Journal of Organometallic Chemistry, 364 (1989) 1–15
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09577

The molecular structure of 1-lithio-2-methoxybenzene in the solid state and in solution

Sjoerd Harder, Jaap Boersma *, Lambert Brandsma,
Department of Metal-mediated Synthesis, University of Utrecht, Padualaan 8,
3584 CH Utrecht (The Netherlands)

Guido P.M. van Mier and Jan A. Kanters
Laboratory for Crystal and Structural Chemistry, University of Utrecht, Padualaan 8,
3584 CH Utrecht (The Netherlands)

(Received September 23rd, 1988)

Abstract

The X-ray structure of 1-lithio-2-methoxybenzene (2-methoxyphenyllithium) has been determined at 298 K by single crystal X-ray techniques. The compound crystallizes in the triclinic system with spacegroup $P\bar{1}$. Cell dimensions: a 8.889(2), b 11.710(5), c 12.941(3) Å, α 80.47(3), β 84.22(2), γ 82.37(3)°. The structure has been refined to $R(F) = 0.069$ for 1300 unique observed reflections with $I \geq 2.5\sigma(I)$. Each unit-cell contains two centrosymmetrically related tetrameric units which show Li $\cdots$ HC interactions with each other. Its structure in solution has been determined by NMR spectroscopy and association measurements. The influence of various Lewis bases on the solution structure has been studied.

Introduction

Information on the structure of organometallic compounds in the solid state and in solution may contribute to the understanding of their reactivity. In the course of a study on the reactivity and structure of aromatic and heteroaromatic organolithium compounds we recently described the crystal structure of [1-lithio-2-methoxybenzene]$_8$ · TMEDA [1] (TMEDA = N,N,N',N'-tetramethylethylenediamine). These crystals were obtained by lithiating methoxybenzene with butyllithium/hexane in the presence of two equivalents TMEDA. The precipitated complex consists of two centrosymmetrically related tetrameric units connected together by a bridging TMEDA ligand. We considered it of interest to compare this structure with that of the TMEDA-free parent compound in order to obtain information about the change in structure when a potential electron-donating atom or group coordinates

0022-328X/89/$03.50

to it. These data can be used to visualize the first step in the reaction of an organolithium compound with an electrophilic reagent containing a potential electron-donating atom (e.g. ethylene oxide). We have thus prepared TMEDA-free 1-lithio-2-methoxybenzene and determined its molecular structure both in the solid state and in solution. Its behaviour towards potential ligands in solution has also been investigated.

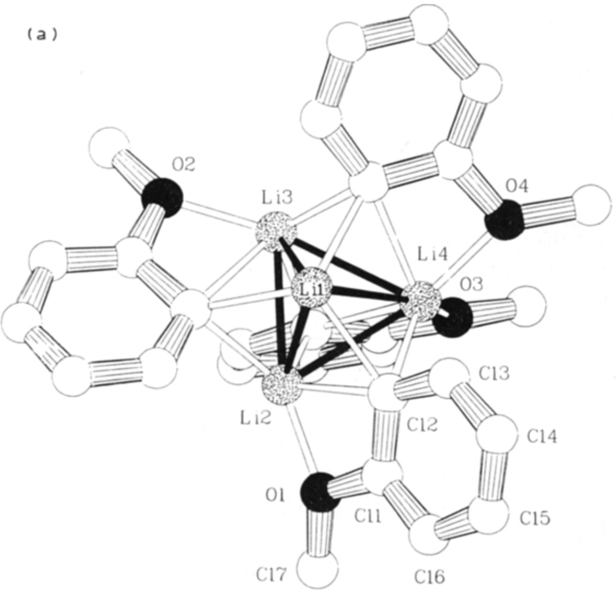
Results and discussion

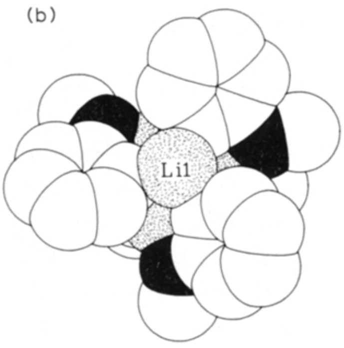
The solid state structure

1-Lithio-2-methoxybenzene was prepared by lithium–bromine exchange between n-butyllithium and 1-bromo-2-methoxybenzene. When this reaction is carried out in pentane a white crystalline product separates from solution in a pure form. It is readily soluble in aromatic solvents and ethers.

The solid state structure of the title compound, illustrated in Fig. 1a, consists of aggregates built-up from four 1-lithio-2-methoxybenzene molecules. The structure of these tetramers is nearly identical to that of the tetrameric units in the solid state structure of $[\text{1-lithio-2-methoxybenzene}]_8 \cdot \text{TMEDA}$ [1]. Fractional coordinates of the non-hydrogen atoms together with their equivalent thermal parameters are given in Table 1, bond distances and angles are tabulated in Table 2 and the geometry of the Li coordination is given in Table 3.

The core of the tetramer is formed by four lithium atoms in a slightly distorted trigonal pyramidal configuration. The lithiated carbon atom of a methoxyphenyl group lies over each triangular side plane of this pyramide and is bonded to three Li atoms via four-center-two-electron bonds. C–Li bond distances are in the range of 2.13(1)–2.51(1) Å and projections of the lithiated carbon atoms on the Li triangles to which they are bonded (Fig. 2) indicate that the four-center-two-electron bonds of C(22), C(32) and C(42) are distorted in the direction of the three-center-two-electron bonding mode; C(12) is more symmetrically bound. The O–Li bond distances are in the normal range of 1.93(1)–2.01(1) Å. Surprisingly the coordination sphere of Li(1) shows no O–Li contacts, whereas Li(4) has two such contacts. A priori, there seems to be no reason for such asymmetry. By rotating the methoxyphenyl group 4 around the C(42)–Li(2) axis, a highly symmetric structure with a fourfold inversion axis can be obtained (cf. Fig. 1c). A Van-der-Waals surface plot (Fig. 1b) of the experimentally found asymmetric tetramer shows that Li(1) is very exposed as a result of its asymmetric coordination sphere. However, a plot of the complete unit-cell (Fig. 1e) shows the short contact between Li(1) and the phenyl ring carbon atom, C(24)′, which belongs to the neighbouring tetramer related by an inversion centre. This Li(1) ··· C(24)′ distance is 2.91(2) Å and the Li–C vector makes an angle of 70.4(5)° with the phenyl ring plane. There is also a short contact of 2.84(2) Å between Li(1) and H(24)′, the proton attached to C(24)′. Li(1) ··· C(23)′ and Li(1) ··· C(25)′ distances are 3.60(1) and 3.14(1) Å, respectively. Probably the mesomeric effect of the methoxy substituent increases the electron density in the *p*-orbital of C(24)′ which results in it having the shortest distance to Li(1). The other short contact of Li(1) to C(25)′ could be the reason for the significantly shorter C(24)–C(25) bond distance of 1.33(1) Å as a result of partial localization of π-electrons from the aromatic system in the C(24)–C(25) π-bond. The interaction of Li(1) with the phenyl ring of its neighbouring tetramer can also be described as an agostic interaction, since the Li(1)–H(24)′ distance is only 2.84(2) Å. The chemical activation of C–H bonds by early main group metal compounds is a well-established aspect of their chemistry. It has been proposed that Li · · · HC interactions





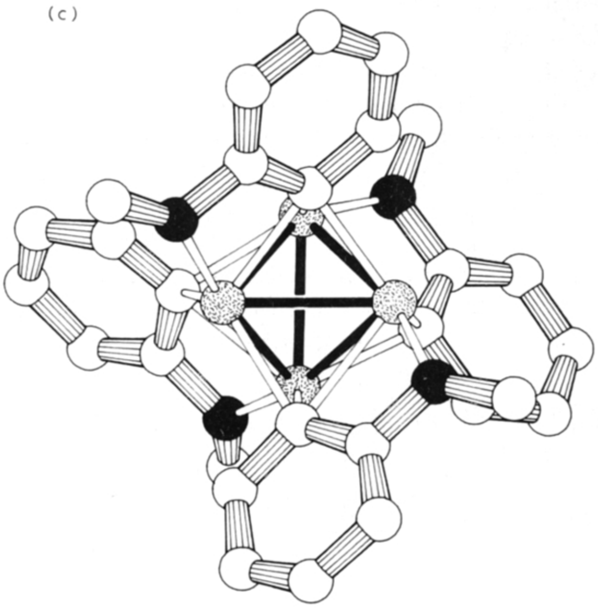
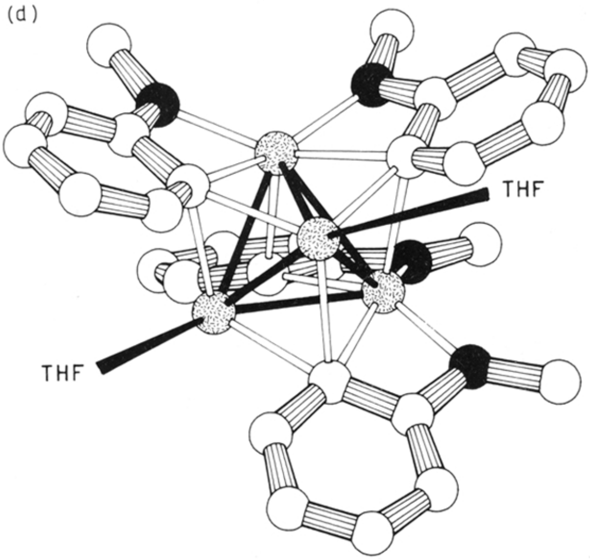


Fig. 1a. Perspective view of the tetrameric aggregate. Li atoms are indicated by speckled spheres and the oxygen atoms by black spheres; the hydrogen atoms have been omitted for clarity. The atom numbering is shown for molecule 1; the first number gives the molecule number and the second the atom number.

Fig. 1b. A Van-der-Waals surface plot of the tetrameric aggregate, showing the exposed Li(1).

Fig. 1c. The highly symmetric structure. This plot is made from Fig. 1a by rotating methoxybenzene anion number 4 on the C(42)–Li(2) axis.



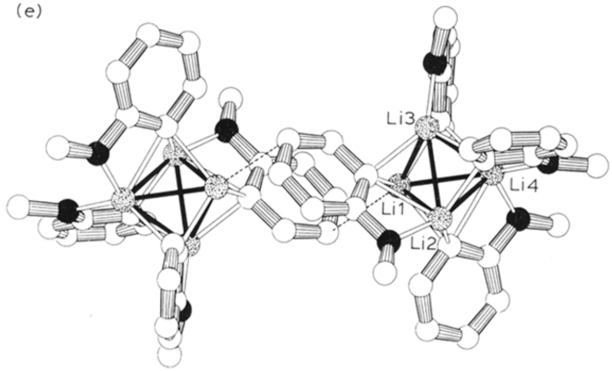


Fig. 1d. Proposed structure for the solid state of 1-lithio-2-methoxybenzene · 1/2THF.

Fig. 1e. Perspective view of the complete unit cell, showing the short contact between Li(1) and the phenyl ring of the inversed neighbouring aggregate (dotted lines).

play a major role in the stereochemistry of (cyclohexyllithium)$_6$ [2] and in the bonding in $LiBMe_4$ [3], in which they may assist in coordinative saturation of the lithium atoms. Recent evidence for such Li · · · HC interactions has been found in the X-ray structure of trimeric dibenzylamidolithium [4], in which the Li · · · H distances vary from 2.60 to 3.05 Å.

The structure in solution

NMR spectroscopy has been shown to be an excellent tool in the structural analysis of organolithium compounds, particularly when they are enriched with 96% ^{6}Li ($I(^6Li) = 1$ and $I(^7Li) = 3/2$) [5,6,7,8,9]. The state of aggregation can be determined from the $^{13}C-^6Li$ coupling pattern and its coupling constant [5]. $^6Li-^1H$ 2D heteronuclear Overhauser spectroscopy, $^6Li-^1H$ HOESY, gives information

Table 1

Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for non-H atoms of the title compound with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	U_{eq} ^{a}
Molecule 1				
Li(1)	0.475(1)	0.123(1)	0.3118(9)	0.065(5)
O(1)	0.6027(6)	0.4118(6)	0.3428(4)	0.079(3)
C(11)	0.6948(9)	0.3468(7)	0.2751(6)	0.055(4)
C(12)	0.6226(8)	0.2593(7)	0.2449(6)	0.057(3)
C(13)	0.7198(9)	0.1932(7)	0.1797(6)	0.065(4)
C(14)	0.872(1)	0.2067(7)	0.1473(6)	0.065(4)
C(15)	0.9326(9)	0.2968(8)	0.1780(6)	0.069(4)
C(16)	0.844(1)	0.3674(7)	0.2434(6)	0.065(4)
C(17)	0.644(1)	0.517(1)	0.3627(7)	0.130(6)
Molecule 2				
Li(2)	0.429(1)	0.327(1)	0.3528(9)	0.070(5)
O(2)	0.0945(6)	0.1672(4)	0.4374(4)	0.069(3)
C(21)	0.212(1)	0.1506(6)	0.5047(6)	0.058(3)
C(22)	0.3543(9)	0.1722(7)	0.4564(6)	0.061(3)
C(23)	0.463(1)	0.1585(7)	0.5277(7)	0.082(4)
C(24)	0.437(1)	0.1273(9)	0.6370(8)	0.102(5)
C(25)	0.297(1)	0.1067(8)	0.6760(7)	0.093(5)
C(26)	0.719(1)	0.1172(7)	0.6116(7)	0.077(4)
C(27)	−0.060(1)	0.1639(7)	0.4766(6)	0.083(4)
Molecule 3				
Li(3)	0.202(1)	0.232(1)	0.3060(9)	0.065(5)
O(3)	0.3091(6)	0.4474(5)	0.0960(5)	0.083(3)
C(31)	0.224(1)	0.4919(9)	0.1808(8)	0.064(4)
C(32)	0.2375(8)	0.4164(7)	0.2746(7)	0.060(4)
C(33)	0.158(1)	0.466(1)	0.3577(8)	0.085(5)
C(34)	0.067(1)	0.575(1)	0.347(1)	0.103(6)
C(35)	0.057(1)	0.6404(9)	0.249(1)	0.117(5)
C(36)	0.137(1)	0.599(1)	0.1628(9)	0.098(6)
C(37)	0.288(1)	0.5060(8)	−0.0069(8)	0.139(6)
Molecule 4				
Li(4)	0.411(1)	0.299(1)	0.1553(9)	0.062(5)
O(4)	0.4103(7)	0.2130(5)	0.0329(4)	0.080(3)
C(41)	0.3309(9)	0.1229(8)	0.0846(7)	0.062(4)
C(42)	0.3108(8)	0.1151(7)	0.1944(6)	0.053(3)
C(43)	0.2325(8)	0.0221(8)	0.2397(7)	0.065(4)
C(44)	0.181(1)	−0.0555(9)	0.187(1)	0.102(5)
C(45)	0.199(1)	−0.039(1)	0.080(1)	0.117(6)
C(46)	0.277(1)	0.051(1)	0.0284(8)	0.102(5)
C(47)	0.442(1)	0.2277(8)	−0.0773(7)	0.121(5)

^{a} $U_{eq} = 1/3\ \Sigma_i\ \Sigma_j\ U_{ij}a_i^{\star}a_j^{\star}\mathbf{a}_i\cdot\mathbf{a}_j$.

about the three dimensional structure of the compound, since by this technique short Li · · · H contacts ($\leq$ 3.5 Å) can be detected [8–11].

^{1}H NMR data of 1-lithio-2-methoxybenzene in benzene-d_6 are given in Table 4. As has been observed for several aryllithium compounds [9,10,12] the signal for the vicinal proton H(3) is shifted downfield relative to the signal in the hydrolysis

Table 2. Selected bond distances (Å) and angles (°)

Molecule X:	1	2	3	4
O(X)–C(X7)	1.39(1)	1.40(1)	1.40(1)	1.39(1)
O(X)–C(X1)	1.40(1)	1.42(1)	1.41(1)	1.41(1)
C(X1)–C(X2)	1.40(1)	1.39(1)	1.38(1)	1.40(1)
C(X1)–C(X6)	1.39(1)	1.39(1)	1.38(1)	1.36(1)
C(X2)–C(X3)	1.40(1)	1.38(1)	1.39(2)	1.39(1)
C(X3)–C(X4)	1.40(1)	1.40(1)	1.41(2)	1.37(2)
C(X4)–C(X5)	1.38(1)	1.33(1)	1.37(2)	1.36(2)
C(X5)–C(X6)	1.39(1)	1.38(1)	1.38(2)	1.38(1)
C(X7)–O(X)–C(X1)	120.5(6)	121.7(6)	118.8(7)	120.7(7)
O(X)–C(X1)–C(X2)	113.3(7)	115.3(7)	112.5(8)	115.4(7)
O(X)–C(X1)–C(X6)	121.9(7)	119.2(8)	119.2(9)	119.8(8)
C(X6)–C(X1)–C(X2)	124.7(7)	125.5(8)	128.3(9)	124.8(8)
C(X1)–C(X2)–C(X3)	111.9(7)	112.2(7)	110.8(8)	11.6(7)
C(X2)–C(X3)–C(X4)	126.5(7)	125.4(8)	125.0(1)	125.9(9)
C(X3)–C(X4)–C(X5)	117.9(7)	118.1(9)	119.0(1)	119.0(1)
C(X4)–C(X5)–C(X6)	119.7(8)	121.5(9)	120.0(1)	119.0(1)
C(X5)–C(X6)–C(X1)	119.3(8)	117.4(8)	117.0(1)	120.0(1)

Table 3. Lithium coordination geometry (distances in Å and angles in °)

Li(1)–C(22)	2.18(1)	Li(2)–O(1)	1.93(1)
Li(1)–C(12)	2.21(1)	Li(2)–C(12)	2.25(1)
Li(1)–C(42)	2.23(1)	Li(2)–C(22)	2.20(1)
		Li(2)–C(32)	2.13(1)
Li(3)–O(2)	1.95(1)	Li(4)–O(3)	1.93(1)
Li(3)–C(22)	2.44(1)	Li(4)–O(4)	2.01(1)
Li(3)–C(32)	2.19(1)	Li(4)–C(12)	2.26(1)
Li(3)–C(42)	2.22(1)	Li(4)–C(32)	2.51(1)
		Li(4)–C(42)	2.40(1)
C(22)–Li(1)–C(12)	107.9(6)	O(1)–Li(2)–C(12)	67.4(4)
C(22)–Li(1)–C(42)	110.6(5)	O(1)–Li(2)–C(22)	134.6(6)
C(12)–Li(1)–C(42)	108.1(6)	O(1)–Li(2)–C(32)	115.9(6)
		C(12)–Li(2)–C(22)	105.8(6)
		C(12)–Li(2)–C(32)	114.3(6)
		C(22)–Li(2)–C(32)	107.8(5)
O(2)–Li(3)–C(22)	63.8(4)	O(3)–Li(4)–O(4)	98.8(5)
O(2)–Li(3)–C(32)	120.7(6)	O(3)–Li(4)–C(12)	129.4(6)
O(2)–Li(3)–C(42)	120.0(6)	O(3)–Li(4)–C(32)	61.2(4)
C(22)–Li(3)–C(32)	98.3(5)	O(3)–Li(4)–C(42)	127.8(5)
C(22)–Li(3)–C(42)	102.4(5)	O(4)–Li(4)–C(12)	116.1(6)
C(32)–Li(3)–C(42)	119.0(6)	O(4)–Li(4)–C(32)	142.0(5)
		C(12)–Li(4)–C(32)	100.7(5)
		C(12)–Li(4)–C(42)	115.1(5)
		C(32)–Li(4)–C(42)	101.3(5)
Li(1)–Li(2)	2.50(2)		
Li(1)–Li(3)	2.59(1)		
Li(1)–Li(4)	2.69(2)		
Li(2)–Li(3)	2.60(1)		
Li(2)–Li(4)	2.65(2)		
Li(3)–Li(4)	2.65(1)		

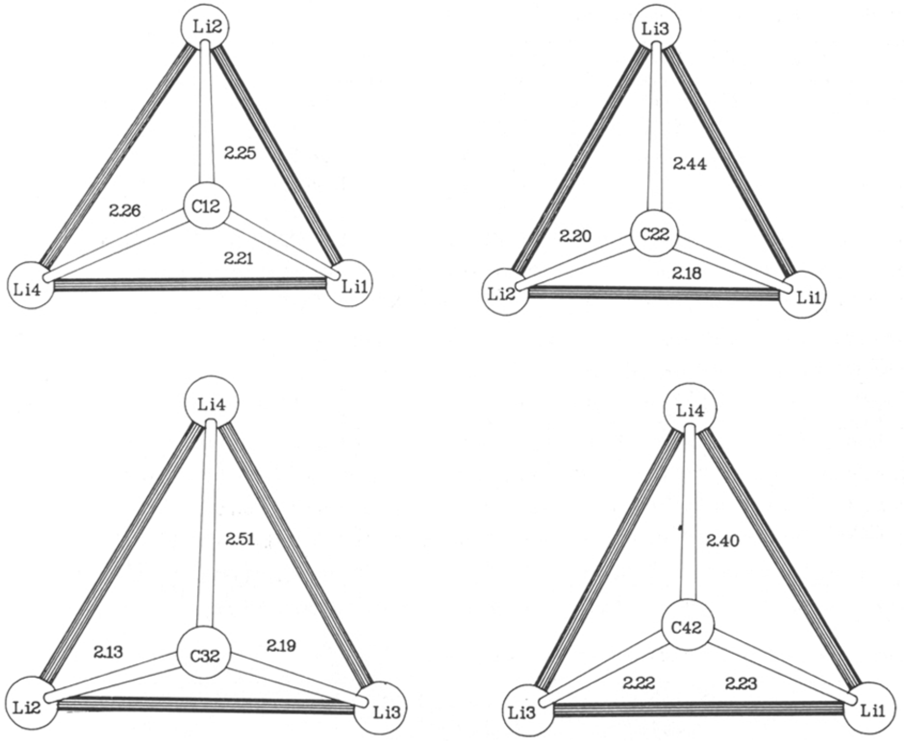


Fig. 2. Plots perpendicular to the four planes of the lithium tetrahedron, showing the distortion of the 4-center-2-electron bonds of C(22), C(32) and C(42).

product, methoxybenzene. This downfield shift is due to the polarized aromatic system and the electric field produced by Li [13]. Further assignments were made by means of decoupling experiments. The value of the vicinal coupling constant, ^3J(H(3)–H(4)) (6.3 Hz), is smaller than the values of ^3J(H(4)–H(5)) (7.2 Hz) and the ^3J(H(5)–H(6)) (8.0 Hz). This is common for aryllithium compounds and originates from a reduced C(3)–C(4) π-bond order [9]. The ^{13}C chemical shifts are tabulated in Table 5. The assignment of signals was made by means of ^{13}C–^{1}H shift-correlation spectroscopy (Fig. 4) [14].

A low temperature ^{13}C spectrum shows that the tetrameric structure is retained in solution (toluene-d_8). At −35 °C the ^{13}C signal of the lithiated carbon at 155.9 ppm is split into seven lines, approximately in the ratio 1/3/6/7/6/3/1 (Fig. 4a),

Table 4

^{1}H chemical shifts (δ_{TMS}, diagonal) and coupling constants (Hz, off-diagonal) of 1-lithio-2-methoxybenzene dissolved in benzene-d_6 (T = 20 °C)

H(3)	H(4)	H(5)	H(6)	OCH_3
7.86	6.3	1.7		
	7.07	7.2		
		7.24	8.0	
			6.51	
				3.08

Table 5

^{13}C chemical shifts (δ_{TMS}) for 1-lithio-2-methoxybenzene dissolved in benzene-d_6 ($T = 20\,°C$)

C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
169.8	155.9	141.6	122.3	129.1	107.0	54.1

which is indicative of a carbon bonded to three ^6Li nuclei (the small signals at the edge of the signal, with a theoretical relative intensity of 1, are hard to see because of broadening of the foot of the signal). Furthermore, the value of the ^{13}C–^6Li coupling constant, which is 5.1 Hz, is typical for carbon bonded to three ^6Li atoms. The NMR data were confirmed by cryoscopic measurements in benzene which yielded a degree of association of 3.96 (conc. = 0.22 molal). The ^6Li NMR spectrum at −90 °C shows only a single sharp signal, so in solution the symmetric (on the NMR time scale) tetrameric structure (Fig. 1b) is proposed. ^6Li–^1H HOESY shows strong dipolar relaxation between lithium and H(3), as expected. Also a weak dipolar relaxation between lithium and the methoxy substituent is observed; this is a proof of its intramolecular coordination to lithium, which is nearly unavoidable as the methoxybenzene anion is rigid (the oxygen atom bonded to the phenyl ring has a fixed position).

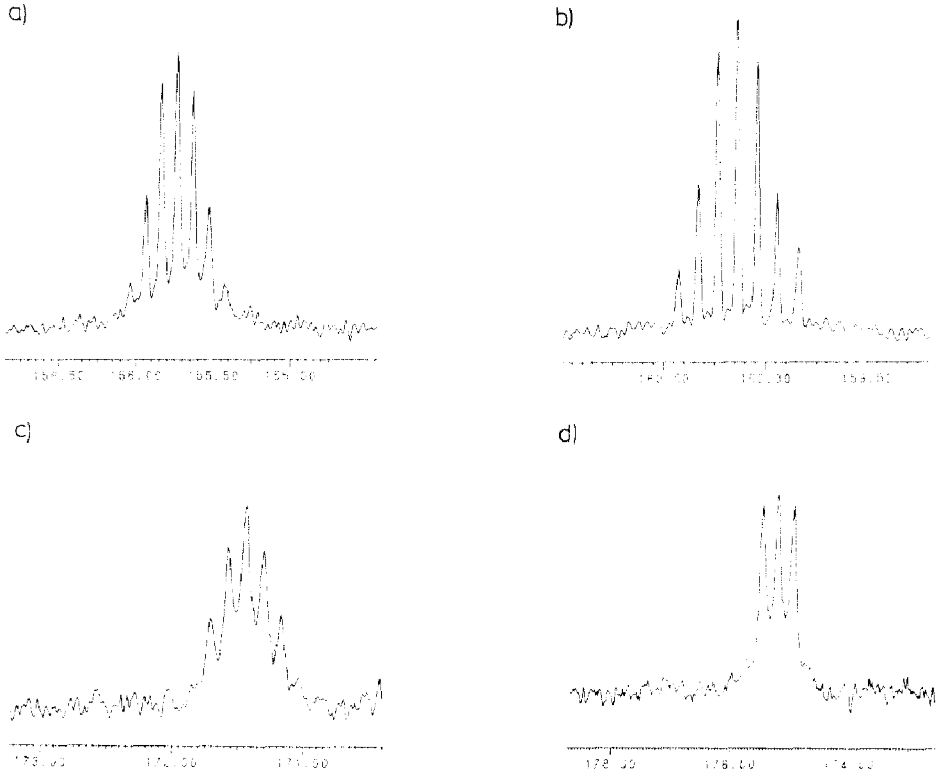


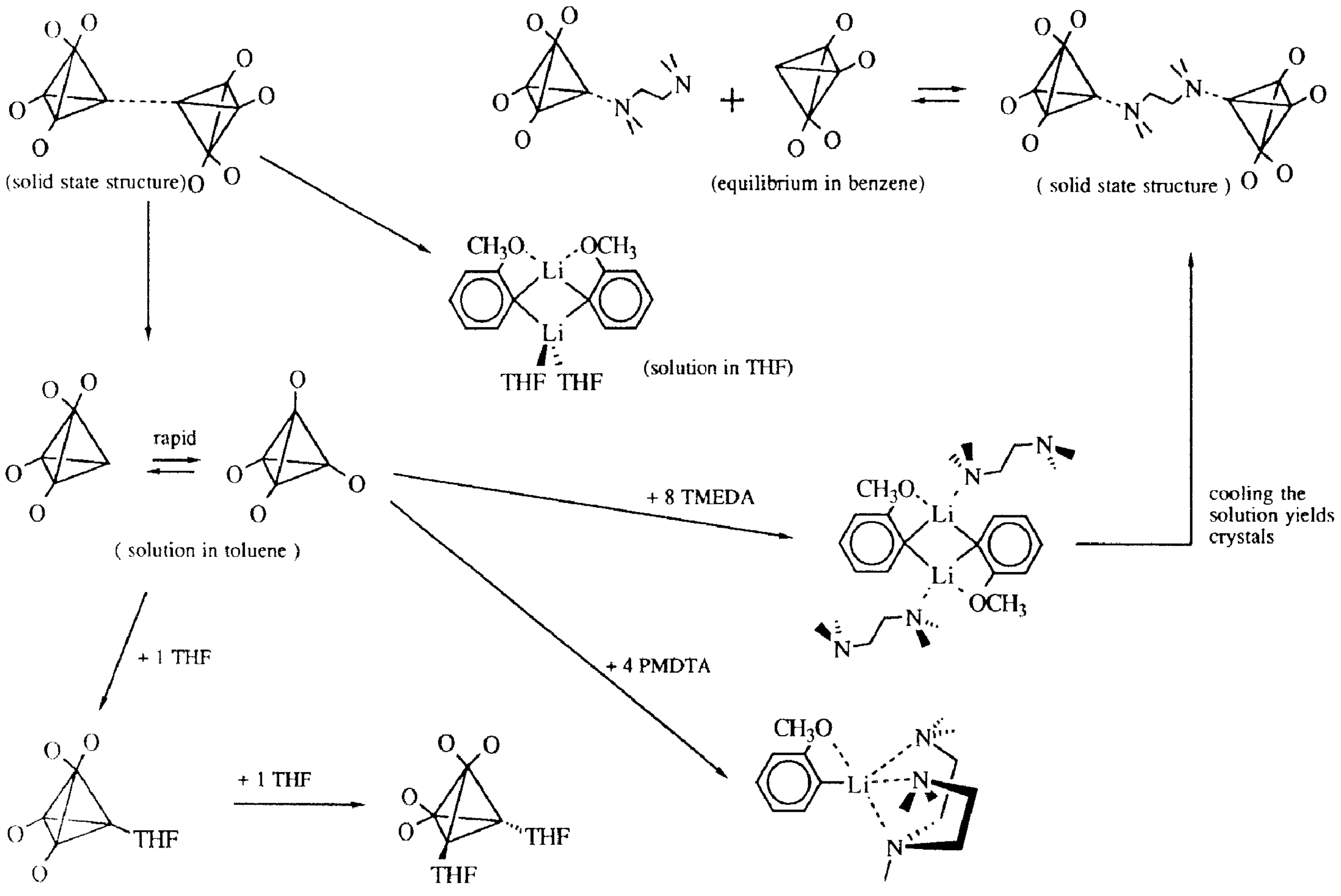
Fig. 4. ^{13}C signals of the lithiated carbon atom in: (a) 1-lithio-2-methoxybenzene dissolved in toluene-d_8 ($T = -35\,°C$); (b) 1-lithio-2-methoxybenzene·1/2THF dissolved in toluene-d_8 ($T = -20\,°C$); (c) sample (a) + two equivalents TMEDA ($T = -60\,°C$); (d) sample (a) + one equivalent PMDTA ($T = -63\,°C$).

The influence of additional ligands

When two equivalents (calculated on lithium) of TMEDA are added to a solution of 1-lithio-2-methoxybenzene in toluene-d_8, the tetramer is broken down to dimeric species. This was concluded from the appearance of a quintet (171.1 ppm; intensity ratio: 1/2/3/2/1) (Fig. 4c) for the lithiated carbon in the ^{13}C spectrum at $-35\,^\circ$C, indicative of a carbon bonded to two ^{6}Li atoms, while the septet at 155.9 ppm disappeared completely. The quintet is shifted downfield with respect to the septet by 15.2 ppm. This is in agreement with the NMR data on different aggregation states of phenyllithium which show a downfield displacement of the lithiated carbon signal going from tetramers to dimers and from dimers to monomers [8]. The ^{13}C–^{6}Li coupling of 6.8 Hz also indicates a carbon atom bonded to two Li atoms. The dimeric species is assumed to have the structure depicted in Scheme 1, which is of the same type as the solid state structure of bis[t-butyl(2-lithiophenyl)sulfide] · TMEDA [15].

When the solution of 1-lithio-2-methoxybenzene containing two equivalents of TMEDA is cooled to $-90\,^\circ$C, crystals of [1-lithio-2-methoxybenzene]$_8$ · TMEDA are obtained. The crystal of this complex that was used for the earlier X-ray study [1] was also formed in the presence of two equivalents of TMEDA. Apparently, the composition of the solution differs from the crystal deposited from it, and the solid state structure only represents the structure of the least soluble species. Crystals of [1-lithio-2-methoxybenzene]$_8$ · TMEDA did not dissolve very well in toluene-d_8, but a ^{13}C spectrum could be obtained at $-35\,^\circ$C. The signal for the lithiated carbon was broad and no splitting could be seen but its chemical shift (157.9 ppm) indicates that this carbon is bonded to three Li atoms. The ^{1}H spectrum at $25\,^\circ$C of this complex showed a reversal of the chemical shifts for the two different TMEDA protons, and an upfield shift for both signals, which is indicative for TMEDA coordinated to Li. Adding a small amount of TMEDA results in the fast exchange of TMEDA molecules and now the $N(CH_3)_2$ signal appears upfield to the $N(CH_2)$ signal. Cryoscopic measurements on crystals of [1-lithio-2-methoxybenzene]$_8$ · TMEDA in benzene (conc. = 0.02 molal, calculated as $[C_7H_7OLi]_8 \cdot$ TMEDA) suggest the equilibrium depicted in Scheme 1 (upper right) with an equilibrium constant of circa 1. However, it should be noticed that cryoscopy on these large aggregates (the aggregate consists of nine molecules) which are moreover slightly soluble (circa 20g/l) and sensitive to hydrolysis can not be very accurate. It seems therefore likely that the solid state structure is retained in solution.

When one equivalent (calculated on lithium) of *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDTA) is added to a solution of 1-lithio-2-methoxybenzene in toluene-d_8, the tetramers break down to monomers. The ^{13}C signal of the lithiated carbon now has a chemical shift of 175.6 ppm and is split into a triplet in the ratio 1/1/1 ($J(^{13}C–^6Li) = 13.6$ Hz) (Fig. 4d), which is indicative of a carbon bonded to one ^{6}Li nucleus. At low temperature ($-63\,^\circ$C) the ^{13}C signals for the PMDTA ligand are split in two sets of signals in a ratio of about 1/4: one set of four small sharp signals, of which the chemical shifts are in agreement with free PMDTA in toluene-d_8 and one of four larger broadened signals which must be caused by lithium-coordinated PMDTA. Its seems likely that the ligand is coordinated to lithium with all its three nitrogen donor atoms, as depicted in Scheme 1. Because of the rigidity of the methoxybenzene anion, at least weak intramolecular coordination of the methoxy substituent must be assumed in this monomer.


(solid state structure)
(equilibrium in benzene)
(solid state structure)
(solution in THF)
THF THF
CH3O
OCH3
Li
rapid
(solution in toluene)
+ 8 TMEDA
+ 4 PMDTA
cooling the solution yields crystals
+ 1 THF
+ 1 THF
THF
N

Scheme 1

The addition of one equivalent of THF does not affect the tetrameric aggregation state as the ^{13}C signal of the lithiated carbon remains a septet (intensity ratio: 1/3/6/7/6/3/1) (Fig. 4b), and even addition of five equivalents does not have any effect on this multiplicity. As the X-ray structures of 1-lithio-2-methoxybenzene with and without TMEDA shows how easy one O–Li coordination bond can be moved, we believe that the structure of the symmetric tetrameric aggregate must be affected upon addition of THF. When one quarter of an equivalent of THF was added to a suspension of 1-lithio-2-methoxybenzene in hexane, in which this compound is slightly soluble, the suspension immediately changed into a clear solution, and after ca. 10 s a white solid separated rapidly. When this experiment was repeated with amounts of THF ranging from one-half to two equivalents, in all cases crystals of 1-lithio-2-methoxybenzene $\cdot \frac{1}{2}$THF were formed. ^{13}C NMR at $-20\,^{\circ}$C of these crystals dissolved in toluene-d_8 shows a septet (intensity ratio: 1/3/6/7/6/3/1) for the lithiated carbon (Fig. 4b). The abnormal ^{1}H chemical shifts of the added THF (1.11 and 2.93 ppm) indicate that it functions as an electron-donating ligand (chemical shifts measured for free THF in toluene: 3.50 and 1.47 ppm). We suggest that the first THF molecule replaces one intramolecular O–Li bond (see Scheme 1) to give a soluble aggregate which reacts with another

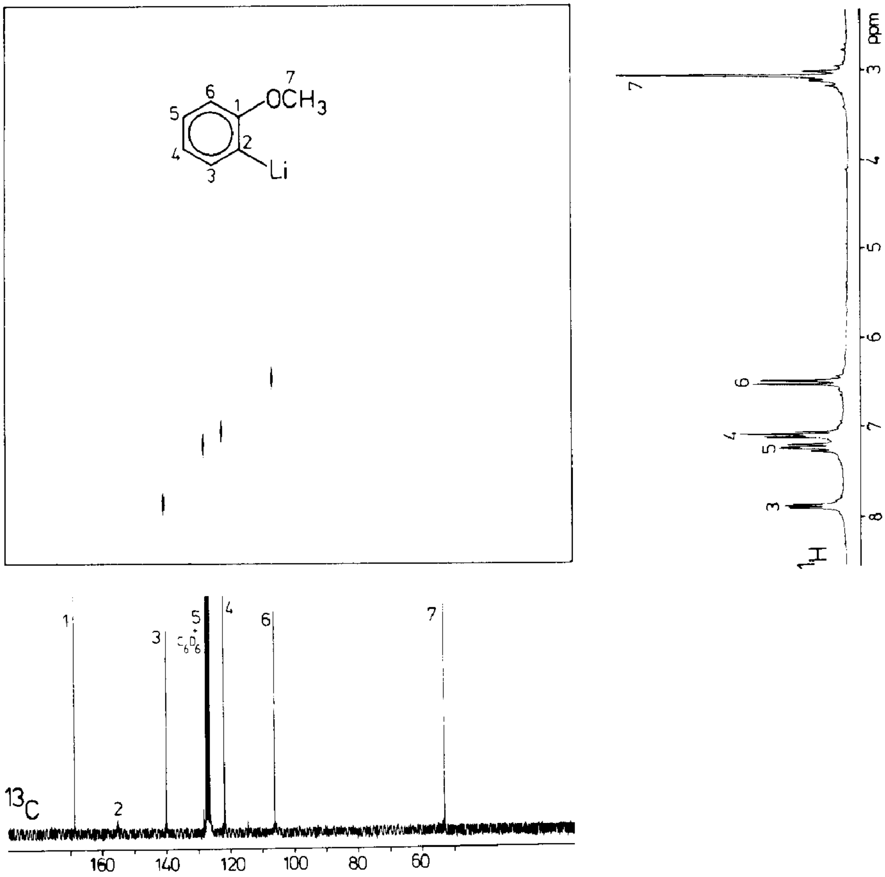


Fig. 3a. ^{13}C–^{1}H shift correlated spectrum of 1-lithio-2-methoxybenzene dissolved in benzene-d_6, contour plot, $T = 20\,^{\circ}$C.

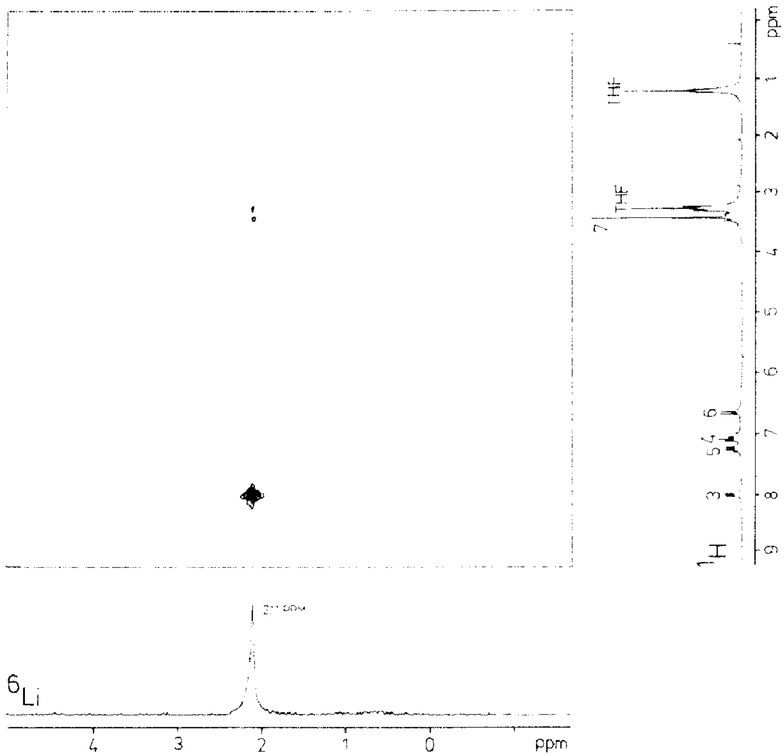


Fig. 3b. ^{6}Li–^{1}H HOESY of 1-lithio-2-methoxybenzene·1/2THF dissolved in toluene-d_8, contour plot, $T = 20$ °C, sample enriched with 96% ^{6}Li, mixing time = 2.0 s.

THF ligand with replacement of a second intramolecular O–Li bond, resulting finally in a rather stable tetrameric aggregate (Fig. 1d) which is not soluble in hexane and is similar to the tetrameric unit of 2,6-dimethoxyphenyllithium [16]. The structure of the latter consists of two planar dimeric units in which the lithiated carbon is planar tetracoordinated. The bonding within the dimeric units is of the 3-center-two-electron type ($C(sp_2) \cdots Li_2$) and bonding between the dimers is achieved by $C(p) \cdots Li$ interaction. It is impossible to add one more THF molecule to this stable crowded aggregate without disturbing this kind of bonding. A ^{6}Li–^{1}H HOESY spectrum of 1-lithio-2-methoxybenzene·$\frac{1}{2}$THF in toluene-d_8 (Fig. 3b), shows a strong Li $\cdots$ H(3) NOE and small NOE's to the methoxy substituent and the α-CH$_2$ of THF. Therefore, in solution THF is coordinated to lithium, but whether one or two THF molecules are coordinated to one tetrameric unit is not clear. We also repeated these experiments with 2-methyl-THF which is sterically more demanding and found the same results as for THF: only one quarter of an equivalent was needed to dissolve the 1-lithio-2-methoxybenzene and crystals of 1-lithio-2-methoxybenzene·$\frac{1}{2}$(2-methyl-THF) precipitated.

1-Lithio-2-methoxybenzene in pure THF has a degree of association of 1.97 (determined by cryoscopy, conc. = 0.17 molal) and therefore dimers are assumed. Whether the lithium coordination proceeds as depicted in Scheme 1 is not clear, but this dimeric species may act as a precursor for the tetramer containing two coordinated THF ligands (Fig. 1d).

Conclusions

1-Lithio-2-methoxybenzene in solution in apolar solvents (benzene, toluene) possesses a tetrameric structure in which each methoxy substituent is coordinated to one lithium atom. This symmetric intramolecular coordination involves a four-membered ring and is not very strong. In the solid state this symmetric intramolecular coordination of the tetramer is disturbed by small electrostatic (or agostic Li–H) interactions between the tetramers. The asymmetric solid state structure can be obtained by simply rotating one of the methoxybenzene anions by ca. 60°. The symmetric intramolecular coordination in solution can be disturbed by adding small amounts of electron-donating ligands.

Experimental

General conditions

All experiments were carried out under nitrogen by use of Schlenk techniques and syringes. Solvents were freshly distilled from sodium/benzophenone prior to use.

Synthesis

1-Lithio-2-methoxybenzene was synthesized by adding one equivalent of butyllithium (1.6 *M* in hexane) to a solution of 1.0 g (5.3 mmol) of 1-bromo-2-methoxybenzene in ca. 10 ml of pentane at room temperature. After a few seconds white crystals grew at the surface of the solution and formed a precipitate. These crystals are washed twice with ca. 10 ml of pentane and dried in vacuo. Yield: 0.5 g; 85%.

X-ray determination

Good quality crystals were obtained by carrying out the procedure described above starting with a very dilute solution of 1-bromo-2-methoxybenzene in pentane (0.5 g in ca. 150 ml). A rod-shaped crystal (0.60 × 0.30 × 0.15 mm), mounted under nitrogen in a Lindemann glass capillary, was used for data collection on an Enraf–Nonius CAD-4F diffractometer with Zr-filtered Mo-K_α radiation. Cell parameters were derived from the least-squares fitting of the setting angles of 18 reflections with $6.3 < \theta < 11.4°$. The intensity data of 4898 unique reflections were collected within one half of the reflection sphere ($-10 \le h \le 10$, $-13 \le k \le 0$ and $-15 \le l \le 15$; $2\theta_{max} = 50°$). Scan mode Ω–2θ with $\Delta\Omega = (0.55 + 0.35 \tan\theta)°$. Two reference reflections (200 and 102) were measured every hour and showed no significant variation. After correction for polarization and Lorentz effects 1300 reflections survived for which $I \ge 2.5\sigma(I)$.

The space group was assumed to be $P\bar{1}$, and this was later confirmed by the refinement. The structure was solved using direct methods (SHELX-86) [17] and subsequent Fourier analysis. Blocked full-matrix least-squares refinement was applied on *F*. During the early stages of the refinement the phenyl rings were refined as a rigid body using fixed distances and angles. In the final stages of the isotropic refinement, when convergence was reached, the restrictions on the rings were removed and anisotropic thermal parameters were calculated. At this stage the H atoms were introduced on calculated positions with C–H = 0.98 Å. All H atoms were refined riding on their carrier atoms. For the H atoms of each molecule two isotropic thermal parameters were calculated, one for the H_{phenyl} atoms and one for the H_{methyl} atoms. The final R-value was 0.069, $wR = 0.066$, $w = 2.3522/[\sigma^2(F_0) + 0.000302(F_0)^2]$, $S = 1.67$. The average and max. shift/error ratios in the final cycles were 0.006 and 0.018. Final residual electron density: $-0.20 < \rho < 0.22$ eÅ^{-3}.

The scattering factors for non-H atoms were taken from Cromer and Mann [18], those for H atoms from Stewart, Davidson and Simpson [19], and anomalous dispersion factors from Cromer and Liberman [20]. Calculations were performed with SHELX-76 (refinement) [21] and the EUCLID package (geometric calculations and illustrations) [22].

NMR-measurements

Spectra were recorded on a Bruker AC200 spectrometer (^{1}H frequency: 200 MHz). Deuterated solvents were dried over sodium sand and kept under nitrogen. Chemical shifts for ^{13}C and ^{1}H spectra are given relative to TMS; chemical shifts for ^{6}Li spectra are given relative to 1 M LiBr in THF at room temperature. In order to simplify the splitting pattern of the ^{13}C signal of the lithiated carbon due to C–Li coupling, samples were enriched with 96% ^{6}Li ($I(^6\text{Li}) = 1$; $I(^7\text{Li}) = 3/2$).

Cryoscopic measurements

The cryoscopic measurements in benzene and THF (freshly distilled from sodium/benzophenone under nitrogen) were carried out under nitrogen in the apparatus described by Seebach and Bauer [23].

Acknowledgement

X-ray data were kindly collected by A.J.M. Duisenberg. We are grateful to Dr. Walter Bauer for introducing the use of ^{6}Li–^{1}H HOESY in our laboratory.

References

1 S. Harder, J. Boersma, L. Brandsma and J.A. Kanters, J. Organomet. Chem., 339 (1988) 7.
2 R. Zerger, W. Rhine and G. Stucky, J. Am. Chem. Soc., 96, (1974) 6048.
3 W.E. Rhine, G. Stucky and S.W. Peterson, J. Am. Chem. Soc., 97 (1975) 6401.
4 (a) D. Barr, W. Clegg, R. Mulvey and R. Snaith, J. Chem. Commun., (1984) 285; (b) D. Barr, W. Clegg, R. Mulvey and R. Snaith, J. Chem. Soc., Commun., (1984) 287.
5 D. Seebach, R. Hässig and J. Gabriel, J. Helv. Chim. Acta, 66 (1983) 308.
6 J.F. McGarrity and C.A. Ogle, J. Am. Chem. Soc., 107 (1984) 1805.
7 R.D. Thomas, M.T. Clarke, R.M. Jensen and T. Corby Young, Organometallics, 5 (1986) 1851.
8 W. Bauer, W.R. Winchester and P.v.R. Schleyer, Organometallics, 6 (1987) 2371.
9 W. Bauer, P.A.A. Klusener, S. Harder, J.A. Kanters, A.J.M. Duisenberg, L. Brandsma and P.v.R. Schleyer, Organometallics, 7 (1988) 552.
10 W. Bauer, T. Clark and P.v.R. Schleyer, J. Am. Chem. Soc., 109 (1987) 970.
11 A. Bax and G. Morris, J. Magn. Res., 42 (1981) 501.
12 W. Bauer, G. Müller, R. Pi and P.v.R. Schleyer, Angew. Chem., 98 (1986) 1130; Angew. Chem., Int. Ed. Engl., 25 (1986) 1103.
13 J.I. Musher, J. Chem. Phys., 37 (1962) 34.
14 C. Yu and G. Levy, J. Am. Chem. Soc., 106 (1984) 6533.
15 (a) S. Harder, L. Brandsma, J.A. Kanters and A.J.M. Duisenberg, Acta Cryst., C43 (1987) 1535; (b) W. Bauer, P.A.A. Klusener, S. Harder, J.A. Kanters, A.J.M. Duisenberg, L. Brandsma and P. von R. Schleyer, Organometallics, 7 (1988) 552.
16 (a) H. Dietrich, W. Mahdi and W. Storck, J. Organomet. Chem., 349 (1988) 1; (b) S. Harder, J.

Boersma, L. Brandsma, A. van Heteren, J.A. Kanters, W. Bauer and P.v.R. Schleyer, J. Am. Chem. Soc., in press.
17 G.M. Sheldrick. SHELX-86. Program for crystal structure determination. University of Göttingen, Federal Republic of Germany (1986).
18 D.T. Cromer and J.B. Mann, Acta Cryst., A24 (1968) 321.
19 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
20 D.T. Cromer, D. Liberman, J. Chem. Phys., 53 (1970) 1891.
21 G.M. Sheldrick. SHELX-76. Program for crystal structure determination. University of Cambridge, England (1976).
22 A.L. Spek, in D. Sayre (Ed.), The EUCLID Package. In Computational Crystallography, Clarendon Press, Oxford 1982, p. 528.
23 W. Bauer and D. Seebach, Helv. Chim. Acta, 67 (1984) 1972.