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Investigations on the Structure of 1-Dimethylaminoallylalkali Compounds

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Abstract: Structural investigations (NMR) show that both 1-dimethylaminoallyllithium (**4**) and potassium (**2**) exist exclusively in the *endo* conformation in THF. *Ab initio* calculations also conclude that the *endo*-structure is thermodynamically more stable than the *exo*-conformation. Cryoscopic measurements indicate that the potassium compound **2** is a monomer under the experimental conditions studied here. The lithium compound **4** exhibits a monomer-dimer equilibrium that lies almost completely on the side of the dimer at higher concentrations. *Ab initio* calculations again support these findings. The effect of specific solvation upon the most stable conformation (η^4-*endo*-in) of both the lithium and the potassium species is investigated at the HF level of theory.

The synthetically very important class of heterosubstituted allyl compounds has received very little interest from structural chemists in the past. This deficit has been recently remedied in the case of silicon[3] and sulphur[4] stabilised allyllithium compounds. However, there is still very little known about the structure of the 1-aminoallylalkali system. The considerable synthetical interest in these compounds is due to their ability to function as homoenolate equivalents.[5] As an example of their significance, we employ 1-aminoallyllithium and potassium compounds[5,6] on a regular basis in our laboratory. Their extremely good regioselectivity and high nucleophilicity make them quite effective homoenolate equivalents, thus enabling the synthesis of 3-substituted carbonyl compounds. This chemistry has received additional attention since the introduction of (+)-(S)-2-methoxypyrrolidine (SMP) as the amine component, resulting in a chiral homoenolate equivalent[7] that can even be used in an asymmetric homoaldol reaction.[8] Connected with our synthetical investigations, we have become increasingly interested in the structure of these organometallic intermediates. We succeeded in determining the X-ray structure of 1-SMP-1,3-diphenylallyllithium[9], which yielded valuable information about the nature and location of the lithium atom. As we have long suspected[5], the structure of the compound can be described as a 3-lithiated enamine. Conformation of the generality of this structure was recently provided by Beak et al. for a sparteine complex of η^3-N-Boc-N-(p-methoxyphenyl)-3-phenylallyl-lithium.[10] Continuing our systematic structural study of these compounds, we now report upon structural details of the two simplest experimentally accessible 1-aminoallylalkali compounds, 1-dimethylaminoallyl-potassium (**2**) and lithium (**4**).

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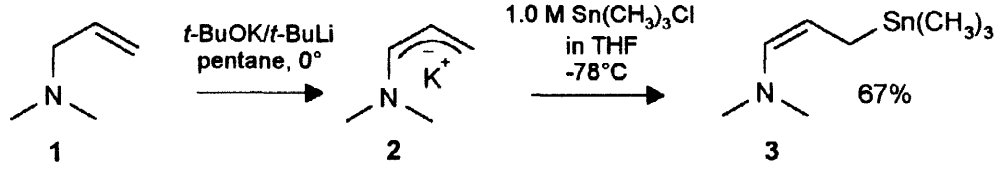
Preparation of *endo*-1-Dimethylaminoallylpotassium and lithium

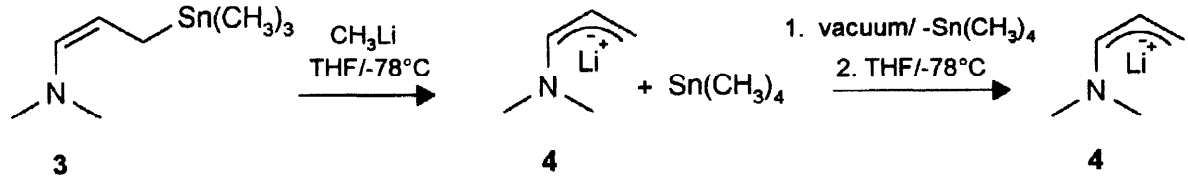
We have known for a relatively long time that the Lochmann-Schlosser base combination *t*-BuLi/*t*-BuOK[11] is capable of directly deprotonating dimethylallylamine (**1**), yielding 1-dimethylaminoallylpotassium (**2**) in nearly quantitative yields[12] (Scheme 1). Obtaining the lithium analogue proved to be a little more difficult since the suitable precursors (dimethylallylamine or 1-dimethylaminopropene) could not be deprotonated with the usual arsenal of lithium bases. Since organolithium compounds can also be generated through a Sn-Li exchange reaction[13], we trapped **2** with a solution of trimethyltin chloride in THF. This resulted in the *Z*-enamine **3**, a suitable precursor for the generation of the desired lithium compound, as the only product in yields of up to 67%.* Assuming a careful work up procedure is employed, compound **3** is obtained stereoisomerically pure.



Scheme 1. Synthesis of *Z*-1-dimethylamino-3-trimethylstannylpropene (**3**).

Transmetallation of **3** with methyllithium in THF is complete within 20 min at -78°C (Scheme 2) and results in a lemon-yellow solution containing an equimolar amount of the lithium species **4** and $Sn(CH_3)_4$. The solution is light sensitive. As indicated in Scheme 2, evaporation of the solvent along with the $Sn(CH_3)_4$ leaves a yellow residue behind that can be redissolved in **cold** THF. Trapping reactions with a couple of electrophiles (Table 1) showed that this purification procedure does not harm the 1-dimethylaminoallyllithium (**4**). Since the $Sn(CH_3)_4$ can be completely removed without affecting the lithium compound in the slightest, we rule out the presence of an at-complex.[14] Furthermore, ^{13}C NMR spectra with and without the presence of $Sn(CH_3)_4$ are identical. Removal of the $Sn(CH_3)_4$ stabilises the lithium compound with regard to its light sensitivity. We suspect that minute traces of organotin radicals, generated by light, are responsible for catalysing a decomposition of the lithium compound. Compound **4** is, regardless of whether $Sn(CH_3)_4$ is present or not, rather sensitive. Temperatures above -50°C and/or minute traces of oxygen in the probe cause decomposition. It proved very difficult to keep probes alive for more than 30 min at -50°C.

The transmetallation reaction is nearly quantitative. However, the products formed from the trapping reactions are 3-substituted enamines, which tend to polymerise upon distillation, thus yielding less than quantitative results. The raw products all possess the *Z*-configuration. Distillation results in partial to complete



Scheme 2. Generation of *endo*-1-dimethylaminoallyllithium (**4**) via a tin-lithium exchange reaction.

* We had a few difficulties in isolating the desired *Z*-enamine **3** before we realised that the potassium compound **2** reacts with the product. If the $(CH_3)_3SnCl$ is added slowly, only black tar is the result. However, if the solution of the electrophile is first cooled down to -78°C and added all at once under wild stirring to a cold solution of the potassium precursor **2**, the desired product is obtained.

Table 1. Reaction of *endo*-1-dimethylaminoallyllithium (**4**) with silyl chlorides in THF at -78°C.

Electrophile	Product	Configuration[a]	Yield (%)[b]	Purification[c]
$(CH_3)SiCl$	**5**	*Z*	83	no
$(CH_3)SiCl$	**5**	*Z*	80	yes
t-$Bu(CH_3)_2SiCl$	**6**	*Z*	75	no
t-$Bu(CH_3)_2SiCl$	**6**	*Z*	76	yes

[a]: Configuration in the raw product. [b]: After distillation. [c]: The $(CH_3)_4Sn$ was removed before the *endo*-1-dimethylaminoallyllithium (**4**) was quenched.

isomerisation of the double bond, depending upon the boiling point of the enamine.

We then tried to make the corresponding *exo*-lithium compound by transmetallating *E*-1-dimethylamino-3-trimethylstannylpropene (**3**). Although the transmetallation reaction succeeded and trapping reactions resulted in the hoped for *E*-enamines, aggregational effects caused the resulting lithium compound to almost immediately flock out of solution as an unstable cheesy solid. Structural investigations proved impossible.

Experimental Structural Investigations

Determination of the molecular weight. Using the cryoscopic method of Bauer and Seebach[15], we determined the molecular weight of both the potassium **2** and the lithium compound **4**. The values given in Table 2 are the average of several measurements performed under the same experimental conditions. The potassium compound **2** is a monomer in THF. A monomer-dimer equilibrium is present for the lithium species **4** with the monomer occurring only at very low concentrations. If the concentration is raised, a dimeric species prevails. These findings are in good accord with the behaviour of allyllithium and potassium. Allyllithium is known to exist as a dimer in THF over a wide concentration range[16] whereas allylpotassium is a monomer under similar experimental conditions.[17]

Table 2. Degree of aggregation (n) of *endo*-1-dimethylaminoallylpotassium (**2**) and lithium (**4**).

endo-1-Dimethylaminoallylpotassium (**2**)			*endo*-1-Dimethylaminoallyllithium (**4**)		
mmol/kg	M[a]	n	mmol/kg	M[a]	n
90.0 ± 0.5	0.10	0.94 ± 0.14	86.5 ± 0.7	0.08	1.04 ± 0.06
120.4 ± 0.5	0.13	1.01 ± 0.12	124.9 ± 0.3	0.11	1.66 ± 0.08
-[b]	-	-	181.0 ± 0.2	0.16	2.00 ± 0.03

[a]: Molar concentration (mol/l). [b]: Concentrations higher than 120 mmol/kg are not soluble at -108°C in THF.

^1H NMR spectra. The ^1H NMR spectral data of both compounds are given in Table 3. Data from the literature[18,19] for the closely related allylalkali compounds are also included in the Table for comparison. The introduction of the NMe_2 group causes a considerable down field shift of the H_α signal (1.74 ppm for the

Table 3. ^{1}H NMR Spectral data of *endo*-1-dimethylaminoallyllithium (**4**) and potassium (**2**) as well as literature values for the closely related allyllithium and potassium.

Compound	H_α	H_β	$H_{\gamma\ in}$	$H_{\gamma\ out}$	NMe_2	$^3J_{\alpha,\beta}$	$^3J_{\beta,\gamma\ out}$	$^3J_{\beta,\gamma\ in}$	$^2J_{\gamma\ out,\gamma\ in}$
allyllithium[a]	1.79	6.22	1.79	2.23	-	-	8.3	14.6	1.6
endo-**4**[b]	3.53	5.65	1.40[c]	1.08[c]	2.22	6[d]	11[d]	10[d]	-[e]
endo-**4** + TMEDA[f]	3.59	5.72	1.48[g]	1.48[g]	2.20	5.5	11.4[g]	11.4[g]	<2[e]
allylpotassium[h]	1.94	6.28	1.94	2.32	-	-	8.2	14.7	2.6
endo-**2**[i]	3.14	5.44	< 1.5[j]	< 1.5[j]	2.24	5.6	8.8	14.4	-

[a]: Literature reference 18. [b]: Measured at -50°C on a 0.32 M solution in d_8-thf. [c]: Assignment uncertain. [d]: The considerable spectral linewidth prevented a more accurate determination. [e]: Geminal coupling was not observed. [f]: Measured at -50°C on a 0.50 M solution with 1.0 equivalent TMEDA. [g]: Both γ-protons are magnetically equivalent. [h]: Literature reference 19). [i]: Measured at -50°C on a 0.50 M probe in d_8-thf. The ^{1}H NMR spectrum of **2** was first obtained 1976 in our group (Lit. ref. 20) and was repeated in this work. [j]: Traces of solvent covered the area of interest.

lithium **4** and 1.20 ppm for the potassium compound **2**). The central proton H_β experiences an upfield shift (0.57 ppm for the lithium and 0.84 ppm for the potassium species). The magnitude of the $^3J_{\alpha,\beta}$ coupling constant (6 and 5.6 Hz) verifies conclusively the *endo*-configuration of both compounds.

Assignment of the γ-protons was not possible for the potassium compound **2**, as signals due to trace amounts of solvent covered the area of interest. The solvent could not be completely removed *in vacuo* without destroying the probe. Problems were also encountered with the assignment of the γ-protons of the lithium species **4**. We observed two dupletts in the ^{1}H NMR spectrum of compound **4**, one at 1.40 and one at 1.08 ppm. The coupling constants are 10 and 11 Hz, respectively. There are several possible interpretations of these findings. One possibility is that only one species with magnetically non-equivalent protons is present. This interpretation is unsatisfactory for two reasons. First, the spectral line width is considerable and second, the magnitude of the coupling constants is wrong. If the γ-protons are really magnetically non-equivalent, coupling constants of ca. 8 and 14 Hz are to be expected. Another possibility is that two equilibrating species with magnetically equivalent γ-protons are present. This is supported by the cryoscopic results, the line width of the ^{1}H NMR spectrum and the magnitude of the coupling constants. Unfortunately, a gs-HOESY spectrum shows a cross peak only to one (the signal at 1.08 ppm) of the dupletts. If there were two species present, two cross peaks would have been seen. Further work needs to be performed in order to clear up this discrepancy. Interestingly enough, the addition of one equivalent of TMEDA causes a noticeable change in the ^{1}H NMR spectrum (Table 3). The line width becomes considerably smaller and the peak at 1.08 ppm is gone. The γ-protons are magnetically equivalent. There is no question as to the assignment of this spectrum. The addition of the chelating agent obviously shifts the equilibrium to favour only one species.

^{13}C NMR Spectra. The introduction of the 1-amino group has, analogue to the ^{1}H NMR spectra, quite some influence upon the ^{13}C chemical shifts of the allylic carbons in **2** and **4**. The signal of the α-carbon in both species is shifted more than 40 ppm downfield as compared to the corresponding allylalkali compound[18,19] (Table 4). The signals due to the β- and the γ-carbon are shifted 14-15 ppm upfield.

A comparison of the chemical shifts of the lithium compound **4** (using the ^{13}C shifts measured for the lowest concentration in order to ensure that the aggregation is the same for both compounds) with those of the potassium compound **2** shows that the identity of the counter ion has a definite influence upon the chemical shift of the γ-carbon. C_γ for the lithium compound is shifted 7.4 ppm upfield of the potassium

species. The chemical shift of the α-carbon is very similar for both species and the signal due to the β-carbon is shifted slightly (0.8 ppm) downfield of the potassium species.

The ^{13}C chemical shifts of the lithium compound show a concentrational dependency. As the concentration is lowered, the signals due to C_α and C_β wander upfield. The signal due to C_γ wanders downfield. Interestingly enough, the 0.32 M probe showed two signals for C_γ. We believe that at -50°C the probe with the lowest concentration is a monomeric species. If the concentration is raised, two species with very similar chemical shifts are present (0.32 M). At still higher concentrations, again only one species, most probably a dimer, is present. To check this, we took the highest concentration (0.50 M) and added an equivalent of TMEDA in the belief that the complexing reagent would break apart the dimer. Indeed, the resulting chemical shifts are directly comparable with those measured for the lowest concentration (0.08 M). Furthermore, the $^1J_{C\text{-}H}$ coupling constants (especially $J_{C\beta\text{-}H}$) with and without TMEDA present are different. Since the coupling constants are quite sensitive of the local structural environment, the very fact that they are different clearly proves the presence of two different aggregates.

Table 4. ^{13}C NMR Spectral data and $J_{C\text{-}H}$ coupling constants of *endo*-1-dimethylaminoallyllithium (**4**) and potassium (**2**).

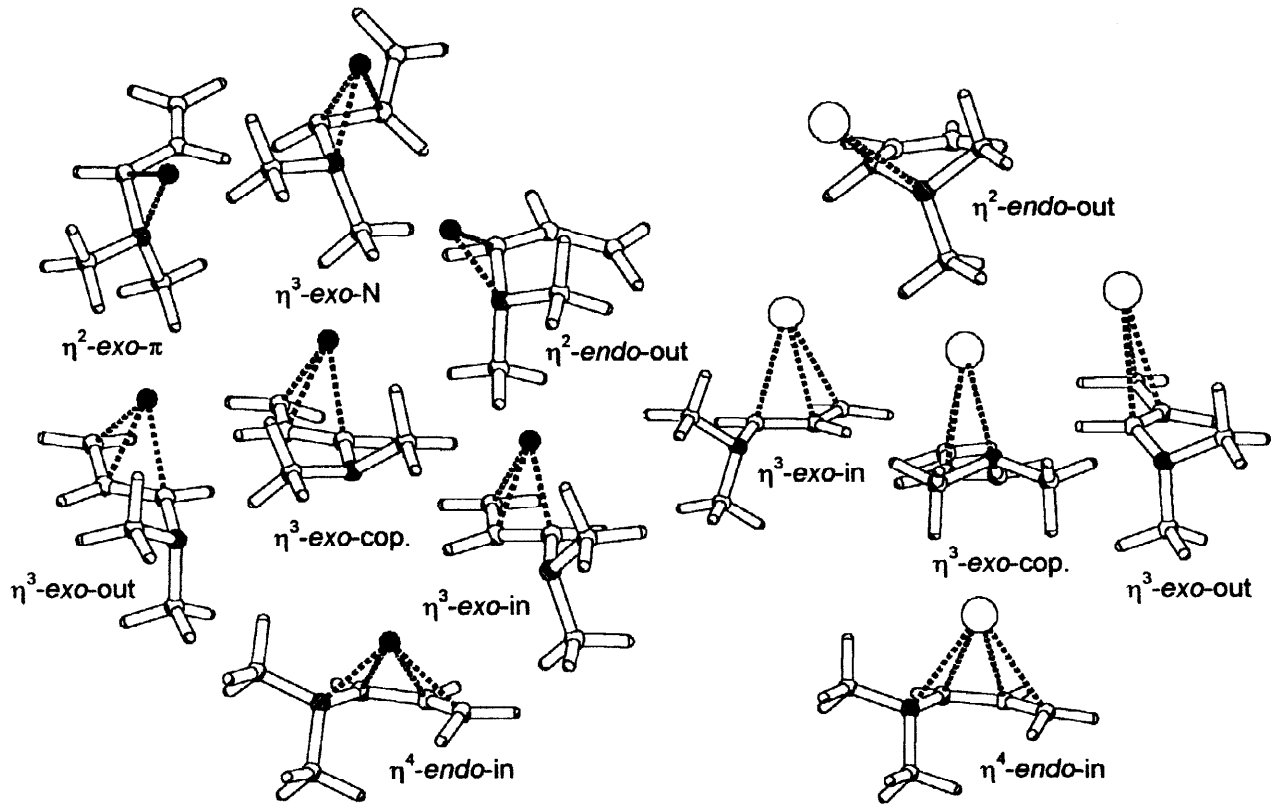
Compound	Conc. (M)	δ (ppm)				$^1J_{C\text{-}H}$ (Hz)			
		C_α	C_β	C_γ	NMe_2	C_α-H	C_β-H	C_γ-H	CH_3
2[a,b]	0.50	94.3	130.4	43.7	45.3	168	134	149 (H_{in}) 153 (H_{out})	132
4[c]	0.50[d]	96.0	131.9	34.9	45.2	173	140	144	133
4[c]	0.32[d]	94.6	131.3	36.1,35.6	45.2	-[e]	-[e]	-[e]	-[e]
4[c]	0.08[d]	94.6	131.2	36.3	45.3	-[e]	-[e]	-[e]	-[e]
4[c]	0.50+TMEDA[f]	94.2	131.0	37.6	45.2	170	150	140	133

[a]: The chemical shifts for allylpotassium have been reported[19] as being 52.8 ($C_{\alpha\gamma}$) and 144.3 ppm (C_β). [b]: Measured at -50°C in d_8-thf The ^{13}C NMR spectrum of **2** was first obtained 1983 in our group (Lit. ref. 12) and was repeated in this work. [c]: Literature values for allyllithium[18]: 50.3 ($C_{\alpha\gamma}$) and 145.9 ppm (C_β). [d]: Measured at -50°C in d_8-thf. [e]: $^1J_{C\text{-}H}$ constants could not be measured at this concentration. [f]: One equivalent of TMEDA was added. The spectrum was taken at -50°C.

Computational Results

Monomeric 1-dimethylaminoallyllithium and potassium. An extended conformational search using the semiempirical PM3 method and reoptimisation at the HF level of theory of all conformers found lead to the seven different conformations of 1-dimethylaminoallyllithium illustrated in Scheme 3. Of these seven conformers, the η^3-*exo*-N structure is most probably a computational artefact. Free optimisation at the MP2 level using the HF η^3-*exo*-N geometry as a starting point resulted invariably in the η^2-*exo*-π conformer. All of the other six conformers are energetical minima at the MP2 level of theory.

Upon sorting the different conformations according to the type of lithium contact present, four completely different structural patterns emerge. In accord with the experimental results, the global minimum is an *endo* conformation. This is not too surprising, as many 1-substituted allylalkali species are known to prefer an *endo* configuration (the well-known cis-effect[21]). The lithium has contact with all three allylic carbon



Scheme 3. Energetically stable conformations found for 1-dimethylaminoallyllithium (**4**) and potassium (**2**) at the MP2 level of theory. Also included is the η^3-exo-N conformation of 1-dimethylaminoallyllithium which is only found at the HF level of theory.

atoms and with the lone electron pair on nitrogen. Interestingly enough, the N-Li contact is quite short* as compared to the Li-C_γ distance (Table 5), leading to a rather asymmetric η^4 bonding pattern with the C_α-Li distance being the shortest C-Li contact. The η^4-*endo*-in conformer is further characterised by slightly alternating allylic C-C bond lengths. C_α is only very slightly nonplanar as measured by the sum of its bond angles. On the other hand, C_γ is noticeably pyramidal in nature. According to its structural features, the global minimum of 1-dimethylaminoallyllithium **4** is most accurately described as being a strongly delocalised, 3-lithiated enamine in which an additional intramolecular Li-N contact is present.

The second structural class found for 1-dimethylaminoallyllithium (**4**) consists at first glance of the three *exo*-conformers. All three structures possess the η^3 bridging pattern typical of allylalkali compounds. A close look at the structural parameters of all three conformers shows, however, that only the η^3-*exo*-in and η^3-*exo*-out rotamers can be classified as being truly 1-amino substituted allylalkali compounds. The amino group, due to the nearly orthogonal orientation of the lone electron pair on nitrogen, does not interact significantly with either the π-system or the lithium. These two conformers are characterised by C-C bond lengths that do not alternate. Both terminal allylic carbons are pyramidal in nature.

* We discuss only our best computational results (MP2 structural parameters in the case of the monomer) in this article. The effect of the method upon the individual structure parameters will be discussed in a future publication.

Table 5. Selected structural parameters for the different conformers of 1-dimethylaminoallyllithium (**4**) and potassium (**2**). All parameters are calculated at the MP2/6-31+G(d) level of theory except for the structural parameters of the η^3-*exo*-N conformer which are given at the HF/6-31+G(d) level of theory.

	C_α-N	C_α-C_β	C_β-C_γ	C_α-Li	C_β-Li	C_γ-Li	N-Li	CCC	CCN	$\Sigma\varphi_{C\alpha}$[a]	$\Sigma\varphi_{C\gamma}$[b]
						1-Dimethylaminoallyllithium (**4**)					
η^4-*endo*-in	145.0	139.4	141.1	206.1	210.2	211.7	198.4	127.0	118.0	359.4	354.8
η^3-*exo*-in	143.2	140.1	140.2	211.1	205.3	208.6	-	126.0	120.0	353.3	354.9
η^3-*exo*-cop.	142.5	139.1	142.6	221.4	206.9	205.1	-	124.8	126.4	356.1	349.5
η^3-*exo*-out	143.5	140.1	141.1	210.4	206.9	207.0	-	125.2	125.6	352.8	355.7
η^2-*exo*-π	148.8	144.6	135.9	196.1	252.1	-	190.3	129.3	112.2	341.8	360.0
η^2-*endo*-out	148.9	145.0	135.9	195.6	-	-	189.6	133.7	122.8	340.4	360.0
η^3-*exo*-N[c]	150.6	149.8	133.4	191.8	-	-	196.8	123.8	111.4	342.9	360.0
						1-Dimethylaminoallylpotassium (**2**)					
η^4-*endo*-in	144.9	139.4	140.7	282.8	287.5	282.6	275.6	130.2	120.4	357.5	354.0
η^3-*exo*-in	143.9	139.8	140.4	289.3	283.2	284.8	398.6	129.5	119.0	352.9	252.9
η^3-*exo*-cop.	145.6	141.4	139.0	279.6	277.3	301.6	290.4	126.8	122.8	352.4	341.9
η^3-*exo*-out	144.6	139.8	140.7	288.1	285.8	282.9	396.8	129.1	123.0	354.6	351.8
η^2-*endo*-out	147.6	143.9	136.9	270.0	399.5	-	267.9	133.9	122.6	342.3	360.0

[a]: Sum of the bond angles at the α-carbon. All parameters are given in pm and degrees. [b]: Sum of the bond angles at the γ-carbon.
[c]: HF/6-31+G(d) structural parameters. This conformer does not exist at the MP2 level of theory.

The coplanar orientation of the lone electron pair on nitrogen in the η^3-*exo*-cop. conformation results in a considerable interaction with the π-system as seen from the strongly alternating C-C bond lengths coupled with the relatively short C-N bond. The polarisation due to n-π interaction is also seen in the sum of the bond angles on C_α and C_γ. In comparison with the other two exo conformers, C_γ is more pyramidal whereas C_α has flattened out somewhat. Instead of building a more or less symmetrical η^3 contact with the allyl system, the lithium is shoved in the direction of C_γ. The C_γ-Li distance is the shortest C-Li contact in the η^3-*exo*-cop. structure. In contrast to the global minimum, the lithium is more or less localised in the neighbourhood of the γ-carbon. The enamine nature is thus enhanced and this conformer is best described as being a 3-lithiated enamine.

Still higher in energy lie two η^2 structures typical of α-lithiated amines.[22] Here the allyl system is decoupled and the resulting C=C double bond can be considered as a „spectator" substituent, thus allowing these two structures to be described as α-lithiated allyl amines. Only in the case of the η^2-*exo*-π conformer is an additional weak π contact present. In keeping with the double bond nature in these allyl amines, C_β and C_γ are purely sp^2-hybridised. C_α is sp^3 in character. Noticeable for these three conformations is a lengthening of the C_α-N bond, indicative of a possible carbenoid nature.[23]

The last structural pattern found (η^3-*exo*-N) exists only at the HF level of theory and exhibits a η^3 contact in which the lithium sits above the $C_\beta C_\alpha N$ plane in complete contrast to the allyllithium-like η^3 contacts

already discussed. This conformer is most probably a computational artefact. No experimental analogue has yet been reported.

Most of the structural motives found for the lithium compound are retained when the lithium is replaced with potassium (Scheme 3 and Table 5). The global minimum of the potassium compound is a η^4-*endo*-in conformation. Two η^3-*exo* conformers and a η^2-*endo*-in structure, both again similar to the corresponding lithium analogues, lie higher in energy (Table 6). Interestingly enough, the η^3-*exo*-cop. conformer of the potassium species differs from that found for the lithium compound. The lone electron pair on nitrogen is now on the side of the allylic π system facing the potassium. Electrostatic contact is made not only with the three allylic carbons, but also with the lone electron pair on nitrogen. In order to improve the contact, the anionic substrate „wraps" itself around the potassium resulting in a considerable deviation from planarity for the CCCN backbone. This is not possible for the lithium species due to the small size of the cation.

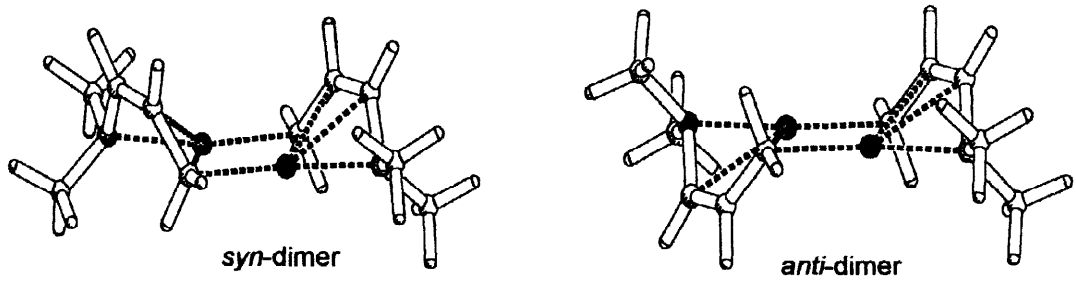
Although the structural motives are mostly retained, there are significant changes in the individual structural parameters when the lithium is replaced with potassium. The localising effect of the small, rather hard lithium is no longer present. The potassium is relatively far away (on average 285 ppm) from the anionic substrate. This enhances the anionic nature of the 1-dimethylaminoallyl substrate and reduces the 3-metallo enamine nature of these conformers.

The stabilisation of the anionic substrate due to the presence of the cation is mostly electrostatic in origin.[24] This stabilisation is known to decrease with increasing ionic radius[24] and is clearly the reason why the relative energies of the potassium conformers are somewhat smaller than the corresponding values for the lithium compound (Table 6). The number of electrostatical contacts present also plays a considerable role in determining how stable a conformer is relative to the others. The larger the number of contacts there are, the more stable the conformation.

Table 6. Relative stabilities (ΔE) of the different conformers of 1-dimethylaminoallyllithium (**4**) and potassium (**2**). All values are calculated at either the HF/6-31+G(d) or the MP2/6-31+G(d) level of theory and are given in kcal/mol.

	η^4-endo-in	η^3-exo-in	η^3-exo-out	η^3-exo-cop.	η^2-exo-π	η^2-endo-out	η^3-exo-N
				1-Dimethylaminoallyllithium (**4**)			
ΔE_{HF}	0.00	9.43	12.45	13.27	16.97	18.80	20.27
ΔE_{MP2}	0.00	13.87	16.60	16.62	17.78	21.32	-
				1-Dimethylaminoallylpotassium (**2**)			
ΔE_{HF}	0.00	6.89	10.02	10.74	-	16.13	-
ΔE_{MP2}	0.00	9.85	12.94	12.31	-	17.96	-

Aggregational effects. An extended conformational search for dimeric stationary points using the semiempirical PM3 method and the reoptimisation of all structures found (around 20) at the HF level of theory resulted in two energetically stable dimers in the case of *endo*-1-dimethylaminoallyllithium (**4**) (Scheme 4). The two dimers are practically isoenergetical in the gas phase. In accord with the experimental findings in THF, dimerisation is strongly favoured. The calculated stabilisation due to dimerisation at the HF/6-31+G(d) level of theory is 36 kcal/mol. This value is only a very rough estimate of the position of the equilibrium in solution. As will be discussed later, specific solvation influences the position of the equilibrium.



ΔE_{rel} = 0.00
ΔE_{dim} = -36.61

ΔE_{rel} = +0.03
ΔE_{dim} = -36.58

Scheme 4. Dimeric aggregate structures found at the HF/6-31+G(d) level of theory for *endo*-1-dimethylaminoallyllithium (**4**). Relative stabilities (ΔE_{rel}) and energies of dimerisation ΔE_{dim}(dimer $\rightleftharpoons$ 2 monomer) are given in kcal/mol.

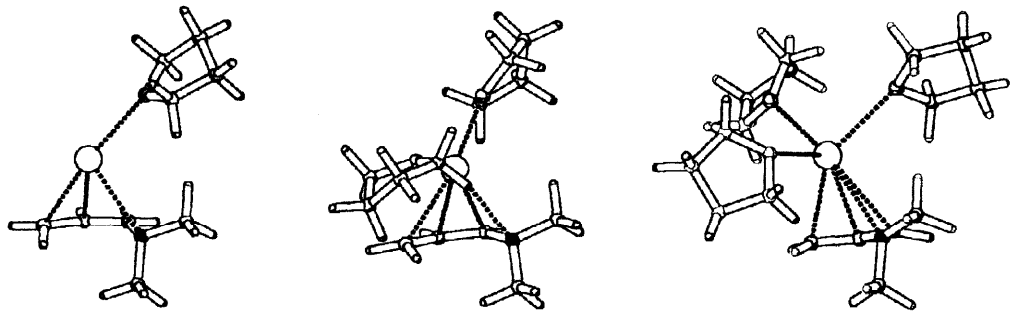
Entropy effects which are not considered by the calculations probably also play an important role in determining the position of the equilibrium in solution.

The basic structural unit underlying both dimers is a 5-4-5 chelate ring system. The monomeric subunits each contain a 5-member chelate ring. These 5-membered rings are fused together in the dimer structure by means of a C_2Li_2 4-membered ring. The resulting dimers are thus structurally very similar and differ only in the *syn* and *anti* bonding pattern of the monomeric subunits. Dimerisation weakens the contact of the lithium to the three allylic carbons in the monomer slightly while maintaining the contact to the nitrogen.* The η^4-*endo*-in structure of the monomeric subunit is otherwise quite well preserved in the aggregate. This 5-4-5 chelate structure is by no means new. The X-ray structure of 1-(+)-(S)-2-methoxypyrrolidino-1,3-diphenylallyllithium[9] possesses a similar dimeric structure with an *anti* bonding pattern. Other organolithium compounds reported in the literature also possess similar 5-4-5 chelate ring structures.[25] The lithium atoms in all of the reported X-ray structures as well as the calculational results have a nearly tetrahedral geometry. The 5-4-5 ring structure occupies three of the four coordination sites at lithium. The fourth coordination site is occupied, at least in the solid state, either with an extra intramolecular chelation or with a solvent molecule. Also worthy of note is the fact that the *anti*-form is overwhelmingly preferred in the solid state.

Interestingly enough, we did not succeed in finding any stationary points for a dimeric aggregate of *endo*-1-dimethylaminoallylpotassium (**2**). Every attempt to optimise the structure of dimeric starting geometries resulted in a smooth convergence of the energy to the sum of two monomers and the monomeric subunits themselves moved further and further away from each other. This finding, together with the cryoscopic results, provide a very good indication that the potassium species, in direct contrast to the lithium compound, is indeed a monomer.

Specific solvent effects. We first considered the effect of specific solvation upon the potassium compound **2** since the complicating effect of aggregation does not need to be taken into account. Specific solvation was simulated by binding THF molecules one after the other onto the potassium and optimising the resulting solvated complexes at the HF/6-31G(d) level of theory (Scheme 5). The complex with only one THF

* A discussion of the individual structure parameters of both dimers is beyond the scope of this article. Those interested should contact the authors for tables of structural parameters.



	one THF	two THF	three THF
$\Delta E_{solv.}$:	-12.60	-21.02	-26.76
$\Delta E_{solv.}$/THF:	-12.60	-8.42	-5.74
N-K:	283.9	285.6	294.1
C_α-K:	288.5	293.0	293.9
C_β-K:	290.8	296.6	299.8
C_γ-K:	285.1	289.9	297.6

Scheme 5. Solvated complexes of *endo*-1-dimethylaminoallylpotassium (**2**). All energies of solvation are calculated according to equation 1 and are given in kcal/mol. Selected structural parameters are given in ppm.

looks a little strange. One would intuitively expect the THF to be more or less directly above the allyl system and not tipped to the side. However, the potential energy surface for this complex is extremely flat, and as long as the THF does not come too close to the *endo*-1-dimethylaminoallyl substrate, it can pretty much do as it likes. We succeeded in binding three THF molecules onto the potassium. There is possibly enough room for a fourth THF in the coordination sphere. Due to the extremely large computational demands, it was not technically possible for us to optimise such a large complex.

Specific solvation increasingly stabilises the potassium species. The stabilisation due to solvation ($\Delta E_{solv.}$) was calculated according to equation 1 and the results are given in Scheme 5.

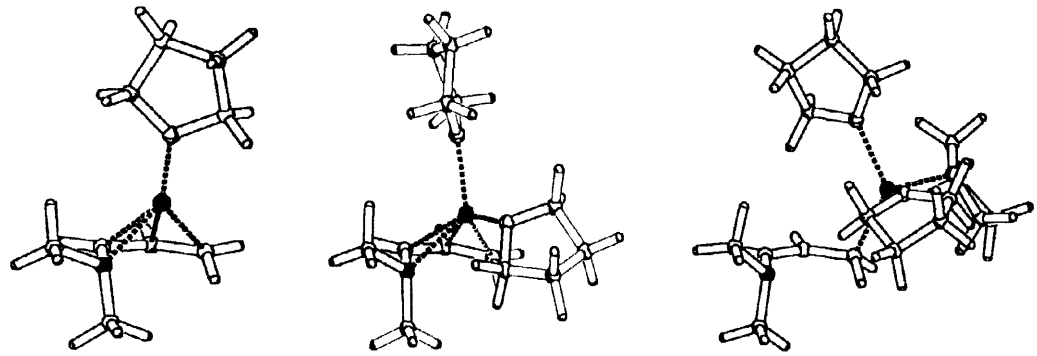
$$\Delta E_{solv.} = E(\text{monomer}\bullet n\,\text{THF}) - n\,E(\text{THF}) - E(\text{monomer}) \qquad \text{(eqn. 1)}$$

The largest contribution to the stabilisation (12.6 kcal/mol) is provided by the first THF molecule. With increasing solvation, the stabilisation gained per introduced THF becomes smaller. This parallels computational results obtained for solvated alkali metal ions [$M^+(H_2O)_n$ complexes, M: Li → Cs][26,27] and is caused by two different effects.[27] First, the solvent molecules already present screen the incoming THF from the electrostatical field of the potassium ion. Second, steric hindrance increases with the degree of solvation and reduces the stabilisation experienced.

Specific solvation does not disrupt the η^4-*endo*-in geometry of the anionic substrate. However, solvation does pull the potassium increasingly away from the allyl system, thus increasing the anionic character in the substrate. The very slight 3-potassioenamine nature of the *endo*-1-dimethylaminoallyl substrate in the unsolvated complex is completely lost upon solvation.

In direct contrast to the potassium compound, solvation has a considerable effect upon the η^4-*endo*-in geometry of the 1-dimethylaminoallyl substrate in the monomeric lithium species (Scheme 6). Binding THF molecules one after another to the lithium causes it to wander in the direction of the γ-carbon. Electrostatic

* A discussion of the effect of solvation upon the individual geometry parameters is beyond the scope of this article. Those interested should contact the authors for tables of structural parameters for the solvated complexes.



	one THF	two THF	three THF
$\Delta E_{solv.}$:	-17.52	-24.11	-27.63
$\Delta E_{solv.}$/THF:	-17.52	-6.59	-3.52
N-Li:	211.4	221.3	(422.4)
C_α-Li:	215.6	239.9	(388.4)
C_β-Li:	216.4	235.0	(305.2)
C_γ-Li:	216.0	218.6	216.0

Scheme 6. Solvated monomeric complexes of *endo*-1-dimethylaminoallyllithium (**4**). All energies of solvation are calculated according to equation 1 and are given in kcal/mol.

contact to the rest of the allyl system as well as to the nitrogen is gradually given up and a 3-lithioenamine is formed. Interestingly enough, a fourth THF cannot be brought into the first coordination sphere of the cation. Several attempts to optimise a complex with four THF molecules at the HF/3-21G level of theory resulted in one of the THF molecules leaving the coordination sphere every time. Although relatively little is known about the first coordination sphere of organolithium compounds in THF, a tetrahedral coordination on lithium has been proven for monomeric hexamethyldisilazide.[28] Theoretical studies on $Li(H_2O)_n^+$ complexes also show that a tetrahedral coordination for the first coordination sphere of the lithium is preferred.[26]

Analogous to the potassium compound, the largest contribution to the stabilisation is provided by the first THF molecule. With increasing solvation, the stabilisation gained per introduced THF becomes smaller. The total stabilisation due to solvation (28 kcal/mol) is on roughly the same order of magnitude as the stabilisation due to dimerisation (36 kcal/mol).

We then investigated the effect of specific solvation upon the dimeric aggregate structures by completing the tetrahedral coordination sphere of the lithium cations. Two THF molecules were necessary, one per lithium ion. Geometry optimisations of the solvated aggregates at the HF/6-31G(d) level of theory lead to two solvated structures directly derived from the *syn* and the *anti* dimeric aggregates. The solvated *anti* species is illustrated in Scheme 7. The stabilisation due to solvation (ΔE_{solv}) was then calculated according to equation 2 and the results are contained in Table 7. The Table also contains the relative stabilities of both solvated dimers.

Interestingly enough, solvation leads to a

Table 7. Relative stabilities and energies of solvation calculated at the HF/6-31G(d) level. All values are in kcal/mol.

	syn-dimer•2 THF	*anti*-dimer•2 THF
$\Delta E_{rel.}$	+2.21	0.00
$\Delta E_{solv.}$	-23.92	-26.25

differential stabilisation of the dimeric aggregates. Although both dimers are practically isoenergetical in the absence of specific solvation, the introduction of two solvent molecules causes the *anti*-structure to become 2 kcal/mol more stable than the *syn*-dimer. This finding parallels the preference for the *anti*-form observed in X-ray structures of related compounds.

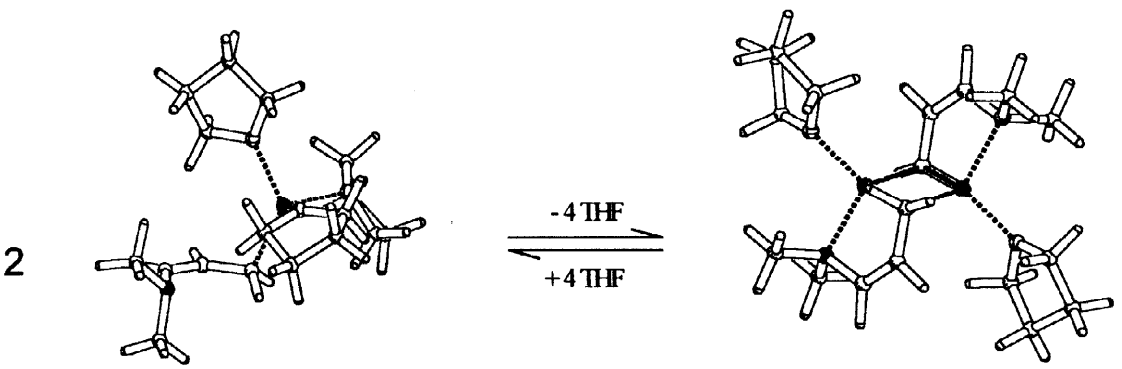
$$\Delta E_{solv.} = E(\text{dimer}\bullet 2\ \text{THF}) - 2\ E(\text{THF}) - E(\text{dimer}) \qquad \text{(eqn. 2)}$$

There is potentially enough space in the solvated dimer structures for binding two THF molecules per lithium atom. Computational limitations prevented us from investigating this possibility.

An estimation of the enthalpy contribution (ΔE) to the dynamical equilibrium ($\Delta G = \Delta E - T\Delta S$) between the monomeric and dimeric species in THF using equation 3 shows that the monomer is slightly preferred (Scheme 7).

$$\Delta E = E(\text{dimer}\bullet 2\ \text{THF}) + 4\ E(\text{THF}) - 2\ E(\text{monomer}\bullet 2\ \text{THF}) \qquad \text{(eqn. 3)}$$

One should bear in mind that, based upon a simple particle count, entropic effects (not considered by the calculations) will shift the equilibrium in the direction of the dimer. It can therefore be expected, and is indeed experimentally observed, that the equilibrium between the monomeric and dimeric lithium species will be a very sensitive function of the temperature and the concentration.



ΔE = +0.5 kcal/mol (*anti*-dimer)
ΔE = +2.7 kcal/mol (*syn*-dimer)

Scheme 7. The monomer-dimer equilibrium of *endo*-1-dimethylaminoallyllithium (**4**) in THF.

^{13}C NMR Chemical shifts of endo-1-dimethylaminoallyllithium. In the hopes that a conformational structure could be unambiguously assigned to the lithium compound in solution, we took both monomer *endo*-conformers found (Scheme 3), calculated their ^{13}C NMR chemical shifts at the HF and the MP2 level of theory and compared them with experimental data (Table 8). Both calculational methods show an extremely large deviation between experiment and theory per carbon atom in the case of the η^2-*endo*-out conformation. Much better results are obtained for the η^4-*endo*-in structure. However, the HF method is not able to describe the allyl system properly. The shift calculated for the α-carbon lies too far upfield and that for the β- and the γ-carbon too far downfield. Only when electron correlation effects are included in the determination of the chemical shifts via the MP2-method is a really good match between experiment and theory found. The correlated results show that there is little doubt that the lithium compound assumes a η^4-*endo*-in conformation in THF.

Unfortunately, it is technically not possible for us at this time to calculate the chemical shifts of the dimer at the MP2 level of theory. Although calculations at the HF level of theory show that the η^4-*endo*-in structure is maintained upon dimerisation, the individual structural parameters do indicate that the 3-lithio enamine nature of the anionic substrate is strengthened somewhat as compared to the monomer. This is also reflected in the calculated (HF) chemical shifts of the dimeric species. We are not certain if the

strengthened enamine character of the dimer is a computational artefact that will disappear at the MP2 level. It could also be possible that dimerisation does indeed strengthen the enamine nature of the lithium compound in the gas phase. Specific solvation would, however, tend to work against this effect.

Electron correlation effects are even more important for the potassium compound than for the lithium compound. Due to lack of computational resources, we could not perform extensive GIAO-MP2 calculations on this system.

Table 8. Theoretical ^{13}C NMR chemical shifts for selected conformations and aggregate forms of *endo*-1-dimethylaminoallyllithium (**4**) as compared with experimental values.

	η^2-*endo*-out		η^4-*endo*-in		*anti*-dimer	Experiment	
	SCF[a]	MP2[b]	SCF[a]	MP2[b]	SCF[a]	0.50 M	0.08 M
C_α	86.0	82.9	86.0	92.3	106.5	96.0	94.6
C_β	146.3	134.7	146.3	129.8	143.5	131.9	131.3
C_γ	66.0	72.8	66.0	36.4	13.1	34.9	36.3
CH_3	41.3	49.2	41.3	49.6	41.2	45.2	45.4
CH_3	40.5	44.4	40.5	45.3	40.2	-	-
$\Sigma\lvert\Delta\delta\rvert/n$[c]	14.5[d]	13.3[d]	6.1[d]	1.5[d]	13.0[e]		

[a]: Calculated at the GIAO-SCF/6-31G(d)//HF/6-31+G(d) level of theory. [b]: GIAO-MP2/dzp//MP2/6-31+G(d) values. [c]: Average deviation between experiment and theory per carbon atom. [d]: Compared with the 0.08 M experimental results. [e]: Compared with the 0.50 M experimental results.

Conclusions

We succeeded in synthesising the two simplest, experimentally accessible, examples of the class of 1-aminoallylalkali compounds, *endo*-1-dimethylaminoallyllithium (**4**) and potassium (**2**). Both compounds exist exclusively in the *endo*-conformation in THF. *Ab initio* calculations and cryoscopic measurements conclude that the potassium compound **2** is a monomer in solution whereas a monomer-dimer equilibrium is present for the lithium species **4**. The global minimum of both species is a η^4-*endo*-in structure. The only other stable *endo*-conformation that could be found on the energy hypersurface of both compounds is a η^2-*endo*-out structure that is a good deal more unstable (ca. 18 kcal/mol at the MP2 level of theory for both species) than the η^4-*endo*-in structure. A comparison of calculated with experimental shifts shows that there is little doubt that the lithium compound **4** assumes a η^4-*endo*-in conformation in THF. Such an assignment could not be performed for the potassium compound **2** due to computational limitations. Based on the experimental and computational evidence presented in this article, however, we are fairly sure that the potassium compound **2** also assumes a η^4-*endo*-in conformation in THF.

Interestingly enough, the η^4-*endo*-in structure is retained upon dimerisation of the lithium compound **4**. Two η^4-*endo*-in units simply come together and form a 5-4-5 chelate ring system. We calculated two such dimeric structures, a *syn*- and an *anti*-form. Without solvation, both dimers are isoenergetical. However, specific solvation preferentially stabilises the *anti*-form. This is in keeping with the experimental fact that X-ray structures of organolithium compounds with 5-4-5 chelate ring structures almost always have the *anti*-structure. The stabilisation gained due to solvation is calculated to be roughly the same order of magnitude as that gained due to dimerisation. One can therefore expect, and it is indeed experimentally observed, that

the position of the equilibrium between the monomeric and dimeric species will be a very sensitive function of the temperature and the concentration.

EXPERIMENTAL

General information. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Brucker AM-400 spectrometer. Chemical shifts for all lithium and potassium species were obtained in d_8-THF. Spectra thus acquired were referenced to the low field d_8-THF signal (3.70 ppm in ^{1}H; 68.6 ppm in ^{13}C NMR spectra). The spectral acquisition temperatures stated have an estimated error of ±5°C. Routine ^{1}H and ^{13}C NMR spectra were recorded in C_6D_6 that had been stored 24h over basic Al_2O_3 to remove all traces of acid. All chemical shifts of routine spectra are reported in ppm relative to TMS. All coupling constants are given in Hz. Combustion analyses were carried out using a Carlo-Erba 1106 instrument. Kugelrohr distillations were performed using a Büchi glass-tube oven GKR-50. The boiling pressures given are only approximate; the boiling points given are the oven temperatures and are ca. 20°C too high. *t*-Butyllithium and methyllithium were purchased from the Metallgesellschaft Frankfurt and their concentration determined by titration of diphenylacetic acid[29] prior to use. All organolithium reagents were handled under a protective argon atmosphere (99.99%, Messer-Griesheim) that had been dried and scrubbed clean from CO_2 by $CaCl_2$ and KOH. Commercial THF was stored several days over KOH, decanted, distilled over fresh KOH, refluxed over Na/benzophenone and distilled before being stored in a brown bottle over Na-wire. Absolute THF intended for cryoscopic measurements was distilled over CaH prior to use. Deuterated THF was distilled and stored over Na/Pb prior to use. Pentane was extracted with conc. H_2SO_4 until the H_2SO_4 was only slightly yellow, refluxed over KOH, distilled, refluxed over Na/benzophenone and distilled before being stored in a brown bottle under Ar and over Na wire. Potassium *t*-butoxide was obtained from Aldrich and dried 12 h at 100°C under continuous stirring *in vacuo* before use. Dimethylallylamine was purchased from Fluka and distilled prior to use. Trimethyltin chloride was obtained from Fluka and used without further purification.

Preparation of Z-1-dimethylamino-3-trimethylstannylpropene (3). Freshly distilled dimethylallylamine (3.4 g; 40.0 mmol) was added to a stirred suspension of potassium *t*-butoxide (4.49 g; 40.0 mmol) in 150 ml dry pentane under an argon atmosphere. The resulting mixture was cooled down to -10°C before 1.0 equivalents of *t*-butyllithium (1.6 M, 25.0 ml) were added dropwise over 30 min. at -10°C. The resulting yellow precipitate of 1-dimethylaminoallylpotassium (**2**) was allowed to stir an additional 30 min. at -10°C before being cooled down to -78°C. The reaction mixture was quenched **all at once** under wild stirring with 40.0 ml of a **cold** (-78°C) 1.0 M solution of trimethyltin chloride in THF [It is very important to react away all the potassium compound as fast as possible, as it attacks with the product]. After stirring an additional 10 min. at -78°C, the now colourless mixture was filtered as rapidly as possible over a glass filter (dry!) under argon, freeing it from precipitated organic salts. The pentane was evaporated away at 50 Torr/r.t. leaving the crude product behind. The tin compound **3** was then distilled at 0.1 Torr/room temperature in a Kugelrohr distillation apparatus, with the collecting ball being continually cooled with dry ice and the vacuum being only occasionally applied. 6.69 g (67%) of a colourless liquid with a rather high vapour pressure was obtained, bp. 25°C/0.1 Torr. Found: 38.64 %C, 7.91 %H, 5.41 %N. Calc. for $C_5H_{19}NSn$ 38.75 %C, 7.72 %H, 5.65 %N. %. δ_H(400 MHz, C_6D_6) 0.14 (s, $SnMe_3$), 1.78 (dd, J = 1.2/8.7,CH_2), 2.30 (s, NMe_2), 4.82 (m_c, 8 signals, H_β) 5.36 (td, J = 1.2/8.0, H_α); δ_C(100 MHz, C_6D_6) -9.5 ($SnMe_3$) 11.4 (C_γ), 44.5 (NMe_2), 112.9 (C_β), 137.7 (C_α).

Preparation of E-1-dimethylamino-3-trimethylstannylpropene (3). 6.69 g *Z*-**3** was stirred together with 30 ml of absolute methanol for 2 h under argon and in the dark. The mixture was then extracted with 3x 20 ml of absolute pentane. The solvent was then cautiously (50 Torr/r.t.) evaporated from the combined pentane phases. The raw product was then distilled as described above. Yield: 1.21 g (18 %) of a colourless liquid possessing a rather high vapour pressure. bp. 25°C/0.1 Torr. Found: 38.09 %C, 8.15 %H, 5.22 %N. Calc. for $C_5H_{19}NSn$ 38.75 %C, 7.72 %H, 5.65 %N. %. δ_H(400 MHz, C_6D_6) 0.11 (s, $SnMe_3$), 1.74 (dd, J = 1.1/8.1,CH_2), 2.31 (s, NMe_2), 4.37 (td, J = 8.1/13.3 H_β) 5.81 (td, J = 1.1/13.3, H_α); δ_C(100 MHz, C_6D_6) -10.6 ($SnMe_3$) 13.1 (C_γ), 41.2 (NMe_2), 98.2 (C_β), 138.3 (C_α).

Note: Both *Z*-**3** and *E*-**3** are extremely toxic and have rather large vapour pressures. Breathing only minute amounts of vapour or minor skin exposure to the compound results in a severe headache that lasts several hours.

Preparation of endo-1-dimethylaminoallyllithium (4). Procedure A: 5.0 mmol of *Z*-**3** and 20 ml of absolute THF were placed in a 50 ml 2-neck flask than had been previously heated under vacuum and then flushed with argon. The flask was wrapped in Al-foil before being cooled down to -78°C under continual stirring. A continuous stream of argon was maintained while 5.0 mmol of methyllithium (1.6 M in ether) was

slowly added over a period of 10 min. The mixture was then stirred a further 20 min. at -78°C, resulting in a lemon yellow solution of compound **4** containing an equimolar amount of $Sn(CH_3)_4$. The mixture is light sensitive as long as $Sn(CH_3)_4$ is present. ***Procedure B:*** *Removal of $Sn(CH_3)_4$.* The solution of *endo*-**4** obtained in procedure A was purified through evaporation of the solvent and $Sn(CH_3)_4$ *in vacuo* at -78°C. After the formation of a glassy yellow solid, the vacuum was replaced by an argon atmosphere and the lithium compound redissolved in 20 ml of **cold** (-78°C) THF.

Preparation of enamines 5 and 6. General Procedure: A solution of *endo*-**4** was prepared according to either Procedure A or Procedure B. This solution was then titrated at -78°C with 5.0 mmol of a silyl chloride dissolved in 2.5 ml of absolute THF. The now colourless solution was stirred a further 10 min at -78°C before being allowed to warm up to room temperature. The ether solvent mixture was then removed *in vacuo*. 20 ml absolute pentane was added to the residue which was then stirred 10 min before being filtered. The precipitate (LiCl) was washed with 5 ml of pentane. The collected pentane phase was then placed in the end ball of a Kugelrohr distillation apparatus and the pentane was removed *in vacuo*. The remaining raw product was then subjected to a Kugelrohr distillation. *1-Dimethylamino-3-trimethylsilylpropene (**5**)*: A volatile colourless liquid with bp. 25°C/0.1 Torr. Found: 60.80 %C, 12.46 %H, 8.52 %N. Calc. for $C_8H_{19}NSi$: 61.07 %C, 12.15 %H, 8.89 %N. *Z-Isomer*: δ_H(400 MHz, C_6D_6): 0.07 (s, $SiMe_3$), 1.66 (dd, J = 1.4/8.6, CH_2), 2.37 (s, NMe_2), 4.53 (m_c, 4 signals, H_β), 5.49 (td, J = 1.4/8.6, H_α). δ_C(100 MHz, C_6D_6): -1.7 ($SiMe_3$), 16.9 (C_γ), 44.5 (NMe_2), 108.0 (C_β), 139.3 (C_α). *E-Isomer*: δ_H(400 MHz, C_6D_6): 0.06 ($SiMe_3$), 1.42 (dd, J = 0.9/7.9, CH_2), 2.32 (s, NMe_2), 4.20 (td), J = 7.9/13.5, H_β), 5.76 (td, J = 0.9/13.5, H_α). δ_C(100 MHz, C_6D_6): -2.0 ($SiMe_3$), 19.4 (C_γ), 41.1 (NMe_2), 95.3 (C_β), 139.8 (C_α). *1-Dimethylamino-3-(dimethyl,t-butyl)silylpropene (**6**)*: A light yellow liquid with bp. 85°C/16 Torr. Found: 66.06 %C, 12.85 %H, 7.04 %N. Calc. for $C_{11}H_{25}NSi$: 66.25 %C, 12.64 %H, 7.02 %N. *Z-Isomer*: δ_H(400 MHz, C_6D_6): 0.03 (s, $SiMe_2$), 0.93 (s, CMe_3), 1.70 (dd, J = 1.3/8.6, CH_2), 2.38 (s, NMe_2), 4.55 (m_c, 4 signals, H_β), 5.49 (td, J = 1.4/7.2, H_α). δ_C(100 MHz, C_6D_6): -6.1 ($SiMe_2$), 12.9 (C_γ), 22.7 ($\underline{C}Me_3$), 26.8 ($C\underline{Me}_3$), 44.6 (NMe_2), 108.8 (C_β), 139.4 (C_α). *E-Isomer*: δ_H(400 MHz, C_6D_6): 0.01 ($SiMe_2$), 0.94 (s, CMe_3), 1.47 (dd, J = 0.9/7.8, CH_2), 2.33 (s, NMe_2), 4.24 (td, J = 7.8/13.6, H_β), 5.75 (td, J = 0.9/13.6, H_α). δ_C(100 MHz, C_6D_6): -6.4 ($SiMe_2$), 15.5 (C_γ), 17.0 ($\underline{C}Me_3$), 27.0 ($C\underline{Me}_3$), 41.1 (NMe_2), 95.7 (C_β), 139.8 (C_α).

Cryoscopic measurements. *Endo-1-dimethylaminoallyllithium (**4**).* The preparation of *endo*-**4** was achieved by placing 5 eq. of methyllithium (0.80 M in ether, titrated immediately before use with a syringe accurate to 0.01 ml) in a cryoscopic flask equipped with a magnetic stir bar that had been previously heated and flushed with argon. The ether was removed by applying vacuum for about 1h before the flask was flushed with argon. The methyllithium was then dissolved in 20 ml of cryoscopic quality THF, the flask wrapped in Al foil and cooled down to -78°C before an exactly determined amount of *Z*-**3** was added under continual stirring. After stirring 20 min, the lithium compound was freed from $Sn(Me_4)$ as described above in Procedure B and dissolved in an exactly determined amount of cold (-78°C) cryoscopic quality THF. The Al foil was then removed from the flask and the magnetic stir bar was exchanged for a new one. The flask was then placed in the cryoscopy apparatus. The measurements themselves are described elsewhere.[15]

*Endo-1-dimethylaminoallylpotassium (**2**)*: The preparation of *endo*-**2** was achieved by placing an exactly determined amount of dry potassium *t*-butoxide in a three-necked flask equipped with a second flask connected through a glass filter that had been previously heated and flushed with argon. 10 ml of absolute pentane and 1.1 eq. of allyldimethylamine (**1**) were then added to the flask. The mixture was cooled to -10°C under continuous stirring before 1.00 eq. of t-butyllithium (0.7 M in hexane, titrated immediately before use with a syringe accurate to 0.01 ml) was added over a period of 10 min. The reaction mixture was stirred for a further 20 min before being cooled down to -78°C. The solvent was then filtered away over the glass filter. The remaining yellow precipitate was washed with 2x5 ml of **cold** (-78°C) pentane. The precipitate was then dried with a steady, strong stream of cold Ar (the Ar was passed through three liquid N_2 cold traps that were connected one after each other in order to cool it down). After the organopotassium compound appeared to be dry, a 0.02 torr vacuum was cautiously applied for ca. 5 min in order to remove as much of the remaining traces of solvent as possible. It is not possible to completely dry the compound *in vacuo* as decomposition, even at -78°C, sets in. The organopotassium compound was then dissolved in an exactly determined amount of cold (-78°C) cryoscopic quality THF. The resulting deep orange solution was then transferred using a syringe to a dry cryoscopic flask containing an Ar atmosphere that had been previously placed in a cold bath (-78°C). The flask was then transferred to the cryoscopy apparatus.

NMR Measurements. *Endo-1-dimethylaminoallyllithium (**4**).* 2-3 mmol of *endo*-**4** were prepared using an appropriate amount of d_8-thf as described above in either procedure A or B. The resulting lemon yellow solution was transferred to a dry NMR tube containing an Ar atmosphere that had been previously placed in a cold bath (-78°C). The NMR tube was then sealed with parafilm and transferred immediately to a waiting NMR apparatus held at -50°C. *Endo-1-dimethylaminoallylpotassium (**2**)*: 2-3 mmol of *endo*-**2** was prepared

using an appropriate amount of d_8-thf according to the procedure given above in the cryoscopic section. The organopotassium compound was then transferred to a dry NMR tube containing an Ar atmosphere that had been previously placed in a cold bath (-78°C). The NMR tube was sealed with parafilm and transferred immediately to a waiting NMR apparatus held at -50°C.

Computational Details

A full conformational search was performed for solvated and unsolvated monomeric and dimeric 1-dimethylaminoallyllithium **4** at the semiempirical PM3 level[30] using the SPARTAN[31] program package. All semiempirical conformers found were then reoptimised at the HF/6-31G(d) level of theory. All *ab-initio* calculations were performed using either the IBM RS/6000 or Fijitsu VP version of GAUSSIAN 94[32]. The optimal HF/6-31G(d) structures of the unsolvated conformers were then used as starting points for optimisation at the HF/6-31+G(d) and, in the case of the monomer, the MP2-full/6-31+G(d) level of theory (which we abbreviate as MP2/6-31+G(d) in this article). All stationary points found at these two levels were then characterised as energy maxima or minima by calculating their vibrational frequencies. Frequency calculations for the solvated complexes were performed at the HF/6-31G(d) level of theory.

We employed a 10-electron effective core potential (ecp)[33] with a (6s6p1d)[4s4p1d] basis set[34] for the valence electrons for the potassium atom in 1-dimethylaminoallylpotassium (**2**). All other atoms were equipped with either a 6-31+G(d) or 6-31G(d) basis set. Due to the lack of good parameters for potassium, an extended conformational search was not performed at the semiempirical level of theory for the potassium compound. The lithium in the conformer of interest was simply replaced with potassium and the structure reoptimised. To be sure that no conformers of importance were missed, we performed, starting with the η^3-*exo*-in conformer, a 360° scan in steps of 15° about one of the $C_\beta C_\alpha NC_{Me}$ dihedral angles at the HF/6-31G(d) level.

All relative stabilities and energies of solvation reported in this article contain a correction for the zero point energy. Zero point energies calculated at the HF level of theory were scaled by 0.894.[35] MP2 frequencies were not scaled.

Optimal HF/6-31+G(d) or MP2-full/6-31+G(d) structures were then used to calculate the chemical shielding using either the GIAO-SCF method as implemented in GAUSSIAN 94[32] or the GIAO-MP2 method as implemented in ACESII.[36] The calculated ^{13}C NMR shielding values were referenced to $SiMe_4$ that had been calculated at the same level of theory.

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