

Figure 2. Thionophosphate (P=S) signals of  $^{31}\text{P}$  NMR spectra of **2** containing  $^{32}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$  (see text).

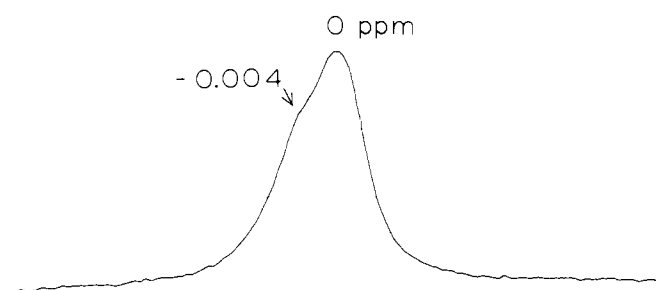


Figure 3.  $^{31}\text{P}$  NMR signal of  $^{34}\text{S}$ - and  $^{36}\text{S}$ -labeled **1** (see text).

The ratio of  $^{34}\text{S}$  to  $^{36}\text{S}$  in compound **2** was determined both from peak heights (0.29:1) in the NMR spectrum (Figure 2) and from molecular peaks in the mass spectrum (0.25:1). The  $^{18}\text{O}$  isotopic shifts (Table I) match previously published values for doubly and

singly bonded  $^{18}\text{O}$  in phosphates.<sup>2</sup>

### Discussion

Despite a large number of experiments involving isotope effects on chemical shifts in NMR spectra,<sup>1</sup> this is the first report of a sulfur isotope effect on a  $^{31}\text{P}$  chemical shift and, to our knowledge, the first time the effects of three different isotopes have been compared. Based on the  $^{18}\text{O}$  isotope effect on  $^{31}\text{P}$  chemical shifts in phosphates,<sup>11</sup> we expected the sulfur isotopes in thiophosphates to shift the  $^{31}\text{P}$  signal upfield. As anticipated,<sup>10,11</sup> the observed upfield shift increased with mass and bond order and decreased with distance.

The isotope shift also increases by roughly a factor of 2 as the mass is increased from 34 to 36 (vs. 32), as predicted.<sup>10</sup> Both the  $^{18}\text{O}$  and S isotope shifts approximately double as the bond order changes from 1 to 2. While there are not enough examples in this case to show whether other factors are involved (e.g., geometry of the molecule), the increase in isotopic shift with bond order has been predicted for diatomic and triatomic molecules<sup>10</sup> and verified experimentally for larger molecules.<sup>1</sup>

The observation that the  $^{18}\text{O}$  isotopic shifts on thiophosphates is larger than on phosphates<sup>11</sup> suggests that the P-O bond order is slightly greater in thiophosphates. The slightly smaller bond order would make the isotopic shift smaller. It would be interesting to see if calculations bear out this decrease in bond order from P-O to P-S.

Registry No. **1**, 16956-55-1; **2**, 15762-04-6.

(10) Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4983-4988.

(11) Tsai, M.-D. In "Phosphorus-31 NMR: Principles and Applications"; Gorenstein, D. G., Ed.; Academic Press: New York, 1984; pp 175-197.

## Communications to the Editor

### Novel 16-Electron Organometallic Complexes of Molybdenum and Tungsten: $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})(\text{alkyl})_2^1$

Peter Legzdins,\* Steven J. Rettig, and Luis Sánchez

Department of Chemistry  
The University of British Columbia  
Vancouver, British Columbia, Canada V6T 1Y6

Bruce E. Bursten\* and Michael G. Gatter

Department of Chemistry, The Ohio State University  
Columbus, Ohio 43210

Received October 11, 1984

The familiar 18-valence-electron rule can often be used to rationalize the stability and reactivity of transition-metal organometallic complexes.<sup>2</sup> It is particularly applicable to compounds possessing monomeric "three-legged piano stool" molecular structures such as  $(\eta^n\text{-C}_n\text{H}_n)\text{M}(\text{L})(\text{L}')(\text{L}'')$  where M is a metal from group 6, 7, 8, 9, or 10 and some of the ligands, L, are good  $\pi$ -acceptors (e.g. CO or NO).<sup>3</sup> We now wish to report the first, thermally stable examples of a class of such molecules that do

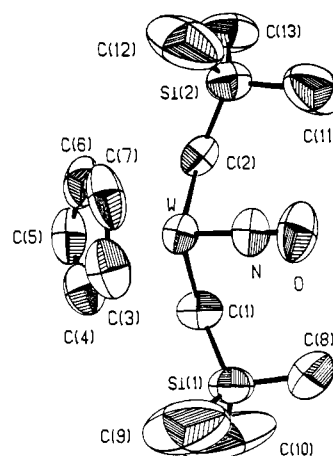


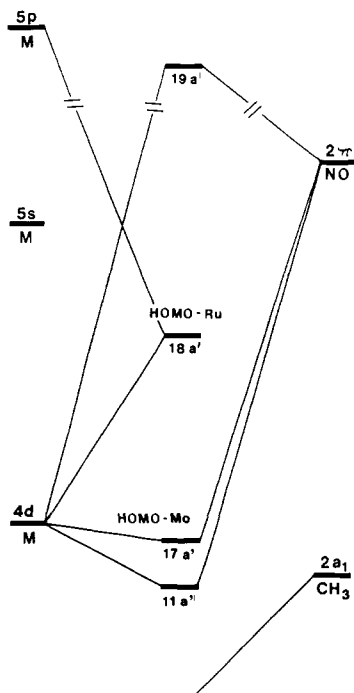
Figure 1. Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles (deg) are W-N = 1.757 (8), W-C(1) = 2.103 (9), W-C(2) = 2.108 (9), W-C( $\text{C}_5\text{H}_5$ , av) = 2.373 (10), N-O = 1.226 (10), Si-C( $\text{CH}_2$ , av) = 1.840 (11), N-W-C(1) = 97.7 (4), N-W-C(2) = 95.7 (4), C(1)-W-C(2) = 109.6 (4), W-N-O = 169.5 (6), W-C(1)-Si(1) = 125.5 (5), W-C(2)-Si(2) = 127.1 (5).

not conform to the rule by virtue of the fact that their lowest unoccupied molecular orbitals (LUMOs) are nonbonding in character. Specifically, we wish to describe the syntheses, characterization, and remarkable properties of the new 16-electron complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$  (**1**),  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$  (**2**), and  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$  (**3**).

(1) Organometallic Nitrosyl Chemistry. 23. For part 22, see: Legzdins, P.; Nurse, C. R. *Inorg. Chem.*, in press.

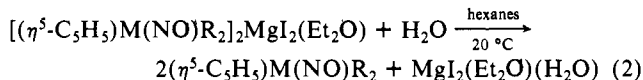
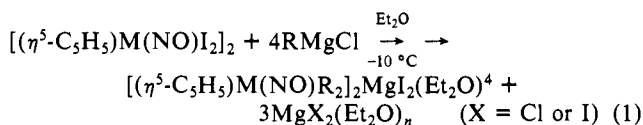
(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; Chapters 25-30.

(3) Jolly, W. L. "Modern Inorganic Chemistry"; McGraw-Hill: New York, 1984; Chapter 16.



**Figure 2.** Molecular orbital diagram of the upper valence orbitals of  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})\text{Me}_2$  ( $\text{M} = \text{Mo}, \text{Ru}$ ).

The complexes may be synthesized by the sequential transformations



where if  $\text{M} = \text{W}$ ,  $\text{R} = \text{CH}_2\text{SiMe}_3$  or  $\text{CH}_2\text{CMe}_3$  and if  $\text{M} = \text{Mo}$ ,  $\text{R} = \text{CH}_2\text{SiMe}_3$ . The desired nitrosyl-containing products of conversions 1 and 2 are isolable as analytically pure crystals<sup>5</sup> from the final reaction mixtures by fractional crystallization.

A single-crystal X-ray crystallographic analysis of **1**<sup>6</sup> confirmed its monomeric nature<sup>8</sup> and revealed its normal "piano stool"

(4) The formulation of the isolable intermediate complexes as  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})\text{R}_2]_2\text{MgI}_2(\text{Et}_2\text{O})$  is based on elemental analyses and preliminary X-ray crystallographic analyses of single crystals of the complexes having  $\text{M} = \text{Mo}$  or  $\text{W}$  and  $\text{R} = \text{CH}_2\text{SiMe}_3$ .

(5) Complex **1**, violet crystals, 85% yield. Anal. Calcd for  $\text{C}_{13}\text{H}_{27}\text{NOSi}_2\text{W}$ : C, 34.50; H, 6.00; N, 3.05. Found: C, 34.43; H, 5.96; N, 3.09. IR (Nujol mull)  $\nu_{\text{NO}}$  1550 (s)  $\text{cm}^{-1}$ ; IR (hexanes)  $\nu_{\text{NO}}$  1600 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.13 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 2.23 (d, 2 H,  $\text{CH}_2$ ,  $J = 8$  Hz), 0.26 (s, 18 H, Si( $\text{CH}_3$ )<sub>3</sub>), -0.58 (d, 2 H,  $\text{CH}_2$ ,  $J = 8$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  101.63 (s,  $\text{C}_5\text{H}_5$ ), 60.78 (s,  $\text{CH}_2$ ), 2.81 (s, Si( $\text{CH}_3$ )<sub>3</sub>); low-resolution mass spectrum (probe 150 °C),  $m/z$  453 ( $\text{P}^+$ ,  $^{184}\text{W}$ ). Complex **2**, red crystals, 35% yield. Anal. Calcd for  $\text{C}_{15}\text{H}_{27}\text{NOW}$ : C, 42.75; H, 6.41; N, 3.32. Found: C, 42.47; H, 6.37; N, 3.20. IR (Nujol mull)  $\nu_{\text{NO}}$  1560 (s)  $\text{cm}^{-1}$ ; IR (hexanes)  $\nu_{\text{NO}}$  1605 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.10 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 3.56 (d, 2 H,  $\text{CH}_2$ ,  $J = 11$  Hz), 1.26 (s, 18 H, C( $\text{CH}_3$ )<sub>3</sub>), -1.57 (d, 2 H,  $\text{CH}_2$ ,  $J = 11$  Hz); low-resolution mass spectrum (probe 100 °C),  $m/z$  421 ( $\text{P}^+$ ,  $^{184}\text{W}$ ). Complex **3**, violet crystals, 60% yield. Anal. Calcd for  $\text{C}_{13}\text{H}_{27}\text{NOSi}_2\text{Mo}$ : C, 42.73; H, 7.39; N, 3.83. Found: C, 42.63; H, 7.38; N, 4.00. IR (Nujol mull)  $\nu_{\text{NO}}$  1587 (s)  $\text{cm}^{-1}$ ; IR (hexanes)  $\nu_{\text{NO}}$  1625 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.18 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 3.17 (d, 2 H,  $\text{CH}_2$ ,  $J = 8$  Hz), 0.31 (s, 18 H, Si( $\text{CH}_3$ )<sub>3</sub>), -0.32 (d, 2 H,  $\text{CH}_2$ ,  $J = 8$  Hz); low-resolution mass spectrum (probe 100 °C),  $m/z$  367 ( $\text{P}^+$ ,  $^{98}\text{Mo}$ ).

(6) Crystals of **1** are monoclinic,  $a = 12.070$  (2) Å,  $b = 12.4360$  (7) Å,  $c = 13.574$  (2) Å,  $\beta = 104.856$  (6)°,  $Z = 4$ , space group  $P2_1/c$ . The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to  $R = 0.048$  and  $R_w = 0.050$  for 2654 reflections with  $I \geq 3\sigma$  collected at 22 °C with Mo  $K\alpha$  radiation on an Enraf-Nonius CAD4-F diffractometer. Hydrogen atoms were fixed in idealized positions. The methylene protons were located on a difference map in normal tetrahedral positions; no evidence for any C-H $\rightarrow$ W agostic<sup>7</sup> interactions was found.

(7) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

molecular structure with a noncrystallographic mirror plane (Figure 1). The most chemically interesting feature of the structure involves the essentially linear (169.5 (6)°) WNO group in which the short W-N (1.757 (8) Å) and long N-O (1.226 (10) Å) bond lengths indicate considerable W $\rightarrow$ NO back-bonding.<sup>10</sup>

Under ambient conditions, the complexes **1–3** are thermally stable, diamagnetic solids which are freely soluble in common organic solvents to give red-to-violet solutions. Their spectroscopic properties<sup>5</sup> confirm that their molecular structures in solution are analogous to that presented for **1** in Figure 1. In particular, the very low  $\nu_{\text{NO}}$ 's (1600–1625  $\text{cm}^{-1}$ ) evident in their IR spectra in hexanes are consistent with a diminished N-O bond order and contrast with the analogous absorption exhibited by the related 18-electron complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{NO})\text{Et}_2$ <sup>11</sup> [1720  $\text{cm}^{-1}$  in  $\text{C}_6\text{H}_6$ ].

In order to address the apparently unusual electronic structure of these compounds, we have performed Fenske-Hall MO calculations<sup>12</sup> on the model 16- and 18-electron systems,  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})\text{Me}_2$  ( $\text{M} = \text{Mo}$  or  $\text{Ru}$ , respectively).<sup>13</sup> As depicted in Figure 2, these calculations lead to the same qualitative MO diagram for both complexes. In contrast to symmetric "three-legged piano stools" such as  $(\eta^n\text{-C}_n\text{H}_n)\text{M}(\text{CO})_3$ , for which the three  $d_\pi$  orbitals form a nearly degenerate set,<sup>15</sup> the replacement of two  $\pi$ -acid ligands by alkyl groups capable of only  $\sigma$ -bonding leads to a large splitting of the  $d_\pi$  orbitals. The highest of these (18a') is localized on the metal center and contains no NO  $2\pi$  character. It follows that this orbital, which is occupied for  $\text{M} = \text{Ru}$  but unoccupied for  $\text{M} = \text{Mo}$ , can have no direct bearing on the extent of M-NO  $\pi$ -back-bonding. Rather, the degree of back-bonding will be controlled primarily by the comparative abilities of Mo and Ru, in the same formal oxidation state, to donate electron density to the nitrosyl ligand. Since Mo is more electropositive than Ru, it is expected to be the better  $\pi$ -donor, and indeed this is indicated by the calculated NO  $2\pi$  populations (1.50 e for  $\text{M} = \text{Mo}$  vs. 1.29 e for  $\text{M} = \text{Ru}$ ). The energies of the 17a' MO for each complex (-9.8 eV for  $\text{M} = \text{Mo}$  and -11.2 eV for  $\text{M} = \text{Ru}$ ) are also consistent with the more electropositive character of Mo.

That the 18a' LUMO is nonbonding also accounts for the thermal stability of **1–3**, as there is no loss of metal-ligand binding in the complexes despite their formal electron deficiency. Moreover, the existence of this metal-localized MO should confer Lewis acid properties on these compounds. However, for steric reasons, the three compounds are most prone to attack by relatively small Lewis bases such as  $\text{H}_2$ , CO, NO,  $\text{O}_2$ , and  $\text{PMe}_3$ . The exact natures of the products resulting from these attacks are currently being investigated.

Finally, it should be noted that the coordination geometries possessed by **1–3** also facilitate their isolation. For instance, it has been shown<sup>14,16</sup> that 18-electron  $(\eta^n\text{-C}_n\text{H}_n)\text{M}(\text{CO})_2$  complexes possess a relatively high, metal-localized nonbonding HOMO. Consequently, by the reasoning outlined above, it is understandable why 16-electron  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$  and  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$ , both generated by matrix photolysis,<sup>17</sup> exhibit decreases in  $\nu_{\text{CO}}$  relative to their 18-electron analogues,  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  and  $(\eta^6\text{-C}_6\text{Me}_6)\text{Fe}(\text{CO})_2$ .<sup>18</sup> Having a higher degree of coordinative unsaturation than **1**, **2**, or **3**, however, these 16-electron carbonyl

(8) In the solid state, weakly associated centrosymmetric dimers are formed via C-H $\cdots$ O hydrogen bonding<sup>9</sup> about the inversion center at ( $1/2, 1/2, 1/2$ ) [ $\text{C}(7)\text{-H}(7)\cdots\text{O}(1-x, 1-y, 1-z)$ , H $\cdots$ O = 2.27, C $\cdots$ O = 3.18 (1) Å, C-H $\cdots$ O = 155°, N-O $\cdots$ H = 126°].

(9) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

(10) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116 and references therein.

(11) Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6110.

(12) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(13) Fenske-Hall calculations were carried out as described in ref 14.

(14) Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 2554.

(15) For leading references, see: (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

(16) Hoffmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

(17) Rest, A. J.; Sodeau, J. R.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1978**, 651.

(18) Weber, S. R.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 45.

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

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. We also thank Professor R. G. Bergman for providing us with a description of his results prior to publication and Professor J. Trotter for permitting us the use of his X-ray diffractometer. L.S. acknowledges the Spanish Ministry of Education for the award of a postdoctoral fellowship.

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

Gregory F. Meyers,<sup>1a</sup> Michael B. Hall,<sup>\*1a</sup>  
John W. Chinn, Jr.,<sup>1b</sup> and Richard J. Lagow<sup>\*1b</sup>

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

Received October 4, 1984

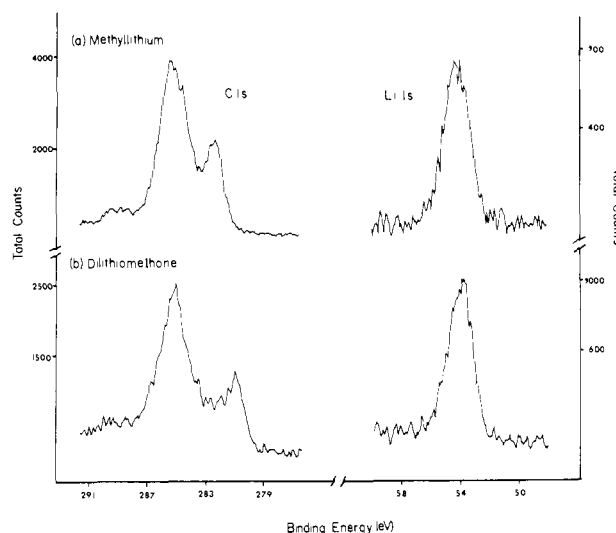
Revised Manuscript Received December 20, 1984

**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.<sup>2</sup> From a theoretical standpoint, however, debate has centered on just how to partition electron density between C and Li atoms in organolithium compounds.<sup>3</sup>

Both semiempirical and ab initio calculations have been used to describe bonding in methyl lithium 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.<sup>4</sup> In the latter description, aggregates are held together by Coulombic forces.<sup>5</sup>

Although the structure of methyl lithium has been known for some 20 years,<sup>6a</sup> 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  $\text{CH}_3\text{Li}$  and  $\text{CH}_2\text{Li}_2$ . For both compounds we observe single carbon and lithium environments. These results are in accord with recent <sup>13</sup>C solid-state NMR studies of the title compounds.<sup>7</sup>

**Experimental Section.** Methyl lithium (bulk purity 100%) and dilithiomethane (bulk purity 96%)<sup>8</sup> were pressed from powders



**Figure 1.** C 1s and Li 1s photoelectron spectra of (a) methyl lithium and (b) dilithiomethane. Contaminant hydrocarbon at 285.0 eV is used as a reference.

into pellets in an argon-filled drybox<sup>9</sup> attached directly to the spectrometer. Core level XPS spectra were recorded on a HP5950A ESCA spectrometer using monochromatic Al  $K\alpha$  radiation (1486.6 eV).<sup>10</sup> 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.  $\pm 0.2$  eV.

**Results and Discussion.** The C 1s and Li 1s core spectra are shown in Figure 1.  $\text{CH}_3\text{Li}$  exhibits three C 1s ionizations while  $\text{CH}_2\text{Li}_2$  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.<sup>11</sup> A weak contribution due to carbonate carbon was also observed in the  $\text{CH}_3\text{Li}$  spectrum at 288.7 eV.<sup>12</sup> Experimental C 1s binding energies for the title compounds are readily observed at 282.6 eV for  $\text{CH}_3\text{Li}$  and at 280.9 eV for  $\text{CH}_2\text{Li}_2$ . Additionally, only one Li 1s ionization is observed at 54.0 eV for  $\text{CH}_3\text{Li}$  and 53.9 eV for  $\text{CH}_2\text{Li}_2$ .

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

(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  $\text{CH}_3\text{Li}$  the flood gun was set at 0.64 eV and 3.00 mA.  $\text{CH}_2\text{Li}_2$  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  $\text{CH}_3\text{Li}$  and  $\text{CH}_2\text{Li}_2$  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) occurring at 531.6 eV and 528.7 eV. These are readily explained by the presence of surface hydroxide and carbonate ( $\text{CH}_3\text{Li}$  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.

(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 <sup>13</sup>C chemical shift for  $\text{CH}_3\text{Li}$  is 16 ppm upfield from  $\text{Me}_4\text{Si}$  while that for  $\text{CH}_2\text{Li}_2$  is 10.5 ppm downfield from  $\text{Me}_4\text{Si}$ .

(8) Both compounds were prepared from published procedures.<sup>7</sup> Bulk purities were determined by D<sub>2</sub>O hydrolysis.  $\text{CH}_3\text{Li}$  (3%) was a minor impurity in  $\text{CH}_2\text{Li}_2$ .