

Preliminary communication

Studies of phenyllithium complexes by ^{13}C CP/MAS NMR spectroscopy**Dan Johnels * and Ulf Edlund***Department of Organic Chemistry, University of Umeå, S-901 87 Umeå (Sweden)*

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Abstract

A ^{13}C CP/MAS study of mono-, di-, and tetrameric phenyllithium complexes was performed. The ^{13}C CP/MAS data can be used to correlate solution NMR data and X-ray structural data.

The structure and reactivity of organolithium compounds continue to be of great interest to organic chemists. A large number of structures have been examined by both X-ray crystallography [1] and by NMR spectroscopy in solution [2]. However, the obvious technique providing a connection between these studies, namely high resolution solid state NMR spectroscopy [3], has been utilized in only a few studies [4]. In an attempt to extend this approach we have carried out a cross polarization/magic angle spinning (CP/MAS) NMR spectroscopic study of various phenyllithium complexes in the solid state. The choice of phenyllithium stems from the fact that this compound is one of the best characterized organolithium systems. This species has been observed in three aggregation states in solution [5] and also in the solid state [6], namely, as a tetramer, a dimer and a monomer. The aggregation state depends on the experimental conditions such as the temperature and on the type of ligand.

The tetrameric species, the structure of which was confirmed by X-ray crystallography, was isolated as an etherate [6a], in which each *ipso*-carbon interacts with three lithium atoms. These aggregates have also been observed in solution by NMR spectroscopy [5a,b].

The dimeric species used for X-ray crystallography was prepared by using *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as the ligand [6b]. In this structure, the *ipso*-carbon is in contact with two lithium atoms. The structure of this species has also been established in solution by NMR spectroscopy [5a–c].

The monomeric species was crystallized by using the terdentate *N,N,N',N',N''*-pentamethyldiethylentriamine (PMDTA) ligand [6c]. In this structure, the *ipso*-carbon interacts with one lithium atom, and the remaining three coordination sites

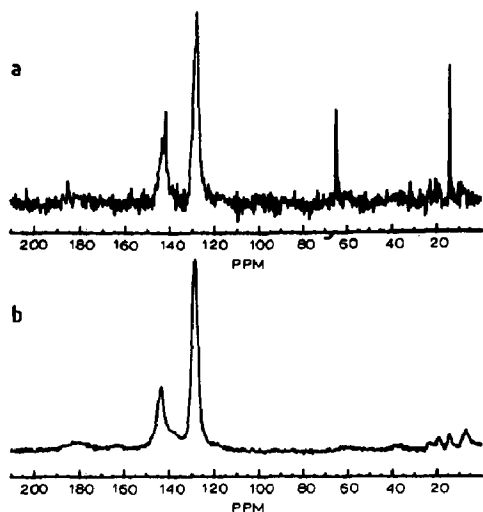


Fig. 1. ^{13}C CP/MAS NMR spectra of (a) phenyllithium coordinated by DEE and (b) phenyllithium without ligand.

on lithium are occupied by the PMDTA ligand. This species has been observed by NMR spectroscopy in THF solution containing one equivalent of PMDTA [5d]. The scalar coupling to one ^6Li was also noticed.

We have prepared the three phenyllithium species and studied them by ^{13}C CP/MAS NMR spectroscopy. The ^6Li and ^7Li isotopes were used together with the appropriate ligand for the preparation of the microcrystalline material [7 *]. However, as noted previously [6a], the DEE-coordinated tetramers are unstable because the ligands are only weakly bonded to lithium. When the complex was kept in an unsealed NMR rotor, with nitrogen as drive and bearer gas, the ether evaporated. However, the ^{13}C CP/MAS spectrum obtained from the DEE-coordinated crystals was identical to the spectrum of phenyllithium prepared directly from hexane without any added ligand (see Figs. 1a and b). The data for uncoordinated phenyllithium were subsequently assumed to apply to the tetrameric species, although there have been some suggestions that these crystals are polymeric in nature, with each *ipso*-carbon in contact with four lithium atoms [5b].

The spectra of the ^6Li and ^7Li isotopomers of the various aggregates are presented in Fig. 2. The chemical shifts are summarized in Table 1. The chemical shifts of the three aggregates in solution are also included for comparison.

It is evident from Table 1 that there is an excellent agreement between the shifts recorded in solution and those recorded in the solid state. Only small displacements are observed for the *ipso*-carbons. It is also evident that the differences in shifts between the isotopomers are small. This is in clear contrast to the differences in the linewidths, as is evident from Fig. 2. These differences in linewidths may be due to differences in dipolar coupling (the quadrupolar moment of ^6Li is only 0.5% of the quadrupolar moment of ^7Li), or differences in scalar coupling (due to differences in spin quantum number I and scalar coupling constant J), or a combination thereof. Quadrupole-induced relaxation by ^7Li would also lead to a line broadening [8].

* Reference number with asterisk indicates a note in the list of references.

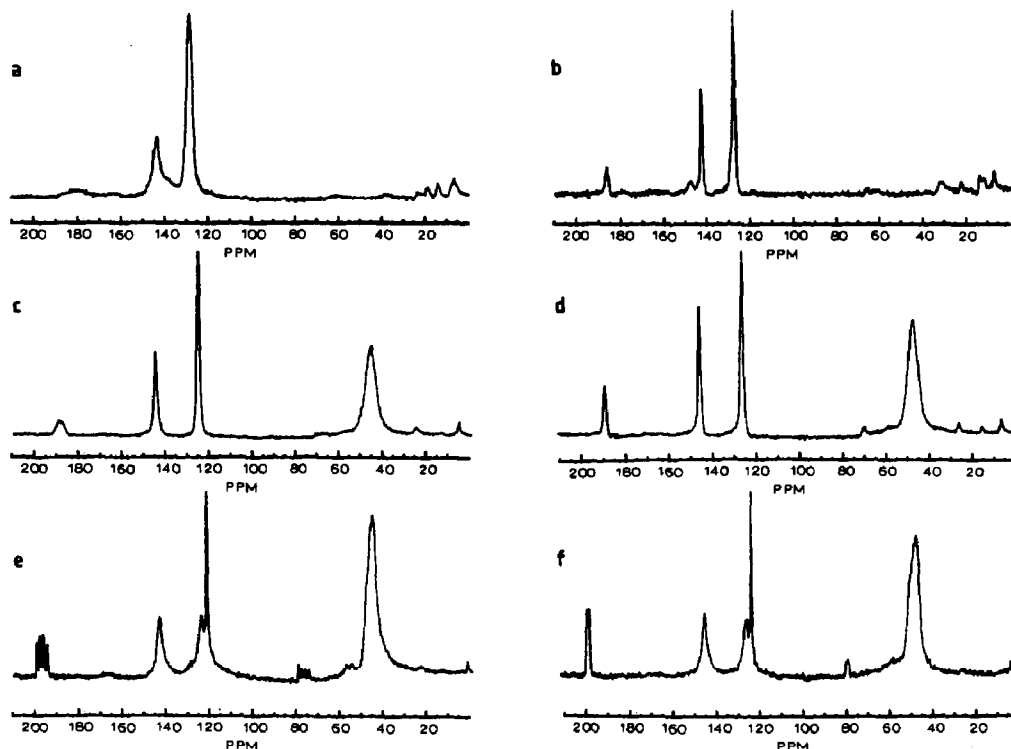


Fig. 2. ^{13}C CP/MAS NMR spectra of the ^7Li (a, c, e) and ^6Li (b, d, f) isotopomers of phenyllithium: (a, b) without ligand, (c, d) with TMEDA as ligand, and (e, f) with PMDTA as ligand, respectively.

It should be noted that only a small additional line broadening due to ^7Li was observed in our earlier study of fluorenyllithium complexes [4c]. The present results also differ from those obtained in a study of methyllithium, where use of ^6Li as well as ^1H decoupling was found to be necessary to give relatively narrow lines [4a,b].

The broadening of the lines due to the *ortho*- and *meta*-carbons indicates that dipolar coupling does indeed make an important contribution, especially in the

Table 1

^{13}C chemical shifts of the phenyllithium complexes in solid state and solution

Isotopomer	Aggregate	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>	Ref.
<i>Solid state data:</i>						
^7Li	"tetramer"	180 ^a	143.3	128.3 ^b	128.3 ^b	
^7Li	dimer	189.1	144.6	124.8 ^b	124.8 ^b	
^7Li	monomer	197.5	143.7	124.6	122.0	
^6Li	"tetramer"	186.3	142.5	127.5 ^b	127.5 ^b	
^6Li	dimer	188.6	144.8	124.9 ^b	124.9 ^b	
^6Li	monomer	197.9	143.8	124.5	122.0	
<i>Solution data:</i>						
^7Li	tetramer	176.2	142.9	127.9	127.1	5a
^6Li	dimer	188.5	144.6	124.8	123.2	5d
^6Li	monomer	196.7	143.4	124.8	120.9	5d

^a Signal broad. ^b Signals not resolved.

tetramer, since the long-range Li–C scalar coupling constants to these positions are expected to be small. However, the somewhat asymmetric quartet observed for the ^7Li isotopomer of the PMDTA-coordinated species is consistent with a monomeric form with a scalar coupling to one lithium atom. The splitting of the lines is about 37–46 Hz, close to the value of ca. 40 Hz calculated from the ^6Li isotopomer in solution [5d]. The observed asymmetry is not solely an effect of the 7% of the ^6Li isotopomer in the ^7Li sample; this was shown by adding up to 20% of the ^6Li to the sample and finding that there was no significant change in the splittings (i.e. in the order of the digitation). The origin of the asymmetry may lie in a combination of scalar and dipolar couplings, as earlier reported [9]. However, the lineshape is determined by many factors, including the nuclear quadrupole moment, the angle and distance between the interacting nuclei, the magnetic field strength, etc. [9a]. Use of a higher magnetic field strength might reduce the dipolar contribution, since the dipolar coupling is field dependent [9a], in contrast to the scalar coupling.

In the higher aggregates, however, all the factors work in the same direction, i.e. to produce greater linewidths. The observed splitting of the lines in the monomer shows that quadrupole-induced relaxation is unimportant in this case. Moreover, the observed splittings indicate that the relaxation time for ^7Li is sufficiently long to prevent self-decoupling of the ^{13}C , ^7Li coupling. The effect of self-decoupling between ^{13}C and ^{14}N has recently been investigated theoretically [11].

The *ipso*-carbon of the ^6Li isotopomer of the monomer has been observed as a triplet with a total line broadening of about 42 Hz in solution [5d]. The corresponding linewidth in the solid is 39 Hz, but unfortunately, no fine structure was visible, due to the limited resolution in solid state NMR.

The broadening of the *ortho*- and *meta*-carbons of the monomeric materials is caused by the asymmetry of the ligand, giving the two *ortho*- and two *meta*-carbons slightly different environments [10], i.e. the rotation about the symmetry axis is evidently slow on the NMR timescale. As expected, the signals from the *ortho*- and *meta*-carbons, together with the signals from the PMDTA ligand, become sharper when the temperature is increased to 60 °C. When the temperature is lowered the signals from the ligand change into three broad peaks, at 41.2, 47.6 and 55.1 ppm, respectively, at –120 °C. This indicates that the dynamic process taking place in the ligand is slowed down, as noted in our previous study of TMEDA-coordinated fluorenyllithium [4c].

In conclusion, we have shown that ^{13}C CP/MAS NMR spectroscopy can give structural information and be used to relate solution NMR data to X-ray structural data. The lower requirement for high quality crystals in the CP/MAS NMR method compared with that in X-ray crystallography, will make it possible to study materials that are difficult to obtain as single crystals. Variable temperature studies [12] give information on dynamic processes in a more direct way than X-ray crystallography.

However, further experimental, as well as theoretical, studies are necessary to reveal the full potential of the application of the CP/MAS NMR spectroscopic technique to organolithium chemistry.

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- 7 *Experimental*: Phenyllithium was prepared by treating iodobenzene with n-butyllithium in hexane. The resulting white microcrystalline material was washed twice with hexane and then dried in vacuum. Commercially supplied n-butyllithium was used for the preparation of the ^7Li isotopomer; ^6Li enriched n-butyllithium was prepared as described earlier [5c]. The crystals of the mono- and dimers were obtained by adding one or two equivalents of the appropriate ligand to a suspension of phenyllithium in hexane. All handling of the materials was conducted under argon. Solid-state ^{13}C CP/MAS spectra were obtained with a Bruker MSL 100 NMR spectrometer. The samples were spun at 3 kHz, the repetition time was 2.5 s, and the contact time 1 ms.
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