J. Am. Chem. Soc. **1995**, *117*, 4179−4180

Lewis Base Complexation, Aggregation, and Reactivity of σ-Organolithiums. Significance of Fractional Reaction Orders in RLi

H. Luitjes, F. J. J. de Kanter, M. Schakel, R. F. Schmitz, and G. W. Klumpp*

Scheikundig Laboratorium, Vrije Universiteit
1081 HV Amsterdam, The Netherlands

Received November 16, 1994
Revised Manuscript Received February 8, 1995

Study of the intramolecularly amine-complexed ((trimethylsilyl)methyl)lithium derivatives **1**−**3**[1] which, according to their NMR spectra,[2] occur in hydrocarbon solvents as tetramer $\mathbf{1}_4$, dimer $\mathbf{2}_2$, and, depending on temperature, either monomers **3a** and **3b** or dimer $\mathbf{3}_2$, has shown that (1) Li−N bond energies decrease in the order $\mathbf{1}_4$, $\mathbf{2}_2$, **3a**, (2) rates of deprotonation of triphenylmethane (TPM) increase in that order, and (3) experimental reaction orders in **1**, **2**, and **3** are fractional, suggesting complexes $\mathbf{1}_2$·TPM, $\mathbf{2}_2$·TPM, and **3**·TPM as the reacting species.

$LiCH_2Si(Me)_2CH_2N(CH_2X)CH_2Y$

1: X = Y = H **2**: X = CH_2NMe_2, Y = H **3**: X = Y = CH_2NMe_2 **4**: $LiCH_2SiMe_3$

Cryoscopy in benzene ascertained the presence of monomeric species **3a** and/or **3b** as the source of the 1:1:1 triplet (−8.31 ppm, pentane) observed in the ^{13}C NMR of **3**-^{6}*Li* at 210 K. Cooling to 153 K converts the triplet into a quintet (−8.60 ppm) stemming from $\mathbf{3}_2$-$^6Li_2$. Since chemical shifts of **3** are practically the same as those exhibited by $\mathbf{3}_2$ (the dimer of **3b**), we assume (encouraged by MNDO calculations)[3] that the proportion of **3b** in hydrocarbon solutions of **3** is considerable and that breaking of a Li−NMe_2 bond in **3a** is about thermoneutral. Rapid equilibration of **3a** and **3b** *plus* fast inversion of NMe_2 nitrogen in **3b** is indicated by the occurrence of a single ^{13}C resonance for *Si*- and *N*-methyl, respectively. Exchange of diastereotopic NMe_2 methyl groups in $\mathbf{2}_2$ ($\rightarrow \mathbf{2}_2$*) occurs through inversion of the free nitrogen in **5**.[4] From four coalescence temperatures of NMe_2 NMR signals were obtained activation parameters for $\mathbf{2}_2 \rightarrow \mathbf{2}_2$* ($\Delta H^{\ddagger} = 54 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = 14 \pm 15$ J K^{-1} mol^{-1}, $r = 0.996$). On the assumptions that the barrier of inversion of nitrogen in **5** is similar to that of trimethylamine ($\Delta H^{\ddagger} = 35$ kJ mol^{-1})[5] and that the enthalpy of activation of Li−N bond breaking in $\mathbf{2}_2$ is smaller than 54 kJ mol^{-1}, a maximum value of *ca.* 20 kJ mol^{-1} is derived for the strength of the Li−N bond broken ($\mathbf{2}_2 \rightarrow \mathbf{5}$). The Li−N bond strength in $\mathbf{1}_4$ is estimated as ≥40 kJ mol^{-1}.[6]

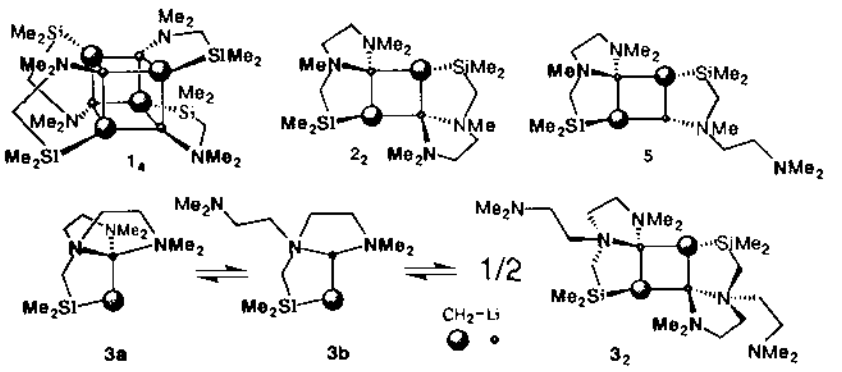


Table 1. Experimental Reaction Orders in $[RLi]_{i,f}$ (x) for **1**−**3** and Relative Rates of Lithiation of TPM by **1**−**4** in Benzene at 23 °C

RLi		exptl reactn order in $[RLi]_{i,f}$ (x)	correlatn coeff	rel rate	
				10^{-3} M[a]	1 M[a]
1	tetramer	0.34	0.982	1	10
2	dimer	0.84	0.993	139	43500
3	monomer	0.59	0.995	3950	215000
4	tetramer[b]	c	c	0.03[d]	

[a] $[RLi]_{i,f}$. [b] Reference 9. [c] Not determined. [d] At $[\mathbf{4}]_{i,f} = [\mathbf{1}]_{i,f} = 0.06$ M.

We propose the decrease of Li−N bond energies in the order $\mathbf{1}_4 > \mathbf{2}_2 >$ **3a** to be a consequence of *Lewis base (LB) assistance of changes in Li−LB (Li−C) bonding*: in coordinatively saturated dimers[7] and monomers of σ-RLi, LB molecules remaining bonded to lithium {LB−Li(1)}, by binding themselves more strongly, compensate for (part of) the bond energy lost upon dissociation of one of their congeners (or by weakening of Li(1)···C in a reaction transition state).[8]

The reactivities of **1**−**3** are assumed to depend (nearly) solely on the mode of aggregation; *i.e.*, the relative reactivities of $\mathbf{1}_4$, $\mathbf{2}_2$, and **3** toward TPM are considered to portray those of different amine-complexed aggregates of 4:[9] $\mathbf{4}_4$·4NMe$_3$, $\mathbf{4}_2$·4NMe$_3$, and 4·3NMe$_3$ ⇌ 4·2NMe$_3$ + NMe$_3$, respectively, and, to some degree, those of $(RCH_2)_mLi_m \cdot nLB$ (*m*, *n*: 4, 4; 2, 4; 1, 3 or 2) in general.

In benzene, initial rates of lithiation of TPM, first-order in the latter, were measured for excess **1**, **2**, and **3**, respectively, by following the increase of absorption by (triphenylmethyl)lithium at 450 nm.[10] Plotting of $\log(\text{rate}/[TPM])_{\text{initial}}$ against $\log\ [RLi]_{\text{formal,initial}}$ (see eq 1) gave reaction orders in $[RLi]_{\text{formal,initial}}$ (x) as the slopes of the lines. They are given, together with the relative rates, in Table 1. The low reactivity of the LB-free parent 4 permitted only a single rate to be measured at the highest concentration at which it still prevails as tetramer.[9]

$$\log \text{rate}_i = x \log\ [RLi]_{i,f} + \log\ [TPM]_i + \log k_{\text{exp}} \qquad (1)$$

i, initial; f, formal organolithium concentration as
obtained by titration with acid

Concentration dependent relative rates increase upon decrease of the degree of aggregation, the change from dimer to monomer being less than that from tetramer to dimer. The relative rates of **1** and **4** testify to intra-aggregate Me$_2$N assistance of Li−C bond breaking in the former. Often, fractional reaction orders ($x \approx 1/m$) in RLi ($\equiv R_mLi_m \cdot nLB$) are assumed to indicate that nonobservable amounts of monomers are the reactive species.[11] Alternatively, Brown suggested that substrate and organolithium aggregate produce a complex whose conversion into product determines the rate (eqs 2 and 3).[12] Values of x depend on complexation constants K_c and on concentrations; roughly: $x \approx 0.1$, relatively high fraction of substrate present as complex; $x \approx 1$, very low fraction of substrate present as complex.

---

(1) **1**−**3** were obtained by lithiation (*sec*-BuLi, pentane) of the corresponding methane derivatives.

(2) *Cf.*: Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.

(3) MNDO indicates **3b** to be more stable than **3a** by 3 kJ mol^{-1}. Hindrance originating from the NMe$_2$ groups seems causative. For the more crowded analog of **3**, neopentyllithium·PMDTA (PMDTA = pentamethyldiethylenetriamine), bidentate complexation of PMDTA is calculated to be more favorable than tridentate complexation by not less than 30 kJ mol^{-1}. Bidentate complexation has also been considered for mesityllithium·PMDTA.[2]

(4) Under the conditions of rapid exchange of NMe$_2$ methyl groups on the ^{13}C NMR time scale (295 K), the $^6Li-^{13}C$ coupling and the diastereotopicity of the *Si*-methyl groups are maintained, indicating that the Li_2C_2 skeleton is essentially unchanged.

(5) Weston, R. E., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2645.

(6) Heat of intra-aggregate Li−OMe complexation in $(CH_3CHLiCH_2CH_2OMe)_4$: Klumpp, G. W.; Geurink, P. J. A. *J. Am. Chem. Soc.* **1986**, *108*, 538. In this system, the strength of binding of NMe$_2$ to lithium is the same as that of OMe: Vos, M. Dissertation Vrije Universiteit Amsterdam, 1989. Due to the primary nature of the carbanion, Li−N bonding in $\mathbf{1}_4$ may be stronger than in $(CH_3CHLiCH_2CH_2OMe)_4$.

(7) Vos, M.; de Kanter, F. J. J.; Schakel, M.; van Eikema Hommes, N. J. R.; Klumpp, G. W. *J. Am. Chem. Soc.* **1987**, *109*, 2187.

(8) Proposed LB assistance in reactions of alkyllithium tetramers: (a) Kaufmann, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560. (b) Hay, D. R.; Song, Z.; Smith, S. G.; Beak, P. *J. Am. Chem. Soc.* **1988**, *110*, 8145.

(9) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664.

(10) Lithiation of TPM by several organolithiums in THF: West, P.; Waak, R.; Purmont, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 840.

(11) For listing, see: Schlosser, M. *Struktur und Reaktivität Polarer Organometalle*; Springer Verlag: Berlin, 1973; p 131.

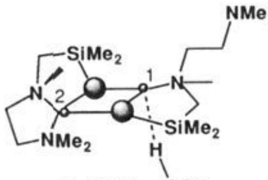
(12) Brown, T. L. *J. Organomet. Chem.* **1966**, *5*, 191; *Adv. Organomet. Chem.* **1965**, *3*, 365.

0002-7863/95/1517-4179$09.00/0

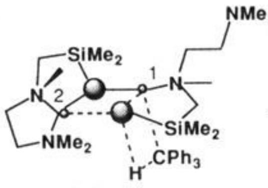
$$\mathrm{R}_m\mathrm{Li}_m\cdot n\mathrm{LB} + \text{substrate} \overset{K_c}{\rightleftharpoons} \underset{\text{complex}}{\text{substrate}\cdot\mathrm{R}_m\mathrm{Li}_m\cdot(n-1)\mathrm{LB}} \xrightarrow{k} \text{product} \quad (2)$$

$$\text{rate}_\mathrm{i} = k[\text{complex}]_\mathrm{i} \quad (3)$$

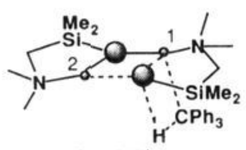
While the reaction order of $\mathbf{1}_4$ is close to that expected for operation of monomer ($x = 0.25$), that of $\mathbf{2}_2$ is incompatible with predissociation for which x would have to be 0.5 or less. Most salient is the finding of a fractional reaction order ($x = 0.59$) for **3** which in no way can dissociate into smaller entities. Involvement of complexes **3**·TPM and $\mathbf{2}_2$·TPM in the rate-determining steps accounts for the reaction orders of **2** and **3** (fractional) and that of TPM (1). Such complexes must be more stable than benzene solvates of alkyllithiums, for, if TPM and benzene would be complexed similarly, the large excess of the latter would cause concentrations of TPM complexes to be so low as to result in $x = 1$. Lithium−hydrogen coordinated structures, *e.g.*, $\mathbf{2}_2$·TPM, are speculative, but we see little choice.[13] Stronger bonding of the nitrogen still ligated to Li(1) in $\mathbf{2}_2$·TPM can compensate for the weak Li•••H−C bonding.[14]



$\mathbf{2}_2$·TPM



$\mathbf{2}_2$·TPM‡



$\mathbf{1}_2$·TPM‡

Having indications that 1:1 complexes, whatever their true structures, intervene in the reactions of $\mathbf{2}_2$ and **3** with TPM, we saw no reason why the less reactive $\mathbf{1}_4$ should behave radically otherwise, *i.e.*, react through energetically unfavorable monomer.[16] Values (M^{-1}) of K_c (eq 2), which, on plotting log([complex]/[TPM])$_{\mathrm{i},K_c}$ *vs* log [RLi]$_{\mathrm{i,f}}$ (eq 4), give slopes that equal the experimental x, are 40 (**3**), 17 ($\mathbf{2}_2$), 65 ($\mathbf{1}_4$).

$$\log([\text{complex}]/[\text{TPM}])_\mathrm{i} + \log k = x \log\,[\mathrm{RLi}]_{\mathrm{i,f}} + \log k_{\exp} \quad (\equiv \log(\text{rate}/[\text{TPM}])_\mathrm{i}) \quad (4)$$

However, a complex $\mathbf{1}_4$·TPM could not be detected by cryoscopy.[17] In hindsight, a reason for its instability can be given: After replacement of N by TPM on $\mathbf{1}_4$, no nitrogen, able to compensate for the weak Li•••H−C bonding, would be present on the lithium involved. To explain the reaction order of $\mathbf{1}_4$, we propose dissociation of $\mathbf{1}_4$ to dimer $\mathbf{1}_2$, which can profit from strengthening of the Li−N bonds.[18] As the actual reactive species, $\mathbf{1}_2$ binds TPM at one of its unoccupied coordination sites (Scheme 1).

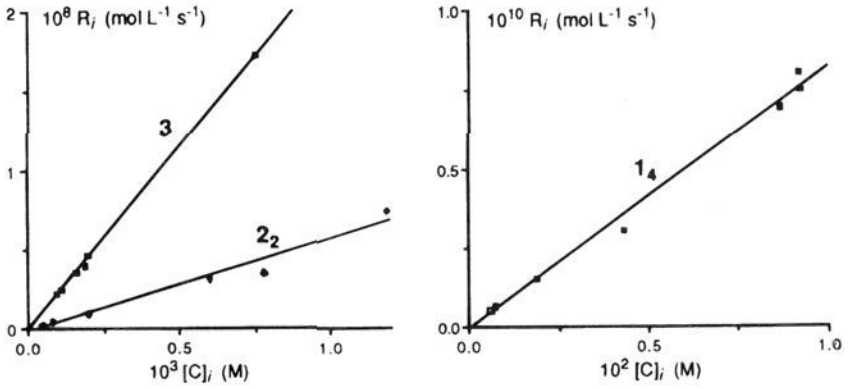


Figure 1. Plots of experimental initial rates of formation of LiCPh$_3$ (R_i) *vs* calculated initial concentration of TPM complex ([C]$_\mathrm{i}$): **3**, $R_\mathrm{i} = 2.30 \times 10^{-5}[\mathrm{C}]_\mathrm{i}$, $r = 0.999$; $\mathbf{2}_2$, $R_\mathrm{i} = 6.14 \times 10^{-6}[\mathrm{C}]_\mathrm{i}$, $r = 0.982$; $\mathbf{1}_4 \rightleftharpoons 2\mathbf{1}_2$, $R_\mathrm{i} = 8.37 \times 10^{-9}[\mathrm{C}]_\mathrm{i}$, $r = 0.995$.

Scheme 1

$$\mathbf{1}_4 \overset{K_d}{\rightleftharpoons} 2\mathbf{1}_2$$

$$\mathbf{1}_2 + \text{TPM} \overset{K_c}{\rightleftharpoons} \text{complex} \xrightarrow{k} \text{products}$$

Equilibrium constants for Scheme 1 were found ($K_d = 1.6 \times 10^{-6}$ M, $K_c = 1.7 \times 10^3$ M^{-1}) giving [complex]$_{\mathrm{i},K_d,K_c}$ which, on plotting of log([complex]/[TPM])$_{\mathrm{i},K_d,K_c}$ *vs* log [RLi]$_{\mathrm{i,f}}$ (eq 4), led to a straight line whose slope, 0.34, equaled the experimental value of x.[19]

Plots of calculated [complex]$_\mathrm{i}$ for $\mathbf{1}_4 \rightleftharpoons 2\mathbf{1}_2$, $\mathbf{2}_2$, and **3** *vs* the experimental initial rates (R_i) are shown in Figure 1. The slopes give the rate constants of the TPM complexes (*cf.* eq 3). Statistically corrected relative rate constants are $\mathbf{1}_2$·TPM, 1; $\mathbf{2}_2$·TPM, 700; **3**·TPM, 5500.

LB assistance of changes in Li−C bonding accounts for the relative reactivities: In $\mathbf{2}_2$·TPM‡, breaking of two partial C−Li bonds can be assisted by three nitrogens complexed to lithiums 1 and 2, while only two such nitrogens are available in $\mathbf{1}_2$·TPM‡. Origins of the relatively small difference in rate derived for $\mathbf{2}_2$·TPM and **3**·TPM are unclear. If **3**·TPM were to contain two Li−NMe$_2$ bonds, steric factors could impede deployment of the full potential for assistance. If it were to contain only one (substitution of NMe$_2$ on **3b** by TPM), NMe$_2$ could bind so strongly that the assistance to be gained were slightly higher than that provided by three nitrogens acting on two partial C−Li bonds in $\mathbf{2}_2$·TPM.

In conclusion, on the basis of our results with **1**−**3**, the following suppositions are proffered with regard to R$_m$Li$_m$·nLB systems:[21] (1) smaller coordinatively saturated aggregates lose LB more easily, because they contain more LB able to provide assistance; (2) fractional reaction orders of RLi (also observed in LB-free systems)[11] are indicative of aggregate−substrate complexes, those of the coordinatively saturated smaller aggregates reacting faster because of more extensive LB assistance; (3) predissociation of tetramer to dimer could be a prerequisite of complex formation for substrates that are weak donors like TPM, but may not be needed for strong donor substrates.[8b]

Supplementary Material Available: Tables of ^{1}H, ^{13}C, and ^{6}Li NMR spectral data of $\mathbf{1}_4$, $\mathbf{2}_2$, **3a/b**, and $\mathbf{3}_2$, DNMR data of $\mathbf{2}_2$, graph of log(rate/[TPM])$_{\text{initial}}$ against log [RLi]$_{\text{formal,initial}}$ and table of initial rates and initial concentrations of reactants used, and derivation of relationship between K_c and x (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA943709C

---

(13) For discussions of many cases of LiM•••H−C coordination in R$_m$Li$_m$, see: Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. A referee suggested that TPM might complex bidentately through two of its phenyl rings. We had rejected this idea earlier, because it does not tally with the easy lithiation of fluorene (Casling, R. A.; Evans, A. G.; Rees, N. H. *J. Chem. Soc. B* **1966**, 519).

(14) Changes of entropy upon formation of loose complexes may be quite small (−40 to −80 J K^{-1} mol^{-1}).[15] In the case of $\mathbf{2}_2 \rightarrow \mathbf{2}_2$·TPM, they will be counteracted by the entropy of opening of a five-membered ring (50 J K^{-1} mol^{-1}).[15]

(15) *Cf.*: Page, M. I. *Chem. Soc. Rev.* **1973**, *2*, 295.

(16) . For the addition of n-Bu$_6$Li$_6$ to 1,1-diphenylethylene, for which the reaction order ($x = {}^1/_6$) suggests operation of monomer, $\Delta G^{\ddagger}$(300 K) is only 100 kJ mol^{-1} (Evans, A. G.; George, D. B. *J. Chem. Soc.* **1961**, 4653), while, on the basis of calculations on methyllithium (Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 1597), formation of monomer is expected to require at least 218 kJ mol^{-1}.

(17) Nor could evidence of $\mathbf{1}_4$·TPM be obtained by NMR and UV spectroscopy, respectively. Analogous experiments were impossible with $\mathbf{2}_2$·TPM and **3**·TPM, due to the fast reactions of these systems.

(18) Some support for the viability of $\mathbf{1}_2$ comes from the occurrence of $[\mathbf{1}_2]^{\bullet+}$ (0.30%) and $[\mathbf{1}_2 - \mathrm{Me}]^{\bullet+}$ (0.36%) in the mass spectrum of **1** (293 K, 70 eV), while fragmentation patterns characteristic of $\mathbf{4}_4$ (Hartwell, G. E.; Brown, T. L. *Inorg. Chem.* **1966**, *5*, 1257) are lacking (B. L. M. van Baar, to be published).

(19) Analogs of Scheme 1 could explain values of x around 1/m of other organolithium reactions[10,11] where a reagent−substrate complex was undetectable[20] and which, for these reasons, were supposed to proceed through monomer.

(20) Smith, S. G.; Charbonneau, L. F.; Novak, D. P.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 7059.

(21) For an overview, also containing references to our earlier work along the present lines: Schmitz, R. F.; de Kanter, F. J. J.; Schakel, M.; Klumpp, G. W. *Tetrahedron* **1994**, *50*, 5933.