Reactivity of Ether- and Amine-Complexed Dimers and Tetramers of Alkyllithiums towards Triphenylmethane

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Abstract: Kinetics of Lewis base (LB) complexed primary and secondary σ-alkyllithiums (RLi) with triphenylmethane (TPMH) are reported. RLis in which one or two LB groups (−OMe, −NMe₂, −NMeR) are part of the molecule form, in benzene, intramolecularly complexed tetramers, for example, **2₄**, or dimers, for example, **4₂**. They are used as models for their intermolecular congeners $R_4Li_4 \cdot 4LB$ and $R_2Li_2 \cdot 4LB$ (LB = NR′₃, OR′₂). Nonunity reaction orders in [RLi] are in line with reactions via as yet unidentified 1:1 complexes formed in an equilibrium (K(stat. corr.) ≈ 1) between aggregated RLi and TPMH. In some cases, a tetramer/dimer equilibrium mixture undergoes complexation/reaction. Reaction rates correlate linearly with calculated concentrations of the complexes. Relative rates of complexes range from 1 [$prim$-$R_4Li_4 \cdot 3LB \cdot$ TPMH (presumed)] to 4250 [sec-$R_2Li_2 \cdot 3LB \cdot$ TPMH (presumed)]. A major role in the reactivity enhancement owing to LB-induced conversion of tetramers into dimers is ascribed to increased LB participation in LB-richer dimer transition states. Amine and ether complexes have practically equal reactivities. Lithiation of TPMH by dimeric RCH₂Li is retarded by a factor of 24000 if a silyl group is linked to the α-carbon.

Keywords: aggregation · kinetics · lithiation · precomplexes · triphenylmethane

Introduction

Despite the importance of σ-organolithiums (RLi) in organic and organometallic chemistry,[1] detailed knowledge of the origins of their multifarious modes of reaction is scant as a result of a characteristic feature of these reagents. In the presence of Lewis bases [LB (ethers, tertiary amines)], which are frequently used to activate RLis, these occur as mixtures of complexes $R_mLi_m \cdot n$ LB (m,n: 4, 1–4; 2, 4; 1, 2 or 3).[2] If, as is often the case, the rates with which equilibria between these species are established are faster than the reaction under investigation, the individual contributions of the various species to the reaction rate,[3] and the chemo-,[5] regio- and stereoselectivity,[6] which are needed for any thorough understanding of RLi reactivity (and its control!), cannot be determined, since the proportions of the various complexes in the mixture are constant throughout the experiment. To avoid this impediment, we are studying RLis with *intramolecular* LB complexation. In most cases, these prevail in hydrocarbon solvents as a single type of aggregate, whose size depends on the steric bulk of R and on the ratio LB:Li. Thus, the primary

RLis **1**–**3** (LB:Li = 1), **4** and **9** (LB:Li = 2)[7] occur exclusively as equilibrating D_2- and S_4-type tetramers **1₄**–**3₄**, **4₄** and **9₄** (the last two with only four of their eight LB groups complexed to lithium), while the secondary RLis **6**–**8** (LB:Li = 2) form dimers (**6₂**–**8₂**). Only the secondary RLi **5** (LB:Li = 1) is present as a 7.5:1 mixture of S_4-type tetramers **5₄** and of dimers whose structure we presume to be **5₂** (Figure 1). With respect to C−Li and Li···LB bond properties, and the reactivities arising from them, we consider these oligomers of **1**–**9** as models of the tetraaminates and tetraetherates of the tetramers and dimers of synthetically important RLis, such as, nBuLi (**10**), sBuLi[2e] and neopentyllithium[2f] (e.g., **10₄** · 4 THF, **10₂** · 4 THF,[2c, 3a,c, 8] Figure 1), which cannot be studied individually as a result of the above-mentioned dynamics of RLi/LB systems.

We now report on the kinetics of **1**–**9**, dissolved in benzene, with triphenylmethane (TPMH). Lithiation of TPMH, one of the simplest RLi reactions, was studied extensively by Waak and co-workers for a variety of RLis in THF.[3a] Primary kinetic isotope effects (k_H/k_D(**10**) = 8.9) established proton transfer as the rate-determining step.[9] Effective reaction orders in formal (i.e., titrimetric) organolithium concentration [RLi]f were around 0.25 for MeLi and vinyllithium and were attributed to reversible dissociation of $R_4Li_4 \cdot 4$THF into the monomer, which is assumed to be the most reactive species. The value found for **10**, 0.33, was thought to arise from contributions of the monomer reaction and of one-step

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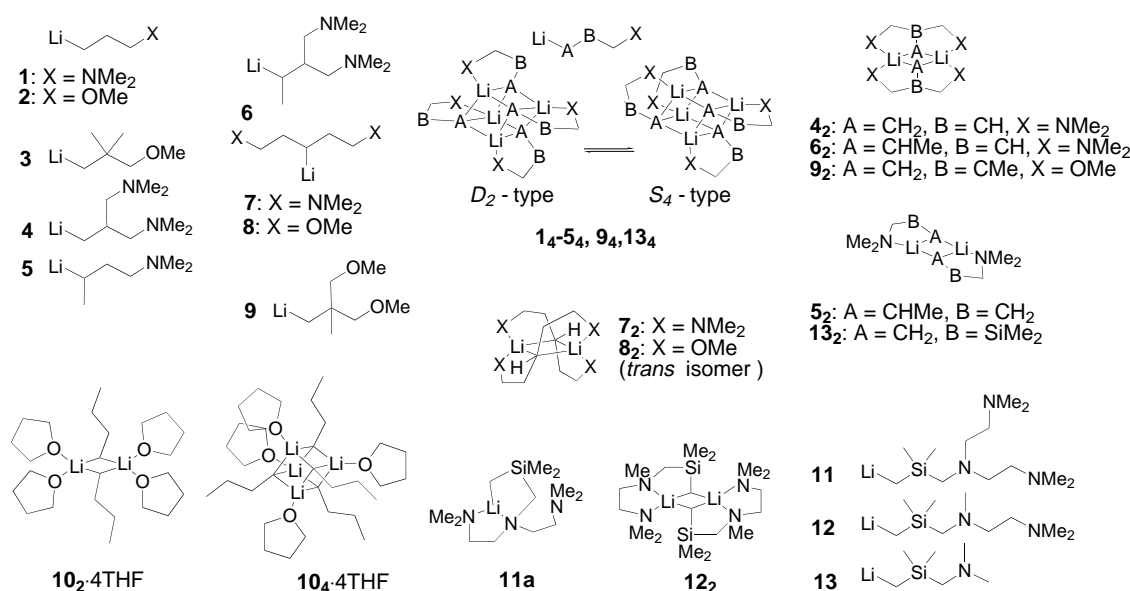Fax: (+31) 20-4447488
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Figure 1. RLis studied and/or discussed in the present work. Structures and modes of aggregation.

reactions between TPMH and solvated aggregates $10_2 \cdot 4\,THF$ and/or $10_4 \cdot 4\,THF$.[3a]

Recently, we have studied the lithiation of TPMH by intramolecularly amine-complexed (trimethylsilyl)-methyllithium derivatives $LiCH_2SiMe_2CH_2-Z$ ($Z = N(CH_2CH_2NMe_2)_2$, **11**; $N(Me)CH_2CH_2NMe_2$, **12**; NMe_2, **13**)[10] that occur in the solvent used, benzene, as monomer **11a**, dimer 12_2 and tetramer 13_4 (Figure 1). At $[RLi]_f = 0.5\,M$, relative reaction rates were 2×10^4, 3×10^3 and 1, effective reaction orders in $[RLi]_f$ were 0.59, 0.83 and 0.34, respectively.

Assuming that in $LiCH_2SiMe_2CH_2-Z$ variation of Z does not affect the intrinsic properties of the $Li-CH_2$ bond,[11] we ascribe the relative rates of **11 – 13** to differences in complexation and aggregation. The reaction order of **11** (0.59) is most illuminating. Commonly, predissociation of R_mLi_m ($R_mLi_m \cdot n\,LB$) is considered to be the cause of nonunity reaction orders in $[RLi]_f$ (see above). An alternative explanation [mechanism 1] was first promulgated by T. L. Brown: formation, in a pre-equilibrium between R_mLi_m ($R_mLi_m \cdot n\,LB$) and substrate (e.g., TPMH), of a complex [$C(m,TPMH)$; Eqs. (1a), (1b)] that is subsequently converted to product in the rate-determining step [Eqs. (2a), (2b), $r = $ rate].[12]

Mechanism 1

$$R_mLi_m \cdot n\,LB + TPMH \xrightleftharpoons{K_m} C(m,TPMH) \tag{1a}$$

$$K_m = \frac{[C(m, TPMH)]}{[R_mLi_m \cdot n\,LB][TPMH]} \tag{1b}$$

$$C(m,TPMH) \xrightarrow{k_m} TPMLi \tag{2a}$$
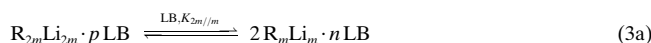
$$r = k_m[C(m,TPMH)] \tag{2b}$$

Depending on the values of K_m and the concentrations of the reaction partners, the effective reaction order in $[RLi]_f$ can have any value between 1 (negligible complexation of substrate) and zero (complete complexation of substrate).[13] Formation of complexes has recently been proven in several

RLi reactions.[5b, 14] As dissociation of monomer **11** into smaller particles is excluded, the finding of a nonunity reaction order can only be attributed to formation of a complex between **11** and TPMH (mechanism 1, $K_m = 40$). However, direct evidence of such a complex is still lacking.[10]

Operation of mechanism 1 is also assumed to be the cause of the reaction order (0.83, $K_m = 17$) of **12**. If, in a family of reagents, the most reactive member (**11**) enters into reaction only after having formed a complex with the substrate, it is unlikely that a less reactive one (**12**) would be able to react directly.[15] By contrast, the reaction order of **13** (0.34) was taken to indicate operation of a more extended mechanism [mechanism 2], in which formation of the reactive complex [Eqs. (1a), (1b), (3b)] takes place after predissociation of a prevailing larger oligomer ($R_{2m}Li_{2m} \cdot p\,LB$, i.e., 13_4) into a smaller one [$R_mLi_m \cdot n\,LB$, i.e., 13_2; Eq. (3a), $m = n = 2$; $p = 4$].

Mechanism 2

$$R_{2m}Li_{2m} \cdot p\,LB \xrightleftharpoons{LB, K_{2m//m}} 2\,R_mLi_m \cdot n\,LB \tag{3a}$$

$$R_mLi_m \cdot n\,LB + TPMH \xrightleftharpoons{K_m} C(m,TPMH) \tag{1a}$$

$$K_m = \frac{[C(m, TPMH)]}{[R_mLi_m \cdot n\,LB][TPMH]} \tag{1b}$$

$$K_m^2 K_{2m//m} = \frac{[C(m, TPMH)]^2}{[R_{2m}Li_{2m} \cdot p\,LB][TPMH]^2} \tag{3b}$$

$$C(m,TPMH) \xrightarrow{k_m} TPMLi \tag{2a}$$
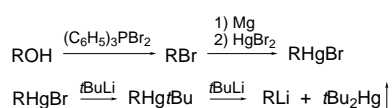
$$r = k_m[C(m,TPMH)] \tag{2b}$$

The present work extends these studies to analogues of synthetically important RLis. In benzene, intramolecular LB complexation provides for the presence of well-defined species. The questions dealt with concern effective reaction orders, precomplexation and mechanism, relative reactivities of tetrameric and dimeric RLis, both for primary and

secondary R, influences on reactivity of the nature of LB (NR$_2'$ vs. OR$_2'$) and of the ratio LB:Li, and the theoretically[16] and practically[17] important effect on rate of α-silicon.

Results

Lithium compounds: X-ray and/or spectroscopic data and colligative properties that together establish the structures in which **1**, **2**, **6**, **8** and **9** prevail have been published.[7] Compounds **3–5** and **7**, like all other RLis used in this study, were prepared by the procedure shown in Scheme 1. Alcohols were converted into alkyl-*tert*-butyl mercury compounds (RHg*t*Bu) via their bromides, Grignard compounds and alkyl mercuric bromides. Treatment of RHg*t*Bu with one equivalent of *t*BuLi gave RLi and *t*Bu$_2$Hg, which was removed by evacuation. The RLis were then dissolved in benzene and sealed under vacuum.

$$ROH \xrightarrow{(C_6H_5)_3PBr_2} RBr \xrightarrow[\text{2) HgBr}_2]{\text{1) Mg}} RHgBr$$

$$RHgBr \xrightarrow{t\text{BuLi}} RHgt\text{Bu} \xrightarrow{t\text{BuLi}} RLi + t\text{Bu}_2\text{Hg} \downarrow$$

Scheme 1. Preparation of lithium compounds.

The identities of **3–5** and **7** were determined from their NMR spectra and the products of quenches with Me$_3$SnCl, benzaldehyde and methanol. Degrees of aggregation (m) were obtained by the method of stationary isothermal distillation (*n*-pentane, 28.4 °C)[18] or (**4**, $m=4$ and **7**, $m=2$) from the nature of ^{13}C-^{6,7}Li coupling.[19] Their colligative properties identified **3** as a tetramer and **5** (0.05 M, 28.4 °C: $m_{av}=3.4$) as mixture of tetramer and dimer in about a 3:1 ratio.

A change from homotopy to diastereotopy observed upon cooling for the OCH$_2$, (CH$_3$)$_2$ and α-CH$_2$ protons as well as for the (CH$_3$)$_2$ carbons of **3** signifies presence of S_4-type tetramers that exchange diastereotopic atoms, at higher temperature, via their D_2-type "chelatomers". At low temperatures, both ^{1}H and ^{13}C NMR spectra of **4** in toluene indicate the presence of at least two species (A,B) whose ratio (1:1) is independent of concentration. The proton-decoupled ^{13}C NMR signal of the α-carbon atom is so broad that its multiplicity cannot be obtained accurately. However, a rough measure of the ^{13}C,^{6,7}Li coupling constants [$J(^{13}$C,^{6}Li$)\approx 5(\pm 0.5)$ Hz, $J(^{13}$C,^{7}Li$)\approx 14(\pm 1.0)$ Hz[19], see Experimental Section] strongly suggests that tetramers **4$_4$** are present, as in the case of **9**. If, as is probable only one dimethylamino group of each monomer subunit **4** is complexed to lithium, akin to methoxy **9**, the β-carbon atom is asymmetric and tetramers can occur as different diastereomers (S_4/R_4, S_3R/R_3S, S_2R_2), each of which may prevail as a D_2-type and/or an S_4-type "chelatomer". This could explain the number and broadness of certain signals. At 183 K, three sharp ^{6}Li resonances occur that are strongly broadened at 273 K and coalesce at 295 K. Coalescence at higher temperatures, due to rapid exchange between different species, is also observed for ^{1}H and ^{13}C NMR signals.

The ^{1}H, ^{7}Li and ^{13}C NMR spectra of **5** taken at temperatures below 250 K in [D$_{12}$]pentane point to the predominance of one type of aggregate, probably the S_4-type S_2R_2 (*meso*)

"chelatomer" **5$_4$** with a single type of lithium and NMe$_2$ groups, which give rise to two signals both in the ^{1}H and the ^{13}C NMR spectrum. Above 250 K, signals of a minor new species come up concommitantly with a broadening and eventual coalescence of the ^{1}H and ^{13}C NMR signals of the NMe$_2$ groups. Both a new broad and structureless α-proton signal and a new 1:1 pair of ^{7}Li signals increase in intensity with temperature and decrease with concentration [area ratios α-H: 0.05 M (0.30 M), major/minor: 294 K, 100/40 (100/17), 254 K, 100/8 (100/0)]. In line with the results of the molecular-weight determination, this indicates the new species to be a smaller aggregate, presumably dimer **5$_2$**. Crystals of **5** are stable in vacuum for short periods. However, at room temperature, pentane solutions of **5** turn yellow and and develop a white precipitate within a few days. Quenches of these solutions with benzaldehyde and trimethyltin chloride formed, in addition to the products expected from **5**, derivatives of 1-dimethylamino-5-lithio-3-methylpentane (**14**), which should result from addition of **5** to ethylene.[4c] Ethylene, we speculate, arises from the isomerisation of **5** into the more stable[16, 20] *N*-methyl-*N*-butylaminomethyllithium (**15**), which in turn could form ethylene and **16** on decomposition[21] (Scheme 2).
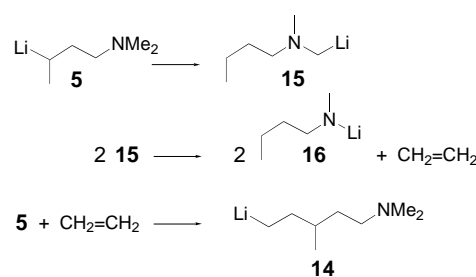
Scheme 2. Possible reaction scheme for the formation of **14**.

In order to exclude complications due to decomposition, NMR spectra of **5** were first recorded at temperatures below 0 °C. Some decomposition/conversion into **14** occurred during the molecular-weight determination: a benzaldehyde quench at the end of the experiment produced 9% of the addition product of **14**. The influence of this on the measurement is not known.

Both ^{1}H and ^{13}C NMR spectra in [D$_{12}$]pentane of **7** at low temperatures indicate the presence of two species in a ratio of 63:37. At 213 K, the proton-decoupled ^{13}C signals of the α-carbon atoms consist of a triplet of triplets [$J(^{13}$C,^{6}Li$)=9.0$ Hz, $J(^{13}$C,^{6}Li$')=5.4$ Hz (major)] and a quintet [$J(^{13}$C,^{6}Li$)=7.6$ Hz (minor)] that indicates the presence of two dimers. At 190 K, three ^{6}Li NMR signals appear in an approximate ratio of 4:1:1. They are ascribed to the major dimer in which the α-hydrogen atoms occupy *trans* positions at the C$_2$Li$_2$ unit, whose lithium atoms are chemically equivalent but magnetically nonequivalent, and to the minor dimer, the corresponding *cis* isomer with chemically nonequivalent lithiums. At 273 K, ^{1}H, ^{13}C and ^{6}Li NMR spectra of the two species are averaged. The overall Li–C–N–Li connectivity of **7$_2$** shown is based on an X-ray crystal structure analysis.[22]

Kinetics: Rates were determined in an evacuated, sealed reactor (Figure 2), which was manipulated as described in the caption of Figure 2. TPMH (10^{-2}–10^{-3} M, benzene) was treated with an excess of **1–9** (10^{-1}–1 M, benzene). The

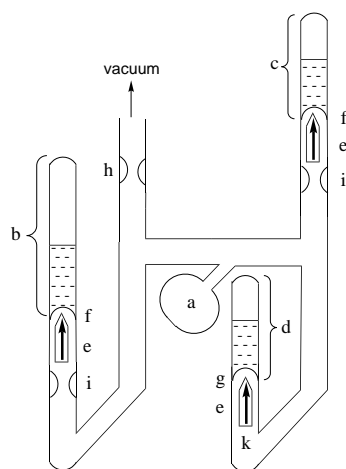Figure 2. Reactor and its use in the kinetic experiments. a: Quartz spectroscopic cell that fits into the thermostatted ($23 \pm 1\,^\circ$C) cell compartment of a Beckman DU-70 spectrophotometer. b–d: Evacuated compartments containing benzene (b) and benzene solutions of RLi (c) and TMPH (d), sealed to the basic apparatus at positions e. f,g: Breakseals. After evacuation, the reactor is sealed at h; b and c are first emptied by breaking breakseals f with the glass-lined magnets k, and then removed by sealing at positions i. The experiment is started by breaking g and mixing the components. The time required for this did not affect measurement of r_i.

absorption of TPMLi at 420 nm ($\varepsilon = 2.0 \pm 0.2 \times 10^4$ L mol^{-1} cm^{-1}) was monitored as a function of time. Ideal first-order behaviour in TPMH was found for **2–5** and **7**, whereas the reactivities of **1**, **6**, **8** and **9** decreased during an experiment.[23] Therefore, and in view of the transformation of **5** into **14**, only initial rates {$r_i = $(d[TPMLi]/d$t$)$_i$, Table 1A, column 2} were used for kinetic analysis.

Values of effective reaction orders in [RLi]$_f$ (x) and of k_{exp} were obtained from Equations (4a) and (4b) by plotting

$\log(r_i/[\text{TPMH}]_i)$ against $\log([\text{RLi}]_{f,i})$ and taking the slopes and the intercepts of the plots. These values are given Table 1A, together with those of **10**[3a] and **11–13**.[10]

$$r = k_{exp}[\text{RLi}]_f^x[\text{TPMH}] \qquad (4a)$$

$$\log(r_i/[\text{TMPH}]_i) = x\log[\text{RLi}]_{f,i} + \log k_{exp} \qquad (4b)$$

Nonunity values of x indicate that mechanisms 1 and/or 2 are operative. An alternative interpretation, concomitant *direct* reaction of coexisting larger and smaller oligomers[15] [cf. Eq. (3a)], without intervention of a complex, is rejected. In such a case, the value of $K_{2m//m}$ should depend on the structure and we would expect the values of x of the tetrameric nBuLi derivative **2** and the tetrameric neopentyl-lithium derivative **3** to differ more strongly than is observed. In a similar vein, dissociation of **12$_2$** should be easier than dissociation of **7$_2$**, because in the former case only Li−C bonds have to be broken, whereas both Li−C and Li$\cdots$NMe$_2$ bonds have to be broken on dissociation of **7$_2$** [$K_{2m//m}$(**12$_2$**) $>$ $K_{2m//m}$(**7$_2$**)]. For direct reaction of TPMH with monomer and dimer of **7** and **12**, respectively, one would expect a greater proportion of monomer reaction in the case of **12** and, by consequence, x(**12**) $< x$(**7**). However, equal values of x are found for **7** and **12**, while ^{6}Li,^{13}C coupling indicates that the C$_2$Li$_2$ core of **12$_2$** is not disrupted on the ^{13}C NMR timescale at $23\,^\circ$C![10]

Support of R$_m$Li$_m \cdot$ TPMH complexation was obtained by FT-IR and UV spectroscopy. Immediately after preparation of a mixture in benzene of **12$_2$** (0.2 M) and TPMH (0.1 M) an IR spectrum was recorded. From this, the IR spectra of benzene and of **12$_2$** were subtracted by computer. Apart from several rather minor differences, the resulting spectrum was practically the same as that of TPMH, except for three bands at 1446 cm^{-1}, 754 cm^{-1} and 464 cm^{-1}, whose relative intensities were only about 1/3–1/2 of those of the signals at the same wave numbers of authentic TPMH. From this we conclude that about half of the amount of TPMH originally added has been consumed by formation of a complex with **12$_2$** and that the IR spectrum of this complex, practically, must be the sum

Table 1. Experimental data relating to Equation (4b) for **1–9**, and **11–13** (benzene, 23 °C) and nBuLi (**10**, THF, 22 °C); **B** interpretation of data according to mechanism 1 (**1–8**, **11**, **12**, K_m) and mechanism 2 (**9**, **10**, **13**, $K_m^2 K_{2m//m}$, k_m).

	A			B		
RLi[a]	r_i[b] [mol L^{-1} s^{-1}]	x[c,d]	k_{exp} [L mol^{-1} s^{-1}]	K_m [L mol^{-1}]	k_m[c] [s^{-1}]	$k_{m,rel}$[e]
1(4)	2.6×10^{-7}	0.72 (0.984)	2.4×10^{-4}	4.0	1.8×10^{-4} (0.996)	1.0
2(4)	2.5×10^{-7}	0.78 (0.981)	1.8×10^{-4}	3.0	2.1×10^{-4} (0.991)	1.2
3(4)	2.0×10^{-7}	0.75 (0.988)	1.9×10^{-4}	6.0	1.0×10^{-4} (0.979)	0.6
4(4)	3.7×10^{-5}	0.56 (0.978)	2.4×10^{-2}	12.0[f]	1.6×10^{-2} (0.974)	89[f]
5(4)	1.3×10^{-5}	0.63 (0.994)	1.0×10^{-2}	10.0[f]	5.3×10^{-3} (0.995)	29[f]
6(2)	7.5×10^{-4}	0.79 (0.995)	4.2×10^{-1}	1.5	4.9×10^{-1} (0.994)	4080
7(2)	1.0×10^{-3}	0.83 (0.998)	5.6×10^{-1}	2.3	5.3×10^{-1} (0.984)	4420
8(2)	8.6×10^{-4}	0.74 (0.998)	4.6×10^{-1}	2.0	5.2×10^{-1} (0.999)	4330
9(4)	4.5×10^{-4}	0.27 (0.904)	1.2×10^{-1}	2.0[g]	1.4×10^{-1} (0.993)[h]	1170
10(4)[i]	3.2×10^{-5}	0.33 (0.957)	7.6×10^{-3}	0.7[g]	1.7×10^{-2} (0.999)[h]	142
11(1)[j]	3.2×10^{-7}	0.59 (0.994)	9.7×10^{-5}	40	2.3×10^{-5} (0.999)	0.4
12(2)[j]	5.2×10^{-8}	0.83 (0.993)	1.8×10^{-5}	17	6.1×10^{-6} (0.982)	0.05
13(4)[j]	1.7×10^{-11}	0.34 (0.982)	4.5×10^{-9}	2.0[g]	8.4×10^{-9} (0.995)[h]	0.00007

[a] Degree of aggregation in parentheses. [b] Calculated for [RLi]$_f$ = 0.5 M and [TPMH] = 0.005 M. [c] Correlation coefficient in parentheses. [d] See ref. [13]. [e] Statistically corrected; in TPMH complexes of tetramers three Rs (see **19**), in complexes of dimers two Rs (see **20**) are assumed to be available for reaction. [f] Alternative interpretation: see below. [g] $K_m^2 K_{2m//m}$. [h] Data refer to dimer (**9$_2$**, **10$_2$**, **13$_2$**) equilibrating with tetramer. [i] Ref. [3a]. [j] Ref. [10].

of those of its components apart from the three TPMH bands mentioned, which are either lacking or of low intensity. Complex formation is also suggested by bathochromic shifts by 70 and 94 nm of the UV bands of TPMH at 262 and 223 nm, respectively, upon addition of excess 2_4 in pentane.

Analysis of the values of x in terms of mechanisms 1 [K_m, Eqs. (1a),(1b)] and 2 [$K_m^2 K_{2m//m}$, Eq. (3b)] was carried out by using Equation (4c), which is obtained if Equation (2b), in logarithmic form and written for $t = 0$ (r_i, [C(m, TPMH)]$_i$), is subtracted from Equation (4b).

$$\log([C(m,\text{TPMH})]_i/[\text{TPMH}]_i) = x\log[\text{RLi}]_{f,i} + \log(k_{\exp}/k_m) \qquad (4c)$$

Compounds **1–5** and **6–8** were supposed to react according to mechanism 1, since their effective reaction orders ($x > 0.5$), on first view, do not tally with predissociation of the prevailing species. Values of K_m [Eq. (1a), (1b)] were chosen such that the values of [C(m, TPMH)]$_i$, calculated from Equation (1b) for the various pairs of [RLi]$_{f,i}$ and [TPMH]$_i$ used in the experiments, when plotted according to Equation (4c) against [RLi]$_{f,i}$ gave straight lines whose slopes equalled the effective reaction orders (x) found for **1–5** and **6–8**. For the tetrameric **9** and for nBuLi (**10**), whose low values of x and high reactivities suggest reaction via more reactive[3c, 4] dimers (mechanism 2), the same procedure was followed with respect to $K_m^2 K_{2m//m}$ [Eq. (3b)]. Plotting of the calculated values of [C(m, TPMH)]$_i$ against r_i [Eq. (4c)] gave the rate constants, k_m, of the TPMH complexes of **1–10**. The results are given in Table 1B together with those of **11–13**.[10] Exemplary plots of Equation (4c) (**1$_4$** and **9$_4$ $\rightleftharpoons$ 2 9$_2$**) are shown in Figure 3.

Discussion

Mechanism 1: Compounds **1$_4$–3$_4$** and **6$_2$–8$_2$** are assumed to react according to mechanism 1. Free energies of dissociation of **1$_4$–3$_4$** and **6$_2$–8$_2$** into smaller oligomers (R$_{2m}$Li$_{2m}$ $\cdot$ nLB $\rightleftharpoons$ 2 R$_m$Li$_m$ $\cdot$ 0.5nLB, $m = 1$, 2; $n = 4$) are prohibitively high [$\Delta G_{2m//m} \gg (\Delta G_{2m}^{\neq} - \Delta G_m^{\neq})$, see mechanism 3 (below) Eqs. (3a) and (6b)] for a reaction via smaller oligomers to be kinetically significant.[25] It turns out that complexation of TPMH has no effect on free energy (Table 1B); for all these oligomers, statistically corrected values of K_m are around one. The free energy of loss of some ligand—LB from the primary complexation sphere or benzene from a secondary solvation shell—must equal the free energy of binding TPMH. The nature of the implied complexes is unkown. However, it is clear that TPMH must bind to R$_m$Li$_m$ $\cdot$ xLB in a way unavailable to benzene,[26] otherwise, while all organolithium would be complexed to excess benzene, TPMH would be free and x would equal one (see above). For the case of TPMH replacing LB, **17** is exemplary of possible complexation modes of TPMH.[27]
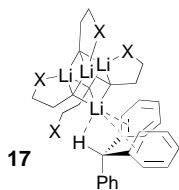
The value of $K_m = 17$[10] for **12$_2$** was used to calculate the degree of TPMH complexation under the conditions of the IR experiment described above
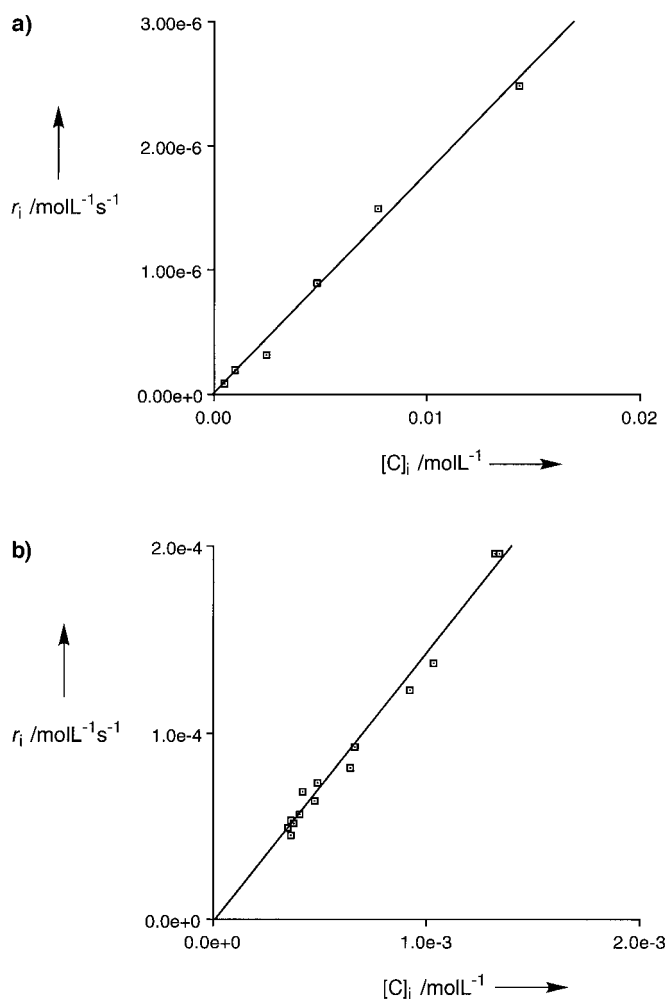
17

Figure 3. Relationship [Eq. (2b)] between experimental initial rate (r_i, mol L^{-1} s^{-1}) and initial concentration of complexes {[C]$_i$($\equiv$ [C(m,TPMH)]$_i$), mol L^{-1})} calculated with the values of K_m and $K_{2m//m}$, obtained by solving Equation (4c) for $x =$ effective reaction order in [RLi]$_f$ [Eqs. (4a), (4b)]; a) **1$_4$** + TPMH $\rightleftharpoons$ C(4,TPMH); b) **9$_4$ $\rightleftharpoons$ 2 9$_2$**, **9$_2$** + TPMH $\rightleftharpoons$ C(2,TPMH).

(0.2 M **12$_2$**, [TPMH]$_0 = 0.1$M). The result, [TPMH] $\approx$ 0.3[TPMH]$_0$, agrees satisfactorily with our estimate from the IR-band intensities. The relatively high value of $K_m(12_2)$ may be due to a symbiotic effect. In the presence of a delocalized α-silyl carbanion, coordination of polarizable TPMH could be slightly more favourable than coordination of NMe$_2$. Clearly, rather favourable steric conditions contribute to the even higher value of K_m of **11**.[10]

Mechanism 2: Dissociation into smaller species can be driven by complexation of additional LB (R$_{2m}$Li$_{2m}$ $\cdot$ nLB + nLB $\rightleftharpoons$ 2 R$_m$Li$_m$ $\cdot$ nLB), as in the case of nBuLi (**10**) dissolved in THF, or intramolecularly (LB:Li = 2), as in the system **9$_4$ $\rightleftharpoons$ 2 9$_2$**. If free energies of dissociation are much lower than the differences of the free energies of activation of the reactive complexes [$\Delta G_{2m//m} \ll (\Delta G_{2m}^{\neq} - \Delta G_m^{\neq})$, see Figure 5 below], only reaction via the smaller oligomer (though it may be undetectable) is significant.
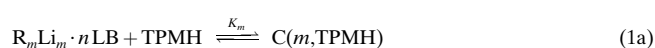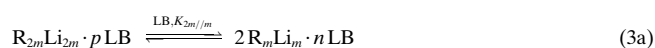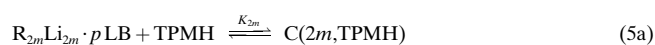
The values of $k_{\exp}$ and x of **9$_4$** and **10$_4$** suggest that mechanism 2 is in operation. This tallies with the observation

that, in THF, nBuLi prevails as an equilibrium mixture of $\mathbf{10_4} \cdot 4\,\mathrm{THF}$ and $\mathbf{10_2} \cdot 4\,\mathrm{THF}$ $[K_{2m//m}(\mathbf{10_4} \cdot 4\,\mathrm{THF})$, Eq. (3a), 22 °C, ca. $10^{-3}\,\mathrm{mol\,L^{-1}}]$.[2c, 3c, 8] On the basis of this and our value of $K_m^2 K_{2m//m} = 0.7$ for $\mathbf{10}$, the value of $K_m(\mathbf{10_2} \cdot 4\,\mathrm{THF})$ must be $26\,\mathrm{mol^{-1}\,L}$, which is about ten times the value of a genuine (intramolecularly complexed, secondary) RLi dimer $[K_m(\mathbf{7_2}) = 2.3]$. Undoubtedly, there are subtle differences in the enthalpy of complexation of TMPH by $\mathbf{10_2} \cdot 4\,\mathrm{THF}$ and $\mathbf{7_2}$; however, we suppose that mainly entropy differences are decisive. In the case of $\mathbf{10_2} \cdot 4\,\mathrm{THF}$, the effects on entropy of one molecule of TPMH being bound may be practically offset by one molecule of THF being freed from complexation, while with $\mathbf{1} - \mathbf{9}$ such compensation should be less, since binding of TPMH is accompanied by the mere opening of a five-membered chelate ring. On the other hand, the tetramer/ dimer dissociation constant of $\mathbf{9_4}$, $K_{2m//m}(\mathbf{9_4}) = 0.5\,\mathrm{mol\,L^{-1}}$, obtained from $K_m^2 K_{2m//m}(\mathbf{9})$ by taking as the value of K_m for $\mathbf{9_2}$ that of the dimers $\mathbf{6_2} - \mathbf{8_2}$, is higher than that of $\mathbf{10_4} \cdot 4\,\mathrm{THF}$. Here, the favouring of $\mathbf{9_4} \rightarrow 2\,\mathbf{9_2}$ over $\mathbf{10_4} \cdot 4\,\mathrm{THF} + 4\,\mathrm{THF} \rightarrow 2\,\mathbf{10_2} \cdot 4\,\mathrm{THF}$ by entropy, due to the different changes in particle numbers, surmounts the adverse influences of the closure of four five-membered rings. The reactivity calculated for $\mathbf{9_2}$ is about ten times that calculated for $\mathbf{10_2} \cdot 4\,\mathrm{THF}$ $[k_{m,\mathrm{rel}}(\mathbf{9_2} \cdot \mathrm{TMPH}) = 8.5\,k_{m,\mathrm{rel}}(\mathbf{10_2} \cdot 3\,\mathrm{THF} \cdot \mathrm{TMPH})]$. More efficient LB assistance (see below and ref. [10]) exerted by the chelate group $-\mathrm{OMe}$, relative to THF, in the lithiation transition state (compare $\mathbf{20}$ below) is believed to be the cause. More importantly, the rather similar reactivitiy of $\mathbf{9}$ *in benzene* compared with that of $\mathbf{10}$ *in THF* demonstrates that the role of LB solvents in organolithium chemistry consists of no more than the provision for the coordinative saturation of all lithium atoms in $R_m \mathrm{Li}_m$.

Mechanism 2 has been proposed before for $\mathbf{13_4}$;[10] this may be surprising in the light of the fact that $\mathbf{1_4}$ follows mechanism 1 and that the two compounds differ only by the presence of $\mathrm{SiMe_2}$ and $\mathrm{CH_2}$, respectively, at the β-position. In the case of $\mathbf{13_4}$, two factors cooperate in favour of mechanism 2 $[\Delta G_{2m//m} \ll (\Delta G_{2m}^{\neq} - \Delta G_m^{\neq})]$: 1) owing to the delocalization of the negative charge in an α-silyl carbanion, Coulomb stabilization in oligomers of (trimethylsilyl)methyllithium derivatives is less—and $\Delta G_{2m//m}$ is accordingly lower—than in corresponding alkyllithiums;[28] 2) activation barriers (and their differences) of oligomers of (trimethylsilyl)methyllithium derivatives are higher than those of $\mathbf{1_4} - \mathbf{3_4}$.

The reaction rates of 4 and 5, mechanism 3: Values of K_m for $\mathbf{4_4}$ and $\mathbf{5_4}$ calculated provisionally on the basis of mechanism 1 (Table 1B) indicate that these species should complex TPMH better than do $\mathbf{1_4} - \mathbf{3_4}$ and $\mathbf{6_2} - \mathbf{8_2}$; this is surprising in view of the sterically more hindered secondary nature of $\mathbf{5}$ and the LB/Li ratio of two in $\mathbf{4}$, which, on statistical grounds alone, should cause the value of $K_m(\mathbf{4_4})$ to be one half of that of $K_m(\mathbf{1_4})$.

Mechanism 3

$$R_m\mathrm{Li}_{2m} \cdot p\,\mathrm{LB} + \mathrm{TMPH} \underset{}{\overset{K_{2m}}{\rightleftharpoons}} \mathrm{C}(2m,\mathrm{TPMH}) \tag{5a}$$

$$R_m\mathrm{Li}_{2m} \cdot p\,\mathrm{LB} \underset{}{\overset{\mathrm{LB}, K_{2m//m}}{\rightleftharpoons}} 2\,R_m\mathrm{Li}_m \cdot n\,\mathrm{LB} \tag{3a}$$

$$R_m\mathrm{Li}_m \cdot n\,\mathrm{LB} + \mathrm{TMPH} \underset{}{\overset{K_m}{\rightleftharpoons}} \mathrm{C}(m,\mathrm{TPMH}) \tag{1a}$$

$$\frac{K_{2m}}{K_m K_{2m//m}^{0.5}} = \frac{[\mathrm{C}(2m,\mathrm{TPMH})]}{[R_{2m}\mathrm{Li}_{2m} \cdot p\,\mathrm{LB}]^{0.5}\,[\mathrm{C}(m,\mathrm{TPMH})]} \tag{5b}$$

$$\mathrm{C}(2m,\mathrm{TPMH}) \xrightarrow{k_{2m}} \mathrm{TPMLi} \tag{6a}$$

$$\mathrm{C}(m,\mathrm{TPMH}) \xrightarrow{k_m} \mathrm{TPMLi} \tag{2a}$$

$$r = k_{2m}[\mathrm{C}(2m,\mathrm{TPMH})] + k_m[\mathrm{C}(m,\mathrm{TPMH})] \tag{6b}$$

As an alternative to stronger complexation of TMPH as a cause of both the relatively low value of x and, relative to $\mathbf{1} - \mathbf{3}$, the enhanced reactivity of $\mathbf{4}$ (which includes an unknown contribution by structural differences), we propose the reaction of both tetramer $\mathbf{4_4}$ and the more reactive dimer $\mathbf{4_2}$ [mechanism 3, $m = 2$, $n = 4$, $p = 8$ [Eq. (6b)]. For $\mathbf{5}$, which has a similar value of x, distinctive concentrations of $\mathbf{5_2}$ in equilibrium with $\mathbf{5_4}$ $[K_{2m//m}(\mathbf{5_4})$, mechanism 3, $m = n = 2$, $p = 4) \approx 5 \times 10^{-3}]$ are evidenced by colligative properties and NMR measurements (see above).

In fact, if the values of K_m and k_m of $\mathbf{4_2}$ are approximated by those of $\mathbf{6_2} - \mathbf{8_2}$ and $\mathbf{9_2}$ and that of K_{2m} of $\mathbf{4_4}$ is derived from those of $\mathbf{1_4} - \mathbf{3_4}$ [i.e., $K_m(\mathbf{4_2}) = 2$, $k_m(\mathbf{4_2}) = 0.125$, $K_{2m}(\mathbf{4_4}) = 1$] use of $K_{2m//m}(\mathbf{4_4}) = 5 \times 10^{-3}$ and $k_{2m}(\mathbf{4_4}) = 0.035$ in the evaluation of initial rates by Equation (6b) leads to a satisfactory match (corr. coeff. $= 0.992$) of experimental (r_i) and calculated (r_{calcd}) reaction rates of $\mathbf{4}$ (Figure 4a).
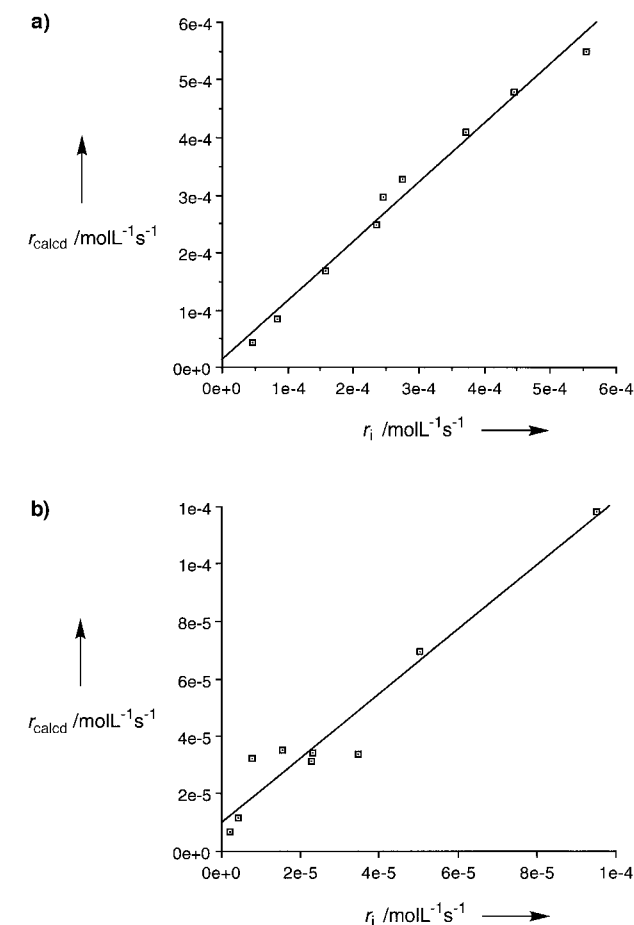

Figure 4. Comparison of experimental initial rate (r_i, $\mathrm{mol\,L^{-1}\,s^{-1}}$) and the rate calculated (r_{calcd}) according to mechanism 3 ($m = 2$). a) $\mathbf{4} + \mathrm{TPMH}$; b) $\mathbf{5} + \mathrm{TPMH}$.

Of the two new parameters required to fit r_{calcd} to r_i, $K_{2m//2}(\mathbf{4_4})$ and $k_{2m}(\mathbf{4_4})$, $K_{2m//2}(\mathbf{4_4})$ is the main cause of the mechanistic difference between $\mathbf{4}$ and $\mathbf{9}$ $[\Delta G_{2m//m}(\mathbf{4_4}) > \Delta G_{2m//m}(\mathbf{9_4})]$, while the increased reactivity of $\mathbf{4_4}$ is the main cause of the mechanistic difference between $\mathbf{4}$ and nBuLi $(\mathbf{10})$ $[\Delta G_{2m}^{\neq}(\mathbf{4_4}) - \Delta G_m^{\neq}(\mathbf{4_2})] < [\Delta G_{2m}^{\neq}(\mathbf{10_4} \cdot 4\,THF) - \Delta G_m^{\neq}(\mathbf{10_2} \cdot 4\,THF)]$ (see Figure 5).
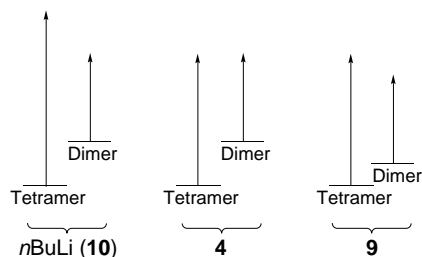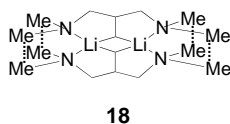

Figure 5. Differences in relative free energies (horizontal lines) and free energies of activation (vertical arrows) that control the differences in kinetics towards TPMH between $\mathbf{4}$, and $\mathbf{9}$ and nBuLi $(\mathbf{10})$ (schematic).

Since a limited set of structures applies to the majority of RLis,[29] the structures of tetramer $\mathbf{4_4}$ and the dimers $\mathbf{4_2}$ and $\mathbf{9_2}$ are assumed to be analogues of those of $\mathbf{9_4}$[7e] and $\mathbf{6_2}$.[7c] On the assumption that the entropies of dissociation into dimers are the same for $\mathbf{4_4}$ and $\mathbf{9_4}$, steric repulsion between the four N-CH$_3$ groups of $\mathbf{4_2}$ as shown in $\mathbf{18}$, which amount to a total of about $11\,kJ\,mol^{-1}$, could explain the lower value of $K_{2m//2}(\mathbf{4_4})$ relative to that of $\mathbf{9_4}$ (which forms $\mathbf{9_2}$ that lacks such interactions). On the basis of mechanism 3, $k_{m,rel}(\mathbf{4_4})$ has a value of 200. The two-hundredfold rate increase relative to $\mathbf{1_4}$ is ascribed to the favourable action of two molecules of LB per lithium involved in bond breaking in the transition state $\mathbf{4_4} \cdot TMPH^{\ddagger}$ (see discussion of $\mathbf{21}$, below).

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We think that mechanism 3 applies also to the reaction of $\mathbf{5}$; however, lack of data (K_m, k_m) of authentic coordinatively unsaturated secondary-$R_2Li_2 \cdot 2LB$ and of secondary-$R_4Li_4 \cdot 4LB$ (k_{2m}) permits only a qualitative discussion. With LB:Li$(\mathbf{5_2}) = 1$, the reactivity ratio $k_m(\mathbf{5_2})/k_{2m}(\mathbf{5_4})$ will be lower, and therefore reaction of $\mathbf{5_4}$, in addition to $\mathbf{5_2}$, is expected to be more probable than in cases in which coordinatively saturated dimers (LB:Li = 2) operate (see below). On the other hand, coordinatively unsaturated $\mathbf{5_2}$ will complex TPMH more strongly than coordinatively saturated dimers $[K_m(\mathbf{5_2}) > K_m(\mathbf{4_2})]$, and the proportion of $\mathbf{5}$ reacting via the dimer complex will be correspondingly higher. An attempt to calculate $r_i(\mathbf{5})$ along these lines $[K_{2m}(\mathbf{5_4}) = 4$, $K_m(\mathbf{5_2}) = 500$ $(\Delta G_m(\mathbf{5_2}) = -13.5\,kJ\,mol^{-1})$, $k_{2m}(\mathbf{5_4}) = 0.002$, $k_m(\mathbf{5_2})/k_{2m}(\mathbf{5_4}) = 2]$ is shown in Figure 4b.

Relative reactivities: Reactivity ratios $(k_{m,rel})$ given in Table 1B and in the discussion $(\mathbf{4_4}, \mathbf{4_2})$ are considered to be representative for the reactivity of the tetraaminates and tetraetherates of the tetramers and dimers of alkyllithiums dissolved in Lewis basic solvents towards TPMH-type substrates and provide guidelines for their controlled use. A summary is given in Scheme 3.
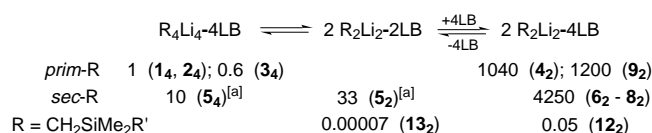

Scheme 3. Relative rates of the complexes of intramolecular tetraaminates and tetraetherates of tetramers and dimers of alkyllithiums with TPMH (benzene, 22 °C). [a] Based on mechanism 3, tentative value.

Going from the coordinatively saturated tetramer (LB:Li = 1) to the coordinatively saturated dimer (LB:Li = 2), the reaction rates of primary alkyllithium complexes increase by factors of about 1000 $[\mathbf{4_2}$ (mechanism 3) vs. $\mathbf{1_4}$, $\mathbf{2_4}]$ and 2000 (neopentyl systems $\mathbf{9_2}$ vs. $\mathbf{3_4}$). In accordance with the Hammond postulate, the rate ratio towards TMPH, $k(\mathbf{4_2})/k(\mathbf{1_4}) \approx 1000$, is about hundred times that found for the highly reactive system nBuLi/THF/benzaldehyde: $k(\mathbf{10_2} \cdot 4\,THF)/k(\mathbf{10_4} \cdot 4\,THF) \approx 10$.[3c] For secondary alkyllithium complexes the tentative rate ratio $k(dimer)/k(tetramer)$ is around 400 $(\mathbf{6_2} - \mathbf{8_2}$ vs. $\mathbf{5_4}$, see footnote [a] in the legend for Scheme 3). The rate enhancement factors for going from primary to secondary alkyllithium tetramers are tentatively 10 $(\mathbf{5_4}$ vs. $\mathbf{1_4}$, see footnote [a] in the legend for Scheme 3)[30] and about 4 for dimers $(\mathbf{6_2} - \mathbf{8_2}$ vs. $\mathbf{4_2}$, $\mathbf{9_2}$). Again, weaker responses of the more reactive systems are in line with the Hammond postulate.

Additional information gained from Table 1B: 1) As evidenced by the relative reactivities of $\mathbf{1_4}$, $\mathbf{2_4}$, $\mathbf{7_2}$ and $\mathbf{8_2}$, amine and ether complexes have practically equal reactivities. 2) α-Silicon retards the rate of lithiation of TPMH by a factor of 24 000 $[k_{m,rel}(\mathbf{9_2}):k_{m,rel}(\mathbf{12_2})]$. 3) Having observed a marked increase of the ease of dissociation of Li–LB in the order $R_4Li_4 \cdot 4LB < R_2Li_2 \cdot 4LB^{[4b,\,10]} < RLi \cdot 3LB$,[10] we proposed LB assistance of Li–X (X = LB, C) dissociation.[4b, 10, 31] By binding more strongly, LB molecules that remain bound to lithium compensate for part of the bond energy lost upon dissociation of one of their congeners or by weakening of an Li–C bond in a reaction transition state. If more LB molecules are bonded to lithium, LB assistance can be stronger. In addition to the earlier results, this inference is nicely illustrated by two cases from the present study. Disregarding the influence of the different structures of $\mathbf{1}$ and $\mathbf{4}$, the relative reactivities of $\mathbf{1_4}$ and $\mathbf{4_4}$ show that doubling of the ratio LB:Li enhances the reactivity of tetramers of primary RLi by a factor between 90 (mechanism 1) and, more probable, 200 (mechanism 3). In similar vein, lifting of a deficiency of LB, as in $\mathbf{13_2} \rightarrow \mathbf{12_2}$, enhances the rate by a factor 700. For the much more reactive species $\mathbf{5_2}$ and $\mathbf{7_2}$ this factor is tentatively taken to be about 130 (see footnote [a] in the legend for Scheme 3). Together with better accessibility of dimers and the reduced shielding of C$^-$ by Li$^+$ in dimers, relative to tetramers,[32] increased LB assistance as a result of the higher ratio LB:Li contributes to the increase of reactivity upon going from a coordinatively saturated tetramer to a coordinatively saturated dimer. For example, in the transition state of an exhaustively LB-complexed tetramer ($\mathbf{19}$), assistance is provided by LB(1) and LB(2) which are bonded to lithium atoms involved in the breaking of three partial carbon–lithium bonds. LB(3) does not participate and LB/C$\cdots$Li is 2/3. In the correspond-

ing dimer transition state (**20**), LB(3) also assists and LB/C ··· Li is 3/2.

19 **20** **21**
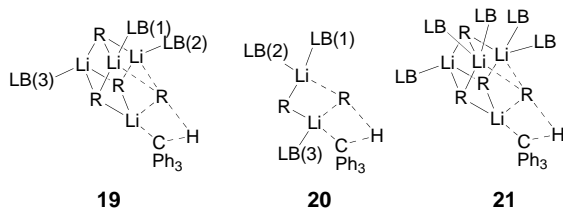
Tetramers with LB:Li = 2 (e.g., **4₄**) might form transition states of type **21** (for clarity, only kinetically important extra LB is shown) whose ratio LB/C ··· Li (4/3) is nearly the same as that of dimer transition state **20**. Similar relative rates [i.e., $k_{m,rel}$: **4₄** (mechanism 3), 200; **10₂** · 4 THF, 140; **9₂**, 1200] are in line with this. The normal coordination number of lithium in σ-organolithium complexes, that is, four, is exceeded in **21**. However, since organolithium transition states are stabilised by Lewis base coordination more strongly than ground states,[4c] we surmise that pentacoordination, while destabilizing ground states, still stabilizes transition states.[5b, 33] A last remark: Evidently, all mechanistic parameters given here for reaction via complexes apply only to assumed mechanisms, which, however, accord well with established principles of RLi chemistry. We feel encouraged by our success in calculating the reaction rate of **4** by use of our tetramer and dimer data and two new parameters [$K_{2m//2}(\mathbf{4_4})$ and $k_{2m}(\mathbf{4_4})$] whose values appear reasonable, although, by no means, can we claim to have reconnoitered all possibilities. Proof and study of the complexes invoked remain of paramount urgency.

Experimental Section

Ether solvents were distilled from Na/K alloy after stirring under nitrogen for at least 16 h. Degassing was realized by freezing and thawing under vacuum. Pentane and benzene were distilled from BuLi (5 mmol L⁻¹). *tert*-Butyllithium was always purified by sublimation (70 – 80 °C, 10⁻⁵ Torr) in portions of 10 to 15 mmol. The sublimate was dissolved in pentane and filtered. The colourless clear solution was free of impurities. It was sealed in evacuated ampoules and stored at -5 °C. All operations involving RLis were carried out in sealed and evacuated glass equipment with break-seal techniques. The concentration of RLi in a sample was determined by Gilman's[34] method of double titration. ¹H, ⁶Li, ⁷Li, and ¹³C NMR spectra were measured on a Brucker WM 250 spectrometer at 250.13, 36.81, 97.20, and 62.89 Hz respectively. ¹H and ¹³C NMR chemical shifts (CDCl₃, δ, ppm) are relative to internal TMS, ⁶,⁷Li NMR chemical shifts are relative to external solutions of 1 M LiBr in THF and 50 % LiBr in H₂O; these were set to 0.00 and – 1.04 ppm (25 °C), respectively.

1-Lithio-3-methoxy-2,2-dimethylpropane (3)

a) 1-Bromo-3-methoxy-2,2-dimethylpropane: Bromine (11.2 mL, 0.210 mol), dissolved in CH₂Cl₂ (100 mL), was added to a solution of triphenylphosphine (54.8 g, 0.210 mol) in CH₂Cl₂ (400 mL) over 30 min at 0 °C under stirring. A mixture of 3-methoxy-2,2-dimethyl-1-propanol[36] (25.0 g, 0.210 mol) and pyridine (16.9 mL, 0.21 mol) in CH₂Cl₂ (100 mL) was added dropwise to the solution of triphenylphosphine dibromide. After stirring for 2 h at room temperature, the solvent was evaporated from the reaction mixture. Petroleum ether 60/80 (500 mL) was added and the mixture was heated to gentle reflux for one hour. The white precipitate of triphenylphosphine oxide was filtered off and washed with cold petroleum ether 60/80. The filtrate was concentrated and cooled to – 80 °C for several hours. The newly precipitated triphenylphosphine oxide was separated by

filtration and after drying over sodium sulfate and removal of solvent the residue was submitted to distillation. Yield: 25.4 g (0.140 mol, 67 %); colourless oil; bp 75 – 79 °C (100 Torr); purity gc > 85 %; ¹H NMR: δ = 3.36 (s, 2H), 3.34 (s, 3H), 3.17 (s, 2H), 0.99 (s, 6H).

b) 3-Methoxy-2,2-dimethylpropylmercuricbromide: 3-Methoxy-2,2-dimethylpropylmagnesium bromide (70 mL, 0.91 M THF, prepared in 9 l% yield from 1-bromo-3-methoxy-2,2-dimethylpropane) was added dropwise to a solution of mercuric bromide (36.30 g, 94.5 mmol) in THF (250 mL) at room temperature under vigorous stirring. Two hours after the addition had been completed, THF was evaporated. The residue was suspended in diethyl ether (300 mL) and was treated once with water (200 mL) and twice with a saturated sodium chloride solution, dried over magnesium sulfate and concentrated. Yield: 15.70 g (41.2 mmol, 59 %); colourless oil; ¹H NMR: δ = 3.38 (s, 3H), 3.05 (s, 2H), 1.73 (s, 2H), 0.99 (s, 6H). Note: The formation of bis(3-methoxy-2,2-dimethylpropyl)mercury (¹H NMR: 3.34 (s, 3H), 3.02 (s, 2H), 0.94 (s, 6H), 0.91 (s,2H)), as a side product in variable yields, was frequently observed. It could be removed by evaporation at room temperature (7.5 × 10⁻⁶ Torr).

c) (3-Methoxy-2,2-dimethylpropyl)-tert-butylmercury: *t*BuLi (3.2 mL, 1.56 M) was added dropwise to a stirred solution of 3-methoxy-2,2-dimethylpropylmercuric bromide (1.905 g, 5.00 mmol) in pentane (100 mL) at 0 °C. After one hour methanol (0.18 mL) was added and the mixture was extracted with water. The organic layer was dried over sodium sulfate and concentrated. The residue (1.90 g) was submitted to a short path distillation at 40 °C, 10⁻² Torr, under cooling with solid CO₂. Yield: 1.400 g (3.91 mmol, 78 %); colourless oil; ¹H NMR: δ = 3.36 (s, 3H), 3.01 (s, 2H), 1.26 (s, ¹⁹⁹Hg-H satellites ³J = 110 Hz, 9H). 0.93 (s, 8H).

d) 1-Lithio-3-methoxy-2,2-dimethylpropane (3): In an evacuated (10⁻⁵ Torr) sealed break-seal apparatus, a solution of sublimed *t*BuLi (2.06 mmol, 0.34 M, pentane) was added under stirring to a solution of (3-methoxy-2,2-dimethylpropyl)-*tert*-butylmercury (0.780 g, 2.06 mmol) in pentane (60 mL) at – 15 °C. After one hour the pentane was evaporated and *t*Bu₂Hg was distilled off (10⁻⁵ Torr, room temperature, 2 h). The solid white residue was redissolved in pentane and filtered. Yield: 90 %. Purity: less than 3.9 % rest base. Average degree of association: 3.71. In agreement with the rest base content, the deviation from the tetramer value is ascribed to the presence of unidentified less-aggregated impurities in a proportion of 3 – 8 % of the RLi concentration. These impurities did not show up in the ¹H and ¹³C spectra. ¹H NMR ([D₈]toluene, 20 °C): δ = 3.09 (s), 3.02 (s), 1.14 (s), – 0.74 (s); ¹H NMR ([D₈]toluene, – 60 °C): δ = : 2.99 (s, 4H)*, 2.93 (s, 0.66H), 2.90 (s 0.33H)*, 1.31 (s, 3H), 1.27 (s, 3H), – 0.63 (AB, 2H) [Note: Part of the OCH₂ signal (*) is hidden under the OCH₃ (*) signal]; ¹³C NMR {[D₈]toluene, 20 °C, (– 70 °C)}: δ = 87.59 (t, J = 141 Hz) (86.86), 58.48, (q, J = 141 Hz) (58.36), 37.91 (s) (37.88), 33.23 (q, J = 121 Hz) (34.22, 34.22 (1:1)), 28.50 (br) (28.23); ⁷Li NMR {[D₈]toluene, 20 °C (– 70 °C]: δ = 1.66 (s) (1.80), with small (< 5 %) signals at 1.07 (1.41), 0.94 (1.17), 0.86 (0.15). Compound **3** could be sublimed at 70 °C, 10⁻⁵ Torr. It did not crystallize from a 0.4 M solution at – 60 °C, but crystals were obtained from a yellow 3.0 M solution at room temperature.

1,1-Bis(dimethylaminomethyl)-2-lithioethane (4)

a) 1,1-Bis(dimethylaminomethyl)-2-ethanol: Finely ground bis(dimethylaminomethyl)malonic acid dihydrochloride[35] (22.9 g, 92 mmol) was added in small portions to a suspension of LiAlH₄ (8.5 g, 220 mmol) in diethyl ether (400 mL). After 3 h reflux, 15 % aqueous NaOH (60 mL) was added. After drying over Na₂SO₄, the mixture was filtered and the residue extracted twice with diethyl ether (100 mL). After drying and removal of the solvent, distillation (85 °C, 16 Torr) gave 9.3 g (58 mmol, 63 %) of 1,1-bis(dimethylaminomethyl)-2-ethanol. ¹H NMR: δ = 6.30 (s, 1H), 3.71 (m, 2H), 2.40 – 2.20 (m, 5H), 2.23 (s, 12H); MS: *m/z* (%): 160 (3.5), 115 (20.9), 98 (6.3), 84 (43.3), 71 (9.9), 70 (5.2), 58 (100).

b) 2-Bromo-1,1-bis(dimethylaminomethyl)ethane: Bromine (6.5 mL, 0.12 mol) dissolved in CH₂Cl₂ (75 mL) was added to a solution of triphenylphosphine (31.4 g, 120 mmol) in CH₂Cl₂ (225 mL) over 45 min at 0 °C under stirring. A mixture of 1,1-bis(dimethylaminomethyl)-2-ethanol (9.6 g, 60 mmol) and H₂O (540 μL, 30 mmol) in CH₂Cl₂ (100 mL) was added dropwise to the solution of triphenylphosphine dibromide. After stirring for 20 h at room temperature, the solution was heated to reflux for 3 h, after which the turbid reaction mixture was cooled and extracted once with H₂O (150 mL) and twice with aqueous HCl (0.1 M, 150 mL). At 0 °C, the combined water layers were set at pH 13 by addition of NaOH (4 M) and

extracted with four portions of diethyl ether (125 mL). After drying over sodium sulfate and removal of solvent, the residue was submitted to molecular distillation (25 °C, 10⁻² Torr, condensation finger cooled by liquid nitrogen). Yield: 8 g (36 mmol, 60 %) of a colourless oil which was stored at −80 °C. ¹H NMR: $\delta = 3.66$ (d, $J = 3.7$ Hz, 2H), 2.40–2.15 (m, 5H), 2.24 (s, 12H).

c) (1,1-Bis(dimethylaminomethyl)-2-ethyl)mercuric bromide: Under reflux, 2-bromo-1,1-bis(dimethylaminomethyl)ethane (4.3 g, 19.4 mmol) dissolved in THF (250 mL) was added under nitrogen over 200 min to magnesium shavings (1.4 g, 58 mmol) in THF (10 mL). After 45 min reflux, filtration through glass wool and titration (yield 90 %), the Grignard reagent was added at room temperature over 180 min to HgBr₂ (9 g) dissolved in THF (150 mL). After centrifugation and filtration the solvent was removed and the residue was stirred with five portions of pentane (60 mL). After drying over sodium sulfate and removal of solvent, a colourless oil (3.1 g, 7.4 mmol, 38 %) was obtained. ¹H NMR: $\delta = 2.40$–2.00 (m, 4H), 2.20 (s, 12H), 1.62 (m, 2H), 1.00 (m, $J_{av} = 5.5$ Hz, 1H).

d) Di(1,1-bis(dimethylaminomethyl)-2-ethyl)mercury(II): A solution of (1,1-Bis(dimethylaminomethyl)-2-ethyl)mercuric bromide (4.65 g, 11.0 mmol) in CH₂Cl₂ (20 mL) was added to a solution of Na₂S₂O₄ (2.8 g, 16 mmol) in 8 % aqueous NaOH (60 mL). After stirring for 20 h, the organic layer was removed and the water layer was extracted twice with CH₂Cl₂ (25 mL). The combined organic layers were dried over CaCl₂. After removal of solvent, molecular distillation (80–90 °C, 10⁻⁵ Torr) gave 1.70 g (3.5 mmol, 63.6 %) of a colourless oil. ¹H NMR: $\delta = 2.20$ (s, ¹⁹⁹Hg-H satellites $^3J = 90$ Hz, 16H), 1.30 (m, 1H), 0.81 (m, 2H).

e) 1,1-Bis(dimethylaminomethyl)-2-lithioethane (4): In an evacuated, (10⁻⁵ Torr) sealed break-seal apparatus, sublimed *tert*-butyllithium (4.3 mmol in 2.5 mL pentane*)* was added under stirring to a solution of di(1,1-bis(dimethylaminomethyl)-2-ethyl)mercury(II) (1.04 g, 2.14 mmol) in pentane (50 mL) at −20 °C. After 90 min at 0 °C, the pentane and *t*Bu₂Hg were distilled off (10⁻⁵ Torr, room temperature, 2 h). The solid, dark yellow residue was redissolved in pentane (50 mL) and filtered (P5). At −80 °C, tiny colourless crystals formed. The identity of **4** followed from the products of quenches with Me₃SnCl, benzaldehyde and methanol.

(1,1-Bis(dimethylaminomethyl)-2-ethyl)trimethyltin: ¹H NMR: $\delta = 2.35$–1.80 (m, 5H), 2.20 (s, 12H), 0.88 (d, $J = 6.0$ Hz, 2H), 0.33 (s, $J(H, ^{117/119}Sn) = 49.6/52.0$ Hz, 9H); Exact mass: 293.1026 (moleculair ion minus CH₃); calcd (C₁₀H₂₅N₂¹²⁰Sn): 293.1038; MS: *m/z* (%): 293 (9.8, Sn-cluster), 165 (5.3, Sn-cluster), 143 (2.1), 98 (24.7), 84 (47.3), 58 (100).

3,3-Bis(dimethylaminomethyl)-1-phenyl-1-propanol: ¹H NMR: $\delta = 7.45$–7.10 (m, 5H), 4.78 (d, $J = 6.0$ Hz, 1H), 2.54–2.07 (m, 5H), 2.27 (s, 12H), 1.87 (m, $J' = 6.0$ Hz, $J'' = 8.0$ Hz, 2H); Exact mass: 250.2050; calcd (C₁₅H₂₆N₂O): 250.2045; MS: *m/z*(%): 250 (1.2), 207 (6.2), 173 (7.1), 129 (3.7), 105 (2.0), 98 (15.8), 84 (18.6), 79 (14.4), 58 (100).

1,3-Bis(dimethylaminomethyl)-2-methylpropane: ¹H NMR: $\delta = 2.17$ (s, 12H), 2.20–2.10 (m, 2H), 2.00 (dd, $J' = 8.35$ Hz, $J'' = 11.94$ Hz, 2H), 1.87–1.67 (br m, 1H), 0.91 (d, $J = 6.33$ Hz, 3H); Exact mass: 144.1630; calcd (C₈H₂₀N₂): 144.1627; MS: *m/z* (%): 144 (3.0), 99 (64.9), 84 (100), 58 (100).

At low temperatures, both ¹H and ¹³C NMR spectra of **4** in toluene indicate the presence of at least two species (A,B) whose ratio (1:1) is independent of concentration. The proton-decoupled ¹³C NMR signal of the α-carbon atom (Cᵃ) is of such broadness that its multiplicity could not be discerned.

A rough measure of the ¹³C,⁶,⁷Li coupling constants was obtained: $J(^{13}C, ^6Li) \approx 5 (\pm 0.5)$ Hz (see Figure 6), $J(^{13}C, ^7Li) \approx 14 (\pm 1.0)$ Hz. At 183 K, three sharp ⁶Li resonances occur at $\delta = 2.51$, 2.23 and 1.95. These are strongly broadened at 273 K and coalesce at 295 K ($\delta = 2.11$). Coalescence at higher temperatures is also observed for ¹H and ¹³C NMR signals.

Li-CᵃH₂CᵇHᵇ(CᶜH₂ᶜNMe₂)CᶜH₂ᶜNMe₂: ¹H NMR ([D₈]toluene, 187 K): Hᵃ: $\delta = −1.333$, −0.914 (dd, $J_{av} = 8.8$ Hz); Hᶜ (or Hᶜ'): $\delta = 2.832$ (dd, $J_{av} = 9.0$ Hz); NMe₂: $\delta = 2.213$ (A), 2.180 (A), 2.168 (B), 2.153 (A), 2.096 (B);
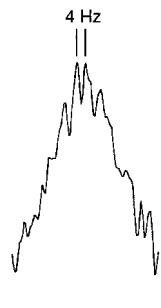
4 Hz

Figure 6. ¹³C NMR trace of C-α of [⁶Li]**4**.

signals of Hᵇ and Hᶜ' (or Hᶜ) between 2.30 and 1.90 are hidden under the NMe₂ signals; ¹H NMR (298 K): Hᵃ: $\delta = −1.150$ (very broad); Hᶜ (or Hᶜ'): $\delta = ?$ (extremely broad); NMe₂: $\delta = 2.138$; ¹³C NMR (213 K): Cᵃ: $\delta = 17.06$, ("t", very broad); Cᵇ: $\delta = 36.29$, 35.94, 35.78 (d, $J(CH) = 120$ Hz); Cᶜ,ᶜ': $\delta = 74.62$, 69.15 (t, $J(C,H) = 127$ Hz); NMe₂: $\delta = 49.53$ (A), 48.43 (A), 46.35 (B), 45.12 (B) 44.06 (A) (q, $J(C,H) = 130$ Hz); ¹³C NMR (298 K): Cᵃ: $\delta = 17.13$ (very broad); Cᵇ: $\delta = 36.55$ (d, $J(C,H) = 120$ Hz); Cᶜ,ᶜ': $\delta = 74.81$, 69.81, (br t, $J(C,H) = 127$ Hz); NMe₂: $\delta = 48.76$ (very broad), 46.37 (q, $J(CH) = 130$ Hz).

1-Dimethylamino-3-lithiobutane (5)

a) 1-Dimethylamino-3-butanol: 1-Dimethylamino-3-butanone[37] (15.0 g, 0.130 mol) was dissolved in diethyl ether (100 mL) and added dropwise under stirring at 0 °C to LiAlH₄ (5.7 g, 0.150 mol) in diethyl ether (400 mL). The mixture was warmed to gentle reflux for 4 h. At 0 °C, H₂O (5 mL) and 15 % aqueous NaOH (5 mL), followed by more H₂O (15 mL) were carefully added under stirring. After warming to room temperature the mixture was dried on MgSO₄ and stirred until the organic layer had become clear. The organic layer was decanted and the residue was washed twice with diethyl ether (100 mL). The combined organic layers were dried over Na₂SO₄ and K₂CO₃, filtered and concentrated (30 °C, 500 Torr). The residue was submitted to distillation and yielded 11.8 g (0.101 mol, 78 %) of a clear oil, b.p. 68 °C (50 Torr) of high purity. ¹H NMR: $\delta = 5.27$ (br s, OH), 3.93 (q, $J = 6.0$ Hz, 1H), 2.32–2.74 (m, 2H), 2.23 (s, 6H), 1.34–1.69 (m, 2H), 1.13 (d, $J = 6.0$ Hz, 3H).

b) 3-Bromo-1-dimethylaminobutane: At 0 °C a solution of bromine (16.1 g, 5.17 mL, 0.101 mol) in CH₂Cl₂ (120 mL) was added dropwise to a stirred solution of triphenylphosphine (27 g, 0.103 mol) in CH₂Cl₂ (450 mL). Then a solution of 1-dimethylamino-3-butanol (11.2 g, 0.096 mol) in CH₂Cl₂ (120 mL) was added dropwise to the mixture, which was still held at 0 °C and stirred. The reaction mixture was slowly warmed (16 h) to room temperature and was once extracted with H₂O (150 mL) and twice with HCl (0.1 M, 150 mL). Pentane (150 mL) was added to the combined water layers and under strong stirring and cooling at 0 °C aqueous NaOH (4 M) was added until pH 13 was reached. The organic layer was separated and aqueous NaOH (4 M, 10 mL) was added to the water layer, which was then extracted twice with pentane (150 mL). The combined organic layers were dried with MgSO₄, filtered and concentrated at 20 °C and 400 Torr. The residue was submitted to a short path distillation with solid CO₂ as coolant (25 °C, 10⁻³ Torr). Yield: 15.0 g (0.083 mol; 83 %) of colourless oil that must be stored at −80 °C. ¹H NMR: $\delta = 4.22$ (m, $J = 6.5$ Hz, 1H), 2.38 (q, $J = 7.0$ Hz, CH₂N), 2.23 (s, 6H), 1.98 (t, $J = 7.0$ Hz, 2H), 1.74 (d, $J = 7.0$ Hz, 3H).

c) Mixture of 3-dimethylamino-1-methylpropylmercuric bromide and bis(3-dimethylamino-1-methylpropyl)mercury: Under gentle reflux and stirring a solution of 3-bromo-1-dimethylaminobutane (5.00 g, 27.8 mmol) in THF (150 mL) was added dropwise to magnesium shavings (1.5 g, 63 mmol) with THF (5 mL). The heating was continued for 0.5 h after the addition had been completed. After cooling to room temperature, the mixture was titrated (yield 85 %) and filtrated. The filtrate was added over 2 h to a strongly stirred solution of HgBr₂ (10.00 g, 27.8 mmol) in THF (100 mL). After standing for 12 h, the mixture, which contained a white precipitate, was concentrated and the viscous residue was extracted immediately with three portions pentane (75 mL). The combined organic layers were dried with Na₂SO₄ and concentrated. The residue was a colourless oil which contained according to ¹H NMR 3-dimethylamino-1-methylpropylmercuric bromide and bis(3-dimethylamino-1-methylpropyl)-mercury in a molar ratio of 93.5:6.5, total yield: 5.81 g (± 15.3 mmol, 55 %). ¹H NMR: 3-dimethylamino-1-methylpropylmercuric bromide: $\delta = 1.61$–2.56 (m, 5H), 2.20 (s, 6H), 1.42 (d, $J = 7.0$ Hz, 3H, ¹⁹⁹Hg-H satellites $^3J(^{199}Hg,H) = 288$ Hz); ¹H NMR: bis(3-dimethylamino-1-methylpropyl)mercury: $\delta = 1.61$–2.56 (m, 10H), 2.18 (s, 12H), 1.24 (br s, 6H, $^3J(199 Hg,H)$ can not be given because of the low intensity of the signal).

d) (3-Dimethylamino-1-methylpropyl)-tert-butylmercury: Over a period of 15 min *tert*-butyllithium (10.5 mL, 1.49 M, 15.6 mmol) was added dropwise to a cooled (−12 °C) and stirred solution of 3-dimethylamino-1-methylpropylmercuric bromide (5.41 g, ca. 13.3 mmol) and bis(3-dimethylamino-1-methylpropyl)mercury (see above) (0.9 mmol) in pentane (800 mL). [Bis(3-dimethylamino-1-methylpropyl)mercury reacts with *tert*-butyllithium to give **5** and (3-dimethylamino-1-methylpropyl)-*tert*-butylmercury as products, of which **5** is hydrolyzed during work up]. Cooling and stirring were continued for 1.5 h. Then methanol (0.56 mL) was added and the mixture was warmed to room temperature. Then it was centrifuged and the

organic layer was decanted, dried on Na_2SO_4, filtered and concentrated. The oily residue was submitted to a short path distillation with CO_2 as coolant. (25 °C, 10^{-3} Torr). The yield was 4.89 g (13.7 mmol, 96%) of a daylight-, temperature- and water-sensitive colourless oil. ^1H NMR: δ = 2.17 – 2.38 (m, 4H), 2.18 (s, 6H), 1.60 – 2.00 (m, 1H), 1.24 (s, 3H), 1.21 (s, 9H, ^{199}Hg-H satellites ^3J(199 Hg,H) = 106 Hz).

e) 1-Dimethylamino-3-lithiobutane (**5**): 3-Dimethylamino-1-methylpropyl)-*tert*-butylmercury (7.67 g, 21.5 mmol) was dissolved in pentane (25 mL) and placed into a glass vessel. The system was degassed and sealed. Then the solution was diluted with pentane (200 mL) and thermostatted at −15 °C. Then *tert*-butyllithium (54 mL, 0.40 M, 21.5 mmol) in pentane was added under stong stirring. After 1.5 h at −15 °C, the reaction mixture was concentrated at 4 °C to 30 mL. After standing for several hours at −15 °C the solution was decanted from the white precipitate. The precipitate was evacuated for 3 h at 20 °C (10^{-5} Torr), redissolved in pentane (75 mL) and filtered. The filtrate was now a clear yellow solution. Titration indicated 17.4 mmol (81%) of total base. The product was further purified by repeated crystallizations at −80 °C until clear colourless crystals were obtained. Yield: ±15 mmol (70%) of **5** in a pure, colourless, clear solution. Double titration with 1,2-dibromoethane indicated less than 0.4% rest base. The identity of **5** followed from the products of quenches with benzaldehyde and Me_3SnCl.

4-Dimethylamino-2-methyl-1-phenyl-1-butanol: ^1H NMR: Two groups of signals of a mixture of diastereomers in a ratio of 1.4. Both had ^1H NMR signals at δ = 7.51 – 7.16 (m, 5H), 2.78 – 2.22 (m, 2H), 2.22 – 1.44 (m, 3H). The major species also had signals δ = at 4.28 (d, J = 7.0 Hz, 1H), 2.28 (s, 6H), 0.80 (d, J = 7.0 Hz, 3H), while the minor species had signals at δ = 4.76 (d, J = 2.5 Hz, 1H), 2.31 (s, 6H), 0.78 (d, J = 7.0 Hz, 3H); ES: m/z (%): 207 (4.1), 107 (1.2), 105 (2.9), 101 (2.5), 79 (5.7), 77 (9.2), 59 (6.0), 58 (100.0), 45 (12.0).

(3-Dimethylamino-1-methylpropyl)trimethyltin, ^1H NMR: δ = 2.40 – 2.13 (m, 2H), 2.22 (s, 6H), 2.00 – 1.51 (m, 2H), 1.33 – 1.11 (m, CH−CH_3), 0.04 (s, J(Sn,H) = 50 Hz, 9H); MS: m/z (%): clusters of signals with maxima at 250 (9.9), 165 (12.0), 150 (2.3), 135 (5.4), 120 (1.7), signals at 100 (24.0), 98 (10.7), 84 (3.0), 58 (100.0).

1,5-Bis(dimethylamino)-3-lithiopentane (7)

a) 1,5-Bis(dimethylamino)-3-pentanol: At 0 °C, 1,5-bis(dimethylamino)-3-pentanone[38] (12.9 g, 0.075 mol) in diethyl ether (500 mL) was added dropwise to a well-stirred suspension of $LiAlH_4$ (2.85 g, 0.075 mol). After completion of the addition, the reaction mixture was warmed to gentle reflux for 4 h. After lowering the temperature to 0 °C H_2O (3.0 mL), aqueous NaOH (15%, 3.0 mL) and H_2O (7.5 mL) were added carefully (dropwise) under strong stirring. This mixture was warmed to room temperature for 1 h, cooled again to 0 °C, after which powdered NaOH (3.0 g) and $MgSO_4$ were added. After strong stirring for 1 h the mixture was filtered, concentrated, dissolved in pentane and dried once more with $MgSO_4$ and some K_2CO_3. Filtration and evaporation of the pentane yielded 12.4 g (0.071 mol; 95%) of a colourless oil. ^1H NMR: δ = 5.95 (br s, OH), 3.64 – 3.97 (m, 1H), 2.24 – 2.56 (m, 4H), 2.19 (s, 12H), 1.31 – 1.70 (m, 4H).

b) 3-Bromo-1,5-bis(dimethylamino)pentane: At 0 °C, bromine (1.95 mL, 6.1 g, 38 mmol) in CH_2Cl_2 (50 mL) was added dropwise to a stirred solution of triphenylphosphine (10.0 g, 38 mmol) in CH_2Cl_2 (100 mL). Then a mixture of H_2O (0.225 mL, 12.50 mmol) and 1,5-bis(dimethylamino)-3-pentanol (4.35 g, 25.0 mmol) was dissolved in CH_2Cl_2 (50 mL) and added dropwise. After the addition had been completed, cooling (−5 °C – 0 °C) and stirring were continued for 16 h. Then, the mixture was warmed to room temperature and extracted twice with HCl (0.10 M, 25 mL). Diethyl ether (200 mL) was added to the combined water layers and solid NaOH was added under strong stirring until pH 13 was reached. After separation of the diethyl ether some extra NaOH was added to the water layer. After this it was extracted twice with diethyl ether (200 mL). The combined organic layers were dried with $MgSO_4$ and K_2CO_3. The mixture was filtered, concentrated, dissolved in pentane and dried once more over $MgSO_4$ and some K_2CO_3. Filtration and evaporation of the pentane at 25 °C yielded 4.45 g (18.8 mmol; 75%) of a colourless oil that must be stored at −80 °C. The product was submitted to a short path distillation (10^{-3} Torr, 20 °C) with liquid N_2 as coolant just before it was used for the synthesis of 1-(2-dimethylaminoethyl)-3-dimethylamino-propylmercuric bromide. ^1H NMR: δ = 4.18 (quintet, J = 6.5 Hz, 1H), 2.26 – 2.60 (m, 4H), 2.22 (s, 12H), 2.02 (t, J = 6.8 Hz, 4H).

c) 1-(2-Dimethylaminoethyl)-3-dimethylaminopropylmercuric bromide: A solution of 3-bromo-1,5-bis(dimethylamino)pentane (4.74 g, 20.0 mmol) in THF (150 mL) was added dropwise to Mg shavings (1.0 g, 40 mmol) with THF (5 mL), under stirring and heating to gentle reflux. Heating and stirring were continued for 0.5 h after the addition had been completed. After cooling to room temperature and titration (yield 70%) the mixture was filtered and added dropwise over 2 h under strong stirring to a solution of $HgBr_2$ (5.75 g, 16.0 mmol) in THF (150 mL). After standing for 16 h, the reaction mixture was filtered and concentrated. The viscous residue was immediately extracted with three portions of pentane (75 mL). The combined pentane solutions were dried with $MgSO_4$, filtered and concentrated. To remove volatile impurities, the residue was evacuated for 2 h (20 °C, 10^{-2} Torr). The yield was 3.93 g (9.0 mmol; 45%) of a colourless oil. ^1H NMR: δ = 2.44 – 2.22 (m, 4H), 2.19 (s, 12H), 1.71-2.00 (m, 5H).

d) 1-(2-Dimethylaminoethyl)-3-dimethylaminopropyl-tert-butylmercury: At −15 °C, *tert*-butyllithium (25 mL, 0.25 M) was added dropwise over 30 min to a well-stirred solution of 1-(2-dimethylaminoethyl)-3-dimethyl-aminopropylmercuric bromide (2.70 g, 6.2 mmol) in pentane (400 mL). Cooling and stirring were continued for 2 h after the addition had been completed. Then the mixture was warmed to room temperature and methanol (0.28 mL) was added and the salts were precipitated. After decantation and concentration of the supernatant the residue was evacuated for 1 h at 10^{-2} Torr (20 °C) to evaporate bis(*tert*-butyl)mercury and volatile impurities. Yield: 2.51 g (6.0 mmol; 97%) of a colourless, daylight-, water- and temperature-sensitive oil. ^1H NMR: δ = 2.41 – 2.12 (m, 9H), 2.20 (s, 12H), 1.21 (s, 9H, ^{199}Hg-H satellites ^3J(^{199}Hg,H) = 110 Hz).

e) 1,5-Bis(dimethylamino)-3-lithiopentane (**7**): A solution of 1-(2-dimethylaminoethyl)-3-dimethylaminopropyl-*tert*-butylmercury (1.04 g, 2.5 mmol) in pentane (10 mL) was put into a glass vessel. Then the solution was degassed and sealed. Pentane (50 mL) was added and the diluted solution was cooled to −15 °C. Then sublimed *t*BuLi (5 mL, 0.53 M) was added under continued stirring for 1.5 h. Then the pentane was evaporated at 5 °C in such a way that the solid residue was spread as a thin film over the glass wall of the vessel. The solid residue was evacuated for 2 h at 10^{-5} Torr (25 °C). The residue was dissolved in pentane (60 mL) and filtered. A yellow filtrate was obtained. Compound **7** was purified by crystallizations at −20 °C and −80 °C until clear colourless crystals were obtained. Analyses of the crystals with NMR and quenches with benzaldehyde and $SnMe_3Cl$ did not show any significant impurities. Yield: ±1.5 mmol of **7** (60%). Solubility of **7** in pentane at 20 °C: ±0.45 M. Crystals of **7** decompose at 125 °C in vacuum. ^1H NMR (C_6D_6): δ = 2.90 – 2.10 (m, 8H), 2.06 (s, 12H), −1.01 (tt, J_{av} ≈ 9.4 Hz, 1H); ^7Li NMR ([D_{12}]pentane): δ = 1.78.

4-Dimethylamino-2-(2-dimethylaminoethyl)-1-phenyl-1-butanol, ^1H NMR: δ = 7.56 – 7.16 (m, 5H), 4.61 (d, J = 4 Hz, 1H), 2.67 – 1.78 (m, 4H), 2.24 (s, 6H), 2.14 (s, 6H), 1.78 – 1.11 (m, 5H); MS: m/z (%): 265 (2.5), 264 (12.0), 220 (6.0), 218 (5.3), 192 (12.1), 112 (24.2), 100 (18.5), 84 (11.0), 77 (12.0), 71 (16.9), 59 (12.5), 58 (100.0), 45 (22.9).

1-(2-Dimethylaminoethyl)-3-dimethylaminopropyl-trimethyltin, ^1H NMR (low resolution): δ = 0.05 (s, 9H), 2.21 (s, 12H). MS: m/z (%): clusters of signals with maxima at 307 (3.2), 165 (2.1), signals at 157 (6.3), 112 (3.0), 98 (9.6), 84 (1.3), 58 (100.0), 55 (2.4).

Kinetics: The apparatus used and the mode of manipulation are described in the Results section (Figure 2). Some of the specific of the experimental conditions and results are provided in Tables 2 – 4.

IR spectroscopy: An ATI Mattson Instruments 6030 Galaxy series FT-IR spectrometer was used. Spectra were recorded of benzene solutions circulated (2 mL min^{-1}, Gilson 300 pump) in a nitrogen atmosphere

Table 2. Experimental data relating to the reaction of **1** with TPMH (benzene, 23 °C, see Figure 3a).

[**1**]$_f$ [M]	[TPMH] [10^{-2} M]	rate [10^{-6} mol L^{-1} s^{-1}]
0.96	3.02	2.4800
0.96	1.00	0.8920
0.64	2.03	1.4900
0.32	1.03	0.3170
0.11	1.00	0.1930
0.11	0.502	0.0902

Table 3. Experimental data relating to the reaction of **9** with TPMH (benzene, 23 °C, see Figure 3b).

$[9]_f$ [M]	[TPMH] $[10^{-3} M]$	rate $[10^{-4} \, mol \, L^{-1} s^{-1}]$
0.18	0.97	0.531
0.18	1.01	0.516
0.22	1.01	0.563
0.35	2.95	1.960
0.35	2.91	1.960
0.16	1.00	0.450
0.36	0.91	0.682
0.36	1.03	0.635
0.35	2.03	1.230
0.14	1.01	0.490
0.14	1.93	0.926
0.66	0.92	0.727
0.65	1.94	1.370
0.96	1.11	0.808

Table 4. Experimental data relating to the reaction of **4** with TPMH (benzene, 23 °C, see Figure 4a).

$[4]_f$ [M]	[TPMH] $[10^{-2} M]$	rate $[10^{-4} \, mol \, L^{-1} s^{-1}]$
0.10	1.40	0.464
0.21	1.73	0.843
0.21	3.48	1.580
0.22	5.02	2.340
0.59	3.54	2.740
0.40	4.42	2.450
0.60	4.40	3.710
0.78	4.40	4.440
1.00	4.41	5.540

between an IR cell (KBr, 0.2 mm) and a storage vessel into which a desired reactant could be introduced by syringe. First, spectra of benzene and of 0.2 M **12₂** in benzene were recorded, then the spectrum of the **12₂** (0.2 M) *plus* TPMH (0.1 M) mixture. Spectra subtraction was carried out with the Enhanced First™ Fourier Infrared Software Tools Subtraction Program.

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[24] For propensities for LB-induced formation of dimers from nBu₄Li₄ and n-pent₄Li₄, see refs. [2c] and [2f], respectively.

[25] Since the bond energy of the Li···NMe₂ bond of **12₂** (LB:Li = 2) that dissociates easiest contributes around 20 kJ mol⁻¹ to the stability of **12₂**,[10] **1₂** with LB:Li = 1, that is, it lacks two such bonds, must be higher

in relative energy by about 40 kJ mol^{-1}, and $\Delta G_{2m//m}(\mathbf{1_4} \rightarrow 2\mathbf{1_2})$ must be higher than $\Delta G_{2m//m}(\mathbf{4_4} \rightarrow 2\mathbf{4_2}$, LB:Li = 2) by about 80 kJ mol^{-1}.

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[30] On the crude assumptions that 1) the entropies of activation of $\mathbf{1_4}$ and $\mathbf{5_4}$ are equal and 2) the change from 100% reactant character to 100% product character of $\mathbf{1_4}$·TMPH$^+$ and $\mathbf{5_4}$·TMPH$^+$ is linear with respect to $\Delta\Delta H^{\ddagger}$ {100% reactant character: $\Delta\Delta H^{\ddagger} = 0$ kJ mol^{-1}; 100% product character ($\Delta\Delta H_{0,rel}$(RH) = 0 kJ mol^{-1}): $\Delta\Delta H^{\ddagger} = 0.25\ \Delta\Delta H_{0,rel}$(R$_4Li_4$) = 9 kJ mol^{-1} (see: P. J. A. Geurink, G. W. Klumpp, *J. Am. Chem. Soc.* **1986**, *108*, 538–539; and ref. [28])} the tentative rate ratio $k_{m,rel}(\mathbf{5_4}):k_{m,rel}(\mathbf{1_4}) = 10$ ($\Delta\Delta H^{\ddagger} = 5.6$ kJ mol^{-1}) indicates 40% reactant character, which is in line with the value of k_H/k_D (**10**) reported.[9]

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