Bicyclo[3.2.1]octa-2,6-dienyllithium and -potassium Chemistry
Solvation, Aggregation, and $^{119}$Sn–$^7$Li Coupling of Stannylated Derivatives

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Dedicated to Prof. Dr. H. P. Fritz on the occasion of his 60th birthday
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Stannylated Bicyclo[3.2.1]octa-2,6-dienyl Anions, Coupling of $^{119}$Sn with $^7$Li, Solvation and Aggregation of $\pi$-Carbanions

The $^1$C NMR spectra of bicyclo[3.2.1]octa-2,6-dienyl anion (1) as the lithium (1Li) and the potassium salt (1K) were recorded at various temperatures and in different solvents. The results show 1K to exist as a contact ion pair (CIP), whereas for 1Li solvent separated ions (SSIP) are also found as the temperature is lowered and when the solvating power of the solvent is increased. In the $^7$Li NMR spectra at very low temperature the signals of the SSIP disappear and only those of a monomeric CIP and a triple ion (1LI1) consisting of two carbanions and one lithium cation are present. For independent confirmation, the hitherto unknown 6-, 7-, and 3-trimethylstannyl substituted bicyclo[3.2.1]octa-2,6-dienyllithium derivatives 2aLi, 2bLi, and 3Li were synthesized and also studied by $^{119}$Sn, $^{13}$C, and $^1$H NMR. According to the temperature dependence of the $\delta$($^1$C)-values the CIP/SSIP-equilibrium of 2aLi in THF/TMEDA is shifted to the CIP side. The observation of a unique $^{119}$Sn–$^7$Li coupling (6.2 Hz) shows that at $-90^\circ$C a species containing 2a and lithium exists under slow exchange conditions. A similar coupling of 3.5 Hz can be estimated for 3Li. A mixture of the epimeric carbanions 2a and 2b yields two sets of $^1$C NMR signals which are due to the diastereomeric triple ions 2aLi2a and 2aLi2b.

Introduction

In the fascinating chemistry of the bicyclo-
[3.2.1]octa-2,6-dienyl anion (1) the controversial discussion concerning the homoaromaticity had to get along without experimental details on the structure until recently. MNDO geometries have been determined as a basis for $ab\ initial$ calculations [1], but only values for two C–C distances are available from these studies [1c]. Our X-ray analysis of 1Li (TMEDA) [2] revealed that the olefin (C6/7) and the allyl (C2–4) part of 1 have a through space distance $r = 237$ pm which is $11$ pm shorter than found in the MNDO calculation [1b].

and that the angle $\alpha$ between the $\pi$-systems (as given by the angle between the normals to planes C2–C3–C4 and C1–C5–C6–C7) is 72.9°. This did not seem to contradict the $ab\ initial$ study by Brown et al. [3], who claimed homoaromatic interaction in 1 based on an optimal interaction of the $\pi$-orbitals for $r$ close to 240 pm and $\alpha > 60^\circ$ and on the analysis of the electronic charges.

A question of central interest was as to whether the lithium cation plays an important role in the structure and the stability of 1. Lindh, Ahlberg et al. in a multiconfigurational SCF study [4] and v. Schleyer et al. in a MNDO study [5], both including lithium, did not find evidence (from bond lengths, charge distribution, orbital interaction, and energy considerations) for homoaromaticity, but a considerable $\pi$-chelating effect of the olefin part of 1 was proposed [5]. The calculated structural parameters are in good agreement with the X-ray results except for the Li–C distances, which deviate owing to the method of calculation.

Obviously, further information on the interaction of 1 with lithium was desirable. We have therefore investigated the structure of 1Li and three unknown stannylated derivatives in solution.

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Results and Discussion

A. Solvation of bicyclo[3.2.1]octa-2,6-dienyllithium (1Li) and -potassium (1K)

When a solution of 1K in THF or 2,5-dimethyltetrahydrofuran (Me₂THF) was studied by $^{13}$C NMR at 0.4 and −74.0 °C only small changes $\Delta \delta$ of the resonance shifts to low frequency were observed for all carbon atoms with $\Delta \delta^{(13)} < 1.1$. $\Delta \delta^{(13)}$ had the same sign and was even smaller when 1Li dissolved in 2,2,5,5-tetramethyltetrahydrofuran (Me₄THF) was measured at 0.2 and −71.5 °C. This contrasted with a solution of 1Li in Me₂THF the $^{13}$C NMR results of which are shown in Fig. 1.

On lowering the temperature all resonances move to high frequency, a behaviour which is characteristic of an equilibrium existing between contact ion pairs (CIP) and solvent separated ion pairs (SSIP) [6]. We conclude that in Me₂THF and above 0 °C 1Li exists predominately as CIP whereas on lowering the temperature to −90 °C an increasing amount of SSIP emerges. By contrast, 1K behaves like other potassium salts of carbanions and is a CIP at all temperatures and for all solvents studied.

The temperature effect is most pronounced for C6/7 of 1Li. This is to be expected if in the CIP the lithium sits in the endo-position of 1 as found in the solid state [2]. The fact that all $\delta$ vs. T-curves are similar means that a conceivable polarization of the carbanion charge by the cation is not reflected in the $\delta^{(13)}$-values. Another remarkable feature of the curves in Fig. 1 is that near −95 °C the shifts of the more affected carbon atoms pass through a maximum. Obviously, the assumption of only one CIP/SSIP equilibrium is too simple to account for this behaviour (see also Section C).

The CIP/SSIP equilibrium should also be influenced by a change of the solvent. This was actually found as demonstrated in Fig. 2. Among the various trends we mention the following: When the solvating power of THF is decreased by introducing methyl groups, $\delta^{(13)}C6/7$ at a given temperature decreased in accord with the expected increase

![Fig. 1. Temperature dependence of the $^{13}$C NMR signal shifts of 1Li in Me₂THF.](image)

![Fig. 2. Solvent dependence of the $^{13}$C NMR signal shifts of 1Li and 1K (lower four traces) at 0 °C except for 1Li in 1,4-dioxane (15 °C) and in benzene (7 °C). a Dimethoxyethane; b 1,4-dioxane; c–e methyl-, 2,5-dimethyl- and 2,2,5,5-tetramethyltetrahydrofuran; f tetramethylene diamine. Some data were taken from ref. [2].](image)
of the CIP concentration. Note that $\delta^{13}(\text{C}6/7)$ is a probe for the CIP/SSIP equilibrium only for a given cation. Thus for the CIP 1K the resonance of C6/7 is found in the same range as for 1Li when it is a SSIP. Similar cation effects have been found for other carbanions [6b].

B. Stannylated bicyclo[3.2.1]octa-2,6-dienyl anions

B.1. Synthesis

We have extended these studies by introducing trimethyltin groups in 1 as shown in Scheme 1. The distannylated precursors 6a and 7 have been prepared by double deprotonation of 5 followed by quenching with (CH$_3$)$_3$SnCl, and by reacting 4 with (CH$_3$)$_3$SnLi [7]. When approximately one equivalent of methyllithium was added to 6a or 7 below room temperature, the stannyl group in the allyl position 4 was split off selectively and the lithium derivatives 2aLi and 3Li were formed. It is noteworthy that 3Li was obtained in only three synthetic steps starting from norbonadiene, which is the shortest synthesis of a bicyclo[3.2.1]octa-2,6-dienyl anion reported to date. Within the limits of detection by $^{13}$C NMR spectroscopy the yields were quantitative. The selectivity of the reaction is in line with the partial quench of doubly deprotonated 5 with THF giving exclusively 1 [7].

After cooling solutions of 2a and 3 in ether yellow microcrystalline materials were obtained which were stable for months at $-78^\circ$ C. In THF 2a was much less stable than 3 and even 1; above 0 °C it decomposed within a few hours as shown in Scheme 2 giving 8 and 9 in a ratio of 9/7 (cf. Fig. 4 below).

Table I. $^{13}$C NMR data for lithium salts of stannylated bicyclo[3.2.1]octa-2,6-dienyl anions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Position</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<td>113.47</td>
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<td>&lt; 3</td>
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<td>61.1</td>
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<td>36.4</td>
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<td>156</td>
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<td>159.2</td>
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<tr>
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<td>163.6</td>
<td>141</td>
<td>158.7</td>
<td>158.7</td>
<td>132.5</td>
<td>127.6</td>
<td>$^a$ For numbering see Scheme 1; $^b$ from top to bottom: $\delta^{13}(\text{C}), \delta^{19(11)}(\text{Sn}-^{13}\text{C}), \delta^{11(13)}(\text{C}-^{1}\text{H}); c$ at 0 °C in Et$_2$O/TMEDA (8/1); $^d$ at $-40^\circ$ C in THF-d$_8$/TMEDA (3/1); $^e$ from two sets of signals (see Section B.4.); $^f$ at 23 °C in Et$_2$O; $^g$ at 23 °C in Et$_2$O; $^h$ no separate signal observed; $^i$ obtained from $^{119}$Sn NMR, solvent Et$_2$O/toluene-d$_8$.</td>
<td></td>
</tr>
</tbody>
</table>
The structure of 2a and 3 was confirmed by $^{13}$C and partly by $^1$H NMR spectroscopy; details are collected in Table I. The signal assignment is based on the comparison with data obtained for 8 and 3-trimethylstannylbicyclo[3.2.1]octa-2,6-diene (10) [8] and the arguments given there. The $^1$H signals of 2a (cf. Experimental) have been assigned using selective homo- and heteronuclear decoupling.

Some interesting changes are evident from the NMR data on going from the hydrocarbons 8 or 10 [8] to the corresponding anions 2a or 3. The average of $\delta(^{13}$C) and $J(^{13}$C-$^1$H) of C6/7 is reduced by 53.6 or 50.6 ppm and 4.1 or 7.8 Hz, respectively. This is similar to what was found for the pair bicyclo[3.2.1]octa-2,6-diene (5) and 1 [9]; it is indicative of negative charge being built up at the olefinic carbon atoms of the anions. The effect is more pronounced for $J(^{119}$Sn-$^{13}$C) which is 16% smaller for 2a as compared to 8. By contrast, a decrease of only 3% is calculated for the pair 3/10. The latter result is in nice agreement with the fact that in 10 the stannyl group is bound to the central carbon atom of an allyl system where only little charge is expected.

B. 2. Solvation

As outlined for 1Li the $\delta(^{13}$C)-values of C6/7 are a good probe for the CIP/SSIP equilibrium. When this is applied to 2a and 3 the values in Table I have to be corrected for the substituent effects of the stannyl groups [7, 8]. Signal shifts between 82 and 85 ppm are then obtained for C6/7 at $-3$ or 23 °C. This points to the predominance of CIPs but the procedure gives only a rough idea. Therefore we have performed a variable temperature $^{13}$C NMR study of 2aLi. The result shown in Fig. 3 is rather different from that for 1Li in Fig. 1. The changes of the $\delta(^{13}$C)-values of 2aLi with temperature are much smaller than those of 1Li, the trend is inverse and resembles that of 1K. We conclude that on substituting 1 with stannyl groups the CIP/SSIP equilibrium is shifted to the CIP which predominates even at $-90$ °C.

B. 3. $^{119}$Sn–$^7$Li coupling

This study offered the possibility of detecting a tin-lithium coupling. In fact, 3Li dissolved in Et$_2$O/toluene-d$_8$ gave a $^{119}$Sn NMR signal which broadened at $-40$ °C and a multiplet as shown in Fig. 4a seemed to emerge below $-70$ °C. However, a detailed analysis was impossible because the small coupling constant (estimated value 3.5 ± 0.5 Hz) was smeared out by temperature instabilities. This was verified by a variable temperature $^{119}$Sn NMR study between $-90$ and 0 °C giving $\delta(^{119}$Sn) = $-0.02153 T - 41.73$. Assuming a temperature instability of ±0.5 K the resonance moves over 2.2 Hz at 100.7 MHz.

The $^{119}$Sn NMR signal shift of 2a turned out to be much less temperature dependent ($\delta = -47.4$ at
Fig. 4. $^{119}\text{Sn}$ NMR spectra of the lithium derivatives of 3 in THF/TMEDA (trace A) and of 2a in Et₂O/toluene-d₈ (trace B) both at -90 °C. For the origin of the signals of 7 and 8 see Scheme 2 and text. C: Model for the pattern of the signal for 2a (cf. text).

0 °C and -47.3 at -90 °C), and the spectrum in Fig. 4b could be obtained. Besides the sharp signals of 8 and 9 (formed in the partial reaction of 2a with THF at 0 °C) a quartet is seen for 2aLi at -90 °C.

It shows the typical 1/1/1/1-pattern expected for the coupling to the spin-3/2 nucleus $^7\text{Li}$ with the inner components having somewhat higher intensity than the outer ones owing to limited resolution. $J(^{119}\text{Sn}-^7\text{Li})$ amounts to 6.2 Hz which is close to the value estimated for 3Li. The quartet is further distorted by the presence of the $^6\text{Li}$-isotopomer which gives a 1/1/1-triplet with $J(^{119}\text{Sn}-^6\text{Li}) = 2.3$ Hz (calculated from $[J(^{119}\text{Sn}-^7\text{Li})]/[y(6\text{Li})/y(7\text{Li})]$ by using the gyromagnetic ratios $\gamma$). Taking into account that a secondary isotope shift $\Delta$ to high frequency usually occurs when a neighbouring nucleus is replaced by its heavier isotope the pattern in Fig. 4b can be understood as being determined by the natural abundance of $^6\text{Li}$ (7.4%) or $^7\text{Li}$ (92.6%) and a superposition as shown in Fig. 4c.

The isotope effect $J(119\text{Sn}-^7\text{Li})$ is estimated to be 30 ppb; a corresponding isotope effect $J(13\text{C}-^7\text{Li})$ is to be observed in the $^{13}\text{C}$ NMR spectrum of $t$-BuLi [10].

This appears to be the first $^{119}\text{Sn}-^7\text{Li}$ coupling detected and one of the few cases for which the coupling of $^7\text{Li}$ to other nuclei could be resolved; recent examples are $^{195}\text{Pt}$ [11a], $^{31}\text{P}$ [11b–c], $^{29}\text{Si}$ [11f], $^{13}\text{C}$ [10, 11g–l], and $^1\text{H}$ [11m]. The mechanism of these couplings is not well understood. However, it is generally believed that small covalent contributions to e.g. the Li–C bond are responsible [12]. In the lithium derivatives of 1, 2a, and 3 covalency should be also small and the coupling of lithium to the ligand nuclei are further reduced by the fact that $\pi$- rather than $\sigma$-type orbitals are engaged in the bonding. Therefore such couplings will be unobservable unless heavy nuclei (which have bigger reduced coupling constants in general) with a high gyromagnetic ratio are present. These requirements are met by $^{119}\text{Sn}$ which we have used in our study. It follows that a species must have been present which contains 2a and lithium in close contact and that the ligand exchange rate at -90 °C is smaller than the coupling constant.

It is enlightening to compare the unique $^{119}\text{Sn}-^7\text{Li}$ coupling to similar data obtained for cyclopentadienyl metal derivatives because carbanions like 1 may be regarded as Cp-like ligands [13]. In fact, couplings between a main group nucleus E and any nucleus of a Cp that has a $\sigma$-bond to E could only be observed when heavy nuclei like $^{117,119}\text{Sn}$ [14a] or $^{203,205}\text{Tl}$ [14b–d] were involved. Evidence has been presented that in decabenzylcyclopentadienyl thallium the $^{203,205}\text{Tl}-^{13}\text{C}$ coupling depends on the Tl–C distance [14d]. Thus the usually accepted Fermi contact [15a] through space interaction [15b] may contribute significantly to the coupling discussed here.

B. 4. Aggregation

The $^{119}\text{Sn}-^7\text{Li}$ couplings confirm that 2a and 3 exist as contact ion pairs. In order to further characterize these species in solution we have generated stannylated derivatives of 1 starting from a mixture of distannylated isomers according to Scheme 3. The expected epimers 2a and 2b should give identical NMR spectra. However, in the $^{13}\text{C}$ NMR spectrum (Fig. 5) two sets of signals were present. Similarly a doubling of resonances was observed by $^1\text{H}$ NMR although the solvent signals did not allow the identification of all protons. The shifts (and their temperature dependence, see Table I and Fig. 3) of one set of $^{13}\text{C}$ signals were practically the same as those found for pure 2a. The second set had signals shifted slightly to high
The doubling of NMR signals may be due to the formation of the endo- and exo-isomers A and B (solvated by S) and their 7-stannylated congeners. However, this can be ruled out for two reasons: (i) The separation of corresponding signals is similar throughout the spectrum in Fig. 5b whereas a much bigger difference of $\delta^{(13)}C6/7$ is expected for A and B. (ii) Pure $2a$ and $3$ should also exist as endo- and exo-isomers but only one set of signals could be observed.

It follows that the doubling of NMR signals must be due to the presence of optical isomers. In fact, our findings are reminiscent of the statistically controlled anisochromism of diastereomeric association (SCADA) [16a] which has also been termed “self induced nonequivalence” or “autoneequivalence” [16b]. SCADA may be observed when at least two optical isomers interact to give diastereomers (e.g. by way of hydrogen bonding) even if the lifetime of the diastereomers is short on the NMR time scale. In our case the nonequivalence of the nuclei of the epimeric carbanions $2a$ and $2b$ is induced by lithium as shown in Scheme 4 rather than being self induced. Similarly higher diastereomeric aggregates of chiral RLi aggregates give rise to more complex NMR spectra [17a, b].

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In the diastereomeric triple ions $2a\text{Li}_2a$ (or $2b\text{Li}_2b$) and $2a\text{Li}_2b$ the lithium fits well between two carbanions so that stable aggregates bigger than dimers are unlikely. The charge of $2a\text{Li}_2a$, $2b\text{Li}_2b$, and $2a\text{Li}_2b$ is most probably balanced by solvated Li$^+$ (see below).

Clearly only $2a\text{Li}_2a$ can be present when $6a$ is converted to $2a$ (cf. Scheme 1). The fact that, in this case, we see only one set of $^{13}$C NMR signals may be understood by assuming a rapid monomer/dimer equilibrium or slow exchange and a small monomer concentration. The latter interpretation is consistent with the appearance of the $^{119}$Sn$-^{7}$Li multiplet at low temperature.

Dimers similar to $2a\text{Li}_2a$ and $2a\text{Li}_2b$ have been shown to exist for peralkylated hexadienyl-lithium compounds by Fraenkel et al. [17c] and very recently for isodicyclopentadienyl- and cyclopentadienyllithium by Paquette et al. [18]. These authors have identified two different lithium cations per dimer, namely a "sandwiched" and an "outer" lithium, and they could also characterize monomeric contact ion pairs.

C. $^7$Li NMR spectroscopy of bicyclo[3.2.1]octa-2,6-dienyllithium ($1\text{Li}$)

Since the detection of triple ions via diastereomers is not possible for $1\text{Li}$ we have studied a solution of $1\text{Li}$ in Me$_2$THF by $^7$Li NMR spectroscopy between 0 and $-126$ °C. On decreasing the temperature the spectra underwent various changes (including the intermediate appearance of a narrow signal due to a solvent separated ion pair with $\delta(\text{Li}) = 2.1$) which will be reported elsewhere. At $-126$ °C the spectrum in Fig. 6 with two signals at unusually low frequency was obtained. The range of $-3$ to $-8$ ppm is characteristic of a lithium cation sensing the magnetic anisotropy of just one $\pi$-carbanion like cyclopentadienyl [18, 19] or hexadienyl anions [17c] whereas $-6$ to $-14$ ppm has been reported for Li$^+$ "sandwiched" between two $\pi$-carbanions [17c, 18, 20]. The actual $\delta(\text{Li})$-values depend on the solvent and on the nature of the carbanion, but in practice the overlap of the two shift ranges poses no assignment problem as long as one signal in each range is observed. We therefore attribute the resonances with $\delta(\text{Li}) = -5.0$ and $-8.5$ to the monomeric contact ion pair $1\text{Li}$ and to the triple ion $1\text{Li}_1$. Above 0 ppm at least four lithium species are seen; among them are most probably methyllithium (1.5 ppm) used to prepare $1$ and lithium acetone enolate (2.5 ppm) resulting from the cleavage of Me$_2$THF by $1$. Hence it is too speculative to locate the "outer" lithium cation balancing the charge of $1\text{Li}_1$ because its signal should appear not far from 0 ppm [17c, 18].

Experimental

All manipulations with sodium or potassium organic compounds were carried out under an atmosphere of purified argon in solvents free of oxygen and water.

6-Trimethylstannylbicyclo[3.2.1]octa-2,6-dienyllithium ($2a\text{Li}$) [21]

To a solution of 0.67 g (1.55 mmol) of $6a$ [7] in 60 ml of Et$_2$O at $-50$ °C were added 1.6 mmol of methyllithium in Et$_2$O and 0.24 ml (1.61 mmol) of TMEDA. While stirring for 6 h at $-25$ °C the yellow solution became cloudy. A yellow microcrystalline solid was obtained after removal of the solvent. The solid could be completely dissolved in THF to give an orange solution which at T $< -20$ °C showed no $^{13}$C NMR signals other than those of $2a\text{Li}$.

$^1H$ NMR (THF-d$_8$/TMEDA, 3/1, 0 °C): $\delta =$ 0.13 (s, (CH$_3$)$_3$Sn, 9 H); $\delta =$ 0.19 (d, Hsyn8, 1 H, $^2$J(Hsyn8$-^1$Hanti8) = 8.2 Hz); $\delta =$ 0.50 (quint, Hanti8, 1 H, $^3$J(Hanti8$-^1$Hsyn8$-^1$Hsyn8) = 8.1 Hz, $^3$J(Hanti8$-^1$H) $\approx$ $^3$J(Hanti8$-^1$H5) = 4.1 Hz); $\delta =$ 2.30 and 2.33 (m, H1 and H5, 2H); $\delta =$ 2.61 (t, H2, 1 H, $^3$J(H2$-^1$H3) $\approx$ $^3$J(H2$-^1$H1) = 6.8 Hz); $\delta =$ 2.92 (t, H4, 1 H, $^3$J(H4$-^1$H5) = 6.4 Hz); $\delta =$ 3.30 (m, H7, 1 H, $^3$J(H7$-^1$H5) = 37.6 Hz); $\delta =$ 5.05 (t, H3, 1 H, $^3$J(H3$-^1$H7) = 37.6 Hz).

![Fig. 6. $^7$Li NMR spectrum of a 0.3 molar solution of $1\text{Li}$ in Me$_2$THF taken at $-126$ °C.](image-url)
A mixture of 0.87 g (2.02 mmol) 6a, 6b, and 6c [7] was dissolved in 60 ml of Et₂O and cooled to −78 °C. When 3.1 ml (2.08 mmol) of TMEDA and 2.14 mmol of methyllithium in Et₂O were added the solution turned yellow and after stirring at −35 °C for 7 h a yellow solid formed. The solvent was removed at −35 °C at reduced pressure and the remainder dissolved in THF. The NMR results described in Section B.4 were obtained from this solution.

3-Trimethylstannylobicyclo[3.2.1]octa-2,6-dienyllithium (3Li)

3.72 mmol of methyllithium in Et₂O were added at 0 °C to a solution of 1.60 g (3.71 mmol) of 7 [7] in 80 ml of Et₂O. The solution turned immediately yellow but, according to ¹³C NMR spectroscopy, the reaction was complete only after stirring for 2 d at 0 °C. Removal of the solvent gave an orange oil. When this was mixed with Et₂O the ¹³C NMR spectrum showed exclusively signals of the solvent and 3Li.

¹⁹Sn NMR (Et₂O/toluene-d₈, 3/2, 0 °C): δ = −47.58.

The NMR spectra were run with a JEOL JNM-GX 270 instrument using tubes with ground-glass joint and stopper; most of the ¹³C NMR data of 1Li and 1K were obtained with a Bruker CXP 200 spectrometer. Solvent signals served as internal standard: δ = 25.80 (C₃/₄ of THF-d₈), δ = 1.73 (H₃/₄ of THF), δ = 14.50 (Cα of Et₂O); for the measurements summarized in Fig. 2 a few drops of cyclohexane (δ(⁶C) = 27.30) were added as internal standard. A solution of LiCl in D₂O was used as external standard in ⁷Li NMR spectroscopy.

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c) Due to a printing error no data for 1 appear in Table I of ref. [1b]; only C₂–C₃ = 139.5 pm and C₂–C₇ = 248.0 pm are given in the text.


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