

# Heats of Lewis base complexation, deaggregation and stabilization by $\alpha$ -silicon in a family of primary alkylolithiums

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For primary alkylolithiums, enthalpies of Lewis base induced tetramer  $\rightarrow$  dimer and dimer  $\rightarrow$  monomer conversion, intramolecular Li–NMe<sub>2</sub>R complexation and stabilization by  $\alpha$ -SiMe<sub>2</sub>R are given.

Any understanding and control of  $\sigma$ -organolithium (RLi) reactivity requires extensive knowledge of each of the various forms in which RLi's occur: aggregates R<sub>m</sub>Li<sub>m</sub> ( $m = 2, 4, 6$ ), complexes of aggregates with Lewis bases [LB (R<sub>2</sub>O, R<sub>3</sub>N)] R<sub>m</sub>Li<sub>m</sub> $\cdot$  $n$ LB ( $m, n = 2, 4; 4, 1-4$ ) and, in relatively rare cases, monomer complexes RLi $\cdot$  $n$ LB ( $n = 2, 3$ ).<sup>1</sup> Nevertheless, fundamental data, such as enthalpies of transfer of RLi from one aggregation state into another, are scarce: BuLi/THF,  $\Delta H$ (complexed tetramer  $\rightarrow$  complexed dimer)  $\approx -2$  kJ (mol RLi)<sup>-1</sup>;<sup>2</sup> Bu<sup>t</sup>Li/cyclopentane–Et<sub>2</sub>O,  $\Delta H$ (uncomplexed tetramer  $\rightarrow$  complexed dimer)  $\approx -38$  kJ (mol RLi)<sup>-1</sup>;<sup>3</sup> neopentylolithium/Et<sub>2</sub>O,  $\Delta H$ (complexed dimer  $\rightarrow$  complexed monomer)  $\approx -3$  kJ (mol RLi)<sup>-1</sup>.<sup>1</sup> For a family of intramolecularly amine-complexed (trimethylsilyl)methylolithium derivatives LiCH<sub>2</sub>Si(Me)<sub>2</sub>CH<sub>2</sub>-Z (**1–3**, Z = N(CH<sub>2</sub>X)CH<sub>2</sub>Y, see Fig. 1)<sup>4</sup> and for the parent (trimethylsilyl)methylolithium (**4**, Z = H),<sup>5</sup> we now present relative stabilities of exhaustively complexed monomer, dimer and tetramer, respectively, as well as uncomplexed tetramer. Inclusion in our study of 3-(dimethylamino)propyllithium (**5**),<sup>6</sup> the analogue of **3** in which SiMe<sub>2</sub> is replaced by CH<sub>2</sub>, provided a measure of RLi stabilization by  $\alpha$ -silicon.

In Fig. 1, heats of protonation of **1–5** by Bu<sup>s</sup>OH [ $\Delta H$ , kJ (mol RLi)<sup>-1</sup>, benzene, 25 °C]‡ are given together with the monomer

(**1**), dimer (**2**) and tetramer [**3**<sub>4</sub>, **4**<sub>4</sub>, **5**<sub>4</sub> (a : b = 6 : 4)] structures in which **1–5** prevail under the conditions of experiment.

The protonation products (H–R, Fig. 1) of **1–5** are assigned equal relative enthalpies since they are devoid of special interactions.§ On this basis, negative differences of heats of protonation equal differences of relative enthalpies (stabilities) of RLi species. We also assume that in **1–4**, variation of Z is of minor influence, if at all, on the nature of C–Li.¶ Thus,  $\Delta H(\mathbf{3}_4) - \Delta H(\mathbf{2}_2) \approx -19$  kJ (mol RLi)<sup>-1</sup> indicates that for type-4 RLi species, amine complexation induced deaggregation of complexed tetramer into dimer is of considerable exothermicity. Further deaggregation of complexed dimer into monomer is nearly thermoneutral:  $\Delta H(\mathbf{2}_2) - \Delta H(\mathbf{1}) \approx -2$  kJ (mol RLi)<sup>-1</sup>.  $\Delta H(\mathbf{4}_4) - \Delta H(\mathbf{3}_4) \approx -40$  kJ (mol RLi)<sup>-1</sup> gives the average strength of an N–Li bond in a tetrameric type-4 RLi complexed by four NMe<sub>2</sub>-type nitrogens.||  $\Delta H(\mathbf{5}_4) - \Delta H(\mathbf{3}_4) \approx -57$  kJ (mol RLi)<sup>-1</sup> provides an experimental measure of the practically<sup>8</sup> and theoretically<sup>9</sup> important carbanion stabilization by silicon. Parenthetically, the close similarity of  $\Delta H(\mathbf{5}_4)$ ,  $-193$  kJ (mol RLi)<sup>-1</sup>, and  $\Delta H$  of tetrameric 3-methoxypropyllithium under the same conditions [ $-190$  kJ (mol RLi)<sup>-1</sup>]<sup>10</sup> testifies to the very similar lithium complexation propensities of –OMe and –NMe<sub>2</sub>.

The energetics found in this study for LB induced tetramer  $\rightarrow$  dimer and dimer  $\rightarrow$  monomer conversion, respectively, are in accord with the results of quantum mechanical calculations on MeLi which indicate the latter to be rather more difficult,<sup>11</sup> although, as the present and the previous experiments show, actual values depend on the nature of R and LB (*cf.* ref. 1). Likewise, as expected,<sup>9</sup> the value found for the energy of stabilization of tetrameric primary RLi by  $\alpha$ -SiMe<sub>2</sub>R [57 kJ (mol RLi)<sup>-1</sup>] is in between those calculated<sup>9</sup> for LiCH<sub>2</sub>SiH<sub>3</sub> (39 kJ mol<sup>-1</sup>) and for –CH<sub>2</sub>SiH<sub>3</sub> (104 kJ mol<sup>-1</sup>). The similarity found for –OMe and –NMe<sub>2</sub> as complexing groups of RLi agrees with the very similar capacities of R<sub>2</sub>O and R<sub>3</sub>N for acceleration of RLi reactions<sup>12</sup> and suggests that the above amine data also approximate those for ethers.

## Notes and References

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‡ Ca.  $8 \times 10^{-4}$  mol dm<sup>-3</sup>; 3–5 measurements per compound; calorimeter: ref. 7.

§ <sup>29</sup>Si NMR of **1** and **2** (H instead of Li) did not indicate N–Si bonding.

¶ This assumption is based on our finding<sup>6</sup> that the C<sub>4</sub>Li<sub>4</sub> cores of **5**<sub>4</sub>a and Et<sub>4</sub>Li<sub>4</sub> are practically the same, *i.e.* introduction of and intramolecular complexation by  $\gamma$ -NMe<sub>2</sub> does not affect C–Li.

|| The first LB unit is bonded more strongly to lithium than the following ones.<sup>5,11</sup>

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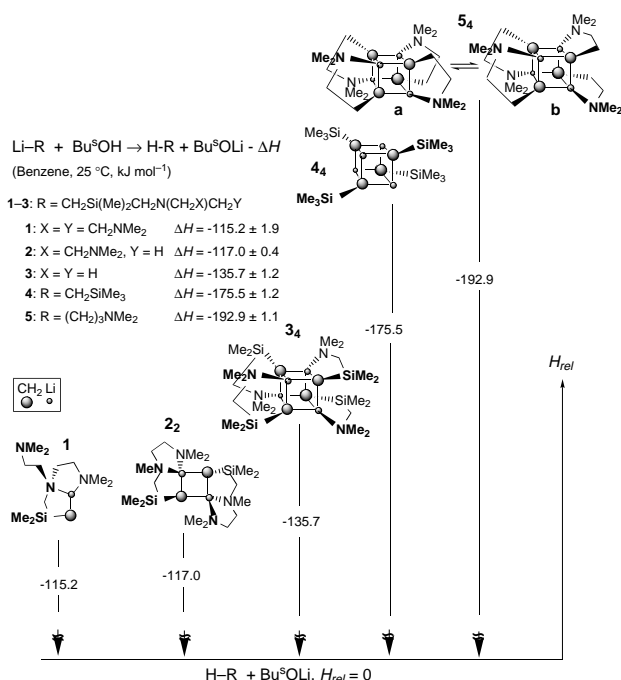


Fig. 1 Heats of protonation by Bu<sup>s</sup>OH [ $\Delta H$ /kJ (mol RLi)<sup>-1</sup>, vertical arrows] and relative stabilities [ $H_{rel}$ /kJ (mol RLi)<sup>-1</sup>]

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