Carbon-13–Lithium-7 Spin–Spin Coupling in Alkyllithium Compounds

Sir:

We wish to report the first observation of spin–spin coupling between ^{13}C and ^{7}Li in alkyllithium compounds. These measurements provide uniquely definitive evidence supporting the existence of electron-deficient bridge bonding in organolithium compounds in ether solution. This is illustrated (Figure 1b) in the ^{7}Li nmr spectrum[1] of a solution of ^{13}C-enriched methyllithium in THF solution.[2] The interpretation of the multiplet pattern supports the tetrameric structure for methyllithium in ether solution.

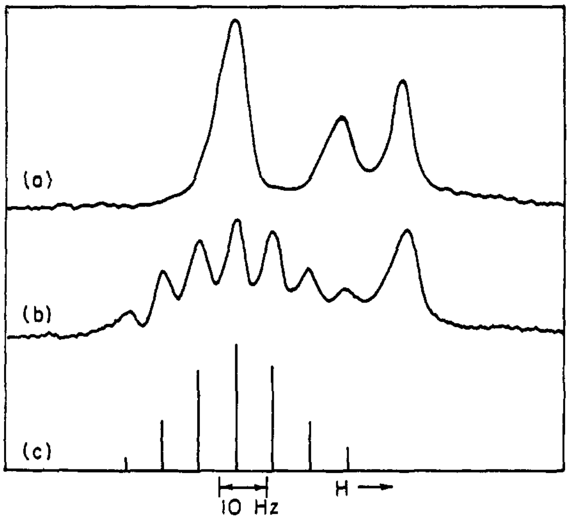

Figure 1. ^{7}Li nmr spectrum of ^{13}C-enriched (57%) methyllithium and lithium iodide in THF solution: (a) ^{13}C-decoupled from ^{7}Li by irradiating at 15.08917 MHz. The ^{13}C nmr spectrum of $^{13}CH_3Li$ in THF solution may be obtained directly or by an INDOR experiment: E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962). The resulting (proton coupled) quartet has δ_{CS_2} (external) +209 ppm at room temperature. The significance of this chemical shift will be discussed in a subsequent publication. (b) ^{1}H decoupled from ^{7}Li by irradiating at 60.009586 MHz. (c) Calculated ^{7}Li spectrum. The resonance lines proceeding from low to high field are methyllithium, methyllithium–lithium iodide mixed aggregate, and lithium iodide.

The room-temperature ^{7}Li nmr spectrum of a solution of ^{13}C-enriched methyllithium and lithium iodide consists of a single sharp line having a chemical shift between that of pure methyllithium and pure lithium iodide, as found in previous studies which illustrated lithium exchange between organolithium compounds and lithium bromide.[3] At −60° (Figure 1b) exchange is sufficiently slow that individual resonances typical of methyllithium, lithium iodide, and the suggested mixed aggregate[3] are resolved. Spin–spin coupling between ^{13}C and ^{7}Li (J = 14.5 Hz) in methyllithium is clearly evident.[4] The multiplet pattern is collapsed by decoupling the ^{13}C in a double-resonance experiment (Figure 1a), thus establishing spin–spin coupling between ^{13}C and ^{7}Li. Also, a distinct sharpening of the lines of the lithium multiplet is observed by decoupling the methyl protons, which is in accord with the previously reported line broadening due to ^{7}Li–^{1}H coupling.[5]

The calculated nmr spectrum (Figure 1c) is based on the previously hypothesized Seitz–Brown local environment model[6] for the tetrameric structure[7] of alkyllithium compounds in solution. This model assumes the four lithium atoms to be situated at the apexes of a tetrahedron and the alkyl groups to be positioned over each facial plane so that each lithium interacts with three neighboring alkyl groups. Assuming the absence of rapid intramolecular exchange,[8] there are four possible environments the lithium can experience in ^{13}C-enriched methyllithium: three ^{13}C; two ^{13}C, one ^{12}C; one ^{13}C, two ^{12}C; three ^{12}C. These environments accordingly determine the multiplicity of the spectrum. Line intensities are calculated from the binomial expansion[9] assuming random distribution of ^{13}C. The agreement between the calculated and the observed spectrum is striking. The ratio of line intensities (relative to the center line of the multiplet) for spectrum 1c is 0.79, 0.36, and 0.08, while that of spectrum 1b is 0.78, 0.38, and 0.10.[10] Alternatively, if rapid intramolecular exchange of ^{7}Li takes place, ^{13}C–^{7}Li coupling would be observed for a fivefold environment.[11] In this case, a nine-line spectrum having line intensity ratios 0.83, 0.46, 0.16, and 0.026 would be expected. The agreement between the calculated (Figure 1c) and observed (Figure 1b) spectrum, however, is clearly better for the fourfold environment.

Therefore, we believe our nmr measurements provide definitive spectroscopic evidence in support of the local environment model[6] for the tetrameric structure of methyllithium in ether solution. Furthermore, it appears that such observations exemplify a novel and presumably general method for studying the structure of electron-deficient bridge-bonded organometallic compounds.

Acknowledgment. The authors wish to thank B. Loy for programming the line-shape calculations and Drs. J. Heeschen and R. Iwamasa for helpful discussions.

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[1] ^{7}Li spectra were measured at 23.3 MHz using the high-resolution nmr spectrometer described by E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **28**, 313 (1957); **34**, 238 (1963). An FTI Model 1052 computer was used for time-averaging.

[2] As a consequence of the preparative procedure, the solution also contains 0.1 mole fraction of lithium iodide; *i.e.*, the solution was prepared by treating 57% carbon-13 enriched methyl iodide with butyllithium in hexane at 0°. Conversion to methyllithium was ~90% with ~10% coupling to give lithium iodide.

[3] R. Waack, M. A. Doran, and E. B. Baker, *Chem. Commun.*, 1291 (1967).

[4] An analogous multiplet pattern (and the same $J_{^{13}C-^{7}Li}$) is observed for solution of methyllithium in diethyl ether at −60°.

[5] T. L. Brown and J. A. Ladd, *J. Organometal. Chem.* (Amsterdam), **2**, 373 (1964).

[6] L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 2174 (1966).

[7] P. West and R. Waack, *ibid.*, **89**, 4395 (1967). Also, X-ray crystallographic studies show methyllithium to be a tetramer in the solid state: E. Weiss and E. A. C. Lucken, *J. Organometal. Chem.* (Amsterdam), **2**, 197 (1964).

[8] The absence of rapid intramolecular exchange of lithium is a hypothesis of the local environment model.[6]

[9] Line intensities are further statistically weighed by analogy with Table I, ref 6.

[10] The reported line intensity ratios for spectrum 1b are an average value for four different spectra. The line-intensity ratios for spectrum 1c were calculated for 57% ^{13}C enrichment (stick model). A calculation of the spectrum using Lorentzian line shapes and a half-width of 4.8 Hz is in good agreement with Figure 1c, indicating that overlap does not significantly alter relative line intensities.

[11] We are indebted to a referee for calling this point to our attention.

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Received March 18, 1968