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On the Reason for Opposite Diastereoselectivities of Benzyllithium Compounds Containing Lithium Amide and Lithium Alkoxide Functionalities

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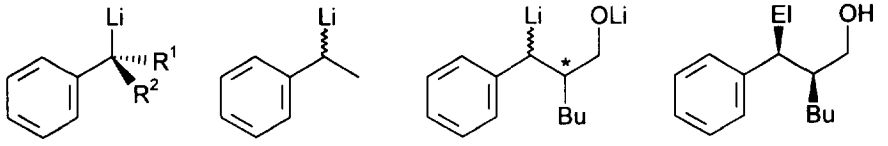
Abstract: The carbolithiation of *N*-methyl-3-phenyl-prop-2-enylamine with *tert*-butyllithium leads to the monomeric benzyllithium compound **7** in good yield. The consecutive reaction with electrophiles exhibits a high *anti* diastereoselectivity, opposite to what has been earlier found for the oxygen analogue **3**. PM3 semiempirical calculations on the intermediates show a preference of the *anti* configuration which is confirmed by ^{1}H NMR. Measurements of the degree of aggregation show the dilithio compound **3** to exist as a dimer and higher aggregates in THF. PM3 calculations on this dimer can explain the different diastereoselectivity.

Introduction

Chiral, α-alkyl-substituted benzyllithium compounds **1** have a low barrier of racemization[3] which depends upon the nature of the substituents R^1 and R^2. For the simplest secondary benzyllithium **2,** the rate of racemization was found to be much faster than its addition to chiral aldehydes, even at low temperatures.[4]

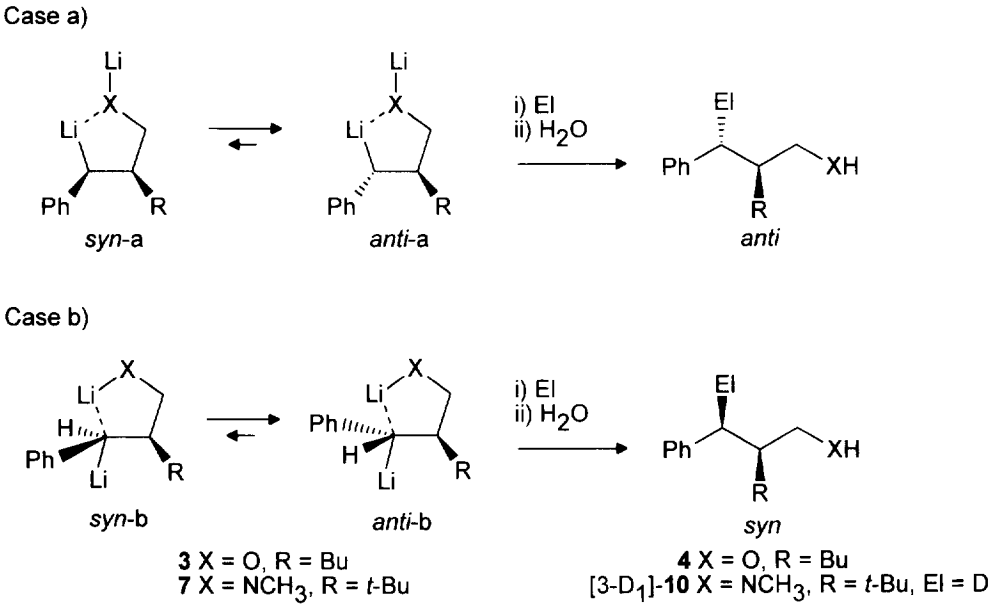


1 2 3 4

Figure 1

With a second chiral centre in the molecule, different configurations at the benzylic position give rise to different diastereomers, the relative stabilities of which determine the configuration at the carbanionic centre. As Kuwajima *et al.*[5] were able to demonstrate, the lithium alkoxide functionality of **3**, obtained upon carbolithiation of cinnamyl alcohol with n-butyllithium in THF, is able to fix the configuration at the benzyl

position and the reaction with some electrophiles gave the *syn* products **4** in high diastereomeric excess. It has been pointed out by the authors that intramolecular chelation giving a five-membered ring is responsible for the observed high diastereoselectivity. Chelation can be imagined in two ways (Scheme 1): Either the benzylic lithium is chelated by the heteroatom and the hetero-lithium is „free" (Case a) or the metal atom at the heteroatom is coordinated to the benzylic carbon (Case b), giving a planar environment with two lithium atoms coordinated from opposite sides of the plane.



Scheme 1

In both cases, the *anti* intermediates are expected to be more stable due to steric hindrance of the phenyl and alkyl groups (the terms *anti* and *syn* in connection with cyclic structures denote the relative position of the aryl and the alkyl group, *i.e.* whether they are on the same or on opposite sides of the ring plane). If the reaction with an electrophile is presumed to take place under retention of the configuration at the benzylic carbon, as the authors do, then the hetero-chelated *anti* diastereomer **3a** is expected to yield the product *anti*-**4**. Therefore, in order to rationalize the experimental results for the oxygen compounds (X = O), Kuwajima proposed *anti*-**3b** to be the reactive species. It has to be stressed that this model is based on the assumption that the electrophilic substitution takes place under retention of configuration at the benzylic carbon. Examples for both inversion and retention can be found in the literature[6] and it is obvious from the theoretical point of view that the activation barriers for retentive and inverse attack at the benzylic carbon will not differ very much.[7]

The analogous carbolithiation of the tertiary *N*,*N*-dimethyl-cinnamylamine with *n*-butyllithium in hexane/TMEDA leads after trapping with several electrophiles to products with a high *anti* diastereoselection,[8] so does cinnamyl methyl ether after addition of *tert*-butyllithium.[9] A secondary cinnamylic amine was shown among other cinnamyl derivatives to add *n*-butyllithium stereoselectively in the

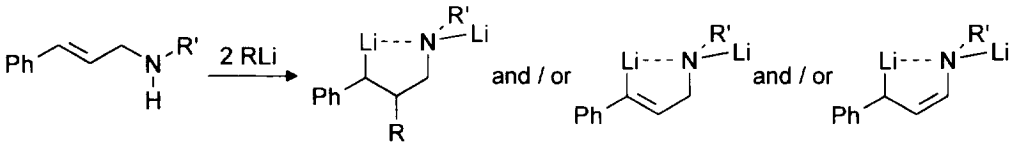
presence of (-)-sparteine,[10] however diastereoselectivity was not investigated in that work.

The aim of our investigations was to examine the diastereoselectivity of a secondary cinnamyl amine in the consecutive reaction with electrophiles. We wanted to gain a closer theoretical insight into the stereochemical course of the reaction and the structure of the intermediate dilithiated species.

Results and Discussion

Experimental results

The interaction of alkyllithiums with the heterometalated secondary cinnamyl amine may lead to deprotonation reactions as well as the expected addition (Scheme 2). Tertiary cinnamyl amines give mainly allylic anions when treated with *tert*-butyllithium. In our experiments we observed no allylic deprotonation (formation of **9**) of the N-lithiated secondary amines, the presence of the anionic centre makes this process more difficult.

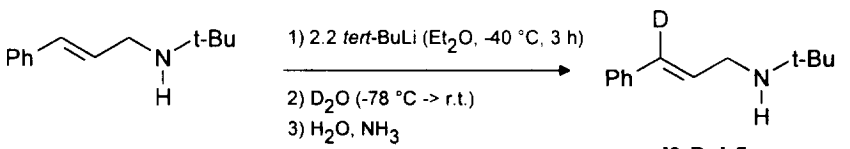


5 R' = *t*-Bu
6 R' = CH_3

7 R' = CH_3, R = *t*-Bu **8** **9**

Scheme 2

The carbolithiation of *N-tert*-butyl-cinnamylamine **5** with *tert*-butyllithium in neat diethyl ether failed. Only deprotonation of the vinylic γ-proton to give **8** is observed, which could be proved by subsequent deuteration (Scheme 3).



5 [3-D_1]-**5**

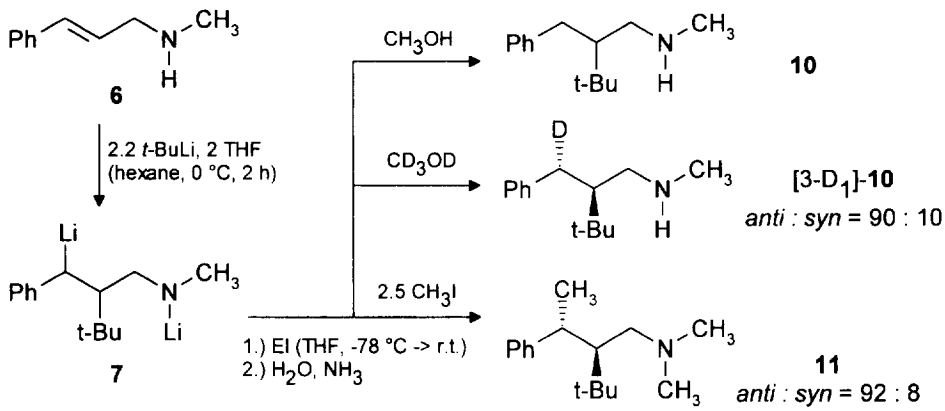
Scheme 3

Secondary allylic amines have been shown before to react in this manner with *tert*-butyllithium.[11] We obtained mixtures of addition and vinylic deprotonation products in THF.

After some fruitless attempts to find conditions that promote addition instead of vinylic deprotonation it emerged that adding the amine together with two equivalents of THF to a solution of the alkyllithium in a nonpolar solvent was the best way to achieve this task. This method proved successful in the reaction of *N*-methyl-cinnamylamine **6** with *tert*-butyllithium (Scheme 4). The dilithio compound formed a dark-red, gumlike solid and could easily be separated from the solution. It was then dissolved in THF and treated with electrophiles at -78 °C.

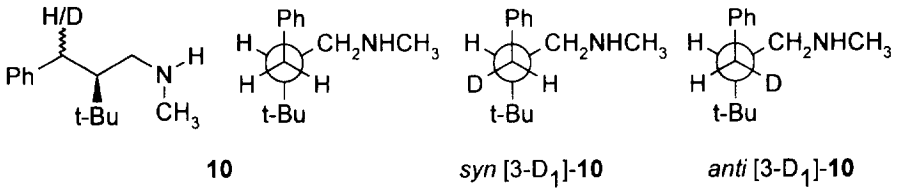
The reaction with iodomethane revealed an inherent problem of this type of dianion. Due to the poor regioselectivity in the alkylation of **7**, which is a known attribute of such species,[12] reaction with one

equivalent of iodomethane gave a mixture of C- and C/N-alkylated products, therefore we alkylated both positions.



Scheme 4

The configuration of the deuterated product [3-D_1]-**10** was determined from its proton NMR spectrum in the following way: The hydrolysis product contains two diastereotopic benzylic ^{1}H NMR signals (400 MHz) which have very different coupling constants $^3J(H_{C3}H_{C2})$ = 10 / 4 Hz. This indicates the preference of the rotamer in which the phenyl and the *tert*-butyl group are *anti* to each other (Scheme 5).



Scheme 5

After deuteration of the benzylic anion, it is obvious from the missing benzylic proton signal in the product, where the deuterium has been incorporated. It emerged to be mainly the *anti* position (d.r. = 90:10). The methylation of **7** also yielded a high excess of the *anti* diastereomer (d.r. = 92:8), as confirmed from the observed vicinal coupling constants between C(3)H and C(2)H in the alkylated product **11**.

These results give rise to questions about the origin of the contrasting diastereoselectivities of *O*,3-dilithio-2-*n*-butyl-3-phenyl alcohols **3** and *N*,3-dilithio-2-*tert*-butyl-3-phenylamines **7**. If the electrophilic substitution takes place in a stereospecific manner, irrespective of the actual mechanism of the process, only one diastereomer of both **3** and **7** is expected to be present in high excess in THF. The cause of the preference of one diastereomeric product could either be (1) different configuration of the dilithio intermediates which react with the electrophile in the same stereospecific way or (2) identical configuration of the dilithio compounds **3** and **7** which react by two different mechanisms to give products of opposing configuration. Therefore more structural information about the nature of the intermediate dilithio compounds is required.

Since organolithium compounds have a marked tendency to form aggregates in solution and in the solid state, these phenomena should also have an impact on the structure of the dilithio compounds **3** and **7**. Using

the cryoscopic method of Bauer and Seebach,[13] we have determined the molecular weight of the adduct from cinnamyl alcohol and *n*-butyllithium (**3**). Under conditions similar to the reaction (-108 °C in THF) we found that a dimeric species and higher oligomers prevail. Two representive aggregation numbers are n = 1.98 (± 0.10) for c = 70 mmol·kg^{-1} and n = 2.31 (± 0.08) for c = 137 mmol·kg^{-1}. This is in good accord with the behaviour of other lithium alkoxides, that form even higher aggregates (n = 4, 6).[14]

On the other hand, the nitrogen compound **7**, stemming from the addition of *tert*-butyllithium to *N*-methyl-cinnamylamine, does not show any tendency to form oligomers at all. We have determined a molecular weight that implies the presence of a monomeric species under the experimental conditions (c = 74 - 136 mmol kg^{-1} in THF, -108 °C). This is not surprising if one takes into account the lower tendency to form aggregates of lithium amides[13a,15] as compared to alkoxides.

The different diastereoselectivities reported might therefore have their genuine origin in the different degrees of aggregation of the intermediates **3** and **7**. The theoretical part of our study consequently intended to elucidate the structure of the dilithio compounds which are present in solution, thereby explaining the different diastereoselection found when the heteroatom is changed from O to N.

Computational results

Taking the experimental results into account, we have carried out a semiempirical investigation of the intermediate dianions, because at this theoretical level even solvation and aggregation can be modelled with reasonable time-effort and trustworthy results. We have chosen the PM3 method[16] for the task because it has proven to perform better than MNDO[17] in the treatment of lithium compounds, at least when the resulting structures are compared with X-ray or ab initio geometries.[18,19,20]

Monomeric species

N,3-Dilithio-propylamines and *O*,3-dilithio-propanols are isoelectronic with 1,4-dilithiobutane **12**, which has been theoretically described by Schleyer *et al.* at a low *ab initio* level (RHF/3-21G//RHF/3-21G).[21] The unsolvated dilithio compound prefers the doubly bridged conformation **12d** by 46.3 kcal mol^{-1} over the open (**12a**) form. This is easily explained in terms of maximized electrostatic stabilization due to the mainly ionic character of the carbon-lithium bond.[22]

We have repeated and extended the calculations on the MP2/6-311+G**//RHF/6-31G* level and compared the results to the semiempirical PM3 method. Figure 2 summarizes the results and gives a comparison of the effect of the heteroatom on the double bridging tendency. It is most pronounced in the case of 1,4-dilithiobutane. The nitrogen compound shows almost the same structural and energetic features as **12**, except a higher double bridging energy. On the semiempirical level, the alkoxide **13** has a lower tendency to form the cage structure **13d**, which is probably due to the shorter Li-O distance in the open chain that has to be notably elongated to achieve double bridging. On the other hand, the energetic difference between chelation by the heteroatom and by the anionic carbon (**13c** *vs.* **13b** and **14c** *vs.* **14b**) is larger for the oxygen compound (PM3: 10.7 kcal) as compared to the nitrogen analogue (PM3: 5.7 kcal).

It must be noted that, although the absolute energetic separations differ for MP2 and PM3, there is a good aggrement in the relative stabilities of the conformers. This agreement is even better between PM3 and RHF/6-31G* energies, which are not listed here.

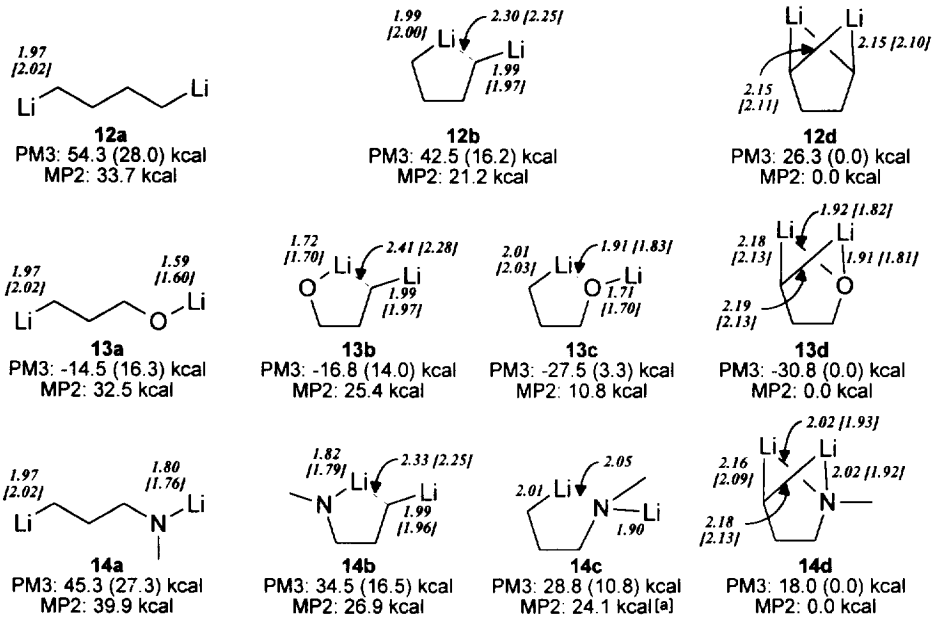


Figure 2: Monomeric 1,4-dilithio compounds **12**, **13** and **14**. PM3 energies are heats of formation, in brackets the energy relative to double bridged conformer **d**. MP2/6-311+G**//RHF/6-31G* energies are relative to the double bridged conformer, no zero point correction was done. PM3 distances, *ab initio*-distances (in square brackets) are given in Å.

[a] MP2/6-311+G**//PM3. The energy of **14c** was obtained with the PM3 geometry, no minimum was found with RHF/6-31G*.

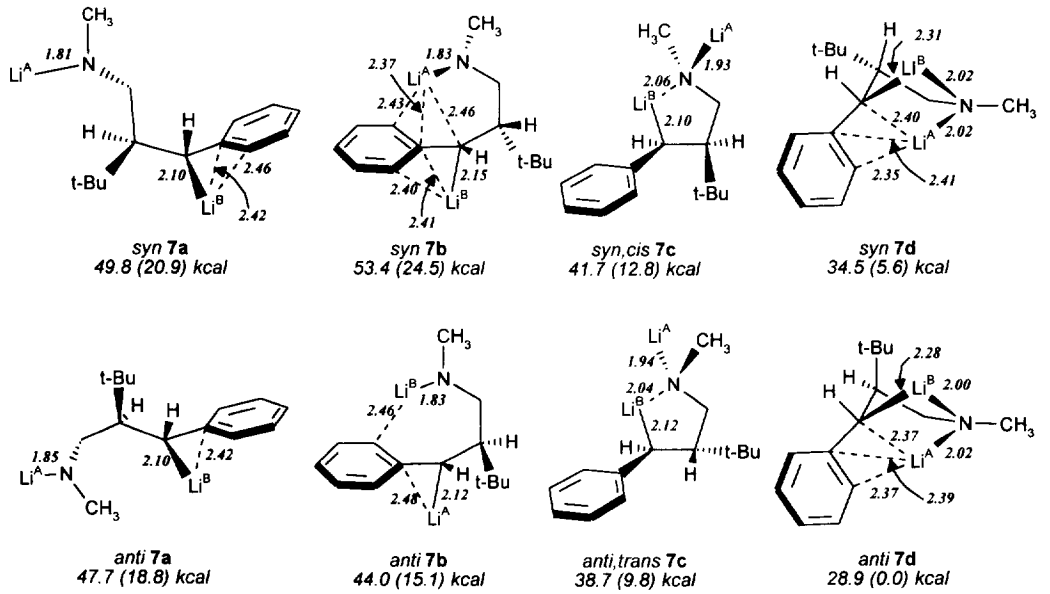


Figure 3: Geometries of the PM3-optimized diastereomers **7a-d**. PM3 heats of formation, values in brackets are relative to the global minimum *anti* **7d**. Distances are given in Å.

In the following part of this work we concentrated on the *N*-methyl-*N*-lithio-2-(phenyl-lithio-methyl)-3,3-dimethylbutylamine **7**. This compound is quite suitable for a model calculation since the alkyl substituent possesses local C_3 symmetry thus making the geometry optimization less ambiguous. Furthermore, it allows a direct comparison with experimental data.

The four possible structural motives (cf. **14a** - **14d**) of the two diastereomers of **7** give rise to eight structural isomers; there are two more if one takes the additional stereogenic centre at the endocyclic nitrogen of **7c** into account. (The configuration at nitrogen is denoted by the terms „*cis*" and „*trans*" describing the relative position of exocyclic lithium cation and phenyl substituent.) However, as indicated in Figure 3, for the unsolvated **7** only two out of the imaginable four are stable minima on the energy hypersurface, the other two structures (*syn,trans*- and *anti,cis*-**7c**) optimized to the doubly bridged **7d**.

As the calculated energies reveal, the relative heats of formation are not drastically changed upon introduction of the aryl and alkyl substituent. Open chained **7a** gains about 20 kcal·mol^{-1} of stabilization energy through double bridging and the single bridged conformations **7b** and **7c** (except *syn*-**7b**) have intermediate energies. As could be expected, in both cases the *anti* diastereomer is calculated to be the more favourable epimer.

The structures exhibit a typical feature of benzyllithium compounds, the solvation of the cation by π-electrons from the aromatic ring, which is expressed in terms of a short distance between the cation and the ortho carbon of the ring. This π-complexation can be observed in X-ray structures,[23] in solution,[24] and in theoretical calculations.[25] It replaces to a large extent the bridging function of the benzylic C3 in *anti*-**7b**. The ortho position is separated by only 2.46 Å from the endocyclic lithium, whereas the distance to C3 falls slightly short of being a bonding one (2.54 Å).

Anti-**7d** is the global minimum due to minimized distance between centres of opposite charge and additional „internal solvation" by the π-electrons. The distance between the π-stabilized cation and C3 is 0.09 Å longer than the separation between C3 and the other cation in both diastereomers of **7d**. Accordingly, the distance to the ortho carbon is of the same length (*anti* epimer) or even shorter (*syn* epimer) than the metal-C3 distance.

The phenyl group allows a deviation from the symmetrical arrangement of unsubstituted **14d** (Figure 2) and causes the orientation of one cation towards the aromatic π-system. This is a first step towards opening of the double bridge, finally resulting in the formation of **7c**.

The bridge-opening process is strongly promoted by external solvation. The first solvation sphere is modeled by association of tetrahydrofuran molecules with the cationic centres. To allow the comparison of unequally solvated associates, one has to find a suitable reference state. This can be done by calculating the hypothetical heat of formation of the species *in the solvated state after removal of the solvent molecules* (ΔH_f^*), the value of which can be obtained by subtracting the enthalpy of the isolated solvent molecules from the enthalpy of the complex:

$$\Delta H_f^* (\mathbf{X \cdot n\ THF}) = \Delta H_f(\mathbf{X \cdot n\ THF}) - n \cdot \Delta H_f(\mathbf{THF}) \qquad (1)$$

One should expect the opening of internal coordinations due to the reduction of the effective positive charge on the cation by σ-donation from the heteroatom lone pairs and a strong increase of steric demand in

the cation surroundings. Beginning with two THF solvent molecules in a (1:1)-solvated complex, we successively introduced up to six (3:3) THF (Table 1). It emerged out of the manifold of solvated structures that those of **7c** are most favourable; *e.g.* **7d** opens upon solvation by three THF (2:1) to give a *cis* **7c**. The maximum possible number of six solvent molecules was only applied to the open chained **7a**. This turned out to be about 15 kcal mol^{-1} less stable than the global minimum **7c** · 5 THF. Even more unfavourable is the C-bridged **7b** · 4 THF (2:2) which therefore should readily open in THF to the unbridged conformer. The reason for the stability of **7c** · 4/5 THF is probably the dominant role of Li-N-interactions that are maximized in this structure. Furthermore, the solvent molecules in **7c** · 4/5 THF are associated with the cations without high steric demands being present.

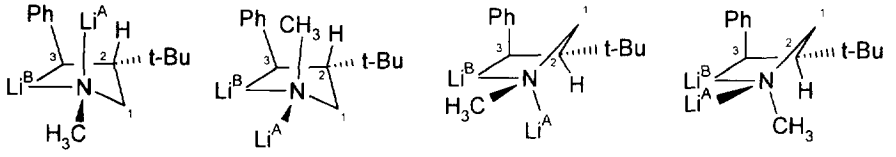
Table 1 PM3 energies of solvated diastereomers of **7**[a]. (ΔH_f^* from eqn. 1[b], values in brackets are relative to the global minimum *anti,cis* **7c** · 5 THF)

Conformer	n THF[c]	ΔH_f (kcal·mol^{-1})	ΔH_f^* (kcal·mol^{-1})	Conformer	n THF[c]	ΔH_f (kcal·mol^{-1})	ΔH_f^* (kcal·mol^{-1})
anti **7a**	5 (3:2)	-238.54	18.1 *(21.2)*	*syn,trans* **7c**	4 (3:1)	-201.03	4.3 *(7.4)*
anti **7a**	6 (3:3)	-291.86	16.1 *(19.2))*	*syn,cis* **7c**	4 (3:1)	-202.18	3.1 *(6.2)*
syn **7a**	6 (3:3)	-292.49	15.5 *(18.6)*	*syn,trans* **7c**	5 (3:2)	-253.80	2.9 *(6.0)*
syn **7a**	5 (3:2)	-243.28	13.4 *(16.5)*	*syn,cis* **7c**	5 (3:2)	-255.06	1.6 (4.7)
syn **7b**	4 (2:2)	-176.44	28.9 *(32.0)*	*anti,trans* **7c**	4 (3:1)	-204.75	0.6 *(3.7)*
anti **7b**	4 (2:2)	-188.45	16.9 *(20.0)*	*anti,cis* **7c**	4 (3:1)	-205.45	-0.1 *(3.0)*
syn,cis **7c**	4 (2:2)	-195.65	9.7 *(12.8)*	*anti,trans* **7c**	5 (3:2)	-257.36	-0.9 *(2.8)*
anti,cis **7c**	4 (2:2)	-199.64	5.9 *(9.0)*	*anti,cis* **7c**	5 (3:2)	-259.79	-3.1 *(0.0)*

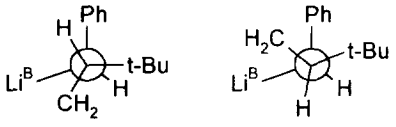
[a] *cf.* Figure 3

[b] ΔH_f(THF) = -51.33 kcal·mol^{-1}; determined in a separate PM3 calculation

[c] The numbers in brackets refer to the ratio of solvent molecules situated on the two distinct lithium cations; thus (3:1) means 3 THF at Li^A, 1 THF at Li^B.



7c



Dihedrals:	*anti,cis*-**7c**	*syn,cis*-**7c**
Ph-C3-C2-(*t*-Bu)	90.7°	59.8°
Ph-C3-C2-(CH_2)	-147.3°	-70.3°

Scheme 6

We confine our discussion of the structures to tetra- and pentasolvated **7c**. As Scheme 6 indicates, the

five-membered rings of the four diastereomers can be idealized as being derived from the envelope conformation of cyclopentane. In all diastereomers, the *t*-butyl group occupies a nearly equatorial position, thus governing the side to which the methylene group is directed out of the plane. The relative configuration of the *syn* diastereomers enforces a destabilizing *gauche* interaction between the phenyl group at C3 and both the alkyl substituent and the methylene bridge of the ring. The dihedral angles between the aryl group and both the alkyl group (90°) and the methylene bridge (147.3°) are larger in the *anti* epimers. This reduced steric strain seems to be the underlying cause of the higher stability of these structures.

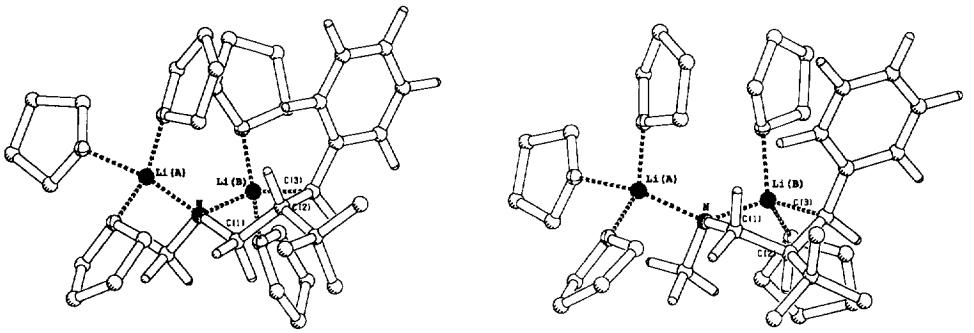


Figure 4: PM3-optimized structures of *anti, cis-* (left) and *syn, cis-* (right) **7c** · 5 THF. Protons of THF and the *tert*-butyl group are omitted for clarity. Selected distances (in Å), *anti, cis*: Li^A-N 2.07, Li^B-N 2.10, Li^B-C(3) 2.19. *syn, cis*: Li^A-N 2.07, Li^B-N 2.12, Li^B-C(3) 2.22.

To summarize these results, we suggest the tetra- or pentasolvated *anti* diastereomer of **7c** to be the major species in a THF solution of **7**. This suggestion is supported by the ^{1}H NMR spectrum of **7** in [D_8]-THF (Figure 5(a), assignment based upon the ^{1}H,^{1}H COSY spectrum). The markedly different chemical shifts of the diastereotopic C(1)-protons H_A and H_B suggest their incorporation into a cyclic structure. Moreover, if one calculates the theoretical vicinal coupling constants $^3J_{HH}$ of the four protons in the propyl chain, which can easily be done using the Karplus relation[26] between $^3J_{HH}$ and the dihedral angle ϕ from our PM3 calculations, the *syn*- and *anti*-diastereomers should be distinguishable from the resulting coupling pattern. Table 2 lists the calculated values for *syn* and *anti* **7c** · 5 THF. The coupling constants $^3J(H_AH_M)$ and $^3J(H_MH_X)$ are of the same magnitude and should give rise to a multiplet structure of the H_M signal that resembles a triplet. This is actually observed in the experimental spectrum. It is obvious that the dihedral angles of the *syn* species would result in a different coupling pattern for H_M; we consider this an indication for the exclusive presence of the *anti*-epimers.

Table 2 Calculated coupling constants between propyl protons of **7c** · 5 THF

	Dihedral angle ϕ / °			^3J (theor.) / Hz[a]		
	H_AH_M	H_BH_M	H_MH_X	H_AH_M	H_BH_M	H_MH_X
anti,cis	-174.9	-62.4	+161.4	9.1 (10)	1.4 (-)	8.3 (10)
anti,trans	+177.7	-67.6	+163.1	9.2	0.8	8.4
syn,cis	-171.2	+74.1	-36.3	9.0	0.3	5.2
syn,trans	-174.4	+71.1	-33.7	9.1	0.5	5.5

[a] $^3J = A + B \cos\phi + C \cos(2\phi)$; A = 4.22, B = -0.5, C = 4.5; first row in brackets: ^3J (expt.)

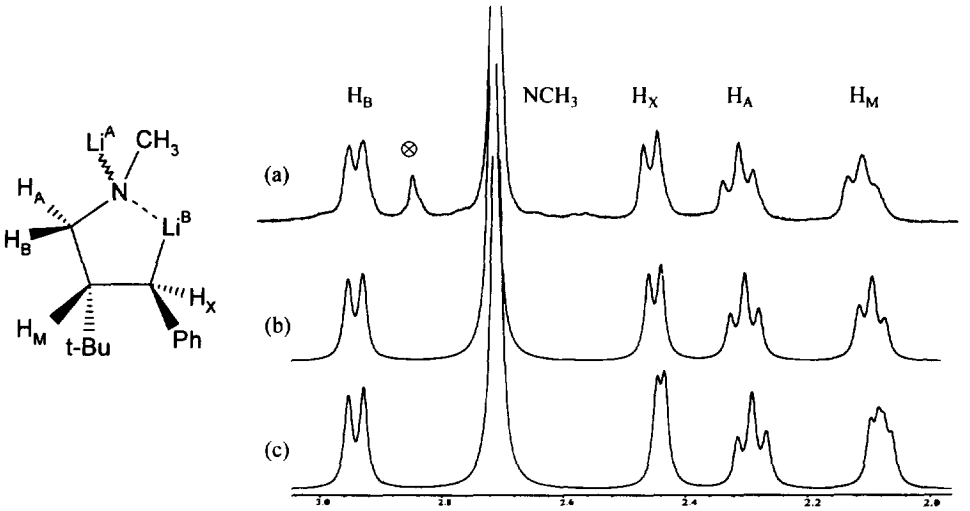
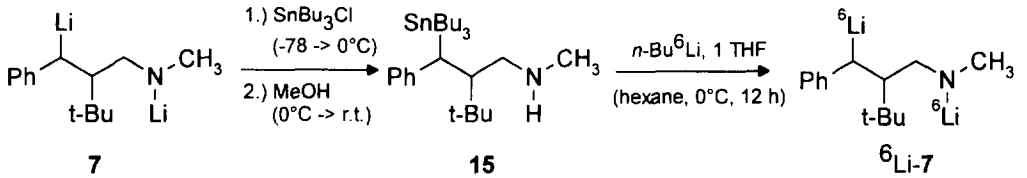


Figure 5: Comparison of calculated and experimental coupling pattern of the ABMX spin system of the propyl skeleton of **7**. (a) experimental ^{1}H spectrum of **7** in [D_8]-THF at 298 K, c ≅ 0.6 M, ⊗ = unknown impurity, (b) *anti,cis*-**7c** · 5 THF (PM3 geometry), (c) *syn,cis*-**7c** · 5 THF (PM3-geometry).

We also have recorded the ^{6}Li NMR spectrum of **7**. The sample was prepared by transmetalation of the corresponding tributyltin compound **15** with *n*-Bu^{6}Li (Scheme 7).



7 **15** ^{6}Li-**7**

Scheme 7

7 shows a temperature dependent ^{6}Li NMR spectrum (Figure 6). At room temperature, only one signal can be observed at 1.5 ppm, indicating a fast exchange of the exo- and the endocyclic lithium atoms Li^A and Li^B. At -39 °C, the signal begins to split into two distinct but still closely neighboured resonances. The relative intensity of these (1:1) implies that they represent either the two different intramolecular lithium sites or two equally populated diastereomers with a faster intramolecular exchange. A rotation of the N-C(1) bond, *i.e.* an equilibrium between *anti,cis*-**7c** and *anti,trans*-**7c** (Scheme 6), does not really exchange the nuclei with regard to one of these epimers (*e.g.* the exocyclic atom in *anti,cis*-**7c** returns to its exocyclic position after being endocyclic in *anti,trans*-**7c**). If the *anti,cis* epimer was the only diastereomer in solution, no coalescence should then be observable.The *cis* and *trans* epimers would have to exist in almost equal amounts, each signal in the ^{6}Li NMR corresponding with one of these diastereomers. In the ^{13}C and ^{1}H NMR we see no indication of more than one diastereomer, so this option can also be excluded.

Instead, the *anti,cis*-**7c** diastereomer exchanges its lithium nuclei by breaking the C-Li^B bond in the rate determining step (Scheme 8), a process facilitated by additional solvation at Li^B. The intramolecular solvent separated ion pair then exchanges the two cations at nitrogen. Finally, the cyclic structure is restored by a ring

closure between the former exocyclic Li^A and the benzylic carbon. The free activation enthalpy of the process is estimated from the coalescence temperature to be $\Delta G^{\neq}$ = 12.4 kcal mol^{-1}. A simulation of the lineshapes[27], assuming mutual exchange and taking the temperature dependance of the chemical shifts and the observed different relaxations times T_2 into account leads to an activation enthalpy $\Delta H^{\neq}$ of 3.1 (± 0.2) kcal mol^{-1}. Both values have to be treated with caution as the change of the chemical shifts can hardly be seperated from the underlying exchange process. Unfortunately, the ^1H and ^{13}C spectra of **7** give no further information about the process. No coalescence phenomena are observed in proton and carbon NMR upon cooling, except that all proton signals loose their coupling structure at low temperatures.

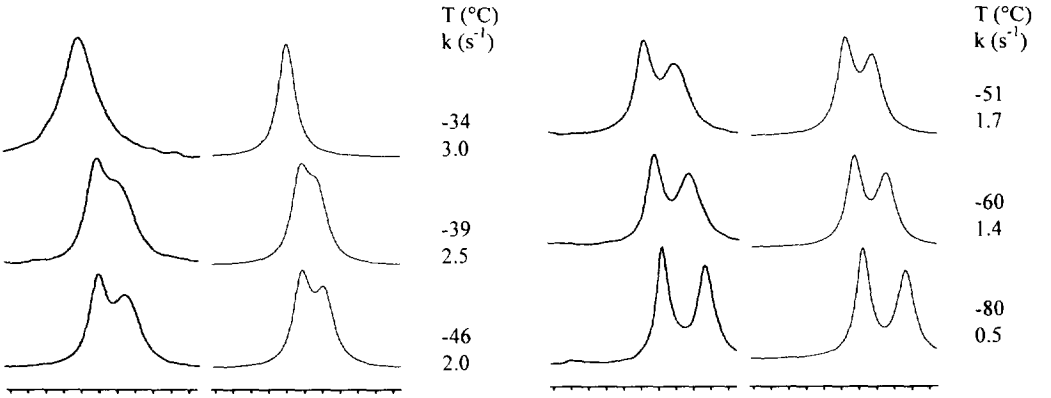
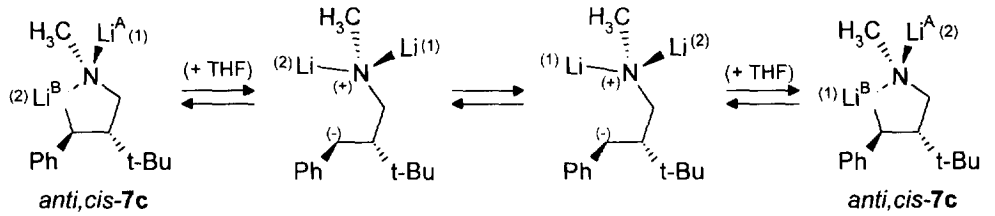


Figure 6 ^6Li spectra (1.30-1.75 ppm) of [^6Li]-**7** at a temperature range between -34 and -80 °C, experimental (left, externally referenced against 0.5 M ^6LiCl in D_2O) and simulated lineshapes (right).



Scheme 8

Dimeric O,3-dilithio-propanols

If the oxygen analogue of **7**, the *O*,3-dilithio-2-butyl-3-phenyl-propanol **3**, exhibited the same preference of chelation by oxygen (**3a** in Scheme 1), the reactions with electrophiles would occur under inversion at the benzylic carbon. The question of the preferred conformation of dimeric *O*,3-dilithio-2-alkyl-3-phenyl-propanols in solution is yet too complex to be answered unambiguously in a satisfying manner. Due to fast exchange between the diastereomeric aggregates, no sharp signals can be found in both the ^1H and ^{13}C NMR spectrum of **3**. In the ^6Li NMR we observed one resonance at ambient temperature. Two signals (relative intensities 5:1) can be seen at temperatures below 0 °C.

Beginning with the „naked" *O*,3-dilithiopropanole **13**, we have assembled the four monomer structures to give dimers [**13a-d**]$_2$ (Figure 7), maximizing the number of O-Li contacts in every case. The pure association of two alkoxide groups in dimer [**13a**]$_2$ already has a large stabilizing effect (-41.6 kcal mol^{-1}) that

is even more pronounced than internal double bridging (2 **13a** → 2 **13d**, $\Delta_R H$ = -32.6 kcal mol^{-1}). **13b** gains about 8 kcal more upon dimerization although there is the same number of additional lithium oxygen contacts. This can be understood as a relief of strain in the pentacycles, indicated by the longer Li-O bond at the bicyclic bridges (1.91 Å instead of 1.72 Å in the monomer). The shorter Li-O distance can be found in the intermolecular bridge.

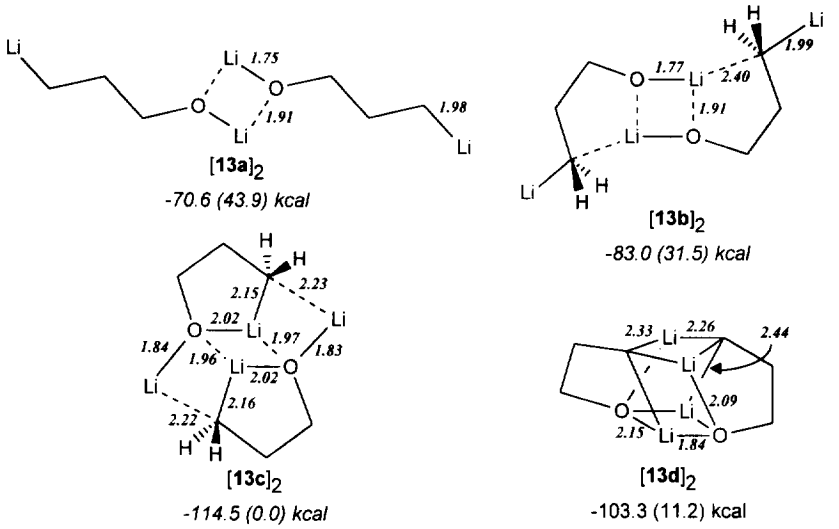


Figure 7: PM3-optimized dimeric O,3-dilithiopropanol **13**. PM3 heats of formation, values in brackets are relative to $[\mathbf{13c}]_2$. Distances are given in Å.

Dimerization of the doubly bridged **13d** is less favourable (2 **13d** → $[\mathbf{13d}]_2$, $\Delta_R H$ = -41.7 kcal mol^{-1}), because the resulting cubic arrangement of the eight charged centres is distorted due to the nonplanar „butterfly" shape of the Li-C-Li-O ring of the monomer. In spite of the larger number of ionic interactions, the average Li-O-distance is 2.02 Å, much larger that the 1.83 Å in $[\mathbf{13a}]_2$. Keeping in mind the insignificance of doubly bridged isomers of **7** after introduction of solvation, this isomer obtained no further attention in the course of this study.

The global minimum of dimeric **13** was found upon assemblence of two O-bridged monomers **13c**. This dimerization process is possible without steric difficulties and maximizes the number of contacts between centres of opposite charges, *esp.* between lithium and oxygen. Moreover, the intramolecular double bridging of **13d** is realized in this isomer in an unexpected way: Both the oxygen and carbon anionic centres are showing double (C) or even triple (O) bridging using additional lithium atoms from the second monomer as counterions.

$[\mathbf{13c}]_2$ is a dimeric equivalent of case a) in Scheme 1 as the lithium atom of the carbon is chelated by the heteroatom. Case b) has its representation in $[\mathbf{13b}]_2$, in which the anionic carbon is coordinated by a second lithium from the back side of the carbon-metal bond. In the following, only the last two dimer types are used for comparison.

If one introduces the phenyl substituent (giving *O*,3-dilithio-3-phenyl-propanol **16**) into the dimeric complexes, they become more complicated in stereochemical terms. With regard to $[\mathbf{16c}]_2$, derived from

$[\mathbf{13c}]_2$, we have investigated only *meso* complexes, *i.e.* the configuration at C(3) and C(3') being either (*R,S*) or (*S,R*), which we denote as *endo, endo* and *exo, exo*, respectively. There are two imaginable diastereomers for $[\mathbf{16b}]_2$ which differ in the relative position of the aryl groups, being either on one side or on opposite sides of the central Li_2O_2-plane (*cis* and *trans*, respectively). The four conformations and the corresponding calculated energies for the unsolvated dimers are displayed in Figure 8.

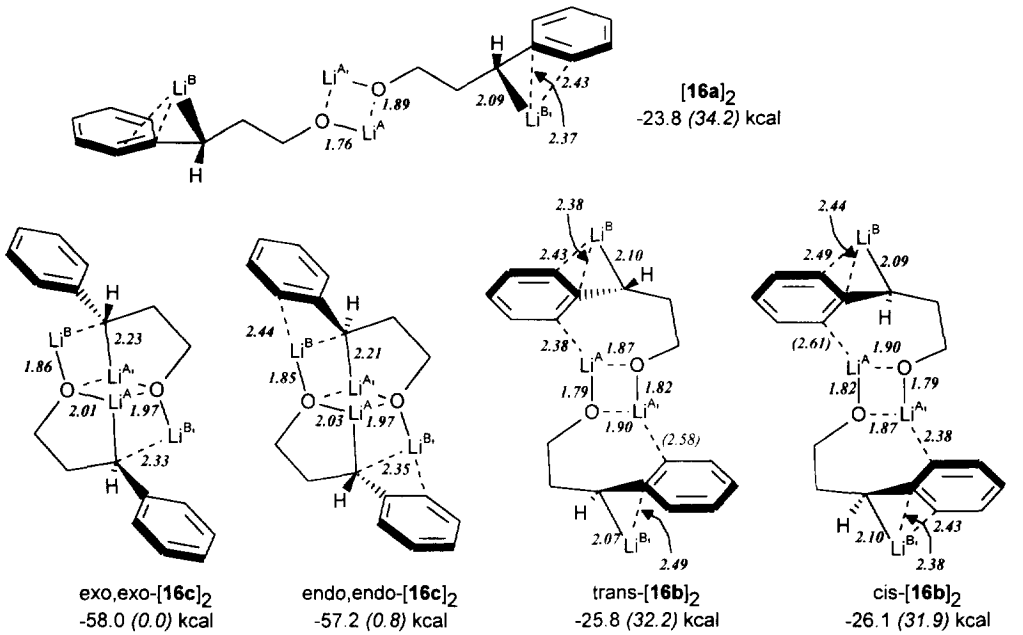


Figure 8 Schematic representation of unsolvated dimers $[\mathbf{16a}]_2$, $[\mathbf{16b}]_2$ and $[\mathbf{16c}]_2$. PM3 heats of formation, values in brackest are relative to isomer *exo, exo*-$[\mathbf{16b}]_2$. Bonding distances are given in Å.

The aryl group obviously does not influence the relative stablitities of the two structural isomers $[\mathbf{16b}]_2$ and $[\mathbf{16c}]_2$ as compared to the dimeric propanolates $[\mathbf{13}]_2$: The energetic separation of *ca.* 32 kcal mol^{-1} remains almost the same.

To investigate solvation effects, we resorted to dimethylether for calculational convenience. The results for the solvated complexes are summarized in Table 3, which lists the heats of formation of the molecules in the solvated state after the hypothetical desolvation (Eq. 1). Surprisingly, the ranking is already reversed when the exocyclic cations are solvated by two or three ether molecules each. The coordinative saturation of the Li^B atoms in $[\mathbf{16b}]_2$ leads to an overproportional stabilization of both diastereomers as compared to the oxygen-bridged $[\mathbf{16c}]_2$. In all structures of the carbon-bridged dimer $[\mathbf{16b}]_2$ the fixation of configuration is achieved by the interaction of Li^A with the ortho carbon of the phenyl ring. Introduction of one dimethylether molecule at the lithium atoms of the central Li_2O_2-square paves the way towards the opening of both dimer types to the open chained $[\mathbf{16a}]_2$. The Li^A-C_{ortho} contact can then no longer compete with the solvent due to the low solvating strength of the π system and the steric demand of the ether molecule. Out of all higher solvates ($n > 3$ per monomer unit) $[\mathbf{16a}]_2$ is the most stable conformer. The carbon bridged $[\mathbf{16b}]_2$, however, maintains

its higher stabilization energy as compared to oxygen bridged $[\mathbf{16c}]_2$.

Table 3 Solvation-corrected PM3 heats of formation ($\Delta H_f^{*[a]}$) of dimeric O,3-dilithio-3-phenyl-propanols **16**, solvated with dimethyl ether, values in brackets are relative to global minimum $[\mathbf{16a}]_2 \cdot 4\ Me_2O$.

n Me_2O[b]	$[\mathbf{16a}]_2$	$[\mathbf{16c}]_2$		$[\mathbf{16b}]_2$	
		exo, exo	*endo, endo*	*trans*	*cis*
0 Me_2O	-23.8 (50.5)	-58.0 (16.3)	-57.2 (17.1)	-25.8 (48.5)	-26.1 (48.2)
2 Me_2O (0:2)	-63.1 (11.2)	-61.9 (12.4)	-54.1 (20.2)	-65.2 (9.1)	-65.9 (8.4)
3 Me_2O (0:3)	-64.5 (9.8)	-67.4 (6.9)	-65.2 (9.1)[c]	-71.6 (2.7)	-72.0 (2.3)
4 Me_2O (1:3)	-74.3 (0.0)	-61.7 (12.6)	-[d]	-63.8 (10.5)	-[d]

[a] conf. eqn. 1; $\Delta H_f(Me_2O) = -48.348$ kcal·mol^{-1}, determined in a separate PM3 calculation

[b] number of solvent molecules per monomer unit; numbers in brackets are ratio of ether molecules at Li^A:Li^B.

[c] partly opened structure, no C-Li^A-contacts

[d] No bridging; open $[\mathbf{16a}]_2$ obtained in geometry optimization

These findings conclude that without solvation the preferred conformation of an *O*,3-dilithio-3-phenyl-propanole for the monomer and dimer is a structure with the benzylic lithium chelated by the oxygen (**13c**, **13d**, $[\mathbf{16c}]_2$). The presence of solvent molecules promotes stabilization of the conformer in which the alkoxide lithium fixes the configuration at the benzylic carbon by an interaction from the opposite side of the benzylic centre ($[\mathbf{16b}]_2$). This is consistent with the assumed presence of *anti* diastereomers of dimeric *O*,3-dilithio-2-alkyl-3-phenyl-propanole in solutions which react with electrophiles in a stereoselective manner under configurational retention of the benzylic carbon to yields 3-substituted *syn*-3-phenyl-2-alkyl-propanols. Nevertheless, the calculations imply that increased solvation destroys the intramolecular interactions of the lithiated positions to give the open chained dimer $[\mathbf{16a}]_2$.

In summary, the different behaviour in ethereal solution of the dilithio compounds obtained from cinnamyl alcohol and secondary (or tertiary) cinnamyl amines upon carbolithiation may be explained by the different aggregation of the species, which allows two different modes of intramolecular chelation.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM-400 spectrometer. Chemical shifts are reported in ppm against tetramethylsilane as an internal standard and *J* values are given in Hertz. Combustion analyses were carried out in a Carlo-Erba 1106 instrument. Mass spectra were taken on a Varian MAT 311 A using an ionization potential of 70 keV.

N-Methyl-cinnamylamine and N-*tert*-butyl-cinnamylamine were prepared following the literature procedure[28] by condensation of the primary amine with cinnamaldehyde and reduction of the imine with sodium borohydride.

tert-Butyllithium was purchased from the Metallgesellschaft Frankfurt and its concentration was determined by titration of diphenylacetic acid[29] prior to use. All lithium compounds were handled under a protective argon atmosphere.

N-*tert-Butyl-3-deutero-3-phenyl-prop-2-enylamine* ([3-D_1]-**5**): To a solution of N-*tert*-butyl-cinnamylamine **5** (947 mg, 5 mmol) in 25 ml diethyl ether, at -40 °C *tert*-butyllithium (11 mmol, 2.2 eq.) was added dropwise. The resulting solution was stirred for 3 hours and the temperature allowed to rise up to -20 °C. During that period the solution turned red. The mixture was cooled to -78 °C and D_2O (600 µl) added during 15 min,

followed by warming up to room temp.. It was hydrolized with 30 ml of aqueous NH_3 (10 %), the aqueous phase extracted with Et_2O and the organic extracts dried over K_2CO_3. After filtration and evaporation of the solvents, distillation gave the amine [3-D_1]-**5** (756 mg, 79 %), b.p. 70 °C / 0.05 torr. (Found: C, 81.6; H/D, 10.4; N, 6.8. Calc. for $C_{13}H_{18}DN$: C, 82.05; H/D, 10.1; N, 7.4%); δ_H(400 MHz, $CDCl_3$) 1.13 (9 H, s, $C(CH_3)_3$), 3.33 (2 H, d, J = 6.4, $C(1)H_2$), 6.30 (1 H, m_c, C(2)H), 7.13-7.38 (5 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 29.1 ($C(CH_3)_3$), 45.1 (C(1)), 50.4 ($C(CH_3)_3$), 126.2, 127.3, 128.3, 129.3 (Ph and C(2)), 130.4 (t $J_{C\text{-}D}$ 23, C(3)), 137.2 (Ph, C_i). (Found: M^+, 190.1600. Calc for $C_{13}H_{18}DN$: M, 190.1580).

N-*Methyl*-N-*lithio*-2-*(phenyl-lithio-methyl)*-3,3-*dimethylbutylamine* (**7**): To a solution of *tert*-butyllithium (8.8 mmol, 2.2 eq.) in 17 ml hexane in a three-necked flask with a second flask connected through a glass filter, a mixture of *N*-methyl-cinnamylamine **6** (589 mg, 4 mmol), tetrahydrofuran (577 mg, 8 mmol) and 3 ml hexane was added dropwise at 0 °C over a period of 30 min.. A red precipitate instantaneously formed that glued together and separated from the red solution. The mixture was stirred for another 1.5 h, then the solvent was removed under vacuum through the glass filter and traces of hexane removed by applying vacuum for 5 min. The solid residue was dissolved in 20 ml of THF and the dark red solution cooled to -78 °C.

^1H and ^{13}C NMR of 7: 2 mmol of **7** were prepared using 2 eq. of [D_8]-THF as described above. After evaporation of the hexane the residue was dissolved in 3 ml [D_8]-THF. The dark solution was transferred into an NMR tube (5 mm) with a syringe. The tube was sealed with parafilm and stored at -78 °C before the measurement (30 min). δ_H (400 MHz, 295 K) 0.89 (9 H, s, $C(CH_3)_3$), 2.08 (1 H, t, J = 10, $C(2)H = H_M$), 2.29 (1 H, t, J = 10, $C(1)H = H_A$), 2.44 (1 H, d, J = 10, $C(3)H = H_X$), 2.71 (3 H, s, NCH_3), 2.94 (1 H, d, J = 9, $C(1)H = H_B$), 4.70 (1 H, t, J = 7.5, p-H), 5.47 (1 H, d, J = 7.5, o-H), 5.66 (1 H, d, J = 7.5, o'-H), 5.94 (1 H, t, J = 7.5, m'-H), 6.12 (1 H, t, J = 7.5, m-H); δ_C (100 MHz, 295 K) 29.2 ($C(CH_3)_3$), 36.9 ($C(CH_3)_3$), 45.7 (NCH_3), 48.4 (C(2)), 64.9 (C(1)), 66.0 (C(3)), 96.2 (C-p), 104.3 (C-o) 114.8 (C-o'), 128.7 (C-m'), 130.7 (C-m), 152.2 (C-i). Assignment of these signals is based on the ^1H-^1H COSY and ^1H-^{13}C-HMQC spectra of the same sample.

^6Li NMR of 7: The solution of 4 mmol of dilithio compound 7 in 20 ml THF was treated with tributyltin chloride (4 mmol, 1.302 g) in 2 ml THF through a syringe. While stirring, the temperature was allowed to rise to 0 °C, then 300 µl MeOH were added. The mixture was hydrolized with a mixture of 10 ml aqueous NH_3 (5 %) and 10 ml NH_4Cl (10 %). The aqueous phase was extracted with Et_2O and the organic extracts dried over $MgSO_4$. After filtration and evaporation of the solvent, distillation gave *N*-methyl-2-(phenyl-tributylstannyl-methyl)-3,3-dimethylbutylamine **15** (0.88 g, 1.8 mmol) along with a not separable by-product.

3 mmol (1.483 g) of the stannylated amine **15** and 3 mmol (240 mg) [D_8]-THF were dissolved in 8 ml *n*-hexane, then 6.3 mmol *n*-Bu^{6}Li were added at 0 °C. The solution was stirred at 0 °C for 12 h, then the solvent was removed through a glass filter, the remaining orange precipitate was washed twice with 5 ml of n-hexane. Vacuum was applied to remove the solvent completely, then 4 ml [D_8]-THF were added and 1 ml of the red solution transferred into an NMR tube (5 mm). Dry, CO_2-free argon was run through the solution to remove traces of oxygen. The sample was stored at -78 °C before the measurement.

The authenticy of the sample was confirmed by hydrolysis of the remaining solution with MeOH, giving **10** as the only product.

N,3,3-*Trimethyl*-2-*benzyl-butylamine* (**10**): The solution of 4 mmol of dilithio compound **7** in 20 ml THF was treated with methanol (650 mg) through a syringe. While stirring, the temperature was allowed to rise to room temp. and the mixture hydrolized with 20 ml aqueous NH_3 (5 %). The water phase was extracted with Et_2O and the organic extracts dried over $MgSO_4$. After filtration and evaporation of the solvents, distillation gave amine **10** (551 mg, 68 %), b.p. 55 °C / 0.01 torr. (Found: C, 81.7; H, 11.8; N, 6.9. Calc. for $C_{14}H_{23}N$: C, 81.9; H, 11.3; N, 6.8%); δ_H(400 MHz, $CDCl_3$) 0.6 (1 H, s(br), N-H), 0.98 (9 H, s, $C(CH_3)_3$), 1.54 (1 H, m_c 8 lines, C(2)H), 2.13 (3 H, s, N-CH_3), 2.36 (1 H, dd, J = 13.6 / 10.1, C(3)H), 2.41 (1 H, dd, J = 12.1 / 6.4, N-CH_2), 2.63 (1 H, dd, J = 12.1 / 3.2, N-CH_2), 2.92 (1 H, dd, J = 13.6 / 3.7, C(3)H), 7.13-7.30 (5 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 28.1 ($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 36.5 (C(3)), 36.6, 50.8 (C(2) and N-CH_3), 53.6 (N-CH_2), 125.7, 128.4, 128.9, 142.5 (Ph).

N,3,3-*Trimethyl*-2-*(phenyl-deuterio-methyl)-butylamine* ([3-D_1]-**10**): The solution of 4 mmol of dilithio

compound **7** in 20 ml THF was treated with CD_3OD (600 mg) through a syringe. While stirring, the temperature was allowed to rise to room temp. and the mixture hydrolized with 20 ml aqueous NH_3 (5 %). The water phase was extracted with Et_2O and the organic extracts dried over $MgSO_4$. After filtration and evaporation of the solvents, distillation gave amine [3-D_1]-**10** (612 mg, 74 %), b.p. 55 °C / 0.01 torr. (Found: C, 81.6; H, 11.0; N, 6.6. Calc. for $C_{14}H_{22}DN$: C, 81.5; H/D, 11.3; N, 6.8%). δ_H(400 MHz, $CDCl_3$) 0.6 (1 H, s(br), N-H), 0.98 (9 H, s, C(CH_3)$_3$), 1.54 (1 H, m_c, C(2)H), 2.13 (3 H, s, N-CH_3), 2.36 (*ca.* 0.1 H, m, *syn*-deut.-C(3)H), 2.40 (1 H, dd, J = 12.1 / 6.4, N-CH_2), 2.63 (1 H, dd, J = 12.1 / 3.1, N-CH_2), 2.89 (*ca.* 0.9 H, m_c, *anti*-deut.-C(3)H), 7.13-7.30 (5 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 28.1 (C(CH_3)$_3$), 33.4 (*C*(CH_3)$_3$), 36.1 (t $J_{C,D}$ = 19, C(3)), 36.6 and 50.8 (C(2) and N-CH_3), 53.6 (N-CH_2), 125.7, 128.3, 128.5, 142.5 (Ph).

N,N,3,3-*Tetramethyl-2-(1-phenyl-ethyl)-butylamine* (**11**): To the solution of 4 mmol dilithio compound **7** in 20 ml THF, iodomethane (1.419 g, 10 mmol) in 3 ml THF was added at -78 °C. While stirring, the temperature was allowed to rise to room temp. and the mixture hydrolized with 20 ml 0.5 n HCl. The acid was neutralized by slow addition of NaOH, the phases separated, the aqueous layer extracted with Et_2O and the organic extracts dried over Na_2SO_4. After filtration and evaporation of the solvents, distillation gave amine **11** (699 mg, 75 %), b.p. 65 °C / 0.07 torr. (Found: C, 82.1; H, 12.1; N, 5.8. Calc. for $C_{16}H_{27}N$: C, 82.3; H, 11.7; N, 6.0%). δ_H(400 MHz, $CDCl_3$) 0.99 (9 H, s, C(CH_3)$_3$), 1.29 (2.75 H, d, J = 7.3, *anti*-C(3)CH_3), 1.44 (0.25 H, d, J = 7.4, *syn*-C(3)CH_3), 1.59 (1 H, m_c, C(2)H), 1.94 (6 H, s, N(CH_3)$_2$), 2.20 (1 H, dd, J = 12.8 / 5.0, N-CH_2), 2.31 (1 H, dd, J = 12.8 / 7.8, N-CH_2), 3.12 (1 H, dq, J = 2.2 / 7.2, C(3)H), 7.05-7.35 (5 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 16.2 (C(3)CH_3), 29.1 (C(CH_3)$_3$), 34.5 (*C*(CH_3)$_3$), 38.5 (C(3)), 45.4 (N-CH_3), 51.0 (C(2)), 57.6 (N-CH_2), 125.0, 127.8, 128.1, 150.0 (Ph).

Cryoscopic measurements: The preparation of both **7** and **3** was achieved by placing an exact amount of the cinnamyl compound (*N*-methyl-cinnamylamine **6** and cinnamyl alcohol, respectively) together with 2 eq. of THF in the cyclindrical flask used for the measurement. The compound was dissolved in 30 ml of *n*-hexane and 2 eq. of alkyllithium reagent was added at 0 °C. After *ca.* 3 h, the solvent was evaporated by applying vacuum for about 1 h. The orange precipitate was then dissolved in an exactly determined amount of dry THF (successively distilled over Na and $LiAlH_4$) and the flask transferred into the apparatus to determine the freezing point of the solution. The measurements themselves are described elsewhere.[13] The following numbers of aggregation were found (c: total concentration of dilithio species): For **3**, 2.0 (±0.1; c=0.07 mol kg^{-1}), 2.16 (±0.2; c=0.093 mol kg^{-1}), 2.29 (±0.08; c=0.136 mol kg^{-1}), 2.76 (±0.13; c=0.16 mol kg^{-1}).
For **7**, 0.98 (±0.06; c=0.074 mol kg^{-1}), 1.04 (±0.06; c=0.1 mol kg^{-1}), 1.03 (±0.09; c=0.136 mol kg^{-1}).

Computational methods

For semiempirical calculations we used the programs MOPAC 93[30] on an IBM RS/6000 workstation and VAMPc 4.5[31] on a IBM compatible 386 PC (the latter only for compounds **12**, **13** and **14**). Geometries were all optimized with GNORM=0.01 without symmetry restrictions on the RHF level. For some molecules, *esp.* the solvated aggregates, it was necessary to use the keywords LET DDMIN=0.00, which turn off some safety checks and allow a temporary rise of the SCF energy during optimization.
Ab initio calculations were carried out with Gaussian 94[32] on a Silicon Graphics Power Challenge workstation.
The local minima were verified by carrying out frequency calculations, which gave no negative eigenvalues of the force constants.

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