Inorganica Chimica Acta, *96* (1985) L75–L77

Solid Phase ^{13}C NMR Techniques, A New Structural Probe for the Study of Solid Organolithium Compounds

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Received August 27, 1984

The first solid phase NMR spectra are reported for $H_3CLi^6)_4$ and the polylithium organic compound dilithiomethane $(CH_2Li_2{}^6)_n$. Although ^{13}C NMR spectra have been frequently employed in structural studies on organolithium compounds in solution [1, 2 etc.], the solid structures of polylithium organic compounds (and even monolithium compounds) are of particular current interest. Solid phase ^{13}C NMR spectra promise to provide a valuable source of structural information.

There is unusual interest in the structures of polylithium compounds such as dilithiomethane [3–6]. Although it may soon be possible to grow crystals of dilithiomethane, its limited solubility has made this initially very difficult. Also it is possible to observe ^7Li resonance in certain solvents for dilithiomethane, at the present time it has proven impossible to find satisfactory solvents to make natural abundance ^{13}C NMR spectra possible for polylithium compounds.

CH_3Li^6 and CH_3Li^7 were synthesized by reaction of ^6Li or ^7Li with $Hg(CH_3)_2$ in ether. Isotopically substituted dilithiomethane was prepared according to an improved version of the Ziegler pyrolysis of methyllithium [6, 7]:

Dilithiomethane

$$(CH_3{}^*Li)_4 \xrightarrow[\text{vacuum stir}]{223-226\ ^\circ C} \underset{95-96\%}{(CH_2{}^*Li_2)_n} + \underset{1-2\%}{(C_2{}^*Li_2)_n}$$

$$+ \underset{0.5-1\%}{(C_3{}^*Li_4)_n} + \underset{2-3\%}{(CH_3{}^*Li)_4}$$

* ^7Li or ^6Li isotope

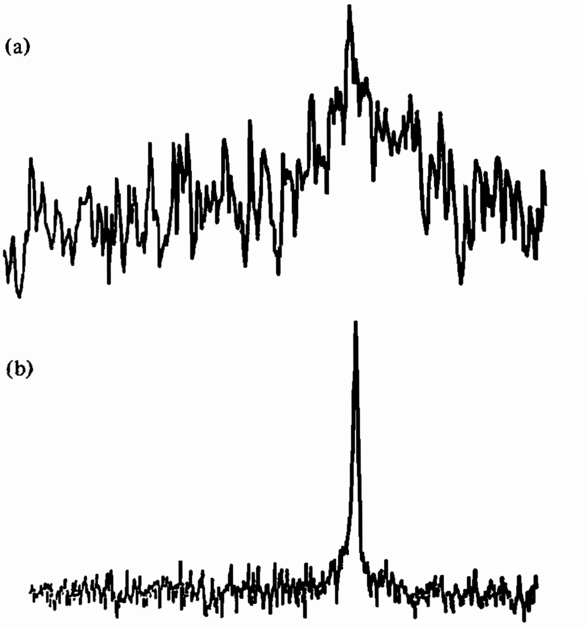

Fig. 1. Proton decoupled solid phase ^{13}C NMR spectrum of dilithiomethane. (a) $CH_2(^7Li)_2$ spectrum obtained at −150 °C. (b) $CH_2(^6Li)_2$ ^6Li decoupled, spectrum obtained at 25 °C. Peak is 10.5 ppm downfield from TMS.

The cross polarization magic angle spinning (CPMAS) NMR technique [8] combines pulsed NMR with high-speed sample rotation and can produce high resolution NMR spectra of a solid material approaching the quality obtained in liquids. The narrow linewidths combined with the high resolution of individual carbon chemical shifts obtained from the CPMAS experiment provide a method for obtaining new information about solid-state structure and dynamics on the atomic level.

The low solubility of polylithium organic compounds such that ^7Li spectra but not ^{13}C spectra are possible in solution makes application of the CPMAS NMR technique to dilithiomethane especially attractive. A detailed account of the CPMAS NMR technique and its chemical application in solids has recently appeared [8].

^{13}C NMR spectra of solid $CH_2(^7Li)_2$, $CH_2(^6Li)_2$, $CH_3{}^7Li$ and $CH_3{}^6Li$ were obtained using $^1H-^{13}C$ CPMAS [8]. Rotors filled with the material were loaded (within seconds) into the spinning apparatus under a strong flow of nitrogen gas after removal from the ampules in which they had been sealed in an argon atmosphere. After loading in the spinner, the samples are continuously bathed in an atmosphere of the helium gas, used for spinning and, if necessary, cooling [9].

The proton-decoupled ^{13}C NMR spectrum (15 MHz) of $CH_2(^7Li)_2$ and $CH_3{}^7Li$ are shown in Figs.

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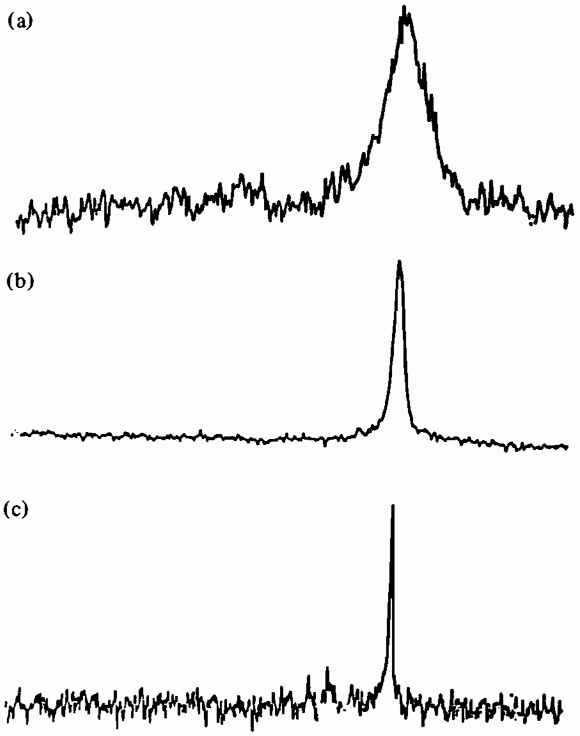

Fig. 2. Proton decoupled solid phase ^{13}C NMR spectrum of methyllithium obtained at −150 °C. (a) $CH_3{}^7Li$; (b) $CH_3{}^6Li$, no ^{6}Li decoupling; (c) $CH_3{}^6Li$, ^{6}Li decoupled. Peak is 16 ppm upfield from TMS.

1(a) and 2(a), respectively. These spectra were obtained at −150 °C, since sensitivity was found to be higher at lower temperatures. Nonetheless, the signal is weak, due to broadening from dipolar coupling with the ^{7}Li nucleus. The ^{7}Li nucleus has a spin quantum number 3/2 and possesses a sizeable electric quadrupole moment. In general, ^{13}C NMR spectral broadening due to dipolar coupling to a quadrupole nucleus cannot be removed either by conventional decoupling techniques, or by magic angle spinning [10]. However, the possibility for removal of this kind of broadening by decoupling or spinning increases as the electric quadrupole moment of the nucleus decreases. Since ^{6}Li has a quadrupole moment which is only ~0.5% of that of ^{7}Li, it was felt that it might be possible to achieve higher resolution in the ^{13}C NMR spectrum of $CH_2({}^6Li)_2$ and $CH_3{}^6Li$ using ^{6}Li decoupling in addition to ^{1}H decoupling.

CH_3Li and CH_2Li_2 were synthesized with an enrichment of 100% in the ^{6}Li isotope (as previously described) and a CPMAS probe was built with the capability of strong irradiation at the ^{6}Li (8.83 MHz), ^{1}H (60 MHz) and ^{13}C (15 MHz) Larmor frequences. The result of a ^{13}C CPMAS experiment at ambient temperatures on $CH_2({}^6Li)_2$ with ^{1}H *and* ^{6}Li decoupling is shown in Fig. 1(b). The spectrum consists of a single line, 80 Hz full-width at half-maximum. The chemical shift is 10.5 ppm downfield from TMS.

The ^{1}H and ^{6}Li decoupled ^{13}C NMR spectrum for $CH_3{}^6Li$ is shown in Fig. 2(c). The spectrum consists of a single line with a chemical shift of 16 ppm upfield from TMS. This value is in good agreement with those obtained in solution. The ^{3}C chemical shifts for $CH_3{}^7Li$ range from 15 ppm (THF) to 11 ppm (Et_3N) upfield from TMS. The small upfield displacement of the ^{13}C chemical shift of methyllithium (relative to methane) was interpreted as evidence for predominent sp^3 hybridization of carbon in this species [12]. Furthermore, excess charge density on the carbon was indicated to be small. The downfield ^{13}C chemical shift is indicative of diminishing charge density on the carbon-bearing lithium upon complexation [12].

The downfield ^{13}C shift in CH_2Li_2 relative to methyllithium may be attributed to an increase in charge density at the methylene carbon with increasing lithium substitution. Electropositive substituents are known to function as effective σ donors [6].

The very small linewidths for $CH_2({}^6Li)_2$ and $CH_3{}^6Li$ compared with that observed for $CH_2({}^7Li)_2$ and $CH_3{}^7Li$ shows that the strategies of using $CH_2({}^6Li)_2$ and $CH_3{}^6Li$ and decoupling ^{6}Li works, and should prove useful for ^{13}C studies of other organolithium materials. Such studies are currently in progress [13].

The fact that a sharp singlet is observed in the ^{13}C NMR spectrum of dilithiomethane is highly encouraging. This implies that solid aggregate $(CH_2Li_2)_n$ may contain only one carbon environment and that the symmetry is very high. This forecasts very favorable conditions for solution of this important and novel structure.

Acknowledgements

We thank Dr. John W. Chinn, Jr. of The University of Texas at Austin for the high-resolution mass spectral analyses. We are grateful for support of this work from the National Science Foundation (CHE-8210708) and for partial support from the Robert A. Welch Foundation (F-700).

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