

A ^7Li NMR SPECTRAL INVESTIGATION OF GROUP III AND IV METALATES IN ETHER SOLVENTS

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Summary

The ^7Li chemical shifts of Et_2O , THF and DME solutions of the metalates LiBMe_4 , LiAlMe_4 , LiGaMe_4 and LiTlMe_4 are reported. These data are correlated with values from the literature. The observed changes in ^7Li chemical shift are discussed in terms of solvation of the lithium ion and ion pair formation in solution. The ^7Li chemical shift of LiSnMe_3 in THF is also reported and a brief discussion of the ^7Li chemical shifts of LiMPh_3 ($M = \text{C, Si, Ge, Sn, Pb}$) is presented.

Introduction

The structure of organometallic derivatives of the type $\text{MM}'\text{R}_4$ ($M = \text{Li, Na, K, Rb}$; $M' = \text{B, Al, Ga, In, Tl}$) have been shown to differ appreciably in the solid state. Grove et al. [1] recently reported that the structure of LiBMe_4 contains two types of $\text{Li}-\text{C}-\text{B}$ bridge bonds, one a very short linear $\text{Li}-\text{C}-\text{B}$ bond as well as a more normal $\text{Li}-\text{C}-\text{B}$ electron deficient bridge system. Previously, it had been shown that a chain structure involving $\text{Li}-\text{C}-\text{Al}$ bridge systems occurred in LiAlEt_4 [2], while other studies have shown that compounds with heavier alkali metal cations [3-5] or large central metals in the anion [4,5], are best described in terms of simple salt-like structures made up of M^+ and $\text{M}'\text{R}_4^-$ ions. The results of several infrared and Raman spectral studies are in general accord with these structures in the solid state [6,7].

In solution the nature of these systems is not understood as well, but in general may be discussed in terms of ion-pair equilibria as described in recent reviews by Szwarc [8,9] and by Smid [10], however the details concerning their behavior remain to be worked out.

Early reports on ^1H NMR spectra and subsequent studies of both ^1H and ^7Li NMR spectra by Brown et al. [2,11,12], suggested ion-pair equilibria in diethyl ether solutions. These studies dealt extensively with the $(\text{LiMe})_4^-$ - LiBMe_4 system, but did not deal with the general problem of solvent dependence

of these equilibria. Later studies by Wilkie and Oliver [13], Gore and Gutowsky [14] and by Ross and Oliver [15] reported additional information on the ^1H NMR spectra of Li^+ and $\text{Na}^+\text{AlMe}_4^-$ species under a variety of conditions and used these results to speculate about the equilibria involved and the various possible distortions, which lead to quadrupolar relaxation of the proton spectra. The proton NMR spectra of these and similar systems have been discussed further by Westmoreland et al. [16] and was recently extended to include variations in the ^{13}C NMR spectra of NaAlEt_4 and $\text{NaAl}(\text{n-Bu})_3$ by this group [17]. Although all of these studies provide information concerning ion-pair formation and the nature of the species present in solution, none of them attack the problem of the coordination directly but infer the nature of interactions from indirect measurements.

The purpose of the present work is to demonstrate that direct measurement of the cation resonance provides a useful approach to the study of ion-pair equilibria for lithium derivatives. This approach can provide significant information which cannot be obtained readily by other means. The choice of ^7Li NMR for this purpose is particularly convenient due to its occurrence in many compounds of interest and its demonstrated sensitivity to detection by NMR methods [18]. Further support for this choice comes from the fact that the ^7Li chemical shift has been shown to be dependent on the anion in the series $\text{LiM}''\text{Ph}_3$ ($\text{M}'' = \text{Si, Ge, Sn and Pb}$) [19] and is enhanced further by the recent report that the chemical shift is determined predominantly by the shielding provided by the surrounding molecules [20], and thus, should serve as a reasonably direct probe for its coordination.

Experimental

All of the compounds used in this study were prepared in vacuo by known procedures. Where possible, the solids were isolated, pumped on at 25° for 24 h and then for 2 h at 50° to remove all volatile materials.

Thus, methyl lithium was prepared by the reaction of lithium metal and dimethylmercury in diethyl ether [21] and isolated. LiBMe_4 [22], LiAlMe_4 [23], LiGaMe_4 [23] and LiTlMe_4 [24] were synthesized as indicated and isolated as the solids. Because LiSnMe_3 decomposes in the absence of solvent and because the PMR spectrum of LiSnMe_3 is affected by the presence of halide ion [25], spectra of this species were obtained on the filtered solutions resulting from the reaction of lithium metal and Me_6Sn_2 in THF [25,26].

^7Li NMR spectra were measured on a JEOL-JNM-4H-100 spectrometer modified to permit internal proton lock with the chemical shifts measured relative to internal TMS by difference as described elsewhere [20]. All NMR samples were 0.02 molar, sealed in 5 mm tubes either in vacuo or under argon and were run at ambient probe temperature (approximately 20°).

Results and discussion

In this paper three points concerning the use of ^7Li NMR studies and their application to the solution behavior of organometallic derivatives are presented.

First, the data obtained in this study and some data on ^7Li chemical shifts

TABLE 1

^7Li CHEMICAL SHIFTS (δ , ppm) FOR DME, THF AND ETHER SOLUTIONS OF LiMMe_4 SPECIES DETERMINED IN THIS STUDY AND SELECTED VALUES OF ^7Li CHEMICAL SHIFTS FROM THE LITERATURE

Compounds	Solvent			
	DME	THF	Et ₂ O	
LiBMe ₄	2.49	1.46	1.82	1.74 ^a (1.63) ^b
LiAlMe ₄	2.55	1.49	1.42	1.41 ^a (1.30) ^b
LiGaMe ₄	2.59	1.46	1.32	
LiTlMe ₄	2.64	1.21	1.35	
LiSnMe ₃		0.41		
EtLi			-0.79	-0.47 ^a (-0.58) ^b
				-0.89 ^d (-1.00) ^c
MeLi			-1.21	-1.21 ^a (-1.32) ^b

^a ^7Li chemical shifts scaled to the standard used in the present study by setting the ^7Li chemical shifts of MeLi equal. ^b Ref. 11. ^c Ref. 2.

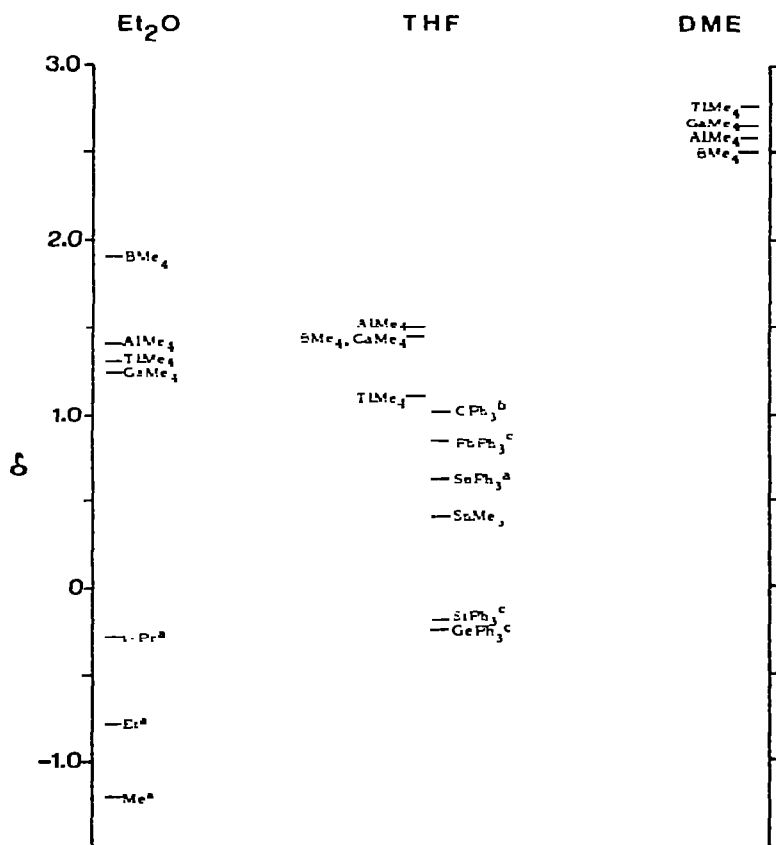


Fig. 1. ^7Li chemical shifts for the derivatives LiMMe_4 ($M = \text{B, Al, Ga, Tl}$), $\text{LiM}''\text{Ph}_3$ ($M'' = \text{C, Si, Ge, Sn, Pb}$), LiSnMe_3 and selected organolithium species in Et₂O, THF and DME. ^a Ref. 20. ^b Ref. 27. ^c Ref. 1.

of similar systems reported in the literature are placed on the same internal reference scale for comparison [20]. The data from this study along with a few of those from the literature are collected in Table 1 and all are given in Fig. 1. Examination of Table 1 shows that the relative ^7Li chemical shifts measured by different groups are consistent to ± 0.1 ppm or better, but also shows that the reported chemical shifts must not be used without referring to a single standard, and further, that values obtained are no better than approximately ± 0.1 ppm, thus making any correlation with chemical shifts obtained from different studies difficult.

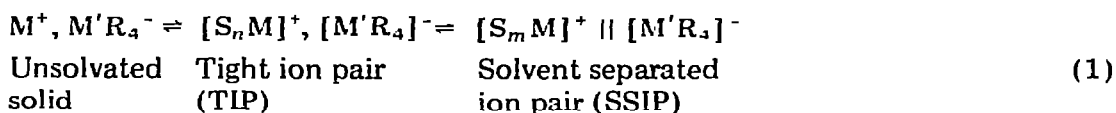
The second observation which is also qualitative in nature is that the relative ^7Li chemical shifts within a solvent system and to some extent between similar solvent systems may be used as a measure of the species present in that solvent system. This is a result of the fact that the ^7Li chemical shift is determined primarily by the shielding provided by its immediate neighbors and thus is determined by the molecules directly coordinated to it [20]. Examination of Fig. 1 makes this point clear. The highly oxygen coordinated ions are observed at the highest chemical shifts, approximately 1.5 ppm and above, while the less strongly coordinated or the lithium ions coordinated to alkyl groups in aggregates occur at substantially lower chemical shifts.

The third and most important feature can be found on closer examination of Fig. 1 and provides much more information concerning solvent interactions involved. The ^7Li shifts for the species LiBMe_4 , LiAlMe_4 , LiGaMe_4 and LiTlMe_4 change their order as a function of solvent (in addition to changes associated with the shifts associated with change in solvent). In DME the order is $\text{Tl} > \text{Ga} > \text{Al} > \text{B}$, in ether it is $\text{B} > \text{Al} > \text{Tl} > \text{Ga}$, while in THF the order is $\text{Al} > \text{B} = \text{Ga} > \text{Tl}$. In each of these series the only change occurring is the solvent, therefore, we must conclude that the solvent interaction determines the relative chemical shifts in each series and serves in some way as a measure of the solvent-metal interaction as well as a measure of the cation-anion interaction.

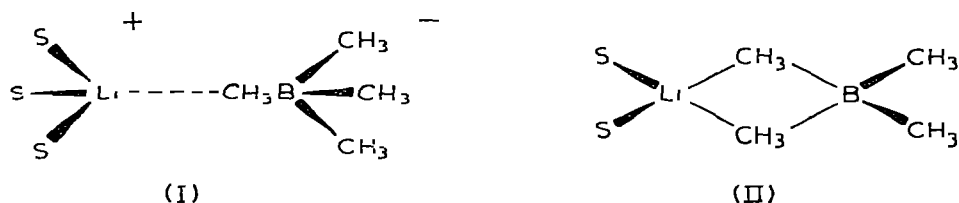
Taking these systems in order it appears quite clear that for DME solutions, we are dealing with systems in which all Li^+ is coordinated strongly by solvent forming solvated ion-pairs with the $[\text{M}^+\text{R}_4]^-$ ion. This conclusion is supported by the ^7Li chemical shifts which shift to lower field with decreasing anion size and by the earlier studies on AlR_4^- systems, which show that in DME solution the tetrahedral field surrounding the aluminum atom is not appreciably distorted. This represents the simplest system which we have to deal with but even in this media ion-ion interaction remains as indicated by the variation in ^7Li chemical shift, a feature not easily detected by other means. For the THF solutions, there is no simple dependence of the ^7Li chemical shifts on anion size, but instead we find three species, BMe_4^- , AlMe_4^- and GaMe_4^- , closely grouped and the LiAlMe_4 at substantially lower resonance. The very narrow range for the three chemical shifts suggests all lithium ions are in nearly the same environment, while the distortion of the field about the ^{27}Al nucleus, as shown by the collapse of $^1\text{H}-^{27}\text{Al}$ coupling, suggests that these species exist in an asymmetric electric field resulting from ion-ion interaction. The ^7Li chemical shift for LiTlMe_4 appears to indicate that this species differs from the others. In Et_2O the three species AlMe_4^- , GaMe_4^- and TlMe_4^- are now grouped together with lower ^7Li chemical shifts than the BMe_4^- derivative.

Examination of data for the Group IV lithium derivatives shows similar trends in THF solution, while comparison between the methyl- and phenyl-tin species shows clearly that the phenyl groups in this derivative are sufficiently close and oriented appropriately to provide some shielding of the ^7Li nucleus, presuming that the solvation of lithium ion remains the same under these conditions.

In all of these systems it appears that the ^7Li chemical shift can be accounted for in terms of the simple ion pair model shown in eqn. 1 similar to one of the



models proposed earlier with the possible exception of LiBMe_4 in ether. In this latter system an additional form may be involved, in which direct interaction occurs between the Li^+ and the BMe_4^- as indicated in I or II. This type of inter-



action seems improbable for the other systems in view of the weaker interactions observed for these species in the solid state [2-7].

One clearly may conclude from the results presented, that direct observation of the metal resonance in these and related systems provides the most direct and sensitive means for the study of ion-pair equilibria and permits distinctions to be made about solvation of the metal center such as the interaction that remains in DME solutions between $[\text{S}_n\text{Li}]^+$ and $[\text{M}'\text{Me}_4]^-$ which cannot be easily detected by other means.

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