Notes

Isolation, Characterization, and Crystal Structure of [MeLi·THF]$_4$

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Received November 25, 1992

Summary: The single-crystal X-ray structure of [MeLi·THF]$_4$ has been determined at 194 K. The lithium atoms are arranged in a tetrahedron with methyls capping each face and a THF coordinating to each lithium. The heat of combustion has been determined to be 9400 ± 300 kcal/mol.

Alkyllithium reagents are some of the most versatile of organometallic reagents, rivaled only by Grignard reagents in their utility.[1] Although it has been accepted for many years that the structure and reactivity of alkyllithium reagents are closely related, it has only recently become evident why this is so. Alkyllithium reagents are generally aggregated, usually as dimers, tetramers, and hexamers.[2,3] The degree of aggregation depends on several factors: steric bulk, temperature, charge delocalization, and solvent basicity. Lower aggregation numbers are favored by bulkier alkyl groups, delocalization of charge, and polar solvents.[2,3] The rule of thumb is that as the aggregation number decreases, reactivity increases. The most dramatic increase in reactivity has been found for the addition of basic solvents such as tertiary amines and ethers.[2,3] This has been attributed principally to the peptizing of the alkyllithium aggregates. It has been forcefully argued that aggregation effects alone do not explain this dramatic difference in reactivity observed in basic solvents.[4] For example, in THF, *n*-butyllithium dimer is only 10 times more reactive than *n*-butyllithium tetramer.[5] This solvent effect is attributed to the transition state being stabilized, the lithium being more highly solvated in the transition state.[6] This has been demonstrated using computational chemistry.[4]

The simplest alkyllithium, methyllithium, is insoluble in hydrocarbon solvents but is readily soluble in ethereal solvents. Methyllithium is known to exist only as a tetramer in ethereal solvents; even the bidentate ligand, TMEDA, fails to break apart the tetrameric aggregate.[7] Methyllithium has been characterized by NMR spectroscopy,[8] mass spectroscopy,[9] X-ray[10] and neutron powder diffraction[11] of polymeric MeLi, and single crystal X-ray crystallography of the TMEDA complex.[7] The monomer, dimer, trimer, and tetramer of methyllithium have been studied computationally.[12] Computational studies have been carried out describing the reaction of methyllithium with ethylene[13] and formaldehyde.[14] Here we report the characterization, isolation, and some properties of [MeLi·THF]$_4$, 1.

Results

Crystalline 1 is obtained by crystallization from a MeLi solution in cumene/THF. Single crystal X-ray analysis reveals the methyllithium to be tetrameric, Figure 1. The lithium atoms are arranged in a tetrahedral array with the methyllithium aggregate sitting on a crystallographic 2-fold axis. The interatomic distances are very typical for alkyllithium tetramers: Li–Li 2.502(4), 2.488(6), 2.502(7), and 2.523(5) Å; Li–O 1.969(4) and 1.948(5) Å; Li–C 2.230(5), 2.248(4), 2.228(5), 2.242(5), 2.241(5), and 2.253(5) Å.

Crystals of 1 are surprisingly nonpyrophoric in air[15] compared to methyllithium uncomplexed. Elemental analysis of these crystals revealed them to contain about

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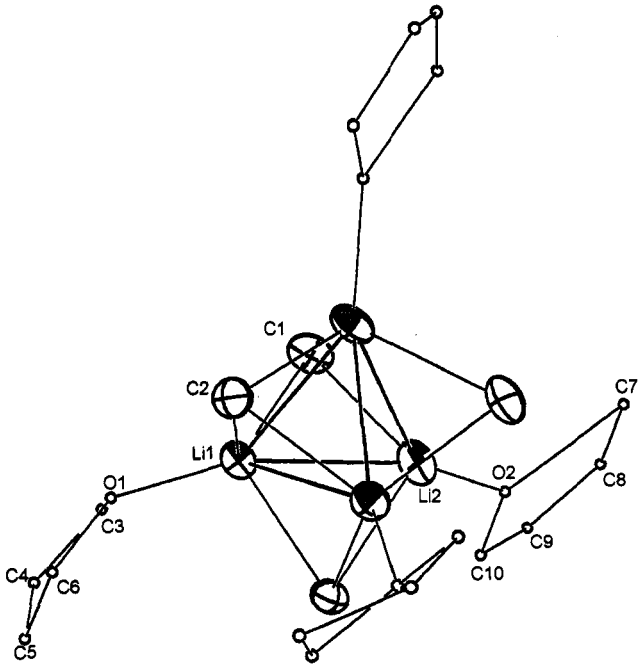

Figure 1. ORTEP drawing of $[MeLi{\cdot}THF]_4$ (1). The hydrogens have been omitted for clarity. The disordered methylenes of the THF are drawn in an average position.

Table I. Selected Interatomic Distances for 1, $[MeLi{\cdot}THF]_4$, and Other Methyllithium Structures

	1[a]	$(MeLi)_4$[10,b]	$(CD_3Li)_4$[11,c]	$(MeLi)_4{\cdot}2TMEDA$[7,b]
Li–Li (Å)	2.51	2.68	2.59	2.56
Li–C (Å)	2.24	2.33	2.26	2.26
Li–O (Å)	1.96			
Li–N (Å)				2.21
Li–C–Li (deg)	68.1		70.1	

[a] 194 K. [b] Room temperature. [c] 1.5 K.

0.90% inorganic chloride.[16] This suggests that lithium chloride either crystallizes out with 1 or a mixed aggregate with methyllithium forms between MeLi and LiCl, 2, $[Me_3Li_4Cl(THF)_4]$.[17] We speculate that the mixed aggregate, 2, having similar size and shape to 1, cocrystallizes with 1. If the chloride is in the form of 2, one in ten of the $[MeLi{\cdot}THF]_4$ would be replaced by 2. Not surprisingly, this cannot be detected in the X-ray structure; however the ^1H and ^7Li NMR spectra at low temperature support this. There is a small peak upfield from the resonances associated with 1 in both ^1H and ^7Li NMR spectra at −80 °C.[19] A tabulation of ^1H, ^7Li, and ^{13}C NMR spectra of 1 in benzene and THF is presented in Table II.

The heat of combustion for crystalline 1 in mineral oil has been determined to be 9400 ± 300 cal/g, Table III.

Discussion

The ^1H and ^{13}C NMR spectra of 1 show a fairly dramatic upfield shift when the solvent is changed from benzene to THF, while the ^7Li signal moves downfield, Table II. Because there does not appear to be space for the coordination of another THF, we do not expect the inner coordination sphere to add another THF on going from benzene to THF. The upfield shift of the ^7Li signal and downfield shifts of the ^1H and ^{13}C signals may be due to the partial displacement of the coordinating THF by benzene,[20] or this difference in chemical shifts may result simply from the difference in the polarity of the solvents.

The lithium atoms are arranged in a tetrahedron with an average Li–Li distance of 2.50(2) Å. A methyl caps each face of the tetrahedron, with an average C–Li bond distance of 2.24(1) Å. There is a THF molecule coordinated to each Li with an average Li–O distance of 1.96(1) Å. A comparison of interatomic distances to similar structures is given in Table I. We note that the Li–Li and the Li–C distances are shorter in the solvated methyllithium structures. The Li–C–Li angle is more acute, making the distance from the methyl to the face of the tetrahedron slightly larger in 1. With the crystallographic data we could neither confirm nor refute the presence of 2 in the solid state.

The crystal of 1 is found to be disordered. Three of the methylenes of the THF and the methyl hydrogens are disordered over two sites. Close examination of the Fourier map has allowed the disorder problem to be solved. The methyl hydrogens are found to be both staggered and eclipsed with respect to the three lithium atoms of the corresponding face of the lithium tetrahedron. An ORTEP[21] plot of one of the methyls on the face of the tetrahedron shows clearly these two conformations, Figure 2.

There has been much interest in the arrangement of the hydrogen atoms around the methyl in methyllithium. One of the first concerns expressed by Weiss in the X-ray powder structure of methyllithium[10] is the position of the methyl hydrogens. This eventually led to the neutron powder diffraction study of CD_3Li at low temperatures.[11] Weiss' crystal data indicate that the carbon bonded to the lithium is pyramidal and the hydrogens are staggered with respect to the triangular lithium face. Schleyer's MNDO

Table II. NMR Chemical Shifts (δ) of 1 in Benzene-d_6 and THF-d_8 at Ambient Temperature

solvent	^1H NMR (H_3CLi)	^{13}C NMR (H_3CLi)	^7Li NMR
benzene-d_6[a]	−1.20	−14.75	2.65
THF-d_8	−2.07	−15.45	3.01

[a] ≈10 μL of THF-d_8 was added to 500 μL of C_6D_6 to clarify the 0.5 M solution.

Table III. Heat of Combustion of 1

run	wt (g) of consumed fuse wire	wt (g) gelatin capsule	wt (g) of mineral oil	wt (g) of 1	ΔT (°C)	ΔH_{comb}(1)[a]
1	0.0100	0.1021	0.2563	0.1944	2.124	9320
2	0.0070	0.1127	0.3359	0.2194	2.631	9635
3	0.0152	0.1187	0.2289	0.1443	1.847	9445
8	0.0186	0.1513	0.3745	0.3409	3.336	9375

[a] Calculated from the following equation: $\Delta H_{comb}(1) = W(\Delta T) - wt(oil)[\Delta H_{comb}(oil)] - wt(gel\ cap)[\Delta H_{comb}(gel\ cap)] - wt(wire)[\Delta H_{comb}(wire)]$. $W_{(bomb)}$ = 2422 ± 9 cal/°C; ΔH_{comb}(mineral oil) = 11 090 ± 160 cal/g; ΔH_{comb}(gel cap) = 4670 ± 50 cal/g; ΔH_{comb}(wire) = 1400 cal/g.

(16) Analysis of the methyllithium crystals was accomplished by ICP. The original solution contained less than 0.3% lithium chloride and about 0.5% dimethylmagnesium. The crystals were found to contain ~100 ppm magnesium, probably from the surface of the crystals.

(17) Mixed aggregates between MeLi and LiBr (Me_3Li_4Br and $Me_2Li_4Br_2$) have been observed previously by Brown.[18]

(18) Novak, D. P.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 3793.

(19) The resonance for the methyl hydrogens of 1 in THF at −80 °C in the ^1H NMR is δ −2.05 and the ^7Li signal is at δ 0.0 (arbitrarily assigned). The signal that we assign to 2 in the ^1H NMR is at δ −2.18. The ^7Li signals are at δ −0.11 and −0.96 in a ratio of 1:3, respectively. The addition of LiCl caused an increase in the signals we attribute to 2. It is interesting to note that even with the addition of large excesses of LiCl we see no evidence for the formation of $Me_2Li_4Cl_2$.

(20) We would like to thank the referee for suggesting this.

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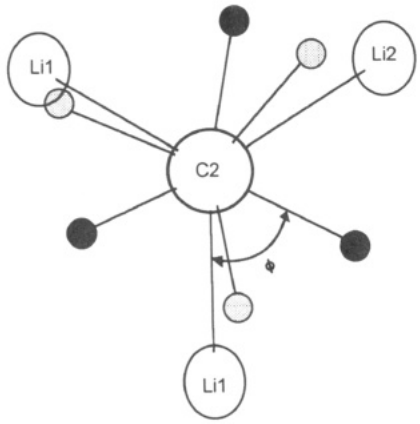

Figure 2. ORTEP drawing of the methyl (C2) on the corresponding triangular face of the lithium tetrahedron. The hydrogens of the methyl are disordered. Both settings are shown. Key: staggered hydrogens (black), eclipsed hydrogens (gray).

and ab initio calculations have suggested that in the gas phase, the eclipsed conformation is favored over the staggered conformation by ≈7 kcal/mol for the unsolvated methyllithium tetramer. This preference for the eclipsed conformation is thought to be largely an agostic interaction between the lithium and the hydrogen.[12] Schleyer argues that the deviation of the experimental structure from the theoretical gas phase structure is due to crystal forces. The methyls of adjoining tetramers are coordinating with lithiums of an adjacent tetramer.

Computationally, the situation is different for solvated methyllithium. Schleyer has calculated that in the ammonia-solvated methyllithium tetramer the staggered conformation is more stable than the eclipsed conformation.[12] It is interesting that in the crystal structure of **1**, both conformations are present and equally populated, indicating that they are close in energy. This agrees with our MNDO[22] calculations on $[MeLi{\cdot}THF]_4$ which indicate that the staggered conformation and the eclipsed conformation become very close in energy with the staggered rotamer slightly more stable than the eclipsed rotamer.[23] The calculations on the various rotamers indicate that although there are local energy minima near the staggered and eclipsed conformations the energy surface is rather flat, Figure 3. This is contrasted to the energy surface for the methyl rotation in $[MeLi{\cdot}NH_3]_4$ where there is only one energy minimum centered at the staggered positions, Figure 3. Space-filling models of **1** in both settings make it apparent that there are no steric reasons for the difference in energies between the two conformations.

The value obtained for the heat of combustion of **1** (ΔH_{comb} = 9400 ± 300 cal/g) leads to a calculated ΔH_f of −196 kcal/mol for **1** or −49 kcal/mol per monomeric unit, MeLi·THF. Unfortunately, we could not obtain ΔH_f for the unsolvated MeLi to enable us to determine the ΔH_{sol}. By taking the experimentally determined ΔH_f for THF, −51.67 kcal/mol,[24] and assuming that ΔH_{sol} is approximately −8 kcal/THF,[25] we estimate a ΔH_f for MeLi of +11 kcal/mol. This value seems to be reasonable, fitting the trend of the experimental values obtained for ΔH_f for liquid *n*-BuLi (−31.6 kcal/mol) and for crystalline EtLi (−14.0 kcal/mol).[24]

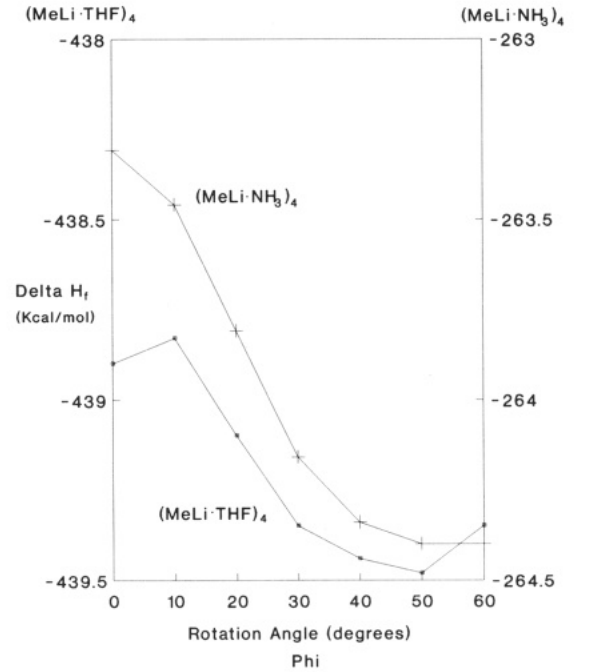

Figure 3. Plot of calculated MNDO energies vs the "dihedral" angle, ϕ, for the methyl hydrogens with the lithium for $[MeLi{\cdot}THF]_4$ and $[MeLi{\cdot}NH_3]_4$.

Experimental Section

The methyllithium solution, MeLi-9307, was obtained from the Lithium Division of FMC. The NMR solvents, THF-d_8 (Cambridge Isotopes Lab) and benzene-d_6 (Aldrich Chemical Co.), were distilled under nitrogen from sodium/potassium alloy (20/80). NMR spectra were obtained on a 7.1-T, broad-band QE300 NMR instrument operating at 300.2 MHz for proton, 75.4 MHz for ^{13}C, and 116.2 MHz for ^{7}Li. Proton chemical shifts are reported relative to residual protic benzene (δ 7.15). Carbon chemical shifts are reported relative to the benzene carbon signal (δ 128.5). Lithium chemical shifts are relative to external LiCl (1.0 M in D_2O; δ 0.0).

Crystals of **1** were obtained by cooling the methyllithium solution in a refrigerator or freezer for several days, at 3 °C; about 20% of the methyllithium crystallizes out. The crystals were separated from the solution by filtering at −50 °C under nitrogen. After the filtration was completed, the crystals were pumped to dryness on the frit at −50 °C. The crystals for X-ray crystallography were kept cold while oil[28] was allowed to cover them. At ambient temperature, in the air, an appropriate crystal was selected from these oil-coated crystals using a stereomicroscope. The oil coating became the glue to cement the crystal to the fiber at low temperature on the diffractometer. Samples for the NMR and combustion studies were removed from the frit in a drybox at ambient temperature. In an attempt to obtain methyllithium without coordinated solvent,[29] crystals of **1** were

(22) J. J. P. Stewart, MOPAC: version 6.0, QCPE, p 455.
(23) The MNDO values we obtained for ΔH_f for **1** with the H's fixed staggered and eclipsed were −439.32 and −438.90 kcal/mol, respectively.
(24) *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed., McGraw-Hill Book Co.: New York, 1985.
(25) ΔH_{sol} values for several organolithium compounds by THF have been measured. These range from 7 to 10 kcal/mol.[26] MNDO calculations on alkyllithium THF complexes also suggest a heat of solvation in this range.[27]
(26) Quirk, R. P.; Kester, D. E.; Delaney, R. D. *J. Organomet. Chem.* **1973**, *53*, 45. Quirk, R. P.; McFay, D. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 827.
(27) Kaufmann, E.; Gose, J.; Schleyer, P. v R. *Organometallics* **1989**, *87*, 2577.
(28) A mixture of one part paratone oil and three parts mineral oil was used to coat the crystals to keep the crystals from reacting with air.
(29) Methyllithium can be obtained without solvent by reaction of *n*-butyllithium with methyl iodide in hexane, but this procedure has not been optimized to reduce the amount of LiI present. See: Rathman, T.; Morrison, R. C., U.S. Pat. 4976886. Methyllithium can be prepared reasonably free of solvent from Me_2Hg and Li.[10,11]

crushed into a very fine powder with an agate mortar and pestle under N_2. We were unable to completely remove the coordinated THF from the powdered MeLi even after 3 weeks at reduced pressure, 10^{-2} T.

Combustion Data. All calorimetry trials were performed with a Series 1300 calorimeter and a Model 1101 double valve bomb from Parr Instrument Co. The combusion was carried out at 35 atm of oxygen as described in the Parr manual (No. 148). The heat capacity of the bomb (2422 ± 9 cal/°C) was determined using a benzoic acid standard. The heats of combustion of the mineral oil (11 090 ± 160 cal/g) and gel capsules (4670 ± 50 cal/g) were each determined in five separate experiments. All weighings were carried out in a drybox and weighed to the nearest 0.1 mg. In a glovebox, crystals of 1 (≈200 mg) were placed in a preweighed 000 size gelatin capsule and covered with mineral oil (≈200 mg) to protect from the air. After the gelatin capsule was removed from the glovebox, a loop of the ignition wire (1400 cal/g) was slipped into the capsule. The heat of combustion of 1 was determined by subtracting out the contributions from the consumed fuse wire, gelatin capsule, and mineral oil.

X-ray Data. A clear colorless, irregular shaped crystal of 1 ($C_{20}H_{44}Li_4O_4$, 376.34 amu) covered with oil (0.32 × 0.26 × 0.18 mm) was selected and mounted on a glass fiber; the oil served to fasten the crystal to the fiber, freezing in the nitrogen cold stream. The X-ray diffraction data were collected at 193 ± 1 K on an Enraf-Nonius CAD4 diffractometer [Mo Kα (λ = 0.709 30 Å)] with a graphite monochromator. The data indicated the monoclinic space group, $C2/c$, with Z = 4. The final cell parameters were a = 17.177(2) Å, b = 8.686(1) Å, c = 19.233(2) Å, and β = 116.89(1)° with a volume of 2559(1) Å^3, giving a calculated density of 0.98 g cm^{-3}. A $\theta/2\theta$ scan with variable scan rate, collected to 2θ = 56.0°, was used to collect 3317 unique reflections. Of these, 1319 having $F_0^2 > 3.0\sigma(F_0^2)$ were used to solve and refine the structure. The background was obtained from the analysis of the scan profile.[30] An empirical absorption correction was applied (from 0.898 to 0.998 on **I**). Scattering factors for neutral atoms and the values for $\Delta f'$ and $\Delta f''$ were taken from ref 31 and the computer program MolEN.[32]

Direct methods were used to solve the structure.[33] A full-matrix least-squares refinement gave R = 0.055 and weighted R = 0.069. The largest residual peak in the final electron density difference map was 0.23(4) e/Å^3. The methyl hydrogen atoms were disordered over two sites and refined with isotropic thermal parameters. Refinement of the occupancy parameter of the methyl hydrogens failed to improve the refinement. The final refinement assumed 50% occupancy.[34] Three methylene groups of the THF molecules were also disordered over two sites. The other hydrogen atoms in the structure were refined isotropically. Attempts to refine the structure in the noncentric space group (Cc) did not improve the R value, and many parameters became unreasnable.

Complete lists of final atomic positions, atomic thermal parameters, bond distances, and bond angles are available in the microfilm edition of this journal. This material as well as observed and calculated structure factors have been deposited with the Cambridge Crystallographic Database. These lists may also be obtained directly from A.A.P.

Acknowledgment. C.A.O. would like to thank the National Science Foundation for their generous support for this research, Grant No. CHEM882154, and the North Carolina Supercomputer Center for computer time. We would also like to thank the Lithium Division of FMC for the donation of organolithium compounds. A.A.P. would like to thank the College of Arts and Sciences of the University of Toledo for their support of the X-ray laboratory.

Supplementary Material Available: Textual presentation of experimental data and tables of positional parameters, thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

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(32) Fair, C. K. *MolEN, An Interactive Intelligent System for Crystal Structure Analysis, User's Manual*; Enraf-Nonius: Delft, The Netherlands, 1990.

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(34) These methyls were calculated to not interact significantly with each other, so the methyls should be considered independently. This gives an energy difference of 0.15 kcal per CH_3, giving a predicted ratio of 60:40, very close to the 50% occupancy.