# Structural NMR Investigations on Allyllithium Compounds

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Received October 16, 1991

**Key Word:** Allyllithium compounds

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Four differently substituted phenylallyllithium compounds Li · **2** have been investigated by dynamic $^1$H- and $^{13}$C-NMR, NOESY and HOESY spectroscopy. It is shown that a considerable barrier of rotation (ca. 40 kJ/mol) between the phenyl and the allyl moiety exists which is only slightly affected by the addition of TMEDA. The lithium atom prefers a bridged position with respect to the allylic part in solution and has HOESY contacts to the *ortho* hydrogen atoms of the aromatic ring.

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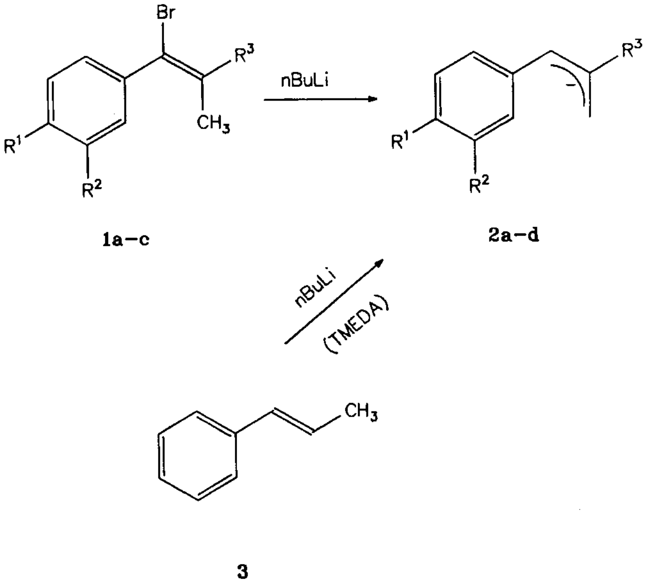
The structure of allyllithium compounds is of fundamental interest and has been extensively investigated in the current literature[1]. Schlosser[2] used the method of isotopic perturbation of equilibrium to conclude that allyllithium forms an unsymmetrical $\eta^3$ complex. Schleyer, who used the same technique, first described a symmetrically bridged structure[3], later, however, his group has found that the asymmetric species in THF is a dimer[4]. Fraenkel extensively applied $^{13}$C-NMR spectroscopy of $^6$Li-labelled compounds and reported recently on the conformation and dynamic behavior of trimethylsilyl-substituted allyl anions[5,6]. To allyllithium a "chameleon behavior" has been ascribed[7], with an ionic and covalent form in an equilibrium. Weiss[8] succeeded in crystallizing the first allyllithium stabilized by TMEDA, and Boche[9] showed that in the solid state the compound is an $\eta^3$ complex. Further light on the structure of allyl anions was shed by an investigation of carbon-carbon coupling constants[10] and very recently by a theoretical comparison of different alkali metals[11], and calculations of NMR spectra using the IGLO approach have been communicated[12]. With modern NMR methods such as NOESY and HOESY spectroscopy it should be possible to assess the structure of these compounds in solution. We have therefore started an investigation to completely characterize some allyllithium compounds by means of these NMR methods. Our choice centered on allyllithium compounds with one phenyl substituent, since these anions are relatively simple to prepare, rather stable, and to our knowledge no stringent NMR analysis has been presented.

## Results and Discussion

### 1. Preparation

The allyl anions **2a – c** have been prepared by reaction of the corresponding vinyl bromides **1a – c** with *n*-butyllithium in hexane. The compounds Li · **2** were obtained in crystalline form and were, after washing with dry *n*-hexane, transferred under argon into the NMR tube. Upon subsequent dissolution in [D$_8$]THF the vinyllithium compounds underwent the transformation described by Knorr and Lattke[13]. **2d** was obtained directly by hydrogen abstraction from olefin **3** as shown in Scheme 1[14]. We restrict the detailed description of the NMR spectra to **2a**. The data of the other compounds are rather similar and given in tabular form.

Scheme 1



| 2 | R¹ | R² | R³ |
|---|---|---|---|
| a | H | H | $CH_3$ |
| b | $CH_3$ | H | $CH_3$ |
| c | H | $CH_3$ | $CH_3$ |
| d | H | H | H |

### 2. $^1$H-NMR Spectra and NOESY Data

The $^1$H-NMR spectrum of **2a** as shown at the axes of the NOESY plot in Figure 1 reveals the signals of the aromatic protons at relatively high field, the vinylic hydrogen 3-H absorbs at δ = 3.81 and the methylenic hydrogens at 3.35 and 2.89 in agreement with the literature[15]. Their individual

*Chem. Ber.* **1992**, *125*, 733 – 737 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1992 0009 – 2940/92/0303 – 0733 $ 3.50 + .25/0

assignments can clearly be derived from the NOESY contours, where the methyl group shows cross peaks to 3-H and 1b-H. The aromatic proton signals may be assigned by inspection of their spin multiplets. Furthermore, the vinylic hydrogen 3-H discloses a NOE contact to the *ortho* hydrogen atoms of the aromatic ring as does the signal of 1a-H. This is indicative of the *endo* structure **2a**.

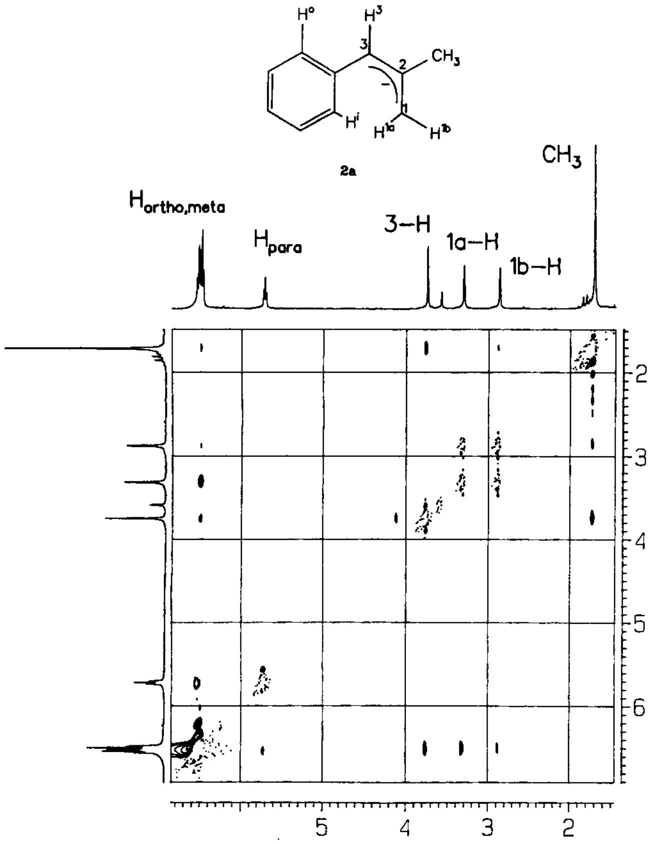
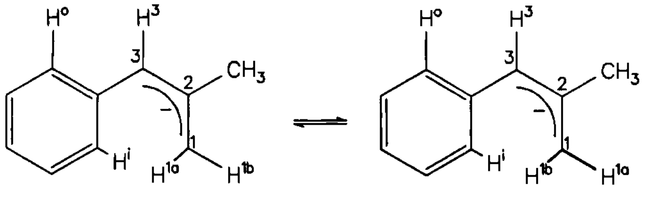


Figure 1. H,H-NOESY spectrum of **2a**, dotted points indicate positive signals. δ scales

A closer inspection of the NOESY spectrum shows two exchange peaks connecting 1a-H and 1b-H, however, with a positive phase. This points to a dynamic exchange process taking place at room temperature. Further warming of the compound leads to decomposition rendering it impossible to proof experimentally this process probably due to the hindered rotation around the partial double bond C-1 – C-2 (**2a** ⇌ **2a'**) interchanging 1a-H with 1b-H[15].



**2a** **2a'**

Furthermore, low-temperature $^1$H-NMR spectra have been recorded. As expected the signals of the *ortho* and *meta* hydrogen atoms broaden by lowering the temperature. At 188 K five absorption signals are recorded in the aromatic region, showing that each aromatic proton is in a different chemical environment (Figure 2). Their individual assignment was straightforward by analyzing their spin multiplets by means of homo decoupling measurements and by use of NOE-difference spectroscopy by which the relative assignment of the two *ortho*- and the two *meta*-proton signals may easily be achieved. Thus, irradiation of the vinylic 3-H gives rise to a NOE at the outer *ortho* hydrogen H°, whereas irradiation of 1a-H yields a NOE at the *ortho* hydrogen Hⁱ. On the firm basis of these assignments the low-temperature $^{13}$C-NMR spectrum is assigned by recording an inverse H,C-correlation[16] at 188 K as shown in Figure 2. At this temperature each carbon atom of the aromatic ring gives an invidivual signal which shows correlation peaks with the attached proton.

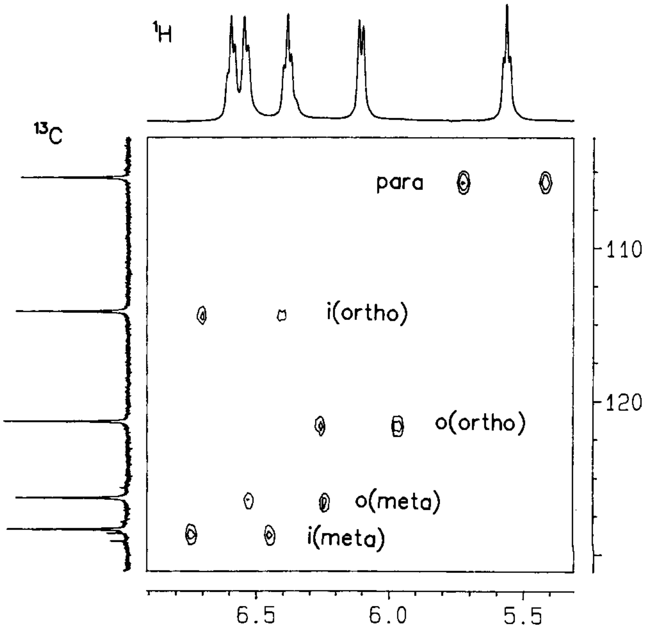


Figure 2. Inverse H,C correlation spectrum of **2a** at 188 K; δ scales

### 3. Temperature-Dependent $^{13}$C-NMR Spectra

As mentioned above, the $^1$H-NMR spectra of the compounds **2** are temperature-dependent. The signals of the *ortho* and *meta* carbon atoms of the aromatic ring broaden whereas the signals of the *para* and *ipso* carbon and the signals of the allyl moiety do not change significantly their line width. By a combined analysis of the carbon and proton line shapes with the DNMR5 program[17] the thermodynamic parameters of this exchange can be obtained (Table 1).

For **2d** a similar analysis is not possible, since already at room temperature the spectra show a slow exchange and further warming leads to decomposition. Since the compound is only handled in the presence of TMEDA a comparison with the values of **2a** – **c** is limited.

We interpret the observed dynamic NMR process as a hindered rotation of the bond $C_{ipso}$ – C-3 which connects the phenyl ring with the allyl moiety. The barrier should be

Table 1. Thermodynamic parameters of the hindered rotation around C-3$-$C$_{ipso}$ in the allyllithium compounds **2a**$-$**c**[a]

| | $\Delta G^{\ddagger}_{298}$ [kJ/mol] | $\Delta H^{+}$ [kJ/mol] | $\Delta S^{+}$ [J/K · mol] |
|---|---|---|---|
| **2a** | 41.9 | 43.2 | −4.3 |
| **2b** | 37.6 | 38.7 | −3.6 |
| **2c** | 40.7 | 42.1 | −4.6 |
| **2a** · TMEDA | 42.9 | 48.1 | −17.3 |

[a] Values are estimated to be correct within a margin of ±1 kJ/mol and 2 J/K · mol respectively. Dynamic NMR measurements and lineshape simulations were performed over a temperature range of 80 K.

mainly caused by a partial double bond character of the C$_{ipso}$$-$C-3 bond. Substitution of a methyl group in *para* position of the aromatic ring (**2b**) should destabilize the delocalization of the negative charge. This is indeed the case as can be seen from the values of $\Delta G^{\ddagger}_{298}$ and $\Delta H^{+}$ in Table 1. Substitution of a methyl group in *meta* position (**2c**) should increase to some extent the steric hindrance and thus destabilize the planar conformers. This could lead to an increase of the energy of the ground state and to a slightly lower activation energy, again as observed. However, since the experimental differences are rather small this interpretation must be viewed with caution. 1,3-Diphenylallyl anions[18] show dynamic NMR spectra, the underlying process being the cisoid $\rightleftharpoons$ transoid equilibration due to rotation around the partial double bond C-2$-$C3. Hindered phenyl rotation in these compounds has not been reported. Whereas with our compounds dynamic processes around the C-3$-$C$_{ipso}$ bond and the C-1$-$C-2 bond are visible we have found no evidence for hindered rotation around C-2$-$C-3. Compared with other formal C$_{sp^2}$$-$C$_{sp^2}$ single bonds, however, such as in acetophenone[19], in the case of compounds **2** we find a considerable enhancement of the rotational barrier around C-3$-$C$_{ipso}$.

## 4. Addition of TMEDA

Compared with alkyl-substituted allyl anions[20] compounds **2** reveal only a small chemical shift difference between the allylic carbon atoms C-1 and C-3 indicating that a considerable amount of charge is delocalized into the aromatic ring[13]. Lowering the temperature further diminishes this difference. This behavior may be interpreted in terms of an ionized and delocalized structure, which at lower temperatures is even more stabilized. Addition of a complexing ligand such as TMEDA should further favor this structure, however, neither the $^{13}$C- nor the $^{1}$H-chemical shifts change significantly in the presence of TMEDA. Apparently, TMEDA is not very effective in THF solution. The dynamic parameters, however, are of interest. We find for the TMEDA-containing solution a large negative activation entropy. Although activation entropies should be interpreted with caution since often their experimental basis is insecure, the difference between the values of **2a** and **2a** · TMEDA is striking. In the TMEDA complex the rotation of the allyl moiety around the phenyl ring apparently requires a more ordered transition state. Schleyer[21] discusses the structure of a dilithiated diphenylhexene where TMEDA is still chelating the lithium "in spite of the presence of a large excess of the donor solvent, [D$_8$]THF". Our dynamic NMR data suggest that there must be a difference between the structure of the lithium compound in THF solution with and without additional TMEDA present, although this is not reflected in a change of chemicals shifts.

## 5. $^{6}$Li,$^{1}$H-HOESY Measurements

The interaction of lithium with organic anions can be probed by two dimensional heteronuclear Overhauser measurements[22] between $^{6}$Li and $^{1}$H. In pioneering work Bauer[23,24] et al. showed the advantages and limitations of this approach. In order to study the chelating effect of TMEDA in a large excess of THF and to understand the difference between the data of **2a** and **2a** · TMEDA, we prepared a solution which contained 2 mmol of this allyl anion in the presence of 2 mmol of TMEDA and 14 mmol of THF/[D$_8$]THF (60:40). The $^{6}$Li,$^{1}$H-HOESY spectrum (not shown) revealed a strong contact of the lithium to the TMEDA-CH$_3$ groups, thus demonstrating that TMEDA competes effectively with THF under these conditions. However, a smaller cross peak was also found for the THF signal at δ = 3.58.

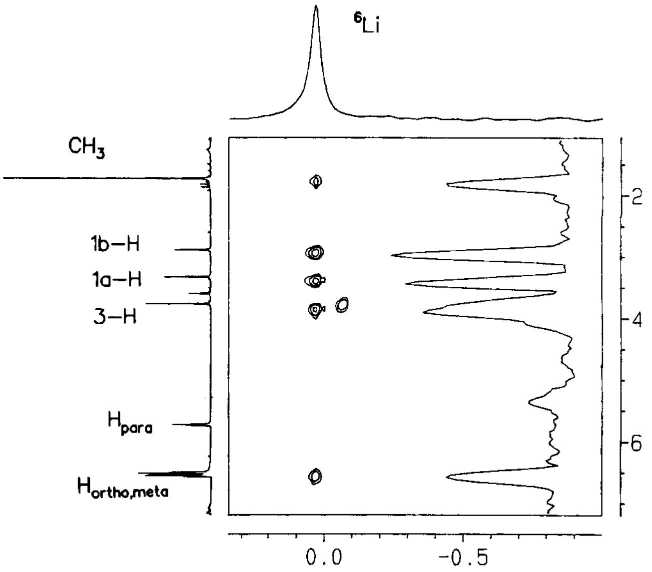


Figure 3. $^{6}$Li,$^{1}$H-HOESY spectrum of **2a** at room temperature; δ scales

Another $^{6}$Li,$^{1}$H-HOESY-spectrum of **2a** taken at room temperature in pure [D$_8$]THF is shown in Figure 3. In addition to the 2-D spectrum, the pertinent column of the 2-D matrix is shown, from which the lithium proton contacts can be estimated, if one corrects for the number of equivalent protons of each site. As expected we find the strongest contact signals for the allyl system, being roughly equally strong for the vinylic hydrogen 3-H and the methylene group hydrogen atoms at C-1. In addition, we find a contact of Li to the methyl group. Most interestingly the spectrum reveals

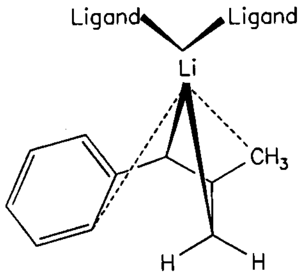
Table 2. $^1$H- and $^{13}$C-chemical shifts of allyllithium compounds **2a–d** at room temperature in [D$_8$]THF measured with solvent resonance as internal standard and calculated with $\delta_C$ = 67.4 and $\delta_H$ = 3.58

| | C-1 (CH$_2$) | C-2 (C$_q$) | C-3 (CH) | C-4 *ipso* | C-5 *ortho* | C-6 *meta* | C-7 *para* | 2-CH$_3$ | C$_6$H$_4$CH$_3$ |
|---|---|---|---|---|---|---|---|---|---|
| **2a** | 67.5 | 145.1 | 80.4 | 148.0 | 120.0 | 128.1 | 109.7 | 29.7 | |
| **2b** | 63.7 | 145.0 | 80.6 | 145.4 | 120.4 | 128.4 | 118.0 | 29.6 | 20.9 |
| **2c** | 67.6 | 144.4 | 80.1 | 147.4 | 119.8[a]<br>117.2 | 135.1[b]<br>127.2 | 110.8 | 29.4 | 22.1 |
| **2d** | [c] | 149.7 | 69.4 | [c] | [c] | [c] | 98.4 | | |

| | 1a-H | 1b-H | 3-H | *o*-H | *m*-H | *p*-H | 2-CH$_3$ | C$_6$H$_4$C*H*$_3$ |
|---|---|---|---|---|---|---|---|---|
| **2a** | 3.35 (d)<br>$^2J$ = 2.76 Hz | 2.89 (s) | 3.81 (d)<br>$^4J$ = 1.23 Hz | 6.63–6.58 (m) | | 5.84 (t) | 1.77 (s) | |
| **2b** | 3.14 (s) | 2.67 (s) | 3.79 (s) | 6.54–6.47 (m) | | – | 1.73 | 2.01 |
| **2c** | 3.30 (d)<br>$^4J$ = 2.6 Hz | 2.84 (s) | 3.72 (s) | 6.36 (s)<br>6.33 (d) | 6.47 (t) | 5.62 (d) | 1.70 (s) | 1.97 (s) |

[a] Top value: carbon atom between methyl group and allyl moiety; bottom value: other *ortho* carbon atom. — [b] Top value: carbon atom bearing methyl group; bottom value: other *meta* carbon atom. — [c] Not observed.

a Li-H interaction to the aromatic *ortho* protons, however not to the *meta*- and *para*-hydrogens. The contact signals for the methyl group and the *ortho* protons must be caused by the spatial vicinity rather than a Li–C$_{ortho}$ bond. Thus, the solution structure **4**, which we propose should have two bonds from lithium to the allyl system and two bonds to a ligand which is either TMEDA or THF, depending on the preparation. The dotted lines indicate the further HOESY contacts.



**4**

In summary, NMR analysis of the phenylallyllithium compounds **2** has shown that their structure is largely delocalized. Addition of TMEDA does not significantly change the spectra. The barrier of rotation between the *ipso* carbon atom of the phenyl ring and C-3 of the allyl moiety amounts to about 40 kJ/mol. From the HOESY measurements we find lithium contacts to both ends of the allyl moiety and a slight but significant interaction with the aromatic ring. On addition of TMEDA, HOESY contacts to the amine are revealed. We therefore propose structure **4** for these anions in solution.

This work was supported by the *Deutsche Forschungsgemeinschaft* (SFB-260) and the *Fonds der Chemischen Industrie*.

## Experimental

*Preparation of the Compounds* **2a–c**: 2.4 mmol of the vinyl bromides **1a–c** was dissolved in *n*-hexane (15 ml). The solutions were cooled to 0°C, and subsequently 1.1 eq. of *n*-butyllithium was added. Upon stirring overnight colorless crystals of the vinyllithium compounds precipitated. They were filtered, washed with *n*-hexane, and dried in vacuo. The crystals were transferred into a 5-mm NMR tube and dissolved in [D$_8$]THF (1 ml). The yellow solutions became dark while the rearrangement of the vinyl anions to the allyl anions took place.

*Preparation of* **2d**: 0.5 g (4.63 mmol) of **3** was dissolved in *n*-hexane (15 ml), subsequently 1 eq. of TMEDA was added. After addition of 1.1 eq. of *n*-butyllithium an intense brown color indicated the formation of the allyl anion. After stirring for 2 h the solvent was removed in vacuo and the residue dissolved in [D$_8$]THF (1.5 ml) and transferred into a 5-mm NMR tube.

In Table 2 the $^1$H- and $^{13}$C-NMR data of the compounds are given.

*NMR Measurements:* All NMR results were obtained on a Bruker AM-400 instrument equipped with a multinuclear probehead and processed on an external data station Bruker X-32. For the NOESY spectra a relaxation delay of 3 s and a mixing time of 1.2 s was used, 128 free induction decays of 4 transients was measured on 1 k data points, after weighting with sinusoidal windows and zero filling a matrix of 512 × 512 real data points was processed in phase-sensitive mode.

The HOESY spectrum was measured by taking 128 $^6$Li free induction decays of 16 transients by using a relaxation delay of 5 s and a mixing time of 1.4 s. The matrix was processed by using sinusoidal windows and zero filling to 1024 × 256 real data points in the magnitude mode.

CAS Registry Numbers

**1a**: 5912-93-6 / **1b**: 100220-01-7 / **1c**: 137966-28-0 / **2a**: 66639-74-5 / **2a** · TMEDA: 137966-29-1 / **2b**: 137966-26-8 / **2c**: 137966-27-9 / **2d**: 34041-44-6 / **3**: 873-66-5

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[1] For a review see: J. L. Wardell in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, **1982**, vol. 1, p. 97.
[2] M. Staehle, M. Schlosser, *J. Organomet. Chem.* **1981**, *220*, 277; M. Schlosser, M. Staehle, *Angew. Chem.* **1980**, *92*, 497; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 487.
[3] W. Neugebauer, P. v. R. Schleyer, *J. Organomet. Chem.* **1980**, *198*, C-1.

[4] W. R. Winchester, W. Bauer, P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.* **1987**, 177.

[5] G. Fraenkel, A. Chow, W. R. Winchester, *J. Am. Chem. Soc.* **1990**, *112*, 1382.

[6] G. Boche, G. Fraenkel, J. Cabral, K. Harms, N. J. R. van Eikema Hommes, J. Lohrenz, M. Marsch, P. v. R. Schleyer, *J. Am. Chem. Soc.*, in print.

[7] G. Fraenkel, A. F. Halasa, V. Mochel, R. Stumpe, D. Tate, *J. Org. Chem.* **1985**, *50*, 4563.

[8] H. Köster, E. Weiss, *Chem. Ber.* **1982**, *115*, 3422.

[9] G. Boche, H. Etzrodt, M. Marsch, W. Massa, G. Baum, H. Dietrich, W. Mahdi, *Angew. Chem.* **1986**, *98*, 84; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 104.

[10] R. Benn, A. Rufinska, *Organometallics* **1985**, *4*, 209.

[11] N. J. R. van Eikema Hommes, M. Buehl, P. v. R. Schleyer, *J. Organomet. Chem.* **1991**, *409*, 307.

[12] M. Buehl, N. J. R. van Eikema Hommes, P. v. R. Schleyer, U. Fleischer, W. Kutzelnigg, *J. Am. Chem. Soc.* **1991**, *113*, 2459.

[13] R. Knorr, E. Lattke, *Tetrahedron Lett.* **1977**, 3969; **1977**, 4655; **1977**, 4659.

[14] V. R. Sandel, S. V. McKinley, H. H. Freedman, *J. Am. Chem. Soc.* **1968**, *90*, 495.

[15] R. Knorr, E. Lattke, *Chem. Ber.* **1981**, *114*, 2116; R. Knorr, M. Hintermeyer-Hilpert, P. Böhrer, *ibid.* **1990**, *123*, 1137.

[16] A. Bax, R. H. Griffey, B. L. Hawkins, *J. Magn. Reson.* **1983**, *55*, 301.

[17] D. S. Stephenson, G. Binsch, *DNMR5, Quantum Chemistry Program Exchange*, **1978**, program 365.

[18] G. Boche, K. Buckl, D. Martens, D. R. Schneider, *Liebigs Ann. Chem.* **1980**, 1135.

[19] T. Drakenberg, J. Sommer, R. Jost, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 363.

[20] S. Bywater, P. Lachance, D. J. Worsfeld, *J. Phys. Chem.* **1975**, *79*, 2142.

[21] W. Bauer, P. v. R. Schleyer, *Magn. Reson. Chem.* **1988**, *26*, 827.

[22] P. L. Rinaldi, *J. Am. Chem. Soc.* **1983**, *105*, 5167; C. Yu, G. C. Levy, *ibid.* **1983**, *105*, 6994; **1984**, *106*, 6533.

[23] W. Bauer, M. Feigel, G. Müller, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1988**, *110*, 6033.

[24] W. Bauer, G. Müller, R. Pi, P. v. R. Schleyer, *Angew. Chem.* **1986**, *98*, 1130; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1103; W. Bauer, T. Clark, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1987**, *109*, 970.

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