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A ß,ß-Shielded Vinyllithium Example for a Quantification of Structure, Monomer-Dimer Equilibrium, and some Reactivity Parameters[1]

Rudolf Knorr*, **Johannes Freudenreich** and **Kurt Polborn**

Institut für Organische Chemie der Universität München, Karlstrasse 23, D-80333 München, Germany

Heinrich Nöth and **Gerald Linti**

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-80333 München, Germany

Abstract: Crystalline 2-(lithiomethylene)-1,1,3,3-tetramethylindan (3) forms the etherate 11 as a centrosymmetric dimer with a LiCLiC four-membered ring. The carbanionic terminal of each of the two CC double bonds is tetracoordinated, being bonded at almost equal distances to the two lithium cations above and below the plane containing both the double bond and the vinylic hydrogen atom. For each lithium cation, tetracoordination is achieved by bonding to two carbanion centers, to the oxygen atom of one ether molecule, and (weakly) to one of the methyl groups. This unstrained dimeric structure is retained in *tert*-butyl methyl ether but not for all molecules in tetrahydrofuran (THF). In THF monomeric 3 predominates at low temperatures and dimerizes endothermically. The two components in equilibrium have characteristically different NMR spectra, in part due to charge polarization by the lithium cation. Their equilibration is the fastest mechanism of C-Li bond breaking. The monomer (15 % at +30°C) in THF is the active base for an allylic deprotonation and shows the expected degree of reactivity. Addition of dimeric 3 to di-*tert*-butyl ketone is rapid, yet measurable and selective; monomeric 3, however, might be more selective.

Introduction

Structural knowledge of organolithium compounds in the solid state and in solution has rapidly developed over the last two decades.[2,3] In the sub-class with sp^2-hybridized carbanionic functions, aryllithium derivatives (1) have provided broad evidence for variability of their ground states. Phenyllithium (1a) in particular can crystallize as a tetrameric etherate,[4] as a dimer[5] if chelated by tetramethylethylenediamine (TMEDA), or as a monomer[6] with N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDTA) in which complex the lithium cation lies slightly off the aromatic plane. ^{13}C-NMR chemical shifts[7,8] and coupling constants[7-9] ^1J(C,Li) to lithium have allowed a ready differentiation of the various phenyllithium aggregates in a variety

of solvents. Corroborating evidence from careful NMR relaxation studies, albeit restricted in applicability[10,11], has also been an important source for evaluation of intramolecular distances[10] or of the coordination sphere[11] of lithium in solution over a broad temperature range. The crystalline dimer[12] of mesityllithium (1b) became exclusively monomeric[7] when sufficiently solubilized in THF by the tightly coordinating chelator PMDTA. As another monomeric example, 2,4,6-tris(*tert*-butyl)phenyllithium ("supermesityllithium", 1c) has been characterized with a chelating base in the solid state[13] and in solution[7]. In order to observe $^1J(^{13}C,^6Li)$ coupling constants of 1 it has typically been necessary to cool the solutions close to the freezing point of the ethereal solvent. At somewhat higher temperatures, the ^{13}C-NMR multiplet of the carbanionic center usually[3] collapsed to a singlet (if ^1H-decoupled) by increasingly rapid intermolecular C-Li bond breaking and bond making.

| 1	R
a	H
b	Me
c	CMe₃
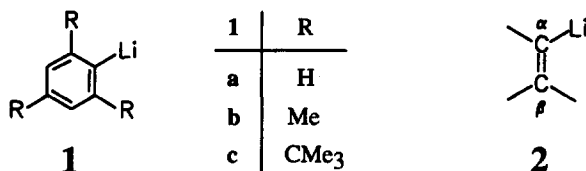
If we were given the opportunity to choose convenient properties for an organolithium model system to be used in investigations of reactivity and reaction mechanisms, which kind of features would be desirable? That the aggregation state may be changed by solvation or with additives such as chelating Lewis bases is interesting but also a source of complication because then one has to consider equilibrating chemical entities of similar constitution but different reactivities. Taking the above-mentioned example of phenyllithium[8], the ground state of 1a is not the same in ether (tetrameric) as it is in THF either without (dimeric) or with PMDTA (monomeric). A monomeric model system without chelation would certainly be preferable, albeit still far from simple if allowance has to be made for further possible equilibria between contact ion pairs, solvent-shared ion pairs, and perhaps even a tiny concentration of highly reactive[14] free carbanions. If an equilibrium of aggregates cannot be avoided, it should be of the simplest type and vary in a predictable way with changing experimental conditions (like solvent or temperature). In view of the mobility of lithium at the carbanionic center, additional conformational ambiguities as in *n*-butyllithium are undesirable for an assessment of the transition state of a chemical reaction: A more convenient carbanion moiety would have to be sufficiently rigid in order to conserve its basic skeletal geometry when substituents or the external conditions are to be varied. A well-defined and rigid geometry might facilitate theoretical calculations as well as an analysis of charge distribution (if possible) as a function of solvation; it is also one of the premises for Jackman's[10,11] methods of estimating distances in solution.

Furthermore, the degree of reactivity should be typical of organolithium compounds but not too high for two reasons. Higher reaction rates are progressively difficult to determine, requiring special techniques[3,15], such that the kinetic order of reaction as an important mechanistic criterion may not be measurable with sufficient precision. Since ethereal solvents can act as proton sources above certain temperatures, high reactivity may result in low stability; this basic practical problem might cause inconvenience when models of the alkyl[8] or benzyl type are subjected to long-term studies. Moreover, organolithium compounds with charge-delocalized anions (benzyl and allyl types) constitute poor model systems in a strict sense because they do not provide direct evidence by NMR coupling constants for the kinetic stability of their C-Li contacts.

An ideal model system with all of the optimal properties may perhaps not be found. However, vinyllithium derivatives **2** possess inherent rigidity together with a broad constitutional variability by substitution at their α and β positions. They can also have stereodynamical properties[16,17] in contrast to most other classes of organolithium compounds, but this feature will not be touched here. We have initiated studies of such model systems for an assessment of how far the above-mentioned ideals may be converted into reality.

A. Preparation and Stability of 2-(Lithiomethylene)-1,1,3,3-tetramethylindan (3)

The Br/Li exchange reaction between 2-(bromomethylene)-1,1,3,3-tetramethylindan[18] (**4**) and n-butyllithium to give 1-bromobutane and the ß,ß-di-*tert*-alkyl substituted vinyllithium derivative **3** required several days in hexane at room temperature[19] but only a few minutes in THF at -78°C. However, this method did not provide stable THF solutions of **3** at ambient temperature because the 2-(pentylidene)indan[18] **6** and LiBr were formed rather quickly by coupling of **3** with the accompanying 1-bromobutane. Even when the latter had been removed by distillation in vacuo, redissolved **3** was protonated by the THF solvent to give the parent olefin **7**[18,20] with $t_{1/2} \approx 29$ h at room temperature. It was therefore better to trap **3** with chlorotrimethylstannane and to purify the α-trimethylstannyl derivative **5**[20,21]. Since **5** is a secondary source of **3** (see below), it was important during its formation to use n-butyllithium in only moderate excess (0.3 equiv.) as required for a fast and complete conversion of the bromide **4**, and to destroy this excess with more chlorotrimethylstannane; remaining n-butyllithium would regenerate **3** from **5** and lead to **7** as a byproduct during workup.

4 - 9	R
4	Br
5	SnMe3
6	n-butyl
7	H
8	SiMe3
9	CO2H
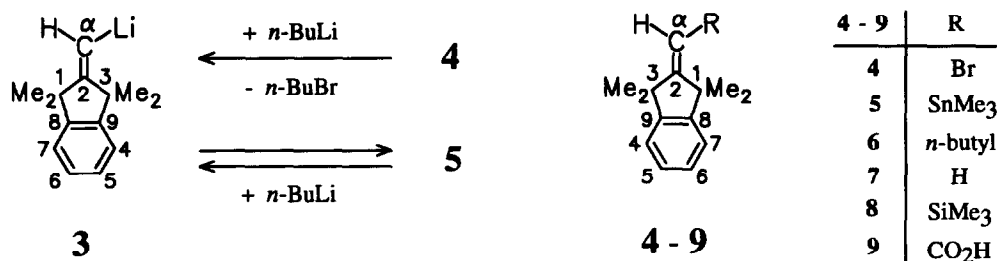
The reduction of bromide **4** with lithium metal was surprisingly sluggish even in THF. Because of the mentioned attack of THF on **3**, this method was of preparative value only with in-situ trapping by an electrophile which is sufficiently unreactive toward lithium: Chlorotrimethylsilane could be applied in this way to prepare **8**[20], whereas chlorotrimethylstannane reacted too quickly with lithium metal under similar conditions, forming hexamethyldistannane ($\delta_H = 0.20$ in CCl_4[22]). The product generated from **4** with activated magnesium[23] was not attacked by chlorotrimethylsilane. On the other hand, the preformed lithium compound **3** had reacted in THF at -78°C with chlorotrimethylsilane completely within 2 min but with chlorotrimethylstannane only after 10 - 15 min. Trapping with dry ice to give the carboxylic acid **9**[19,20] was a convenient criterion for formation and consumption of **3** under the various conditions.

The Sn/Li exchange of **5** with n-butyllithium proceeded without side-reactions in THF (instantaneously) or in ether ($t_{1/2} \approx 15$ min at +30°C). The presence of two equivalents of ether was necessary for the very slow conversion (17 h at room temperature) in pentane, whereas immediate conversion took place in cyclopentane with 2 equivalents of TMEDA. The lithium compound **3** was totally stable in ether but only sparingly soluble, depositing single crystals which were shown to be the monoetherate of **3** by the integration of NMR signals and by X-ray structural analysis.

B. Crystal Structure of the Monoetherate 11

Solid-state structural analyses of genuine vinyl(*mono*)lithium derivatives are very rare[24]. The only example with lithium as the sole constitutional heteroatom was the unsolvated trimer **10**[24]; a reason for this very unusual type of CLi aggregation was suspected in destabilization of an alternative dimeric structure, caused by intermolecular repulsion in **(10)₃** between α-phenyl and the methyl groups. The present substance **3** lacks this α-phenyl group; indeed, its X-ray structural analyses at +21°C and -80°C revealed the monoetherate **11** as a centrosymmetric dimer of **3**, shown in the ORTEP drawing of Figure 1. The central four-membered ring is therefore planar, unlike the C₂-symmetric core of dimeric phenyllithium[5]. The atomic coordinates from measurement at -80°C have been collected in Table 1. Bond lengths and angles are given in Table 2.

Each lithium cation is coordinated at a normal Li-O distance to a molecule of diethyl ether which is partially disordered at room temperature. The central core of **(11)₂** is best compared to that of the centrosymmetric (THF)₄ solvate of dimeric mesityllithium **(1b)** analyzed[12] at -133°C; indeed, for these two compounds the corresponding Li-C-Li' and C-Li-C' angles (66.4° and 113.6° for **(1b)₂**) are almost exactly equal thus giving rise to the same core shape. The O and O' atoms of **(11)₂** with almost coplanar (sp²) ligands are merely 0.322 Å off the central core plane which is tilted by only ≈ 15° from the "oxygen plane". Even if the Li-O interactions were counted as σ and π donation in parallel, this would not satisfy the coordination power of Li completely because the two sp²-electron pairs at C(14) and C(14') are shared with Li' in two three-center bonds. However, C(12) is separated by only 2.827 Å from Li, suggesting a stabilizing interaction by one of the CH bonds with Li-H(12a) = 2.34 (5) Å and an angle Li-H(12a)-C(12) = 109 (3)°. While such distances appear to be too large for an "agostic" interaction, they may indicate an electrostatic attraction[25]: Without stabilization

Table 1. Positional[a] and equivalent thermal parameters for **(11)₂** at -80°C

atom	x/a	y/b	z/c	U_{eq}[b]
Li	0.1080 (8)	0.4825 (2)	0.6240 (8)	0.042 (3)
O	0.2577 (3)	0.4548 (1)	0.8457 (3)	0.044 (1)
C(1)	0.1538 (4)	0.6618 (1)	0.7273 (4)	0.030 (1)
C(2)	0.1296 (4)	0.6076 (1)	0.6226 (4)	0.027 (1)
C(3)	0.2588 (4)	0.6069 (1)	0.5462 (4)	0.031 (1)
C(4)	0.5413 (4)	0.6603 (1)	0.6636 (4)	0.034 (2)
C(5)	0.6386 (4)	0.7012 (2)	0.7723 (5)	0.038 (2)
C(6)	0.5791 (5)	0.7320 (2)	0.8696 (5)	0.039 (2)
C(7)	0.4218 (4)	0.7222 (1)	0.8601 (5)	0.036 (2)
C(8)	0.3253 (4)	0.6806 (1)	0.7525 (4)	0.028 (1)
C(9)	0.3837 (4)	0.6498 (1)	0.6543 (4)	0.027 (1)
C(10)	0.0228 (5)	0.7053 (2)	0.6243 (6)	0.043 (2)
C(11)	0.1451 (5)	0.6526 (2)	0.8972 (5)	0.040 (2)
C(12)	0.3367 (5)	0.5496 (2)	0.5572 (5)	0.038 (2)
C(13)	0.1797 (5)	0.6259 (2)	0.3579 (5)	0.042 (2)
C(14)	0.0201 (4)	0.5673 (1)	0.5994 (4)	0.032 (1)
C(15)	0.2721 (6)	0.4889 (2)	0.9919 (6)	0.062 (2)
C(16)	0.1947 (8)	0.4625 (3)	1.0913 (7)	0.080 (3)
C(17)	0.3438 (7)	0.4033 (2)	0.8858 (6)	0.062 (2)
C(18)	0.3815 (7)	0.3856 (2)	0.7430 (6)	0.063 (2)
H(12a)	0.2530 (51)	0.5226 (16)	0.4837 (50)	0.060
H(12b)	0.3852 (48)	0.5337 (16)	0.6753 (52)	0.060
H(12c)	0.4259 (50)	0.5506 (16)	0.5174 (49)	0.060
H(14)	-0.0469 (46)	0.5777 (15)	0.6607 (45)	0.050

[a] Symmetry transformation: -x, +0.5 + y, +0.5 - z.
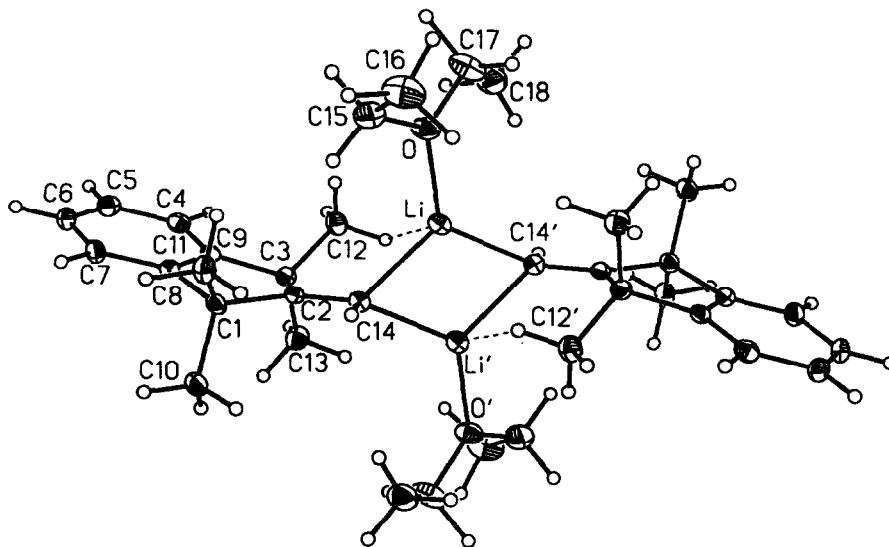[b] Equivalent isotropic U (Å²) defined as one-third of the trace of the orthogonal U_{ij} tensor.
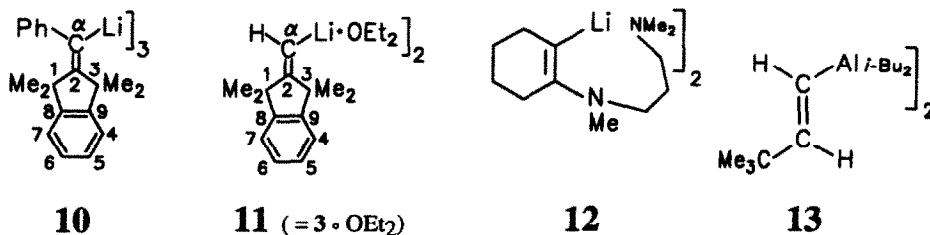
Figure 1. The dimeric etherate (11)$_2$ of **3** at -80°C, viewed in a direction approximately parallel to the vinylic C(14)-H bonds, with crystallographic numbering and thermal ellipsoids of the non-hydrogen atoms at the 25% probability level.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for (11)$_2$ at -80°C

Li-Li'	2.375 (13)	Li-O	1.970 (9)	Li-H(12a)	2.339 (52)
Li-C(12)	2.827	Li-C(14)	2.160 (10)	Li'-C(14)	2.185 (10)
O-C(15)	1.501 (8)	O-C(17)	1.416 (7)	C(1)-C(2)	1.566 (7)
C(1)-C(8)	1.492 (7)	C(1)-C(10)	1.538 (7)	C(1)-C(11)	1.566 (8)
C(2)-C(3)	1.549 (8)	C(2)-C(14)	1.318 (7)	C(3)-C(9)	1.515 (7)
C(3)-C(12)	1.524 (7)	C(3)-C(13)	1.590 (7)	C(4)-C(5)	1.392 (7)
C(4)-C(9)	1.372 (7)	C(5)-C(6)	1.400 (8)	C(6)-C(7)	1.365 (8)
C(7)-C(8)	1.396 (6)	C(8)-C(9)	1.400 (7)	C(12)-H(12a)	0.991 (37)
C(14)-H(14)	0.990 (47)	C(15)-C(16)	1.471 (11)	C(17)-C(18)	1.507 (10)

Li'-Li-O	169.9 (7)	Li'-Li-C(14)	57.4 (3)
Li'-Li-C(14')	56.4 (3)	O-Li-C(14)	118.6 (4)
O-Li-C(14')	126.7 (4)	C(14)-Li-C(14')	113.7 (3)
Li-O-C(15)	117.6 (4)	Li-O-C(17)	127.3 (4)
C(15)-O-C(17)	114.8 (4)	C(2)-C(1)-C(8)	102.4 (4)
C(2)-C(1)-C(10)	109.4 (3)	C(8)-C(1)-C(10)	109.4 (4)
C(2)-C(1)-C(11)	114.3 (3)	C(8)-C(1)-C(11)	110.9 (3)
C(10)-C(1)-C(11)	110.2 (4)	C(1)-C(2)-C(3)	109.4 (3)
C(1)-C(2)-C(14)	127.7 (4)	C(3)-C(2)-C(14)	122.8 (4)
C(2)-C(3)-C(9)	100.2 (3)	C(2)-C(3)-C(12)	111.8 (4)
C(9)-C(3)-C(12)	113.1 (3)	C(2)-C(3)-C(13)	113.0 (3)
C(9)-C(3)-C(13)	110.6 (4)	C(12)-C(3)-C(13)	108.0 (4)
C(5)-C(4)-C(9)	118.4 (4)	C(4)-C(5)-C(6)	121.9 (4)
C(5)-C(6)-C(7)	120.1 (4)	C(6)-C(7)-C(8)	117.8 (4)
C(1)-C(8)-C(7)	126.7 (4)	C(1)-C(8)-C(9)	110.9 (3)
C(7)-C(8)-C(9)	122.4 (4)	C(3)-C(9)-C(4)	126.9 (4)
C(3)-C(9)-C(8)	113.8 (4)	C(4)-C(9)-C(8)	119.4 (3)
Li-H(12a)-C(12)	109.4 (3 4)	Li-C(14)-Li'	66.3 (3)
Li-C(14)-C(2)	118.4 (4)	Li'-C(14)-C(2)	127.2 (4)
H(14)-C(14)-C(2)	106.8 (2 1)	O-C(15)-C(16)	113.4 (5)
O-C(17)-C(18)	108.5 (4)		

Ph$\overset{\alpha}{\underset{}{C}}$Li]$_3$ H$\overset{\alpha}{\underset{}{C}}$Li·OEt$_2$]$_2$

10   **11** (= 3 ∘ OEt$_2$)   **12**   **13**

by an ethereal donor, the Li-C(12) bond in unsolvated (**10**)$_3$ was shorter[24] by more than 0.3 Å. The vinylic hydrogen atom is much more remote with Li-H(14) = 2.753 and Li'-H(14) = 2.774 Å but nevertheless also able to interact with Li in solution to give NMR cross-relaxation (Section C).

According to *ab-initio* calculations[26] on monomeric models, ethenyllithium has a normal C=C double-bond length and a shorter C-Li distance than phenyllithium. Using Bader's criterion of the C-Li bond critical point, these calculations suggested a highly ionic character of this bond with an integrated charge of +0.92 on lithium. The experimental geometries of (**11**)$_2$ and of dimeric mesityllithium[12] are actually reconcilable with the electrostatic model[27,28] because the sp^2-hybridized carbanionic electron pairs are expected to be located almost within the core plane, pointing between the two lithium cations. Given the C(14)-C(14') distance of 3.638 Å for (**11**)$_2$, the separation of the two spatial density maxima of negative charge should be comparable to the Li-Li' distance of 2.375 (13) Å. Almost the same CLiCLi bonding geometry applies to the lithiated enamine **12**[29], while the 1-alkenylaluminum dimer **13**[30] has a similar shape but a wider (79°) angle Al-C-Al.

The common plane of C(1), C(2), C(3) and C(14) is almost perpendicular (86.1°) to the core plane. The C(2)-C(14) double bond is as short as in **12**[29] and does not coordinate to Li since Li-C(2) = 3.019 Å (and Li'-C(2) = 3.162 Å), in contrast to (**10**)$_3$ with 2.719 (7) Å[24]. The dihedral angle C(2)-C(14)-Li-C(14') = -120.9 (5)° corresponds to a tilt of Li toward C(12) owing to the "agostic" interaction.

The five-membered ring forms an envelope which is tilted along the line C(1)-C(3) by about 20°. The further geometrical parameters of the 1,1,3,3-tetramethyl-2-indanylidene substituent are similar to those in (**10**)$_3$[24], except for an even weaker back-bending of the four methyl groups: With an angular average of 111.0 (4)° for CH$_3$-C(1,3)-C(8,9) and strong tilting, (**11**)$_2$ appears to be free of front strain along the CC double bond[31]. Unusually short non-bonded distances were not observed.

C. Ground State Properties of the Vinyllithium-Derivative 3 in Solution

Blind faith that the structure of a crystalline organolithium compound might be preserved in solution would be an imprudent attitude. Using the ^{6}Li-labelled etherate 3∘OEt$_2$, we have therefore applied the concept of searching for atomic contacts of lithium at bonding and non-bonding distances. The latter may be detected by the two-dimensional NMR technique of (^{6}Li,^{1}H) HOESY[32,33] which showed quickly that ^{6}Li in 3∘OEt$_2$ is correlated by cross-relaxation with α-H and with 3-CH$_3$ (the low-field methyl signal) in *tert*-butyl methyl ether (tBuOMe) and in [D$_8$]-THF at +25°C[34]. Coordination with tBuOMe solvent was also visible, but the one equivalent of diethyl ether was no longer coordinated (no cross peak). Hence the basic geometrical relation between cation and anion is similar to that in the crystal, but the aggregation state still obscure.

The number of carbanion bonding contacts to ^{6}Li cations follows from the ^{13}C-NMR multiplet shape of the C-α signal[3,9,35,36]. Examples from the family of genuine vinyllithium derivatives are the CLi$_1$ triplets of **14** (^1J = 10.6 Hz at -91°C in [D$_8$]-THF)[37] and of **15** (^1J = 14 Hz at -80°C in [D$_8$]-THF)[38], and the CLi$_2$

quintet of **16** (^1J = 9.0 Hz at -112°C in 2-methyl-THF)[9]. In tBuOMe our model exhibited the CLi_2 quintet with ^1J = 9.5 Hz at *all* temperatures between -106°C to +25°C. The coalescence temperature +37 (±5)°C was unusually high for an ethereal solvent; it corresponds to ΔG^* = 16.3 (±0.3) kcal/mol for the interaggregate exchange of cations and hence to a kinetically rather stable CLi bond. However, CLi_2 contacts are compatible with the structures of $(11)_2$ as well as with a cyclic trimer like $(10)_3$ or further aggregates. Therefore, the degree of aggregation was finally measured to be 2.0 (±0.1) by isopiestic molecular mass determinations[39].

14   **15**   **16**
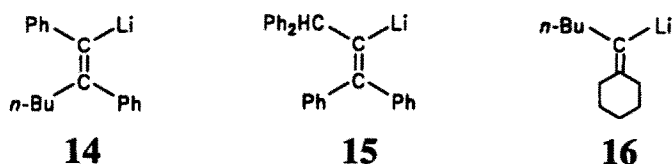
Thus the etherate of **3** in tBuOMe has the same structure $(11)_2$ as in the crystal by the criteria applied above. In spite of its narrow angle C(2)-C(14)-H(14) = 107 (2)°, it is still unstrained by the criterion of its ^1J(C-α,α-H) coupling constant, which is 91.9 Hz in this solvent and precisely equal in THF solution to that of vinyllithium (88 Hz)[40]. By way of contrast, front strain along the C=C bond of **5** and **8** (and of the adduct **25c**) was already noticed[20] from diminished $^1J_{CH}$ values, and the coupling constants involving ^{119}Sn in **5** also point to angular distortion: The magnitudes of ^2J(Sn,α-H) and ^3J(Sn,C-1/-3) are considerably decreased (see Experimental), whereas ^2J(SnMe_3) and both ^1J(Sn,C) have their normal[41] values, which is also true for both $^1J(^{29}$Si,C) of **8**. Compared with **5** and **8**[20], the ^2J(C-2,α-H) = 10.2 Hz is slightly increased in **3**.

Like many other vinyllithium derivatives, 3•OEt_2 is insoluble in pure saturated hydrocarbon solvents. Thus tBuOMe was one of the least polar solvents which could be used, and most ^{1}H- and ^{13}C-NMR chemical shifts δ were slightly temperature-dependent (measured at +45, +25, -90 and -106°C)[34]. However, this was not caused by lithium but is rather a property of the hydrocarbon skeleton of **3** because the corresponding δ values of the parent olefin **7** exhibited just this behaviour[34]. Therefore, the lithiation shifts Δδ, defined as δ(3) - δ(7) and shown in **17**, are totally independent of the temperature, reinforcing the previous conclusion of a single (CLi_2) aggregate.

17   **18**   **19**   **20**

(dimeric **3** in tBuOMe)   (dimeric **3** in THF)   (monomeric **3** in THF)   (in THF)
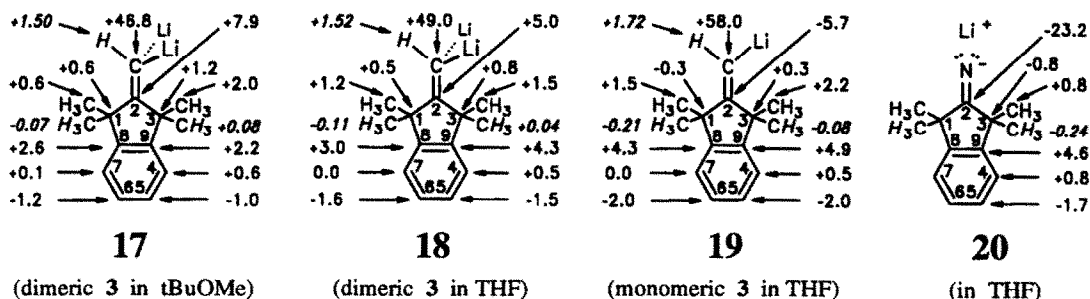
This behaviour was quite different in THF solution. The NMR chemical shifts (assigned at 25°C by NOE, HOESY and the previously[20] described selective decoupling) changed gradually on cooling, with final doubling of the resonances except for C-4 and C-7. The lowfield C-α absorption was clearly due to monomeric **3** for reasons of its triplet splitting (CLi_1) with $^1J(^6$Li,C) = 15.9 Hz; from its coalescence above -90°C, the cation exchange requires only ΔG^* = 9.2 (±0.5) kcal/mol, much less than in tBuOMe. The second C-α had a

linewidth compatible with a CLi_2 quintet but was never resolved; however, its δ value was sufficiently close to that of **3** in tBuOMe for a reasonable assignment to the dimeric aggregate. The lithiation shifts $\Delta\delta$ are depicted in formulae **18** for the dimer and **19** for the monomer. As expected from "IGLO" calculations[42] on dimeric and tetrameric models of vinyllithium, $\Delta\delta$ in **17** and **18** is positive (downfield) for C-β and much more so for C-α. But the monomer has a negative $\Delta\delta$ (in **19**) for C-β as if there were now more negative π charge[43] induced at this atom. The aromatic rings in **17-19** show a pattern of $\Delta\delta$ values similar to that of the isoelectronic lithium imide[44] **20**. This has been ascribed to π electron polarization[20] in front of the π-insulator atoms C-1 and C-3; it is consistent with a high ionicity of the CLi_2 group in **17-18** and perhaps a slightly more ionic CLi_1 bond in **19**. Indeed, the $\Delta\delta$ sums of negative (C-5 + C-6) and positive (C-8 + C-9) induction fall close to the correlation line[45] connecting also **20, 4, 5, 8, 9** and **25c**. Such data might bear some significance for comparisons with theoretical charge calculations[25] on the aggregates.

D. Monomer-Dimer Equilibrium in THF

Energy parameters can be important data in consideration of reaction mechanisms, especially for a ground state in equilibrium. The present case comprises the formation of 0.5 dimers (D) from one monomer (M) in eq. (1). The equilibrium constant is $[D]^{0.5} \cdot [THF]^m/[M]$ such that all data refer to the monomer. Experimental determinations of the concentration ratios $[D]/[M]$ were performed at low temperatures (down to -107°C) by integrations of corresponding ^{1}H- and ^{13}C-NMR signals and checked by ^{6}Li NMR at -104°C where >50% of the material is monomeric. With increasing temperatures all separate resonances of **M** and **D** became coalesced and their averaged positions tended toward those of the dimer which is therefore formed endothermically. Analysis by the correspondingly temperature-dependent $\Delta\delta$ values, shown in Figure 2, was chosen in order to eliminate the intrinsic temperature dependence explained in Section C. The solid and (at or below coalescence) broken curves were calculated from the reaction enthalpy $\Delta H^o = +1.2$ (±0.2) kcal/mol and a reaction entropy $\Delta S^o = +16.9$ (±1) cal/(K·mol) for a 0.5 F solution of **3** without correction[37,46,47] for the density change of THF. A 0.3 F solution had similar experimental and theoretical curves (not shown) slightly displaced toward the monomer **M**, as expected on dilution.

$$M \cdot (THF)_{n+m} \quad \rightleftharpoons \quad 0.5 \; D \cdot (THF)_{2n} \; + \; m \; THF \tag{1}$$

The thermodynamic parameters include an averaged concentration $[THF] = 10.5$ M in the solvent under our conditions, and the postulate of m = 2 in eq. (1) such that the monomer **M** would be trisolvated if n = 1 for **D** as in $(11)_2$. An increase of m by one unit would change only the entropy by $\Delta\Delta S = m \cdot R \cdot ln[THF] = +4.7m$. For comparisons, the following published data were converted to values ΔS^m and ΔH^m normalized to one formal equivalent of lithium in the *less* aggregated component considered to be the starting material, although the per mol basis and the inclusion of solvent were not always stated explicitly in the literature. The resultant ΔS^m of aggregation for a half-dimer of *n*-butyllithium were +3.5[48], +4.7[15], +6.6[15], or +11.2[49] in THF. Similarly, aggregation of *tert*-butyllithium gave $\Delta S^m = +39$ (for 2 Et_2O per Li)[50], $(Me_3Si)_2NLi$ +8.5 in THF[51], and lithium phosphides ≈ +5 in ether[52]. The positive values mean that coordinating donor (solvent) molecules become mobilized on aggregation[53]. Due to its rigid carbon skeleton, fluorenyllithium is a good model suggesting ≈ +28 entropy units[53-55] (e.u.) for the two solvent molecules released. Our value $\Delta S^o = +16.9$ e. u. would leave ≈ -11 e.u. for the aggregation of the two half-monomers without solvation, in good accord with the literature data recalculated for one equivalent of the smaller aggregates of *n*-propyllithium[36], *iso*-propyllithium (-15)[56], 2-butyllithium (-9)[57], or 2-pentyllithium (-8)[56], all in cyclopentane solution.
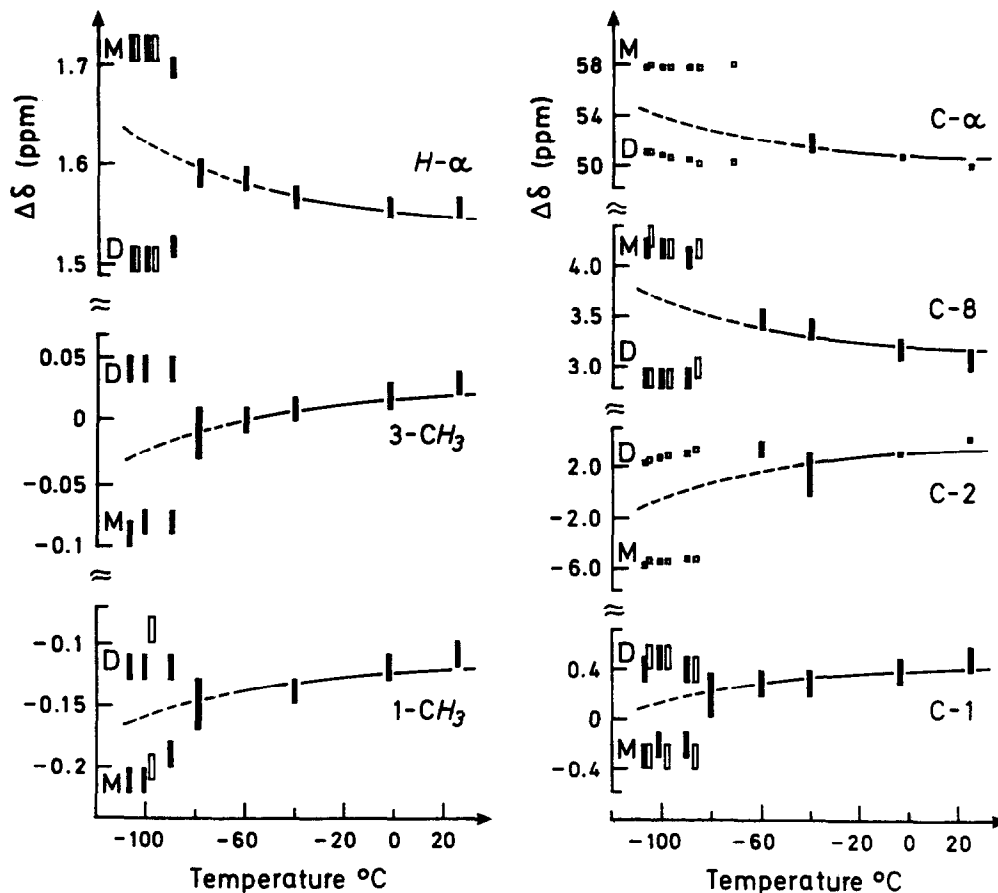
Figure 2. Lithiation shifts Δδ of 3·OEt₂ (0.5 F in THF) as a function of the temperature, with theoretical curves computed for eq. (1) from ΔH° = +1.2 kcal/mol and ΔS° = +16.9 e. u.; M = monomer, D = dimer, open symbols for a 0.3 F solution; ¹H NMR on the left, ¹³C NMR on the right.

This analysis implies that two coordinating THF molecules will be replaced in the monomer of **3** on dimer formation. The observed ΔH° = +1.2 kcal/mol agrees with ΔH^m (again normalized) for n-butyllithium (≈ +0.6)[15,48] or (Me₃Si)₂NLi (+2.0)[51], but this must be fortuitous if the former loses only one THF per lithium. The relevant coordination energy of THF as a solvent, ≈ 5.2 kcal/mol as obtained from ion-pair equilibria[47,54,55], is of course different from the value ≈ 7 determined[15,58-60] in hydrocarbon solvents. An energetic penalty for monomeric **3** would then amount to +10.4, such that -9 kcal/mol is left for the attraction of a second monomer without production of strain. This estimate is reasonably more negative than ΔH^m ≈ -2[36], -4.3[56], -2.3[57], or -1.8[56] kcal/mol for an increasing association of the higher aggregates in cyclopentane. Thus the thermodynamic properties of **3** do not contradict the few literature data most of which had been determined from more complicated systems. We finally mention some qualitative reports on monomers of even extremely basic substances, like tert-butyllithium[61] and 2-butyllithium[61] in THF, or 7-lithionorbornadiene[62] in dimethyl ether. The decrease in solvation power of diethyl ether in comparison with THF suffices to tip the balance toward the more aggregated forms[50,61,63].

We estimated the rate constants of monomer/dimer interconversion for **3** at eleven coalescence temperatures (between -95 and -60°C), some of which may be gleaned from Figure 2. All of them were compatible with a single value of $\Delta G^* = 9.0$ (±0.1) kcal/mol. Therefore, the carbanion exchange between the aggregates needs the same activation as the cation exchange reported in Section C. Hence the fastest mechanism of C-Li bond breaking appears to be the de-aggregation of dimers in THF.

E. Reactivity

n-Butyllithium is decomposed by the solvent THF with a half-conversion time ($t_{1/2} = 10$ min at +35°C)[64] which is much shorter than that of **3** (29 h). On the other hand, *n*-butyllithium and **3** as a mixture have a roughly comparable reactivity toward chlorotrimethylsilane at -78°C; however, the question of the aggregation state of **3** in presence of *n*-butyllithium has not yet been addressed.

A THF solution of **3** contains ≈ 85 (±3)% of the material in the dimeric form **D-3** at +30.3°C (see Figure 2). An "acid" like 2-methyl-1-phenylpropene (**21**) might protonate the dimer directly to give the parent olefin **7** of **3** together with the allyllithium compound[65,66] **22**. The kinetics would then obey a normal rate law of second order, with the formal concentrations [**3**] and [**21**] both in first order. But if the minor component **M-3** in a mobile equilibrium were the kinetically more active base, then the rate would be proportional to $[3]^{0.5}$ and to $[21]^{1.0}$ (total kinetic order 1.5). Fractional orders of reaction are an important mechanistic criterion and quite common[67] in organolithium chemistry. We have applied this concept to **3** as follows.
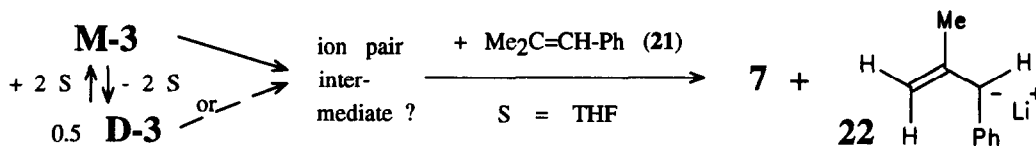
The time-dependent concentrations of **3**, **7**, **21**, and **22** could be followed by ^{1}H-NMR spectroscopy[66] for an initially 0.67 F solution of **3** after the addition of **21** (0.14 equiv.). The pseudofirst-order (with respect to [**21**]) rate law expected for this setup was observed[34] with a rate constant $k_\psi = 4.74 \cdot 10^{-5}$ s^{-1}. After the quantitative consumption of **21** and formation of **22**, another 0.30 equivalent of **21** was introduced and reacted distinctly slower. However, both experiments gave the same value of $k_{1.5}' = k_\psi [3]^{-0.5} = 6.0 \cdot 10^{-5}$ l$^{0.5}$ mol$^{-0.5}$ s^{-1}, using the time-averaged formal concentrations [**3**] for division. Thus the presence of 0.14 equivalent of **22** had not changed the rate constant. An independent run with an initial [**3**] = 0.34 F increased $t_{1/2}$ to 327 min (from 244 min). Combination of the results from all three runs provided an experimental order $r = 0.41$ (±0.1) with respect to **3**. These error limits are not atypical in the field but suffice to exclude a first-order dependence on [**3**] and thus a direct attack of **21** on the dimer. The decision for $r = 0.5$ will be obvious in view of the equilibrium results in Section D. The factor[66,67] $r^r = 0.71$ may then be used for a final improvement of $k_{1.5}'$ to the correct value.

Thus the monomer **M-3** is the base predominantly responsible for deprotonation of **21**. In tBuOMe, in which **3** is exclusively dimeric (Section C), this reaction did not occur at all over a period of more than two days ($t_{1/2} > 300$ h). We suspect that the deprotonation requires THF for the generation of a reactive intermediate[66] of a nature such as to leave the 1.5th order of reaction unaffected. The rate constants in THF transform into $\Delta G^* = 23.7$ kcal/mol, whereas 2-methyl-1-phenyl-1-propenyllithium[66] (**23**) had $\Delta G^* = 21.5$ under the same conditions. Assuming that $\Delta S^* = -44$ e. u.[66] of **23** is approximately also valid for **3**, we estimate a $\Delta G^* \approx$

19 kcal/mol at -70°C for this protonation by **21**; monomer-dimer equilibration with the much lower value 9.0 (Section D) is therefore not the rate-determining step. Further comparison of the k_ψ value given above reveals that *n*-butyllithium in THF at +30°C is merely 7 times more reactive than **3** (and **23** ≈ 60 times, judged from the $k_{1.5}'$ value), whereas ethenyllithium is ≈ 50 times less reactive[65].

24, 25	R
a	$CH(CH_2)_2$
b	$CHMe_2$
c	CMe_3
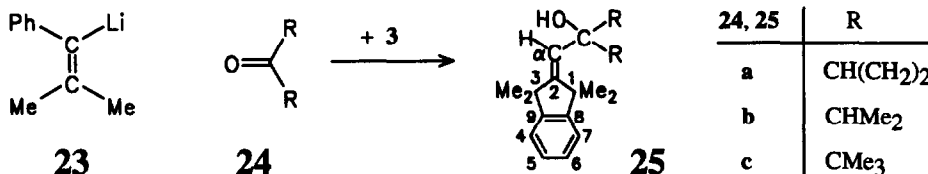
The addition of di-*tert*-butyl ketone (**24c**) to **3** in THF was sufficiently slow ($t_{1/2}$ ≈ 30 min) at -34°C for crude ^{1}H-NMR measurements to give ΔG^* ≈ 17.6 kcal/mol under pseudofirst-order conditions as above. The monomer-dimer equilibration is therefore again not rate-determining. As the temperature dependencies are not known, only a very rough comparison is possible with values at +25°C of ΔG^* = 14.3 for tetrameric methyllithium in ether[68] and ΔG^* ≈ 15 for *n*-butyllithium in hydrocarbons[69,70] in their additions to aryl ketones. Unfortunately, our NMR integrations were not good enough for a determination of the reaction order. Furthermore, the product alcoholate of **25c** might change the reactivity[50,68,69,71] of **3** by mixed aggregation to cause formidable problems[72]. Consequently, **3** should be used in a higher stoichiometric excess over **24** and this would necessitate a more sensitive analytical method. We therefore preferred to determine relative rates k_a/k_b by the addition of **3** to known mixtures of dicyclopropyl (**24a**) and diisopropyl (**24b**) ketones, despite published[73] pessimism. These competition constants, shown in Table 3, were 4.4 (±0.5) in tBuOMe and in THF at +25°C, where the dimer **D-3** predominates, but 12 (±2) at -78°C in THF for the **M-3/D-3** mixture. As the results did not depend significantly on the amount of **3**, the product alcoholates either changed k_a proportionally to k_b or not at all. Although these data point to a higher selectivity of the monomer **M-3**, they do not yet tell us if this depends on the solvent or temperature.

Table 3. Competition Constants k_a/k_b of the ketones **24a,b** for **3·OEt₂**.

Solvent	x + y ml[a]	Temp. °C	3·OEt₂ mmol	24a mmol	24b mmol	25a / 25b ratio	(mg)	k_a/k_b
tBuOMe[b]	2.0 + 0.5	+25	0.07	0.58	2.89	43/57	(18)	3.9
tBuOMe[b]	2.0 + 1.5	+25	0.21	0.58	2.89	47/53	(36)	4.6
tBuOMe[b]	2.0 + 2.0	-78	0.17	0.83	0.42	90/10	(50)	4.9
THF	2.0 + 1.0	+25	0.13	0.52	5.19	32/68	(16)	4.6
THF	3.0 + 1.5	-78	0.23	0.67	0.67	91/9	(36)	10.8
THF	3.0 + 1.5	-78	0.24	1.05	3.49	75/25	(34)	10.6
THF	3.0 + 1.5	-78	0.27	0.53	5.33	57/43	(25)	14.0

[a] See Experimental. -   [b] *tert*-Butyl methyl ether.

The absolute rates with **24a,b** must be significantly higher than with **24c**, because the latter competing with either **24a** or **b** in tBuOMe at +25°C gave no trace of the product **25c** but only **25a** or **b**. Reversibility was excluded by a control experiment in which the lithium salt of **25c** did not react with **3** equivalents of **24a** during 3 h at +25°C in tBuOMe (89% recovery of **25c**). No addition of **3** to **24a,b** had occurred at -104°C on quenching with methanol after 60 min in THF; this fact implies $t_{1/2}$ >10 h and hence ΔG^* >13.3 kcal/mol, to be compared with ΔG^* ≈ 9.8 for the addition of *n*-butyllithium at -86°C to benzaldehyde in THF[71].

Conclusion

Vinyllithium was reported to be tetrameric in THF[74] and ether[75]. Its β,β-shielded derivative **3** is much more reactive as a base toward the olefin **21** and provides a simpler mechanistic model. The disolvated dimer **D-3** (**11**) appears to permit a relatively unhindered approach (Figure 1) of even bulky reagents (**24c**), adding ketones with moderate selectivity in tBuOMe solvent. The invariance of its lithiation NMR shifts $\Delta\delta$ (indicative of charge polarization) is a useful criterion for no changes in aggregation or solvation equilibria over a temperature span greater than 150 degrees. Even the kinetic cohesion of **D-3** is high, as judged from an unusual persistence of the C-Li contacts.

In THF solution, **D-3** is in a mobile equilibrium with the monomer **M-3** which is thought to have a C-Li geometry like the aryllithium monomers[6,13]. **M-3** has a different charge polarization and should be trisolvated like phenyllithium[6], in accord with our thermodynamical results supplied by a multitude of NMR data. The efficient donor THF (but not tBuOMe) can promote the de-aggregation of **D-3** because increased solvation surpasses the enthalpy required for separation of the monomers. **M-3** is energetically favoured in THF and probably more selective toward the ketones, but disfavoured as usual by its more negative entropy. It is the minor component at +25°C but the kinetically more active base toward **21**, causing a 1.5th order of reaction.

Our model is free of the complication[37] caused by TMEDA in the formation of monomeric **14**. But mechanistic studies are still[67] "in their early days"[76], and a purely monomeric model might provide better prospects to elucidate finer details.

EXPERIMENTAL

IR: Perkin-Elmer 125 or Bruker IFS-45. - UV/Vis: Perkin-Elmer Lambda 3 and DMR-10, or PRQ 20 (C. Zeiss). - MS: Finnigan MAT 90. - NMR: Varian VXR-400S and HA-60-IL, or Bruker WP-80-CW; internal standard TMS, or external LiBr in THF for ^{6}Li. All coupling constants are given as absolute values.

General Comments. Carefully dried 5-mm NMR tubes were used for experimentation under a stream of dried and deoxygenated argon. THF was freshly distilled from the potassium/benzophenone radical anion. Diethyl ether and *tert*-butyl methyl ether (tBuOMe) were dried over solid KOH and distilled from sodium/benzophenone. [^{6}Li]-*n*-butyllithium in cyclopentane was made[9] from ^{6}Li metal (at least 91% labelled). The preparations[18] and spectra[18,20] have been described for compounds **4**, **6** and **7**.

2-(Lithiomethylene)-1,1,3,3-tetramethylindan (3)

The bromide **4** (500 mg, 1.89 mmol) in a hexane solution of *n*-butyllithium (3.0 ml, 3.9 mmol) required 4 d at room temperature for total conversion. The constitution **3** of the precipitate was proven by carboxylation with CO_2 to give the acid **9**. The small amount of **3** remaining in solution seemed to form a mixed aggregate with *n*-butyllithium because the ^{1}H-NMR signal of the latter was broadened or invisible but appeared after THF addition; simultaneously, the olefinic α-H absorption was strongly shifted by such additives. - ^{1}H NMR (hexane): δ = 6.00 (s, α-H); (pentane with 2 equiv. of ether): δ = 6.09 (s); (cyclopentane with TMEDA): δ = 6.41 (s); (ether): δ = 6.49 (s); (tBuOMe, THF or [D$_8$]-THF): δ = 6.57-6.88 (s), see below.

2-(Lithiomethylene)-1,1,3,3-tetramethylindan Monoetherate (3·OEt$_2$)

A dried 5-mm NMR tube containing the stannane **5** (168 mg, 0.48 mmol) in anhydrous diethyl ether (0.8 or 0.3 ml) was cooled to -78°C under streaming Ar. After the introduction of 0.63 mmol of *n*-butyllithium (2.1 F in hexane) or of [^{6}Li]-*n*-butyllithium[9] (1 F in cyclopentane), the tube was sealed with a tight rubber stopper and cautiously shaken to mix the contents thoroughly, then kept at room temperature in a vibrationless condition. Formation of crystals started after 3 h and may be induced by short recooling of the yellow solution to -78°C. A microcrystalline first precipitate could be redissolved by gentle warming in a water bath with violent shaking perpendicular to the tube axis. Such recrystallizability is not very common for vinyllithium derivatives and disappeared after aging for 12 h to afford colourless, transparent single crystals. With cooling (0°C to -78°C) under Ar, the supernatant liquid containing *n*-butyltrimethylstannane and olefin **7** was cautiously removed by syringe and replaced by dry cyclopentane. In the same way, the crystals were washed with two 0.4 ml portions of pentane or cyclopentane and dried in vacuo or in a slow stream of dry Ar (yield 68 mg, 53%, or up to 90% in larger runs). They could be stored in a Schlenk tube at room temperature for weeks. A sample did not melt when heated in a sealed capillary up to 300°C but deposited a yellow oil on the crystal surface at 120-126°C and became opaque above 130°C. NMR samples were prepared by weighing **3** in the tube filled with Ar and cooling to -78°C before addition of the solvent and a trace of TMS. [D$_{12}$]-Cy-

clohexane (10-15% by volume) was added for locking at the 400 MHz machine, except for $[D_8]$-THF solvent.

NMR Spectra of 3∘OEt₂ (0.4 F in tBuOMe at +25°C): ¹H NMR: δ = 1.25 (s, 2 1-CH₃), 1.41 (s, 2 3-CH₃, assigned by HOESY), 6.57 (s, α-H), 7.05 (mc, 5-/6-H), 7.10 and 7.15 (2 mc, 7-/4-H). - ¹³C NMR: δ = 32.7 and 34.1 (2 qq, ¹J = 125, ³J = 4.6 Hz, 2 1-CH₃ and 2 3-CH₃, respectively), 47.7 (m, C-1), 48.3 (m, C-3), 123.1 (dm, ¹J = 155 Hz, C-7), 123.6 (dm, ¹J = 155 Hz, C-4), 126.4 (dm, ¹J = 158 Hz, C-6), 126.6 (dm, ¹J = 158 Hz, C-5), 151.2 (dqi, ¹J = 91.9 Hz, ¹J(⁶Li,C) = 9.5 Hz, C-α), 151.9 (m, C-9), 152.3 (m, C-8), 179.4 (m, C-2); assignments by selective {¹H} decoupling[20] on CH₃ which gave also the long-range ¹³C,¹H coupling constants as ³J(C-1,α-H) = 9.5 Hz (d), ³J(C-1,7-H) = 1.9 Hz (d), ³J(C-3,α-H) = 14.2 Hz (d), ³J(C-3,4-H) = 1.9 Hz (d), ³J(C-8,6-/4-H) = ³J(C-9,7-/5-H) = 6 Hz (2 t), ²J(C-2,α-H) = 10.2 Hz (d). - ⁶Li NMR: δ = +2.3.

NMR Spectra of 3∘OEt₂ in THF or $[D_8]$-THF at +25°C: ¹H NMR (0.5 F in $[D_8]$-THF) : δ = 1.24 (s, 2 1-CH₃), 1.38 (s, 2 3-CH₃), 6.65 (s, α-H, NOE +15% on irradiation at δ = 1.24), 7.03 (mc, 5-/6-H), 7.11 and 7.15 (2 mc, 7-/4-H); (0.3 F in THF): δ = 1.22, 1.36, 6.64, 7.01, 7.10. - ¹³C NMR (0.5 F in $[D_8]$-THF): δ = 33.1 and 33.7 (2 qq, ¹J = 125, ³J = 4.5 Hz, 2 1-CH₃ and 2 3-CH₃, respectively), 47.6 (m, C-1), 47.9 (dm, C-3), 123.1 (dm, ¹J = 153 Hz, C-7), 123.5 (dm, ¹J = 153 Hz, C-4), 126.0 (2 coincident dm, ¹J = 158 Hz, C-5/-6), 152.9 (m, C-8), 153.4 (m, C-9), 154.2 (dm, ¹J = 88 Hz, C-α), 175.5 (m, C-2); (0.3 F in THF): δ = 32.9, 33.5, 47.3, 47.6, 122.8, 123.3, 125.7, 152.8, 153.4, 154.6, 174.2; assignments by selective {¹H} decoupling[20] on CH₃ or on the aromatic region to give also the long-range ¹³C,¹H coupling constants as ³J(C-1,α-H) = 9.5 Hz (d), ³J(C-1,7-H) = 1.8 Hz (d), ³J(C-3,α-H) = 14.5 Hz (d), ³J(C-3,4-H) = 2.0 Hz (d), ³J(C-8,6-/4-H) = ³J(C-9,7-/5-H) = 6 Hz (2 t), ³J(C-8,1-CH₃) = 3.7 Hz (m), ³J(C-9,3-CH₃) = 3.8 Hz (m). - ⁶Li NMR: δ = +1.2.

Averaged Shift Values for the two Equilibrium Components M and D of 3 in THF or $[D_8]$-THF (-90, -99, -101, -106 and -107°C): ¹H NMR: Monomer **M** δ = 1.14 (1-CH₃), 1.27 (3-CH₃), 6.88 (α-H), 7.03; dimer **D** δ = 1.24, 1.39, 6.68, 7.09. - ¹³C NMR: Monomer **M** δ = 33.0 (1-CH₃), 33.7 (3-CH₃), 46.4 (C-1), 47.0 (C-3), 122.9 (C-7), 123.4 (C-4), 125.3 (C-6), 125.3 (C-5), 153.3 (C-8), 154.0 (C-9), 162.5 (t, ¹J(⁶Li,C) = 15.9 Hz, C-α), 164.5 (C-2); dimer **D** δ = 32.7, 33.0, 47.1, 47.4, 122.9, 123.4, 125.7, 125.8, 152.0, 153.4, 155.6 (unresolved qi, C-α), 172.5, the last two slightly temperature-dependent (compare Figure 2). - ⁶Li NMR: Monomer **M** δ = +0.6 and dimer **D** δ = +0.9 (≈ 60:40 at -104°C).

X-Ray Data Collection and Structure Solution: A crystal (0.3 x 0.3 x 0.45 mm³) of 3∘OEt₂ was transferred under Ar from the Schlenk tube to a glass capillary which was sealed for diffraction at -80°C.

$(C_{18}H_{27}LiO)_2$: M = (266.4)₂; space group P2₁/c (no. 14); monoclinic with a = 8.76 (3) (Å), b = 24.07 (7) (Å), c = 8.93 (3) (Å), β = 115.1 (2)°; volume = 1705.1 (9) Å³; Z = 4; d_c = 1.037 g/cm³; absorption coefficient = 0.061 mm⁻¹; F(000) = 584. - Diffractometer: Nicolet R3; radiation Mo-$K_α$ 0.71073 cm⁻¹; oriented graphite monochromator: 2Θ range = 2.0 to 45.0°; scan type = ω; scan speed in ω = 2.00 to 29.30 deg/min; scan range (ω) = 1.10°; scan range to background = 0.5; index ranges = ±h,k,l; no. of reflections collected = 2465; no. of unique reflections = 2231 (R_{int} = 2.82%); no. of observed reflections = 1714 (F > 3.0σ(F)); Lorentz and polarization corrections applied. - Program used: Siemens SHELXTL PLUS PC; solution by direct methods; refinement by full matrix least-sq.; w(F_o-F_c)² minimized; hydrogen atoms with fixed isotropic U; weighting by w⁻¹ = σ²(F_o); no. of variables = 262; final R (obs. data) = 0.058; final wR (obs. data) = 0.059; final R (all data) = 0.078; final wR (all data) = 0.071; goodness of fit = 1.04; largest difference peak = +0.49 e/Å³.

Tables of thermal parameters, fractional coordinates including hydrogen atoms, and structure factor amplitudes will be deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information m.b.H., D-76344 Eggenstein-Leopoldshafen.

Isopiestic Molecular Mass Determination of 3 in tBuOMe: The apparatus was similar to that described before[39]. The substance flask was charged with a 0.132 F solution of the crystalline 3∘OEt₂ (210.67 mg, formally 0.791 mmol) in tBuOMe (6.00 ml). The reference side, connected to a quartz cuvette, contained a 0.0514 M ballast solution prepared by dissolving fluorene (34.17 mg, 0.206 mmol) in 4.00 ml of a 7.00∘10⁻⁵ M tBuOMe solution of the indicator dye[77] N-(2,5-di-tert-butylphenyl)-3,4-coronenedicarboximid. Isothermal distillation under high vacuum at +28°C was followed by UV/VIS until equilibrium was established within 8 h. From the quotient of final and initial extinctions, E_f/E_i = 0.384/0.326, the true initial concentration of 3 was calculated[39] as [(4 ml/6 ml + 1)E_f/E_i - (4 ml/6 ml)]∘0.0514 M = 0.0666 M. Hence the degree of association was 0.132/0.0666 = 1.98 (4), or 2.11 in an independent experiment. - After several repetitions of forced distillation and re-equilibration, the recovered solution contained 3 and the olefin 7 (75:25 by ¹H NMR).

1,1,3,3-Tetramethyl-2-(trimethylstannylmethylene)indan (5)

Anhydrous THF (10.0 ml) was stirred under Ar at -78°C during the addition first of n-butyllithium (12.26 mmol, 2.5 F in hexane) and then of small batches of the solid bromoalkene[18] 4 (2.50 g, 9.43 mmol). After 20 min of further stirring and subsequent addition of solid chlorotrimethylstannane (2.44 g, 12.26 mmol), the mixture was warmed up to room temperature during 2 h and then poured on iced water (50 ml). The combined ethereal extracts (3 x 40 ml) were washed neutral and dried with K_2CO_3. The residue (3.70 g) obtained after concentration was distilled at 84-92°C/0.013 mbar to afford 2.51 g (76%) of pure 5 as a colourless oil. This initially odourless material may develop an awful smell on standing without any spectral change.

IR (film): ν = 3018 cm⁻¹, 2962, 2918, 2859, 1610 (s), 1483, 1360, 1025, 813, 754. - ¹H NMR (CCl₄): δ = 0.25 (s, SnMe₃), 1.32 (s, 2 3-CH₃), 1.35 (s, 2 1-CH₃), 5.73 (s, α-H), 7.03 (s, C_6H_4); (CDCl₃): δ = 7.17 and 7.21 (2 mc, 2 + 2 H), rest as in ref.[20]; ¹¹⁹Sn satellites (CCl₄ or CDCl₃): ²J = 54.2 Hz for SnMe₃, ²J = 46.4 Hz for α-H. - ¹³C NMR (CDCl₃): See ref.[20]; ¹¹⁹Sn satellites: ¹J = 350.6 Hz (SnMe₃), ³J = 20 Hz (C-1), ³J = 64.0

Hz (C-3), ^1J = 471.5 Hz (C-α). - MS: No M$^+$; m/z (%) = 335 (M$^+$ - CH$_3$, 22), 185 (M$^+$ - SnMe$_3$, 100). - C$_{17}$H$_{26}$Sn (349.1): calcd. C 58.49, H 7.51; found C 58.85, H 7.37. - An attempted chromatography on SiO$_2$ with light petroleum ether destroyed **5** with formation of olefin **7**, as usually observed[78].

1,1,3,3-Tetramethyl-2-(trimethylsilylmethylene)indan (8)

n-Butyllithium (10.8 mmol) in hexane (6.75 ml) and THF (8 ml) was reacted with bromide **4** (1.91 g, 7.2 mmol) and then chlorotrimethylsilane (1.40 ml, 11.1 mmol) in the manner described for **5**. The same workup procedure furnished a crude product containing **8** and the olefin **7** (87:13). (The presence of TMEDA in the reacting mixture did not change this result.) Distillation at 132-143°C/13 Torr in a small Vigreux column and chromatography on basic alumina with light petroleum ether afforded 950 mg (51%) of the colourless oil **8** which was redistilled. - IR (film): ν = 2958 cm^{-1}, 2927, 2897, 2835, 1617, 1483, 1361, 1248, 870, 844, 753. - ^{1}H NMR (CCl$_4$): δ = 0.22 (s, SiMe$_3$), 1.30 (s, 2 3-CH$_3$), 1.41 (s, 2 1-CH$_3$), 5.42 (s, α-H), 7.03 (s, C$_6$H$_4$); (CDCl$_3$): See ref.[20]. - ^{13}C NMR (CDCl$_3$): See ref.[20]; ^{29}Si satellites: ^1J = 67.5 Hz for C-α at δ = 117.9, ^1J = 52.7 Hz for SiMe$_3$. - C$_{17}$H$_{26}$Si (258.5): calcd. C 79.00, H 10.14; found C 79.49, H 9.89.

Competition of 3 and *n*-Butyllithium for Chlorotrimethylsilane: The bromide **4** (50 mg, 0.19 mmol) was added to *n*-butyllithium (0.76 mmol in 0.30 ml of hexane) and TMEDA (0.120 ml, 0.80 mmol) in anhydrous THF (2 ml) under Ar at -78°C. After 10 min of stirring, when 0.19 mmol of **3** and 0.57 mmol of *n*-butyllithium should be present, chlorotrimethylsilane (0.050 ml, 0.40 mmol) was added by syringe. The mixture was stirred for 4 min and poured on dry ice. The residue after complete evaporation of CO$_2$ was taken up in 2 N NaOH and ether. The usual workup procedure gave 20 mg of a neutral product mixture containing **8** and **7** (56:44). Acidification of the NaOH layer and extraction with ether furnished 20 mg of **9** and pentanoic acid (70:30). Thus **3** had been partially silylated in the presence of the threefold amount of *n*-butyllithium.

2-(1,1,3,3-Tetramethyl-2-indanylidene)acetic Acid[19] (9)

Samples of **3** of diverse qualities were poured on dry ice and left at room temperature for complete evaporation of CO$_2$. The residue was taken up in 2 N NaOH and ether. The purified aqueous layer was acidified and extracted with ether which was washed neutral and dried with Na$_2$SO$_4$. Concentration and recrystallization from CCl$_4$ gave colourless, glistening platelets of **9** with m. p. 199-201°C[19]. - IR (KBr): ν = 3200-2500 cm^{-1} (br., CO$_2$H), 2963, 2930, 2865, 1695 (C=O), 1648 (C=C), 1412, 1260, 1227, 762. - ^{1}H NMR (CCl$_4$): δ = 1.42 (s, 2 3-CH$_3$), 1.64 (s, 2 1-CH$_3$), 5.90 (s, α-H), 7.09 (mc, C$_6$H$_4$), 10.0 (br. s, CO$_2$H). - ^{1}H and ^{13}C NMR (CDCl$_3$): See ref.[20]. - C$_{15}$H$_{18}$O$_2$ (230.3)[19]: calcd. C 78.23, H 7.88; found C 78.30, H 7.80.

Rate Measurement of 3·OEt$_2$ with 2-Methyl-1-phenylpropene (21): The ^{1}H-NMR spectrometer temperature was 30.3 (±0.7)°C during integrations on **3·OEt$_2$** (114 mg, 0.428 mmol) reacting with **21** (0.006 ml, 0.06 mmol by integral) in anhydrous [D$_8$]-THF; total volume 0.636 ml. The first-order plot of ln[(% **3** - 86)/14] vs. time was linear for at least 2 $t_{1/2}$. More **21** (0.012 ml, 0.13 mmol) was injected for the second run.

1,1-Dicyclopropyl-2-(1,1,3,3-tetramethyl-2-indanylidene)ethanol (25a)

n-Butyllithium (1.75 mmol) in hexane was added dropwise under Ar to a solution of the bromide **4** (400 mg, 1.51 mmol) in anhydrous THF (6.0 ml) at -78°C. After stirring for another 20 min at -78°C, dicyclopropyl ketone (**24a**, 0.200 ml, 1.77 mmol) was added and the mixture stirred at room temperature for 2 h. It was quenched with methanol (1.0 ml) and poured into ice-cold 0.4 M HCl (50 ml). The ethereal extracts (3 x 50 ml) were washed neutral, dried with Na$_2$SO$_4$ and concentrated. The crude material (496 mg) contained 20% of the olefin **7** and a trace of the *tert.* alcohol derived from **24a** and *n*-butyllithium. The pure, colourless oil **25a** (349 mg, 78%) was collected at b. p. 116-140°C (bath temp.)/0.013 mbar. - ^{1}H NMR (CDCl$_3$): δ = 0.42 and 0.47 (2 mc, 8 cyclopropyl-H), 1.06 (pseudo-qi, 2 *tert*-H), 1.31 (s, 2 3-CH$_3$), 1.35 (s, OH), 1.57 (s, 2 1-CH$_3$), 5.05 (s, α-H), 7.17 (mc, C$_6$H$_4$); (CCl$_4$): δ = 0.40, 0.92, 1.29, 1.15 (OH), 1.52, 5.00, 7.02. - ^{13}C NMR (CDCl$_3$): δ = 1.04 and 1.05 (2 tm, ^1J = 162 Hz, 2 + 2 diastereotopic cyclopropyl-CH$_2$), 21.5 (dm, ^1J = 156 Hz, 2 *tert.* C), 31.4 and 32.9 (2 qq, ^1J = 127 Hz, ^3J = 4.5 Hz, 2 1-CH$_3$ and 2 3-CH$_3$, respectively), 46.2 (m, C-1), 48.9 (m, C-3), 74.5 (s, COH), 122.3 and 122.6 (2 dd, ^1J = 156 Hz, ^3J = 7.5 Hz, C-7/-4), 124.0 (dq, ^1J = 143.2 Hz, C-α), 126.5 and 127.0 (2 ddd, ^1J = 158.7 Hz, ^3J = 7.5 Hz, C-5/-6), 148.0 (m, C-8), 151.9 (m, C-9), 158.7 (m, C-2). - C$_{21}$H$_{28}$O (296.5): calcd. C 85.08, H 9.52; found C 84.27, H 9.41.

Attempts to crystallize **25a** from methanol led to the corresponding methyl ether (not purified). - ^{1}H NMR (CDCl$_3$): δ = 0.42 and 0.54 (2 mc, 8 cyclopropyl-H), 1.08 (mc, 2 *tert*-H), 1.29 (s, 2 3-CH$_3$), 1.54 (s, 2 1-CH$_3$), 3.47 (s, OCH$_3$), 4.90 (s, α-H), 7.17 (mc, C$_6$H$_4$). - ^{13}C NMR (CDCl$_3$): δ = 0.4 and 2.9 (2 tm, 2 + 2 diastereotopic cyclopropyl-CH$_2$), 16.0 (dm, 2 *tert.* C), 31.0 and 33.0 (2 qq, 2 1-CH$_3$ and 2 3-CH$_3$), 48.7 (q, OCH$_3$), 46.8 (m, C-1), 49.1 (m, C-3), 79.7 (s, COH), 122.3 and 122.6 (2 dm, C-7/-4), 123.2 (dt, C-α), 126.3 and 126.9 (2 ddd, C-5/-6), 147.9 (m, C-8), 152.3 (m, C-9), 159.4 (m, C-2).

2-Isopropyl-3-methyl-1-(1,1,3,3-tetramethyl-2-indanylidene)-2-butanol (25b)

The preceding experiment was repeated with diisopropyl ketone (**24b**, 0.250 ml, 1.75 mmol) in place of **24a**. The crude material (383 mg) contained ≈ 30% of olefin **7** and was distilled at 116-126°C (bath temp.) /0.12 mbar to give 265 mg (58%) of the colourless oil **25b** which crystallized slowly; m. p. 69-71°C. - IR (KBr): ν = 3571 cm^{-1} (sharp OH), 3440 (br. OH), 2955, 2924, 2871, 1484, 1468, 1456, 1358, 763. - ^{1}H NMR (CDCl$_3$ or CCl$_4$): δ = 0.93 and 0.94 (2 d, ^3J = 6.8 Hz, 2 + 2 diastereotopic isopropyl-CH$_3$), 1.20 (d, ^4J = 1.3 Hz, OH), 1.35 (s, 2 3-CH$_3$), 1.58 (s, 2 1-CH$_3$), 1.88 (spt, ^3J = 6.8 Hz, 2 *tert*-H), 5.09 (^4J = 1.3 Hz, α-H), 7.18 (mc, C$_6$H$_4$). - ^{13}C NMR (CDCl$_3$): δ = 16.8 and 18.5 (2 qm, ^1J = 126 Hz, ^3J = 4.8 Hz, 2 + 2 diastereotopic

isopropyl-CH$_3$), 31.5 and 33.0 (2 qq, ^1J = 127 Hz, ^3J = 4.6 Hz, 2 1-CH$_3$ and 2 3-CH$_3$, respectively), 35.2 (dm, ^1J = 127 Hz, 2 tert. C), 45.9 (m, C-1), 49.2 (m, C-3), 81.5 (m, COH), 122.3 and 122.7 (2 dd, ^1J = 156 Hz, ^3J = 7.5 Hz, C-7/-4), 123.3 (ddt, ^1J = 140.0 Hz, ^3J = 5 and 3 Hz, C-α), 126.4 and 126.9 (2 ddd, ^1J = 159 Hz, ^3J = 7.5 Hz, C-5/-6), 148.1 (m, C-8), 152.0 (m, C-9), 158.4 (m, C-2). - C$_{21}$H$_{32}$O (300.5): calcd. C 83.94, H 10.73; found C 83.85, H 10.59.

3,3-Dimethyl-2-tert-butyl-1-(1,1,3,3-tetramethyl-2-indanylidene)-2-butanol (25c)

As described for 25a, n-butyllithium (2.40 mmol) and the bromide 4 (534 mg, 2.01 mmol) were combined in THF and treated with di-tert-butyl ketone (24c, 0.380 ml, 2.20 mmol) in place of 24a. The crude material (659 mg) consisted of 25c, olefin 7 and the coupling product 6 in a 59:9:32 ratio. Byproducts were removed by chromatography on silicagel (12 g) with light petroleum ether, and subsequent elution with ether and chloroform gave 407 mg of 25c; from methanol 235 mg (36%) of colourless rhombohedra with m. p. 127-128°C. - IR (KBr): ν = 3630 cm^{-1} (w), 3601 and 3567 (3 sharp OH), 2958, 2917, 2878, 1485, 1456, 1109, 753. - ^{1}H NMR (CDCl$_3$): δ = 1.14 (s, 2 tert-butyl), 1.39 (s, 2 3-CH$_3$), 1.59 (s, 2 1-CH$_3$), 1.77 (OH) and 5.69 (AB system, ^4J = 1.6 Hz, α-H), 7.19 (mc, C$_6$H$_4$); (CCl$_4$): δ = 1.12, 1.36, 1.55, 1.64, 5.62, 7.00. - ^{13}C NMR (CDCl$_3$): $^3J_{CH}$ ≈ 7 Hz (t) for C-8/-9 by methyl-proton decoupling, rest as in ref.[20]. - C$_{23}$H$_{36}$O (328.5): calcd. C 84.08, H 11.04; found C 84.11, H 11.06.

Competition of Ketones 24a and 24b for 3·OEt$_2$:

A solution of 3·OEt$_2$ in anhydrous tBuOMe or THF (x ml) was added dropwise under Ar during 3 min to a well-stirred solution of 24a and 24b in the same solvent (y ml). After 5-30 min at the reaction temperature, the mixture was kept at +25°C for 20 min and worked up as described for 25a. The ketones and part of the olefin 7 were removed in vacuo (2 h at <0.01 Torr), and the remaining mixture with 25a/b was analyzed by ^{1}H and ^{13}C NMR at 400 MHz for[79] k_a/k_b = [ln(24a - 25a) - ln24a] / [ln(24b - 25b) - ln24b].

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