$$\frac{Y}{F} = \frac{\left(\frac{(1/2)(k_2)}{k_2 + k_3P}\right)\left(\frac{k_1}{k_1 + k_M}\right)}{\left(\frac{(1/2)(k_2)}{k_2 + k_3P}\right)\left(\frac{k_1}{k_1 + k_M}\right) + \left(\frac{k_3P}{k_2 + k_3P}\right)\left(\frac{k_1}{k_1 + k_M}\right) + \left(\frac{k_M}{k_1 + k_M}\right)} \quad (7)$$

This equation can be inverted and simplified to show a linear pressure dependence, as in (8), and is actually

$$\frac{F}{Y} = \left[\frac{k_1 + 2k_M}{k_1}\right] + \left(\frac{k_1 + k_M}{k_1}\right)\left(\frac{2k_3}{k_2}\right)P \quad (8)$$

plotted in the form given in (9).

$$\frac{1}{Y} = \frac{1}{F}\left[\frac{k_1 + 2k_M}{k_1}\right] + \frac{1}{F}\left(\frac{k_1 + k_M}{k_1}\right)\left(\frac{2k_3}{k_2}\right)P \quad (9)$$

The intercept of Figure 2 is simply the reciprocal of the yield of $CHCl{=}CH^{38}Cl$ at zero pressure and has a value of about 5, or a fractional yield of $CHCl{=}CH^{38}Cl$ at zero pressure of 0.20, regardless of the values of F and (k_M/k_1).

The information desired from the slope ($=0.6$ cm^{-1}) of the straight line in Figure 2 is actually the ratio k_3/k_2, and is somewhat uncertain to the extent that the value of $(1/F)[(k_1 + 2k_M)/k_1]$ is known to be 5 from the slope, but what is needed is $(1/F)[(k_1 + k_M)/k_1]$. In one limit, $k_M << k_1$, the ratio $(2k_3/k_2)(5) = 0.6$ cm^{-1}, while in the other, $k_M >> k_1$, $(2k_3/k_2)(5/2) = 0.6$ cm^{-1}. Therefore, $0.06 \text{ cm}^{-1} \leq k_3/k_2 \leq 0.12 \text{ cm}^{-1}$. Actually, since F by definition cannot exceed unity, the intercept of 5 requires a finite upper limit of 2 for the ratio k_M/k_1, and an upper limit for k_3/k_2 of ≤ 0.10 cm^{-1}. From the intermediate value of $k_3/k_2 = 0.08$ cm^{-1}, and the assumption of deexcitation in a single collision, decomposition and stabilization of the trichloroethyl radical compete equally at 12 cm pressure, *i.e.*, $k_2 \cong 2 \times 10^9$ sec^{-1}.

A more exact calculation would require that the products from (1) + (3) be distinguished from those of (5), or from (6), in order to measure k_M and F.

The reaction rates of thermal Cl atoms with CH_3Cl and with $CHCl{=}CHCl$ in 35-fold excess of the former are estimated to be comparable, with a large uncertainty,[5,10] and $k_M/k_1 \sim$ unity is not an unreasonable value. Experimentally, isotopic ^{38}Cl exchange should be expected for $H^{38}Cl$ and any products of $^{38}ClO_2$ reactions.

A Nuclear Magnetic Resonance Study of Structure and Bonding in Methyllithium

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Abstract: Structure and bonding in methyllithium have been examined using carbon, lithium, and proton nuclear magnetic resonance measurements. The observation of ^{13}C–^{7}Li spin–spin coupling in tetrahydrofuran, ether, and triethylamine defines the structure of the methyllithium tetramer in these solutions. The small upfield displacement of the ^{13}C chemical shift of methyllithium (relative to methane) is interpreted as evidence for predominant sp^3 hybridization of carbon in this species. The use of existing linear relationships between ^{13}C chemical shifts and substituent electronegativity indicates that lithium in the tetramer is substantially more electronegative than atomic lithium. Similar relationships between charge density on carbon and ^{13}C chemical shifts for substituted methanes infer that charge separation in the carbon–lithium bond of methyllithium is $\sim$0.1 electron. Calculation of the ionicity of the carbon–lithium bond from Pauling's equation infers that bonding is predominantly covalent.

Abundant experimental evidence supports the use of nuclear magnetic resonance measurements as a probe for studying molecular structure and bonding. For example, the recently reported observation of ^{13}C–^{7}Li spin–spin coupling in methyllithium[1] provided novel evidence supporting the tetrameric structure suggested[2,3] for methyllithium in donor solvents.

Carbon-13 chemical shifts and ^{13}C–^{1}H coupling constants have been shown to be sensitive measures of the hybridization of the examined carbon. Such measurements have been used, for example, to study hybridization in arylmethyllithium reagents.[4] ^{13}C chemical shifts have further been shown to relate to charge density at carbon or electronegativity differences between carbon and a substituent X.[5]

We report measurements of ^{13}C, ^{7}Li, and ^{1}H chemical shifts for methyllithium in tetrahydrofuran, diethyl ether, and triethylamine solutions. These results are discussed in terms of the structure of methyllithium

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(1) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Am. Chem. Soc.*, **90**, 3244 (1968).

(2) R. Waack and P. West, *J. Organometal. Chem.* (Amsterdam), **5**, 188 (1966); *J. Am. Chem. Soc.*, 89, 4395 (1967).

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(5) See, *e.g.*, P. Bucci, *ibid.*, 90, 252 (1968).

Table I. Nuclear Magnetic Resonance of CH_3Li

Solvent	$\delta_{^7Li}$,[b] ppm	$\delta_{^{13}C}$, ppm Ext CS_2	Ext CH_4[f]	$\delta_{^1H}$ (int TMS),[g] ppm	$J_{^{13}C-^1H}$, Hz	$J_{^{13}C-^7Li}$, Hz
THF (7.4)[a]	-1.71[c]	$+209$[e]	$+13$	$+2.1$	98	15
Et_2O (4.3)	-1.33[d]	$+206$	$+10$	$+1.9$	99	15
Et_3N (2.4)	-1.71[c]	$+205$	$+9$	$+2.1$	97	15
THF/Et_2Zn[h]	$+1.30$	$+202$	$+6$	$+0.9$	116	..

[a] Dielectric constant (ϵ) at 25°. [b] Relative to external 0.5 *M* LiBr in THF. [c] δ_{measd} at $-80°$. [d] δ_{measd} at $-60°$. [e] $\delta_{^{13}C}$ is essentially temperature independent, *i.e.*, $\delta_{^{13}C}$ $+209.5$ at $-60°$. Note that ϵ (THF) at $-60° = 11$: C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965). [f] $\delta_{^{13}CH_4}$ $+195.6$ ppm (relative to external CS_2): H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1962). [g] It is noteworthy that the substantial upfield displacement from TMS of the protons of methyllithium is approximately twice that found for the α-H in other alkyllithiums. [h] CH_3Li/Et_2Zn ratio = 1:6; remainder of solution is THF. The methylene protons of Et_2Zn are shifted upfield 0.17 ppm in the CH_3Li complex relative to uncomplexed Et_2Zn. This chemical shift is not absolute but is an exchange average.

and the nature of carbon–lithium bonding. Bonding is discussed in terms of hybridization of carbon, charge distribution, electronegativity of lithium, and ionic character of the carbon–lithium bond.

Experimental Section

^{13}C INDOR[6] and ^7Li spectra were obtained on the previously described high-resolution nmr spectrometer.[7]

Methyllithium was prepared from 51–57% ^{13}C-methyl iodide (Merck Sharp and Dohme, Ltd.) by treatment with equimolar *n*-butyllithium in hexane solution. The temperature of the reaction mixture was raised from an initial -78 to $-30°$ where a cloudiness developed (methyllithium precipitation) and finally to 0° over a 20-min period. Vpc analysis using toluene as an internal standard indicated nearly complete conversion of *n*-butyllithium to *n*-butyl iodide. The methyllithium was centrifuged and then washed with two portions of hexane. Varying amounts of lithium iodide (~5% and less) were produced in these preparations.

Foote Mineral methyllithium (^{12}C) was also used in preparing samples examined in these studies.

All nmr samples were prepared on a vacuum line using solvents freshly distilled from lithium dispersions. Solution transfers were made under an argon atmosphere using Hamilton gas-tight syringes.

Results

^7Li, ^{13}C, and ^1H chemical shifts and ^{13}C–^1H and ^{13}C–^7Li spin-spin coupling constants for methyllithium in various solvents are given in Table I. Observed and calculated line intensity ratios for ^7Li nmr spectra are summarized in Table II.

Example ^7Li and ^{13}C spectra are shown in Figures 1–3. Figure 1 shows the ^{13}C-coupled ^7Li nmr spectrum in THF solution at $-80°$. Notable changes in line intensities arise from varying ^{13}C concentrations. In Figure 2, the ^7Li nmr spectrum in triethylamine solution at $-80°$ is shown. Figure 3 illustrates the ^{13}C INDOR spectrum of methyllithium in tetrahydrofuran solution. Splitting arises from coupling with the methyl protons. The proton spectrum in these 50% ^{13}C-enriched samples is a "triplet" in appearance. The ^{13}C satellites are symmetrically disposed about the central ^{12}C proton resonance. $J_{^{13}C-^1H}$ values are identical with those obtained from the ^{13}C INDOR spectrum.

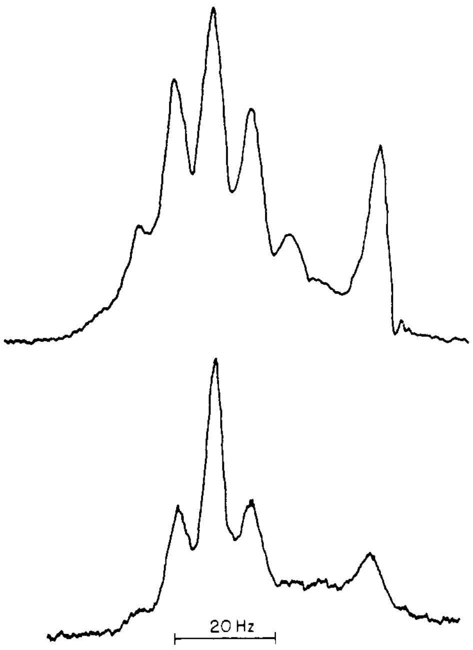

Figure 1. ^7Li nmr spectrum of ^{13}C-enriched methyllithium and lithium iodide in THF solution at $-80°$: upper, 51% ^{13}C enrichment; lower, 25% ^{13}C enrichment. High-field resonance is lithium iodide.

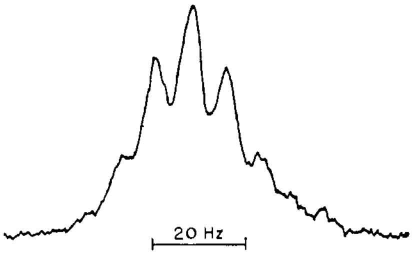

Figure 2. ^7Li nmr spectrum of 51% ^{13}C-enriched methyllithium in triethylamine solution at $-80°$.

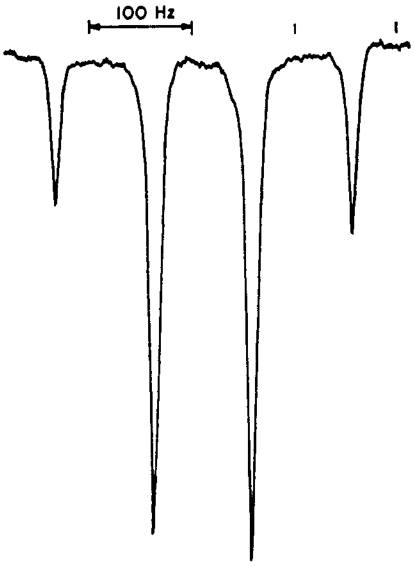

Figure 3. ^{13}C INDOR spectrum of methyllithium in tetrahydrofuran (0.6 *M*) at 27°.

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Table II. Line Intensity Ratios from ^{7}Li Nmr of CH_3Li

		Intensity ratios[a]		
Mole % ^{13}C	Solvent	Observed	Calcd 7-line	Calcd 9-line
25	THF	0.48, 0.10	0.44, 0.07 (0.53, 0.15)[b]	0.54, 0.13 (0.61, 0.21)[b]
51	THF	0.74, 0.34, 0.10	0.76, 0.31, 0.05 (0.78, 0.38, 0.12)[b]	0.81, 0.41, 0.12, 0.03 (0.83, 0.47, 0.18, 0.07)[b]
51	Et_3N	0.76, 0.35, 0.12	0.76, 0.31, 0.05 (0.78, 0.38, 0.12)[b]	0.81, 0.41, 0.12, 0.03 (0.83, 0.47, 0.18, 0.07)[b]

[a] Calculated for a stick model. Intensity ratios are relative to center line of multiplet which has a defined intensity 1.00. [b] Calculated spectrum using Lorentzian line shapes and a half-width of 5.0 Hz. The approximation, analogous to the stick model, favors the seven-line spectrum.

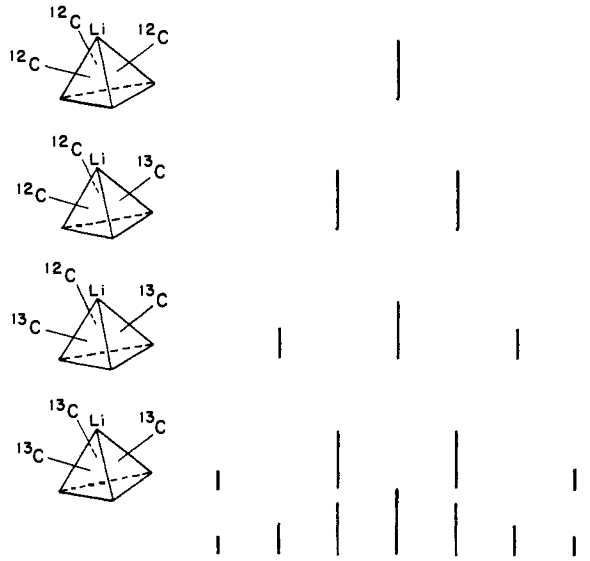

Figure 4. Methyllithium tetramer illustrating the fourfold environment which determines the multiplicity of the spectrum.

Discussion

The observation of ^{13}C–^{7}Li spin–spin coupling,[1] illustrated in Figures 1 and 2, provides novel and definitive evidence supporting a tetrameric structure[2] for methyllithium in each of the solvents. As indicated in Table I, these solvents span a range of dielectric constants and solvating capability. Clearly, the tetramer structure is preferred in these solvents. The agreement between calculated and observed spectra supports the concept that inter- and intraaggregate exchange is sufficiently slow such that the environment of each lithium is due to interaction with three adjacent methyl groups. These observations are in accord with the local environment hypothesis of Seitz and Brown.[3] By analogy with the crystal structure reported for methyllithium,[8] and earlier studies suggesting symmetrical tetrameric aggregates for alkyllithium species in solution,[9] the hypothesis, as illustrated in Figure 4, 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. Thus, each lithium interacts with three neighboring alkyl groups and *vice versa*. The absence of rapid intraaggregate exchange is further assumed. Occurrence of rapid intraaggregate exchange would lead to a different splitting pattern as discussed below.

As reported in Table II, the validity of the proposed structure for the methyllithium tetramer in solution is definitively tested using the ^{13}C–^{7}Li spin–spin coupling probe. Although X-ray studies established the structure of the tetramer in the solid state, this method provides a unique structure test for methyllithium in solution. The predicted seven-line spectrum which arises from the four distinct lithium environments (*i.e.*, intraaggregate exchange is slow on the nmr time scale) agrees well with the observed spectrum. The alternative fivefold lithium environment arising from the presumption of rapid intraaggregate exchange (each lithium would interact with a maximum of four carbon-13's) is predicted to give a nine-line coupling pattern. The intensities are similar but less agreeable with the observed ratios than the former model. Moreover, the outside lines of the nine-line model would not likely be discernible from noise.

It is noteworthy that the tetramer structure is preserved in triethylamine. Brown, Gerteis, Bafus, and Ladd[10] in contrast reported complex formation between ethyllithium and triethylamine in benzene in which increasing triethylamine concentration causes the ethyllithium hexamer to dissociate into a coordinated dimer. This may infer stronger aggregate bonding in methyllithium than in ethyllithium and warrants further study. Even the addition of the strong chelating agent TMEDA (tetramethylethylenediamine) to methyllithium (1:1) in THF solution did not disrupt the tetramer structure at low temperature. Hence, a duplicate of the coupling pattern in Figure 1 is observed. Addition of higher levels of TMEDA resulted in decomposition. Excess of the strongly interacting Lewis acid, diethylzinc,[11] presumably disrupts the tetrameric structure.[12] No ^{13}C–^{7}Li coupling was observed at temperatures as low as −100°. By analogy with methyllithium–dimethylzinc studies[12] facile alkyl group exchange among the complexes could also be responsible for the lack of observed coupling. The chemical shifts (Table I) change in the expected man-

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(10) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1966).

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(12) L. M. Seitz and T. L. Brown, *ibid.*, **88**, 4140 (1966).

ner. Complexation lowers the charge density on both the carbon and methyl protons; hence, a downfield shift (relative to methyllithium in pure THF) of both the ^{13}C and ^{1}H resonance was observed. The value of $J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ increases toward a more normal value for sp^{3} carbon. This is in accord with the suggested tendency of excess charge density to decrease $J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$.[4] The ^{7}Li chemical shift of the complex moves substantially upfield from methyllithium in pure THF. Such $\delta_{^{7}\mathrm{Li}}$ are characteristic of freer lithium (*e.g.*, lithium in arylmethyllithium reagents[4]) than lithium in alkyllithiums which are bound in tetrameric or hexameric electron-deficient aggregates.

Detection of ^{13}C–^{7}Li coupling at temperatures higher than −60° is considered to be limited by interaggregate exchange of methyllithium with itself or with lithium iodide "contaminant" in solution.[13] Coupling is observable but not well defined in THF at −45° and in triethylamine at −30°. Onset of the multiplet structure and hence separation into individual components occurs at a higher temperature in triethylamine, indicating that the exchange rate is slower in this medium. Also, lithium iodide is less soluble in triethylamine than in THF and precipitates from solution at reduced temperature. Examination of salt-free ^{13}C-enriched methyllithium could be fruitful since the temperature dependence of the spectrum should yield information on MeLi–LiI and MeLi–MeLi exchange.

Brown, Seitz, and Kimura[14] reported the absence of observable ^{6}Li–^{7}Li scalar coupling in alkyllithium compounds. This markedly contrasts the observed ^{13}C–^{7}Li scalar coupling[1] and has been interpreted[14] to infer a near-zero Li–Li bond order in the tetramer. These findings indicate that most of the bonding electron density is distributed in the region about the bridging alkyl carbon and that it is multiple bridge bonding betwee Li–C–Li, as contrasted with Li–Li bonding,[8] which results in aggregate formation. Accordingly, the cubic structure for the methyllithium tetramer, illustrated in Figure 5, would appear to be most suitable. Although essentially equivalent to the tetramer model of Figure 4, Li–C–Li bonding is better conceptualized. Precedent for such a cubic structure is found in an X-ray study of electron-deficient bonding in which Rundle[15] reported the tetramethylplatinum tetramer has a cubic structure.

The ^{13}C nmr spectrum of methyllithium in THF is illustrated in Figure 3. Notably, $\delta_{^{13}\mathrm{C}}$ (Table I) is only slightly upfield from that of methane. Owing to the symmetry of the methyllithium tetramer and the small size of lithium, $\delta_{^{13}\mathrm{C}}$ is not expected to be appreciably affected by the magnetic anisotropy of lithium.[16]

In previous studies[4] of arylmethyllithium reagents, in which there is appreciable electron delocalization, substantial differences between the ^{13}C chemical shift of the lithium reagent and the corresponding hydrocarbon were observed. The downfield shifts of the organolithium relative to the hydrocarbon were explained to be a consequence of substantial sp^{2} hybridization of the carbon bound to lithium.

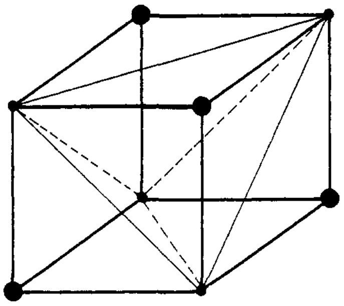

Figure 5. Cubic structure of the methyllithium tetramer. Large spheres represent the carbon atoms of the methyl groups, and small spheres represent lithium atoms.

Based on the ^{13}C chemical shift, predominant sp^{3} hybridization of carbon in methyllithium is inferred. Furthermore, excess charge density on carbon is indicated to be small.

The relationship between charge density and ^{13}C chemical shift of sp^{2}-hybridized carbon was evaluated to be ~160 ppm/electron.[17] Theoretical treatments suggest an analogous relationship for sp^{3} carbon,[18] and the proportionality constant is indicated to be of similar magnitude. It follows from the similarity of $\delta_{^{13}\mathrm{C}}$ of methyllithium with that of methane that excess charge density on carbon in methyllithium cannot be large, implying that bonding is primarily covalent. Presuming charge density on sp^{3} carbon affects C shielding to an extent similar to its effect on sp^{2} carbon,[18] the estimated fractional excess charge density at carbon in methyllithium over that in methane is ~0.1 electron. A possible small contribution to the difference between the chemical shift of methyllithium and methane could be deviation of carbon hybridization in methyllithium from that in methane. The significant point is that the charge separation in methyllithium is indicated to be small. This is supported by the following considerations.

In a recent study, Sichel and Whitehead[19] used extended Hückel theory to calculate charge distributions in a series of substituted methanes. It was demonstrated that the carbon chemical shift in methyl derivatives, CH_3X, was approximately linear with the computed charge on methyl carbon. This correlation of chemical shift with charge density on carbon is consistent with the conclusion that the ^{13}C shift value implies only a small amount of excess negative charge on methyllithium carbon relative to methane. A recent report of theoretical studies[20] of methyllithium pro-

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(16) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1962).

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(20) A. H. Cowley, Abstracts, 3rd International Symposium on Organometallic Chemistry, Munich, Germany, Aug 1967, p 64.

posed the excess charge density on carbon to be of the order of 0.3 electron, a value somewhat higher than that estimated from the ^{13}C chemical shift.

Several authors have presented correlations of ^{13}C chemical shifts with substituent electronegativity for a series of CH_3X derivatives. Comparison of the methyllithium ^{13}C chemical shifts indicates the electronegativity of lithium in the bridge bonded aggregate to be substantially larger than the Pauling or other values.[21] From a series of CH_3X, where X is a first-row element, a value of 1.5[16] and, from an equation based on a more encompassing series,[5] a value of 1.6 are obtained for the effective electronegativity of lithium (Pauling scale) in the electron-deficient aggregate. By comparison, the Pauling electronegativity of atomic lithium is 1.0. Using the value of ~1.5 for the electronegativity of lithium (and 2.5 for that of carbon), a value of 17% ionic character is calculated[22] for the carbon–lithium bond in methyllithium in ether solution. This contrasts with 35–40% ionic character[23] calculated using the electronegativity of atomic lithium and the 27% ionic character calculated by Ebel.[24]

As reported in Table I, the value of $J_{^{13}C-^{1}H}$ of methyllithium is appreciably smaller than that usually found for sp^3 hybrids.[25] To some extent, the negative charge is indicated to cause small $J_{^{13}C-^{1}H}$ values.[4,26] Presuming the charge is not the only cause of the small $J_{^{13}C-^{1}H}$, the value infers more p character (than in sp^3) to the carbon–hydrogen orbitals, leaving the carbon–lithium orbital high in s character, *i.e.*, ~40%.[27] It seems reasonable that increased s character of this orbital allows better overlap in the composite orbital formed between carbon and the three lithium orbitals. On the other hand, changes in effective nuclear charge can contribute to changes in carbon–proton coupling.[28]

The conclusions regarding the nature of the carbon–lithium bond in methyllithium are expected to be general and relate to other alkyllithium reagents.

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On the Kinetics and Mechanism of the Decomposition of Hydrogen Peroxide, Catalyzed by the Cu^{2+}–2,2′-Bipyridyl Complex[1,2]

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Abstract: The decomposition of H_2O_2, catalyzed by the Cu^{2+}–2,2′-bipyridyl system, was investigated by measuring the initial velocity, v_0, of the decreasing concentration of H_2O_2 (25°). The results found can be summarized in the equation $v_0 = -d(H_2O_2)/dt = k[Cu(bipy)][H_2O_2]^2/[H^+]$. A mechanism which is in accord with this equation is discussed as is the structure and the subsequent reactions of the probable active complex. The proposed mechanism can be written without the formulation of *free* radicals.

The systematic investigation of the decomposition of H_2O_2 (eq 1), catalyzed by Cu^{2+} complexes as well as

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \qquad (1)$$

catalase, showed that Cu^{2+} complexes are catalytically active only if the coordination sphere is not saturated by the ligand.[3] This result gives evidence that ternary Cu^{2+}-peroxo-ligand complexes are involved during the reaction. Indeed these can be demonstrated by spectrophotometric measurements.[3,4]

Investigations of the kinetics of the Cu^{2+}–ethylenediamine–H_2O_2 system showed that in this case the reaction probably goes over a binuclear complex,[5] while in the phosphate-buffered Cu^{2+}–histamine–H_2O_2 system, probably a monomeric complex is involved.[6] To learn more about the mechanism of such a catalysis, we investigated the kinetics of the decomposition of H_2O_2 with the Cu^{2+}–2,2′-bipyridyl system as a catalyst.

Experimental Section

2,2′-Bipyridyl and $Cu(ClO_4)_2 \cdot 6H_2O$ were from Fluka AG, Buchs,

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