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Bimetallic complexes containing lithium and boron. Studies on the reactions of $(ArBMe_3)Li \cdot OEt_2$ complexes with the electron donors OEt_2 and THF by means of ^1H, ^7Li, ^{11}B, and ^{13}C NMR spectroscopy *

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Abstract

The stabilities of the toluene and THF solutions of complexes $(Ar^1BMe_3)Li \cdot OEt_2$ (I), $Ar^1 = C_6H_4CH_2NMe_2$-2 and $(Ar^2BMe_3)Li \cdot OEt_2$ (II) and $Ar^2 = C_6H_4$-(*S*)-CHMeNMe$_2$-2 were investigated at various temperatures by means of ^1H, ^7Li, ^{11}B, and ^{13}C NMR spectroscopy. I is stable in toluene and only inversion of configuration on nitrogen and on C(1) aromatic carbon was observed. II is less stable in toluene than I, and beside the intramolecular dynamic processes dissociation with release of ether was detected.

Complex I reacts with THF with donation of ether to THF and product IV, $(Ar^1BMe_3)Li \cdot THF$, was isolated and characterized in toluene solution. IV reacts further with THF forming V, $[LiMe]_n \cdot [THF]$, with cleavage of the LiC_2B bond. II dissolved in THF leads to the (Ar^2BMe_3) $(Li \cdot n THF)$ complex, VI. The mechanism of the bond cleavage of the LiC_2B core in I and in II in the reaction with THF is discussed.

Introduction

Studies on the structure of organolithium complexes show that the stability and the structure of these compounds strongly depends on the basicity of the donor ligand molecules. Solvation changes the degree of association of organolithium compounds and influences polarization of the lithium–carbon bond [1–7].

Our most recent interest concerns the properties of the bimetallic lithium organoborate complexes $(ArBR_3)Li \cdot D$, I: $Ar = Ar^1 = C_6H_4CH_2NMe_2$-2, R = Me, $D = OEt_2$; II: $Ar = Ar^2 = C_6H_4$-(*S*)-CHMeNMe$_2$-2, R = Me, $D = OEt_2$; IV: $Ar = Ar^1$, R = Me, D = THF. Isolation and characterization of these complexes are described elsewhere [8]. NMR spectra data reveal the structures of these complexes in toluene solution as involving bridging aryl group and alkyl ligand, four coordinative boron atoms and one lithium (Fig. 1). The complexes are unstable in solution.

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* In commemoration of Professor Piero Pino.

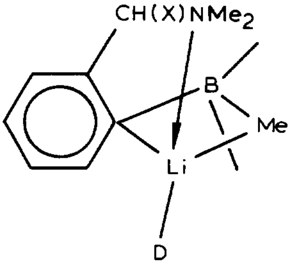


Fig. 1. Structure of the complexes $(ArBR_3)Li \cdot D$ (I, II).

Such intramolecular processes as dissociation of the N → Li bond and inversion of the configuration at the asymmetric aromatic carbon C(1) proceed in solution [8]. The purpose of this work was to explore the dissociation reaction of complexes in nonpolar solvent and to explain the exchange of donor ligands in these complexes.

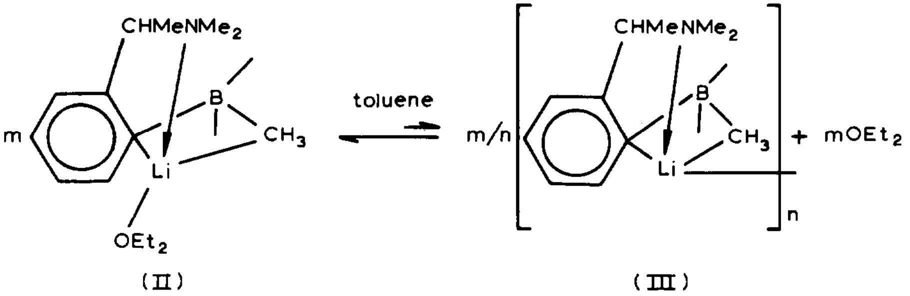
Results and discussion

Dissociation of the $(Ar^2BMe_3)Li \cdot OEt_2$ complex in nonpolar solvent with release of an ether molecule

On dissolving in toluene $(Ar^1BMe_3)Li \cdot OEt_2$ (complex I) remains stable up to 323 K. But $(Ar^2BMe_3)Li \cdot OEt_2$ (complex II) dissociates with release of ether (Scheme 1), over the range of temperatures from 173 to 323 K, according to ^1H NMR spectra.

The ^1H and ^{13}C NMR spectra of complex I show the presence of strongly coordinated ether. The well resolved quartet of OCH_2 protons is observed at 2.83 ppm and is shifted upfield about $\Delta\delta = 0.33$ ppm from the value for free ether. The OCH_2 carbons were recorded at 66.27 ppm and shifted about 0.37 ppm from the values of OCH_2 carbons of noncomplexed ether.

For complex II also the complexed ether molecule is observed on ^1H and ^{13}C NMR spectra. The corresponding $\Delta\delta$ values are 0.21 ppm (^1H NMR) and 0.13 ppm (^{13}C NMR) (Table 1). However the ^1H NMR spectra exhibit a complicated multiplet for OCH_2 protons instead of a well resolved quartet. We believe this is due to the ether exchange reaction (Scheme 1). It cannot be explained by the presence of diastereotopic OCH_2 protons of ether being bonded to the asymmetric



Scheme 1

Table 1

^{1}H and ^{13}C NMR chemical shifts [a] of OCH_2 group of the ether molecule complexed in I and II

Compound	^{1}H NMR		^{13}C NMR	
	OCH_2	$\Delta[\delta(OCH_2) - \delta(OCH_2)]$ free)	$\delta(OCH_2)$	$\Delta[\delta(OCH_2) - \delta(OCH_2)]$ free)
$(Ar^1BMe_3)Li \cdot O(CH_2CH_3)_2$ (I)	2.83q	−0.33	66.27	0.37
$(Ar^2BMe_3)Li \cdot O(CH_2CH_3)_2$ (II)	2.95m	−0.21	66.07	0.17
$O(CH_2CH_3)_2$ (free)	3.16q		65.9	

[a] δ (ppm) in toluene-d_8, at room temperature, q = quartet, m = multiplet.

lithium centre since attempts to decouple OCH_2 protons from the protons of the CH_3 group were unsuccessful.

In order to support the proposition of an ether exchange reaction we measured the ^{1}H NMR spectra of complex II with a 1.5 mole excess of ether added by means of a Hamilton syringe. No signals of free ether were recorded under 190 K. The addition of an excess of ether does not change the character of the OCH_2 multiplet but the δ values are shifted in the direction of non-coordinated ether (Table 2). The ^{1}H NMR spectra of complex II and complex II + 1.5 OEt_2 in toluene lead to the conclusion that for complex II the fast dissociation reaction proceeds and its equilibrium is shifted to the left (Scheme 1).

Obviously the ether molecule in II is coordinated more weakly than in I because the acidity of lithium atom is decreased by the stronger $CHMeNMe_2$ donor ligand. As previously mentioned the chemical shifts of OCH_2 protons in ^{1}H NMR and OCH_2 carbons in ^{13}C NMR for complex II are closer in value to those of the noncoordinated ether than for complex I (Table 3). The approximate values of $\Delta G^{\ddagger}$ (calculated on the basis of VT NMR according to equation: $\Delta G^{\ddagger} = 19.14\ T_c\ (9.97 + \log T_c/\delta)$ [J/mol]) for the dissociation of N → Li coordination bond is 64.78 kJ/mol for complex II and 59.37 kJ/mol for complex I. Increasing the electron density on nitrogen of the amine ligand $CH(Me)NMe_2$ decreases the stability of the O → Li bond and the dissociation reaction in toluene is then observed for complex II.

Table 2

^{1}H NMR chemical shifts [a] of OCH_2 protons of complex II in the presence of excess ether

Compound	^{1}H NMR	
	$\delta(OCH_2)$	$\Delta[\delta(OCH_2) - \delta(OCH_2)$ free]
$(Ar^2BMe_3)Li \cdot O(CH_2CH_3)_2$	2.94	−0.22
$(Ar^2BMe_3)Li \cdot O(CH_2CH_3)_2 + 1.5\ OEt_2$	3.13	−0.03
$O(CH_2CH_3)_2$ (free)	3.16	

[a] δ(ppm) in toluene-d_8 at room temperature.

Table 3

^{1}H and ^{13}C NMR chemical shifts [a] of the CH(X)NMe$_2$ ligand (X = H, Me) in I and II

Compound	^{1}H NMR		^{13}C NMR		T_c (NMe$_2$)
	δ(NCH$_3$)	$\Delta[\delta$(NCH$_3$) $-\ \delta$(NCH$_3$)] free)	δ(NCH$_3$)	$\Delta[\delta$(NCH$_3$) $-\ \delta$(NCH$_3$)] free)	
$(\mathrm{Ar^1BMe_3})\mathrm{Li\cdot OEt_2}$ (I)	1.80	−0.28	45.23	−1.07	243
$\mathrm{Ar^1H}$ (free)	2.08		46.30		
$(\mathrm{Ar^2BMe_3})\mathrm{Li\cdot OEt_2}$ (II)	2.08	0.48	41.67	−1.59	288
$\mathrm{Ar^2H}$ (free)	1.60		43.26		

[a] δ(ppm) in toluene-d_8 at room temperature.

The structure of the ether-free complex III was not fully established. However on the basis of NMR spectra we conclude that a $\mathrm{LiC_2B}$ core is present in the complex III product as in complex II. The resonance of ^{7}Li at −0.72 and ^{11}B at −17.17 in toluene and ^{7}Li at −0.99 and ^{11}B at −17.98 in OEt$_2$ also indicates that the $\mathrm{LiC_2B}$ ring is retained in the presence of an excess of donor solvent. The coordination of the nitrogen to lithium is not disturbed in the presence of free ether since the splitting of a NMe$_2$ ^{1}H NMR singlet into two singlets is observed at low temperature. The degree of association of the $[(\mathrm{Ar^2BMe_3})\mathrm{Li}]_n$ III species cannot be established.

Donor exchange reaction

Complex I and II react with boiling THF to form respectively $(\mathrm{Ar^1BMe_3})\mathrm{Li\cdot THF}$ (IV) by the donor exchange reaction 2, and $(\mathrm{Ar^2BMe_3})$ $(\mathrm{Li}\cdot n\mathrm{THF})$ (VI) by reaction 3. Complex IV was isolated and characterized but the structure of III remains unclear. In reaction 2 excess THF is required for complete replacement of OEt$_2$ by THF.

$$\underset{(\mathrm{I})}{(\mathrm{Ar^1BMe_3})\mathrm{Li}\cdot\mathrm{OEt_2}} + \mathrm{THF} \rightleftarrows \underset{(\mathrm{IV})}{(\mathrm{Ar^1BMe_3})\mathrm{Li}\cdot\mathrm{THF}} + \mathrm{OEt_2} \tag{2}$$

III dissolved in noncoordinating solvent has the same structure as complex I, with bridging aryl ligand and the amine ligand coordinated to lithium. The ^{1}H and ^{13}C NMR chemical shifts of NCH$_2$ and NCH$_3$ groups indicate that the presence of a stronger donor such as THF destabilizes the N → Li coordination. The chemical shifts have values closer to those of free amines of complex III than of complex I (Table 4 and 5). However, the N → Li coordination is still present in toluene at low temperature as can be deduced from the presence of two singlets assigned to NCH$_3$ groups in ^{1}H and ^{13}C NMR.

When complex I is dissolved in THF the coordination of N → Li is broken. The CH$_2$ and NCH$_3$ protons are observed as singlets over the whole temperature range investigated. The CH$_2$NMe$_2$ ligand remains uncoordinated. When THF molecules are present in excess they can compete successfully with the CH$_2$NMe$_2$ ligand.

Table 4

^1H NMR chemical shifts [a] of the CH_2NMe_2 ligand in I and IV

Compound	^1H NMR				T_c (NMe_2)
	$\delta(NCH_2)$	$\Delta[\delta(NCH_2) - \delta(NCH_2)]$ free)	$\delta(NCH_3)$	$\Delta[\delta(NCH_3) - \delta(NCH_3)]$ free)	
$(Ar^1BMe_3)Li \cdot OEt_2$ (I)	3.41	−0.17	1.80	−0.14	243
$(Ar^1BMe_3)Li \cdot THF$ (IV)	3.76	0.18	2.10	0.02	223
Ar^1H (free)	3.58		2.08		

[a] δ(ppm) in toluene-d_8 at room temperature.

Table 5

^{13}C NMR chemical shifts [a] of the CH_2NMe_2 ligand in I and IV

Compound	^{13}C NMR			
	$\delta(NCH_2)$	$\Delta[\delta(NCH_2) - \delta(NCH_2)$ free]	$\delta(NCH_3)$	$\Delta[\delta(NCH_3) - \delta(NCH_3)$ free]
$(Ar^1BMe_3)Li \cdot OEt_2$ (I)	65.16	−2.85	45.23	−1.07
$(Ar^1BMe_3)Li \cdot THF$ (IV)	66.16	−1.85	45.14	−1.17
Ar^1H (free)	68.01		46.30	

[a] δ(ppm) in toluene-d_8 at room temperature.

Raising the temperature to about 323 K results in the appearance of new resonances. Beside $\delta(^{11}B) = -16.09$ and $\delta(^7Li) = -0.46$ new signals at $\delta(^{11}B) = 5.93$ and $\delta(^7Li) = 0.72$ (Fig. 2) were detected. The chemical shift of ^{11}B and ^7Li nuclei are listed in Table 6. The new resonances of ^7Li at 0.72 and ^{11}B at 5.7 ppm show the presence of organolithium and organoboron compounds. The broadening of the signals suggests that exchange reactions occur in solution. The observed changes are reversible. If the sample is cooled to room temperature again only complex I is observed. The compound V is formed only at increased temperature in solution, and

Table 6

^7Li and ^{11}B NMR chemical shifts for $(Ar^1BMe_3)Li \cdot OEt_2$ in THF-d_8 at various temperatures

Compound	T (K)	^7Li NMR		^{11}B NMR	
		δ (ppm)	1/2 halfwidth (Hz)	δ (ppm)	1/2 halfwidth (Hz)
$(Ar^1BMe_3)Li \cdot OEt_2$	323	0.72	broad	5.93	60
		−0.47	14	−16.06	17
	293	0.72	broad	5.68	60
		−0.46	11	−16.09	17
	193			broad	
		−0.25	4	−16.19	28

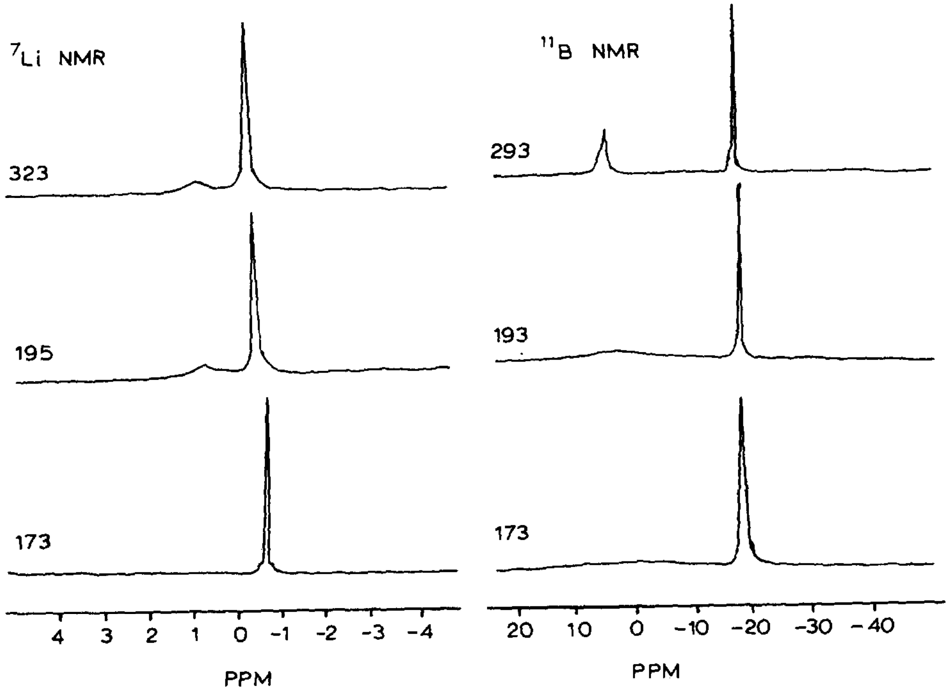
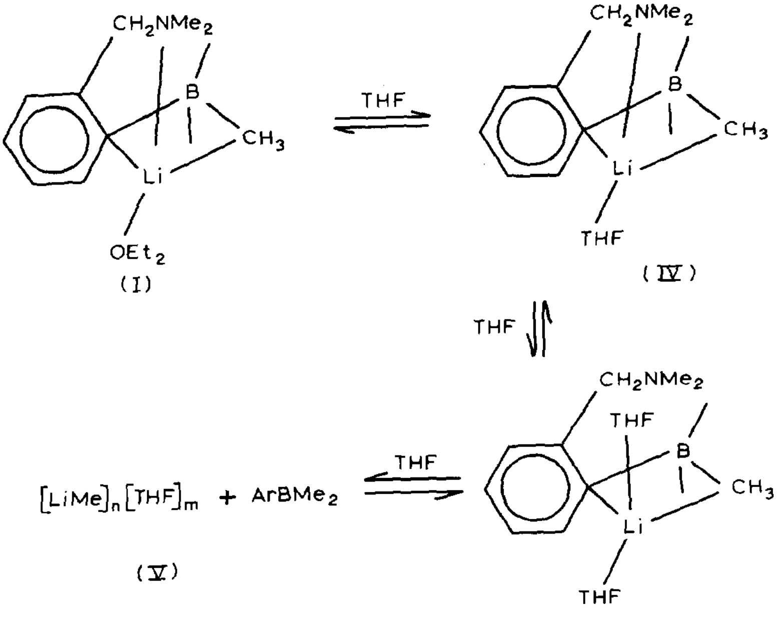


Fig. 2. Temperature dependence of ^{7}Li (relative to LiCl(D$_2$O)) and ^{11}B (relative to BF$_3$·OEt$_2$) NMR spectra of the complex (Ar^{1}BMe$_3$)Li·OEt$_2$ in THF-d_8 solution.



Scheme 2

cooling of the sample shows that all reactions are reversible (Scheme 2). Because the isolation of the product from THF solution gives only complex IV the structure of V could not be established definitely. On the basis of multi-nuclear NMR measurements the following reaction scheme can be proposed (Scheme 2).

As a first stage complex IV is formed, which can be isolated and characterized in nonpolar solution. In THF solution this product reacts immediately with further molecules of THF and the disproportionation of the bimetallic intermediates occurs.

Complex II reacts with excess THF in a different manner. The product is isolated as a solid melting at room temperature. The molecule of OEt_2 is replaced in the original complex by THF, but the structure of product VI differs from that of substrate complex II. The ^1H NMR spectra of toluene-d_8 solution run at various temperatures are complicated. The NMe_2 groups do not split at a low temperature which indicate that the C(1) aromatic carbon originally bonded to both boron and lithium is not chiral. The number of THF molecules bonded in the complex is about 3 and can be only estimated due to overlapping of the signals. The ^{11}B NMR indicate the presence of the BR_4^- species $\delta(^{11}B) = -17.4$ and $\delta(^7Li) = -0.98$ is assigned to the highly shielded lithium nuclei. NMR methods are not sufficient to establish the definite structure of the complex, but the results suggest that the ionic structure $(Ar^2BMe_3)(Li \cdot n THF)$ (VI) with charge separation should be taken into consideration.

$$\underset{\text{(II)}}{(Ar^2BMe_3)Li \cdot OEt_2} + nTHF \rightarrow \underset{\text{(VI)}}{[Ar^2BMe_3][Li \cdot nTHF]} \qquad (3)$$

Comparison of the products of the reactions with THF (Scheme 2 and reaction 3) shows that the reactions of I and II complexes with THF can proceed via different pathways, depending on which electron donating ligands are bonded to lithium.

Conclusions

The results presented show the different reaction mechanisms for the bimetallic complexes I and II with THF. The acidity of the lithium atom was lower in complex II than in complex I. The O → Li bond has different stability in complexes I and complex II as shown by the NMR measurements in a noncoordinating solvent, namely toluene. The coordination of nitrogen to lithium in complex II is stronger than in I and results in destabilization of the O → Li bond in II leading to equilibrium between complex II and free ether (Scheme 1).

The acidity of lithium in complexes I and II determines the course of the reaction with THF. For complex I the reaction with THF leads to the formation of $[LiMe]_n[THF]_m$ (V) and $ArBMe_2$ compounds via complex IV. As a first stage the replacement of OEt_2 by THF occurs and the structures of the bimetallic complexes I and IV are the same. In following steps THF competes with the CH_2NMe_2 ligand and the aromatic ring and finally the bimetallic complex disproportionates to the products V and $ArBMe_2$.

The reaction of complex II in THF is different. The binding properties of the $ArCHMeNMe_2$-2 ligand do not permit disproportionation of complex II to monometallic compound, but the LiC_2B ring is broken by THF. The $[Ar^2BMe_3][Li \cdot nTHF]$ complex VI was detected with a broken LiC_2B ring and most probably it has an ionic structure.

Experimental

All experiments were carried out under deoxidized and dried nitrogen. Solvent were deoxidized and dried prior to use.

The NMR spectra were recorded with a Bruker WM 250 apparatus, ^{7}Li (97.2 MHz, relative to LiCl(D_2O)), ^{11}B (80.17 MHz relative to $BF_3 \cdot OEt_2$) in a sample concentration of 1% of in toluene-d_8 and in THF-d_8.

The complexes I, II, IV, VI were prepared as described in ref. 8.

Acknowledgments

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