complexes are apparently stronger Lewis acids and are unisolable as such.

Registry No. 1, 94620-67-4; **2**, 94620-68-5; **3**, 94620-69-6; [(η^5-C$_5$H$_5$)W(NO)I$_2$]$_2$, 71341-43-0; [(η_5-C$_5$H$_5$)Mo(NO)I$_2$]$_2$, 12203-25-7; ClMgCH$_2$SiMe$_3$, 13170-43-9; ClMgCH$_2$CMe$_3$, 13132-23-5; (η^5-C$_5$H$_5$)Mo(NO)Me$_2$, 94620-70-9; (η_5-C$_5$H$_5$)Ru(NO)Me$_2$, 94620-71-0.

Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for **1** (3 pages). Ordering information is given on any current masthead page.

X-ray Photoelectron Spectra of Methyllithium and Dilithiomethane

Gregory F. Meyers,[1a] Michael B. Hall,*[1a]
John W. Chinn, Jr.,[1b] and Richard J. Lagow*[1b]

*Departments of Chemistry, Texas A&M University
College Station, Texas 77843
University of Texas, Austin, Texas 77812*

*Received October 4, 1984
Revised Manuscript Received December 20, 1984*

Introduction. The degree of ionic character in carbon–lithium bonds continues to be controversial. From a practical standpoint organolithium compounds are often employed in nucleophilic additions as lithium salts of the corresponding carbanion.[2] From a theoretical standpoint, however, debate has centered on just how to partition electron density between C and Li atoms in organolithium compounds.[3]

Both semiempirical and ab initio calculations have been used to describe bonding in methyllithium monomers and aggregates. Bonding descriptions have ranged from covalent C–Li bonds with little charge separation to purely ionic bonds with complete charge separation. In the former description, aggregation occurs via electron deficient, multicenter interactions.[4] In the latter description, aggregates are held together by Coulombic forces.[5]

Although the structure of methyllithium has been known for some 20 years,[6a] little direct experimental evidence of C and Li charges has been forthcoming. As yet the structure of dilithiomethane is unknown. Here we report results of core level X-ray photoelectron spectra of CH$_3$Li and CH$_2$Li$_2$. For both compounds we observe single carbon and lithium environments. These results are in accord with recent ^{13}C solid-state NMR studies of the title compounds.[7]

Experimental Section. Methyllithium (bulk purity 100%) and dilithiomethane (bulk purity 96%)[8] were pressed from powders

(1) (a) Texas A&M University. (b) University of Texas at Austin.

(2) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: New York, 1974.

(3) (a) Lipscomb, W. N.; Graham, G. D.; Marynick, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 4572. (b) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 5818.

(4) (a) Cowley, A. H.; White, W. D. *J. Am. Chem. Soc.* **1969**, *91*, 34. (b) Peyton, G. R.; Glaze, W. H. *Theor. Chim. Acta* **1969**, *13*, 259.

(5) (a) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (b) Baird, N. C.; Barr, R. F.; Datta, R. K. *J. Organomet. Chem.* **1973**, *59*, 65.

(6) (a) Weiss, E.; Lucken, E. A. C. *J. Organomet. Chem.* **1964**, *2*, 197. (b) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265.

(7) Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J.; Steinfink, H.; Yannoni, C. S. *Inorg. Chem.* **1984**, *23*, 3717, in press. The ^{13}C chemical shift for CH$_3$Li is 16 ppm upfield from Me$_4$Si while that for CH$_2$Li$_2$ is 10.5 ppm downfield from Me$_4$Si.

(8) Both compounds were prepared from published procedures.[7] Bulk purities were determined by D$_2$O hydrolysis. CH$_3$Li (3%) was a minor impurity in CH$_2$Li$_2$.
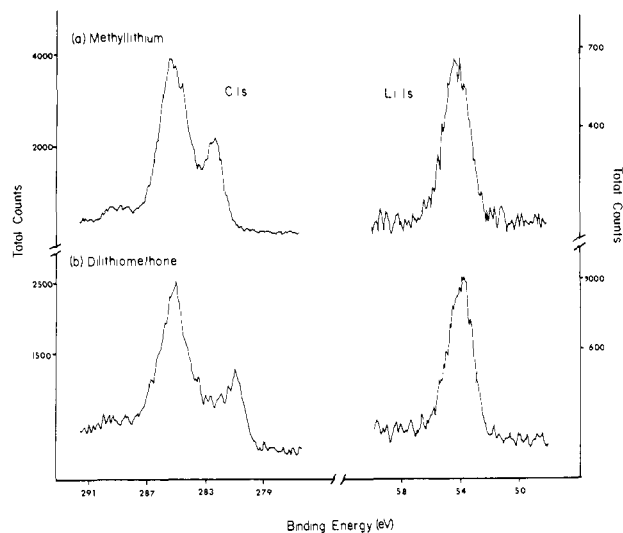
Figure 1. C 1s and Li 1s photoelectron spectra of (a) methyllithium and (b) dilithiomethane. Contaminant hydrocarbon at 285.0 eV is used as a reference.

into pellets in an argon-filled drybox[9] attached directly to the spectrometer. Core level XPS spectra were recorded on a H-P5950A ESCA spectrometer using monochromatic Al Kα radiation (1486.6 eV).[10] Sample exposure time to the X-ray was kept to a minimum without sacrificing signal intensity. No visible degradation of the samples or spectra was noted. There was less than 10% change in relative intensities during the sample analysis period. To ensure reproducibility spectra were recorded with fresh samples at a later date. The standard deviation in binding energies observed for replicate runs was ca. ±0.2 eV.

Results and Discussion. The C 1s and Li 1s core spectra are shown in Figure 1. CH$_3$Li exhibits three C 1s ionizations while CH$_2$Li$_2$ shows only two. The dominant carbon species at 285.0 eV in both spectra is due to residual hydrocarbon from pump oil in the vacuum system. This was verified by comparison of intensity for the same carbon species found in C 1s spectra of LiCl.[11] A weak contribution due to carbonate carbon was also observed in the CH$_3$Li spectrum at 288.7 eV.[12] Experimental C 1s binding energies for the title compounds are readily observed at 282.6 eV for CH$_3$Li and at 280.9 eV for CH$_2$Li$_2$. Additionally, only one Li 1s ionization is observed at 54.0 eV for CH$_3$Li and 53.9 eV for CH$_2$Li$_2$.

Significantly, we observed only one type of low-binding-energy carbon and lithium environment in both compounds. For CH$_3$Li

(9) Vacuum Atmospheres HE-493 equipped with recirculating Dri-Train. Atmosphere integrity was monitored by measuring filament lifetimes of exposed 40-W bulbs (14–24 h) and exposure of Na–K alloy beads, which fogged only after several hours.

(10) Beam power was 800 W. Flood gun settings were determined by gold decoration of samples and then adjusting the flood gun current and energy so that the Au 4f$_{7/2}$ level appeared at 84.0 eV. The spectrum of the undecorated sample was then determined with the same flood gun settings. For CH$_3$Li the flood gun was set at 0.64 eV and 3.00 mA. CH$_2$Li$_2$ was conducting and did not require the use of the flood gun. This procedure was checked by recording the Li 1s and Cl 2p core binding energies for LiCl which were found to be 55.9 eV and 198.5 eV (weighted average Cl 2p), respectively, in excellent agreement with published values: Morgan, W. E.; Van Wazer, J. R.; Stec, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 751.

(11) When normalized to the same scan time, the relative ratios of adventitious carbon in LiCl to CH$_3$Li and CH$_2$Li$_2$ were determined to be 1.6 and 2.2, respectively, based on spectral deconvolution (Gaussian fit routine, Surface Science Laboratories) and atomic cross sections from: Andrade; J. D.; Doyle, C.; Elliot, I. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *28*, 303.

(12) Additionally, two O 1s ionizations were observed for both compounds (spectra not shown) occuring at 531.6 eV and 528.7 eV. These are readily explained by the presence of surface hydroxide and carbonate (CH$_3$Li spectrum only) in the higher binding energy band and surface oxide in the lower energy band. The intensity of the former decreased while the latter gained intensity with time, suggesting dehydration of the hydroxide to surface oxide. Similar results are observed for reactions of clean polycrystalline Li films with residual gas under UHV conditions. See: Hoenigman, J. R.; Keil, R. G. *Appl. Surf. Sci.* **1984**, *18*, 207.

Table I. Binding Energies, Chemical Shifts, and Calculated Charges

compd	C 1s BE, eV	C 1s shift, eV	calcd q_C	Li 1s BE, eV	calcd q_{Li}
C_3H_6	285.0[a]	0.0	−0.03		
CH_3Li	282.6	−2.4	−1.02	54.0	+0.86
CH_2Li_2	280.9	−4.1	−1.55[b]	53.9	+0.71[b]
			(0.07)		(0.04)

[a] Used as reference. [b] Average of monomer, dimer, and trimer structures (see text). Standard deviation in parentheses.

this is to be expected both from the structure[6] and the observation of a single line in the solid state ^1H- and ^6Li-decoupled ^{13}C NMR spectrum for $CH_3{}^6Li$.[7] For CH_2Li_2 the presence of one carbon environment is also supported by a single line in the ^{13}C NMR spectrum of $CH_2(^6Li)_2$.[7] Furthermore, the direction of the C 1s core level shifts and ^{13}C chemical shifts suggests an increased charge density of the methylene carbon in CH_2Li_2.[7] Our results also indicate the presence of one Li environment, which suggests that CH_2Li_2's solid-state structure will be highly symmetric.

As a comparison, the groups IV, V, and VI interstitial carbides exhibit C 1s chemical shifts in the range of −2.0 to −4.0 eV relative to contaminant hydrocarbon.[13] The C 1s chemical shift for CH_2Li_2 (−4.1 eV) is significantly greater than that for TiC (−3.3 eV) for which APW band structure calculations have indicated charge transfer of nearly one Ti 3d electron to the C 2p band.[14] To our knowledge, the C 1s binding energy of CH_2Li_2 is the lowest ever reported.

Fenske–Hall molecular orbital (MO) calculations[15] were performed on cyclopropane (a hydrocarbon reference) and the CH_3Li tetramer, using geometrical parameters from published electron diffraction[16] and X-ray data,[6b] respectively. As the structure of CH_2Li_2 is unknown, calculations were performed on model monomeric,[17] dimeric,[18] and trimeric[19] structures of CH_2Li_2. The monomeric and dimeric structures are among the lowest energy (ab initio geometry optimization) structures in which C and Li atoms are of one chemical type. The trimeric CH_2Li_2 structure was one suggested by Schleyer et al. in which C and Li atoms are in equivalent environments.[19]

Experimental binding energies, chemical shifts, and gross Mulliken charges are listed in Table I. Average calculated values are reported for all three CH_2Li_2 model structures as similar results were obtained.

As Table I indicates, the presence of one Li in CH_3Li shifts the carbon binding energy by 2.4 eV. The presence of a second Li in CH_2Li_2 shifts the carbon binding energy by an additional 1.7 eV. The carbon charge increases from −1.02 in CH_3Li to −1.55 in CH_2Li_2. This is shown in Figure 2 where the calculated carbon charge is plotted against the C 1s chemical shift. A line has been drawn through points for C_3H_6 and CH_3Li as these represent known structures. The average value of the carbon charge in the CH_2Li_2 models is placed on this curve at the observed chemical shift. The excellent correlation ($r^2 = 0.994$) suggests that the carbon potentials in these compounds are well represented by the calculations.

The calculations also predict that the Li positive charge should decrease slightly on going from CH_3Li to CH_2Li_2 (Table I), but

Figure 2. Fenske–Hall MO charges for C in C_3H_6 (**1**), CH_3Li (**2**), and CH_2Li_2 (**3**) plotted against observed C 1s chemical shift. Vertical bars represent uncertainty of ±0.2 eV in binding energy. The horizontal bar represents the standard deviation in the average charge of three CH_2Li_2 model structures (see text).

the magnitude of these changes is small ($\Delta q_{Li} = -0.15$), and we observe a small decrease in Li 1s binding energy ($\Delta BE = 0.1$ eV). The Li 1s binding energies for CH_3Li (54.0 eV) and CH_2Li_2 (53.9 eV) are closer to those of LiOH and Li_2O[20] than to other lithium salts containing noncoordinating anions like $ClO_4{}^-$ and $PO_4{}^{3-}$.[10] Thus, the overall Li potential in these lithiocarbon compounds is similar to that for lithium in extended oxidic structures.

(13) Rumqvist, L.; Hamrin, K,; Johansson, G.; Fahlman, A.; Nordling, C. *J. Phys. Chem. Solids* **1969**, *30*, 1835.

(14) Conklin, J. B., Jr.; Silversmith, D. J. *Int. J. Quantum Chem.* **1968**, *2*, 243.
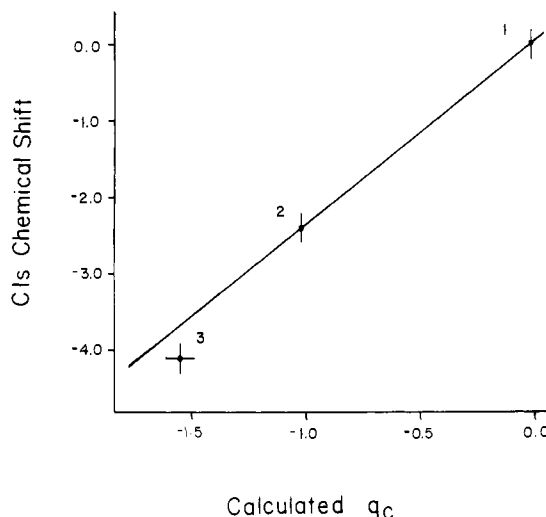
(15) Fenske, R. F.; Hall, M. B. *Inorg. Chem.* **1972**, *11*, 768. The Slater orbital basis set functions were taken from: Clementi, E. *IBM J. Res. Dev.* **1965**, *9*, 2. No Li 2p functions were included. An exponent of 1.20 was used for the H 1s function.

(16) Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538.

(17) Laidig, W. D.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 5972. The cis planar singlet structural parameters were used.

(18) See Structure VIII in: Jemmis, E. D.; Schleyer, P. v. R.; Pople, J. A. *J. Organomet. Chem.* **1978**, *154*, 327.

(19) The D_{3h} structure is best viewed as a trigonal prism of Li atoms with methylene groups bridging rectangular faces (see Structure XIII[18]). Geometrical parameters are as follows: C–C (2.87 Å), C–H (1.10 Å), Li–C (2.10 Å), Li–Li (2.1 Å, triangular faces), Li–Li (2.97 Å, rectangular faces). These parameters are idealized and not the result of geometry optimization.

Resonance Raman Spectra of Ground and Low-Lying Excited States of Ruthenium(II) Pentaammine Pyridine Derivatives

Y. C. Chung, N. Leventis, P. J. Wagner,* and G. E. Leroi*

Department of Chemistry, Michigan State University East Lansing, Michigan 48824

Received August 27, 1984

Raman spectra of electronically excited molecules have been reported for polypyridine complexes of d^6 transition metals.[1–5] The prototypical case has been tris(2,2′-bipyrdine)ruthenium(II) [$Ru(bpy)_3{}^{2+}$], for which it has been demonstrated that the electron promoted by metal-to-ligand charge-transfer (MLCT) absorption is localized (on the Raman time scale) on one of the bipyridine ligands.[1–4] We describe here observations on two pentaammineruthenium(II) pyridine complexes, models of another system for which the photochemistry and photophysics have received considerable recent attention.[6–10] The results are consistent

(1) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391.

(2) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.

(3) Forster, M.; Hester, R. E. *Chem. Phys. Lett.* **1981**, *81*, 42.

(4) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067.

(5) McClanahan, S.; Hayes, T.; Kincaid, J. *J. Am. Chem. Soc.* **1983**, *105*, 4486.

(6) Malouf and Ford (Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213) provide a summary and references to 1977.