence of alkoxides has a large effect on the reactivity of organolithium compounds.<sup>4,5a,6b,10</sup> In the presence of lithium alkoxides, organolithium compounds are known to be thermally less stable, eliminating lithium hydride.<sup>11</sup>



**Figure 1.** <sup>6</sup>Li NMR spectrum (44 MHz) at  $-20\text{ }^{\circ}\text{C}$  with (a) and without (b) <sup>1</sup>H decoupling of a 0.9:1 mixture of <sup>6</sup>BuOH/<sup>6</sup>BuLi in cyclopentane (2 M Li) after exposure to daylight at room temperature. (c) <sup>6</sup>Li NMR spectrum at  $-20\text{ }^{\circ}\text{C}$  of a 0.9:1 mixture of <sup>6</sup>BuOH/(CD<sub>3</sub>)<sub>3</sub>C<sup>6</sup>Li in cyclopentane (3 M Li) after exposure to light and heat.

Here we provide evidence that the decomposition of *tert*-butyllithium/lithium *tert*-butoxide mixtures (prepared from mixtures of <sup>6</sup>BuOH/<sup>6</sup>BuLi > 0.7)<sup>12</sup> in cyclopentane solution leads to a *hydrocarbon soluble* form of LiH, i.e., mixed LiH/LiO<sup>6</sup>Bu aggregates. Two different LiH-containing aggregates could be identified, one from photochemical decomposition and one from thermal decomposition.

We have recently demonstrated that 0.7:1 mixtures of *tert*-butyl alcohol and *tert*-butyllithium-<sup>6</sup>Li in cyclopentane consists of a variety of aggregates: the tetramers R<sub>4</sub>Li<sub>4</sub> and (RO)<sub>3</sub>Li<sub>4</sub>, as well as the mixed hexamers (RO)<sub>4</sub>R<sub>2</sub>Li<sub>6</sub> and (RO)<sub>5</sub>RLi<sub>6</sub>, and [ROLi]<sub>n</sub>.<sup>13</sup> At an alcohol/alkyllithium ratio of 0.9:1, only the mixed hexamers (vide supra) and [ROLi]<sub>n</sub> are present.<sup>14</sup> Upon standing over a period of weeks at room temperature and under normal daylight, the solution gradually decomposes. During that time, all of the mixed hexamers are consumed. Apart from the <sup>6</sup>Li resonance for lithium *tert*-butoxide at  $-0.78\text{ ppm}$ , the <sup>6</sup>Li{<sup>1</sup>H} NMR spectrum contains two additional resonances at  $-0.96$  and  $-1.08\text{ ppm}$  (Figure 1a).<sup>15</sup> The latter two resonances were shown by 2D <sup>6</sup>Li,<sup>1</sup>H-HOESY NMR to correlate to *tert*-butoxide groups, but not *tert*-butyl groups. Without <sup>1</sup>H decoupling, the <sup>6</sup>Li resonances at  $-0.96$  and  $-1.08\text{ ppm}$  each split into doublets with *J*(<sup>6</sup>Li,<sup>1</sup>H) couplings of 2.2 and 1.7 Hz, respectively (Figure 1b). Likewise, for a sample which was prepared from deuterated *tert*-butyllithium, (CD<sub>3</sub>)<sub>3</sub>C<sup>6</sup>Li, each resonance is a triplet (Figure 1c), with couplings of 0.34 Hz ( $-0.96\text{ ppm}$ ) and 0.25 Hz ( $-1.08\text{ ppm}$ ). We interpret these results in terms of the formation of two mixed LiH/LiO<sup>6</sup>Bu (or LiD/LiO<sup>6</sup>Bu, if deuterated *tert*-butyllithium was used) aggregates. Semiempirical MNDO calculations indicate that the formation of such complexes is energetically very favorable.<sup>16</sup> The multiplicity of the lithium resonances indicates that the lithium atoms are only coupled to one hydride (or deuteride) ion within each aggregate. However, no structural assignments can be made from the lithium spectra.

Scalar spin–spin coupling between lithium and hydrogen has been observed for cp\*IrH<sub>2</sub>SiMe<sub>3</sub>Li(PMDTA)<sup>17</sup> and cp\*IrH<sub>3</sub>Li-

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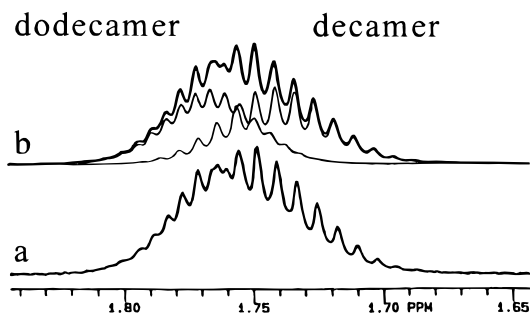
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(15) All NMR spectra were run on a Varian VXR-300 NMR spectrometer at 300, 44, and 46 MHz, for <sup>1</sup>H, <sup>6</sup>Li, and <sup>2</sup>H, respectively. <sup>1</sup>H chemical shifts are referenced to TMS by setting cyclopentane to 1.51 ppm. The <sup>6</sup>Li chemical shifts are referenced to (<sup>6</sup>BuLi)<sub>4</sub> at 0.0 ppm. <sup>2</sup>H chemical shifts are relative to TMS by setting the methyl peaks of toluene to 2.2 ppm.

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**Figure 2.** (a) 46-MHz  $^2\text{H}$  NMR spectrum at  $-29^\circ\text{C}$  of a 0.9:1 mixture of  $^t\text{BuOH}/(\text{CD}_3)_3\text{C}^6\text{Li}$  in toluene after exposure to daylight at room temperature. (b) Simulated spectra for the dodecamer at 1.765 ppm and decamer at 1.74 ppm and the resulting sum of the spectra with relative intensities of 1.014:1.0 (dodecamer:decamer).

(PMDTA) $^{17}$  (PMDTA = *N,N,N',N'',N''*-pentamethyldiethylenetriamine;  $\text{cp}^* = \text{C}_5(\text{CH}_3)_5$ ), as well as  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlH}_2\text{Li}\cdot 2\text{Et}_2\text{O}$ . $^{18}$  The  $J(^7\text{Li}, ^1\text{H})$  coupling constants in these complexes are 8.4, 6.4, and 10.5 Hz, respectively. On the basis of the ratio of the magnetogyric ratios of the  $^7\text{Li}$  and  $^6\text{Li}$  isotopes, 2.641, these couplings correspond to  $J(^6\text{Li}, ^1\text{H})$  couplings of 3.2, 2.4, and 4.0 Hz. Thus, the  $J(^6\text{Li}, ^1\text{H})$  values we observed are similar in magnitude.

In addition to the correlations noted above for the *tert*-butoxide groups, a 2D  $^6\text{Li}, ^1\text{H}$  HOESY spectrum revealed that the  $^6\text{Li}$  signal at  $-0.96$  ppm is correlated to a proton resonance at 1.59 ppm, while the  $^6\text{Li}$  signal at  $-1.08$  ppm is correlated to a proton resonance at 1.56 ppm. Selective  $^1\text{H}$  decoupling experiments confirmed that these protons were the source of the observed coupling in the  $^6\text{Li}$  spectrum. While hydride ions in transition metal complexes generally $^{19}$  appear upfield from TMS, $^{17,20}$  main group metal complexes typically resonate downfield from TMS. $^{21}$  IGLO chemical shift calculations $^{16}$  on several LiH-containing model tetrameric and hexameric aggregates predict an even greater downfield shift for LiH/LiOtBu species (shift range: ca. 3.5–4.0 ppm relative to TMS).

Despite these correlations, and confirmation from selective decoupling experiments, no *visible* signals could be identified in this region in the  $^1\text{H}$  NMR spectra in either cyclopentane or toluene. We reasoned that the  $^1\text{H}$  signal might be too small to observe if the hydride ion were incorporated into a fluxional aggregate. However, for samples which contained LiD/LiO $^t$ -Bu aggregates, the signals could be observed in the  $^2\text{H}$  NMR spectrum. The deuteride peak region in the  $^2\text{H}$  NMR spectrum of a mixture of the two LiD/ $^t\text{BuOLi}$  compounds in toluene is shown in Figure 2a. In toluene, the resonances are shifted to 1.74 and 1.765 ppm, respectively. There are clearly two overlapping peaks with the expected couplings of 0.25 Hz (downfield multiplet) and 0.34 Hz. Most noteworthy is the fact that both multiplets clearly contain too many peaks and have the wrong relative intensities to be hexameric or smaller aggregates. The overlapping multiplets are best described as a

downfield 25-line multiplet centered at 1.765 ppm, resulting from coupling to 12 equivalent  $^6\text{Li}$  nuclei, and an upfield 21-line multiplet centered at 1.74 ppm, resulting from 10 equivalent  $^6\text{Li}$  nuclei. A simulation of two such peaks is shown in Figure 2b.

Since (1) the aggregates contain no alkyl groups, (2) the  $^6\text{Li}$  nuclei are coupled to only one hydride, and (3) the hydride proton is coupled to either 10 or 12  $^6\text{Li}$  nuclei, respectively, we assign these aggregates to fluxional aggregates of the form  $(\text{RO})_9\text{HLi}_{10}$  and  $(\text{RO})_{11}\text{HLi}_{12}$ . Such large aggregates for what is primarily lithium *tert*-butoxide was surprising, since lithium *tert*-butoxide in hydrocarbon solvent $^{22}$  and the solid state $^{23}$  is hexameric. X-ray analysis of crystals from this solution has shown a complex mixed aggregate,  $(\text{LiH})_{17}(\text{LiO}^t\text{Bu})_{16}$ . $^{24}$  However, this structure does not appear to be consistent with the solution data. We suspect it is not representative of the solution structures.

Variable-temperature  $^6\text{Li}\{^1\text{H}\}$  NMR spectra for the proton-containing compound are consistent with this explanation. The decamer is a single peak at  $-0.96$  ppm for all temperatures studied,  $-95$  to  $+40^\circ\text{C}$ , although the peak broadens below  $-90^\circ$ . The  $^6\text{Li}$  singlet for the dodecamer at  $-1.08$  ppm broadens below approximately  $-50^\circ$  and is no longer observable below  $-80^\circ$ . Three new broad peaks appear below  $-90^\circ$ , with relative intensities at  $-95^\circ$  of 2.96:4.34:4.7. As noted above and shown in Figure 1b, both the decamer and dodecamer are doublets at higher temperatures without proton decoupling. However, at  $-95^\circ$ , only the most upfield of the three dodecamer peaks is a doublet; the other two dodecamer peaks are very broad singlets. All spectral changes as a function of temperature are reproducible upon raising the temperature. These observations suggest that the decamer is fluxional at all temperatures studied, while the fluxional exchange process of the dodecamer is slowed at low temperature. Although the integration of the three low-temperature dodecamer peaks suggests a structure with three types of nonequivalent lithium atoms in the ratio of 3:4:5, we do not know the structure.

Separate experiments revealed that the two LiH/LiO $^t$ Bu complexes are formed via two different decomposition pathways. Photolysis $^{25}$  of a freshly prepared 0.9:1 *tert*-butyl alcohol/*tert*-butyllithium mixture exclusively yields the decameric aggregate, while heating an identical mixture under exclusion of light leads to the formation of the dodecamer. The photochemically generated decameric aggregate is slowly converted to the dodecamer by heat.

The presence of the hydride ions in these compounds was further confirmed by reacting them with 3,3-dimethyl-2-butanone (pinacolone). The reaction produced the anticipated lithium enolate and hydrogen gas. It is noteworthy that these hydrocarbon soluble LiH aggregates are considerably more reactive than commercially available lithium hydride, which is not capable of deprotonating pinacolone. $^{26a,b}$

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