

Stereochemistry of Polynuclear Compounds of the Main Group Elements. A Neutron and X-Ray Diffraction Investigation of Lithium-Hydrogen-Carbon Interactions in $\text{LiB}(\text{CH}_3)_4$

Wendell E. Rhine,^{1a} Galen Stucky,*^{1a} and S. W. Peterson^{1b}

Contribution from the Department of Chemistry and Material Research Laboratory, University of Illinois, Urbana, Illinois 61801, and the Argonne National Laboratories, Argonne, Illinois 60439. Received January 23, 1975

Abstract: The role of the bridging methyl groups and the effect of lithium-H₃C interactions on the geometry of the CH₃ group have been investigated by single-crystal neutron and X-ray diffraction studies in the compound, $\text{LiB}(\text{CH}_3)_4$. The structure of $\text{LiB}(\text{CH}_3)_4$ consists of planar sheets of lithium atoms, which are bridged by the tetramethylboron groups through linear B-CH₃-Li and multicenter fragments. The structural features in the linear B-CH₃-Li moiety are similar to those found in the intermolecular interaction between tetrameric units in CH_3Li with a trihydrogen bridged group. The other methyl bridging arrangement is similar to that first proposed by Pitzer and Gutowsky for $\{(\text{CH}_3)_3\text{Al}\}_2$ with a dihydrogen bridged linkage. The bridged hydrogen atoms, Li-H_B-C, form an average H_B-C-H_B angle of 108.8 (2.4)° while the H_B-C-H_T (H_T = terminal hydrogen atom) angles are 103.5 (1.0)°. Mass spectroscopic studies show that $\text{LiB}(\text{CH}_3)_4$ is also associated in the gas phase. Crystals of $\text{LiB}(\text{CH}_3)_4$ possess orthorhombic symmetry, space group *Pnma* with *a* = 10.80 (2), *b* = 9.77 (2), and *c* = 5.883 (9) Å. The observed density is 0.830 (6) g/cm³, which agrees well with the calculated density of 0.826 g/cm³ for four molecules of $\text{LiB}(\text{CH}_3)_4$ per unit cell. A total of 513 unique X-ray reflections were utilized to refine atomic parameters, including hydrogen atoms, to *R*_F = 0.029 and *R*_{wF} = 0.022. Neutron data were also utilized to accurately determine hydrogen atom positions (378 unique reflections) to give *R*_F = 0.032 and *R*_{wF} = 0.029.

It is now apparent that the lithium atom is able to stabilize a number of unusual transition metal organometallic species. The enhanced stability is manifested in a number of ways, for example, Me_2Mn readily detonates, but LiMnMe_3 is comparatively stable (100°C dec). Similarly, a series of novel organochromium "ate" complexes, such as $\text{Li}_4\text{Cr}_2(\text{CH}_3)_8 \cdot 4\text{THF}$, have been described by Kurras and coworkers²⁻⁷ and by Hein.⁸⁻¹² An extremely interesting lithium "ate" system, $\text{Li}_6\text{Ni}_2(\text{N}_2)(\text{C}_6\text{H}_5)_6 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, contains an N₂ molecule which is side bonded to the Ni atom. This compound is formed by the reaction of phenyllithium, cyclododecatrienenickel(0), and nitrogen.¹³ Finally, the reaction of organolithium reagents with biscyclopentadienylmolybdenum dihydride has been shown to give a lithium stabilized complex, $\text{Li}_4\text{Mo}_4\text{C}_{40}\text{H}_{44}$.¹⁴ This reaction appears to be general for a number of transition metal hydride systems.

A characteristic of the compounds which have been prepared in basic solvents such as diethyl ether, tetrahydrofuran, and tertiary amines is that in spite of the fact that one associates a large solvation energy with the lithium cation, the number of base molecules coordinated to the lithium atom is usually two or less. The implication is that lithium-organic group interactions are stronger and more important than lithium-base (solvent) interactions. An examination of the crystal structures of LiCH_3 ,¹⁵ LiC_2H_5 ,¹⁶ $\{\text{LiTHF}\}_4\text{Cr}_2(\text{CH}_3)_8$,⁷ and cyclohexyllithium¹⁷ suggested to us that the Li-H-C interaction is a stereochemically important property of alkyl organolithium compounds. A simple system in which to investigate this feature is $\text{LiB}(\text{CH}_3)_4$. As we have noted earlier, many of its physical properties are those of a covalent substance.¹⁸ A preliminary X-ray investigation¹⁸ demonstrated that two lithium-methyl group configurations are present as shown below. A knowledge of



the precise positions of the hydrogen atoms in this structure is essential to understanding the bonding in this and the lithium "ate" complexes described above. With this in mind, complete neutron and X-ray diffraction studies of $\text{LiB}(\text{CH}_3)_4$ were undertaken and are reported here.

Experimental Section

$\text{LiB}(\text{CH}_3)_4$ was prepared by previously published procedures.¹⁹ Crystals for X-ray and neutron diffraction experiments were grown by sublimation in evacuated glass tubes at ~100°C. X-Ray precession photographs revealed that the crystal system is orthorhombic and belongs to one of the space groups, *Pnma* or *Pn2₁a*. Statistical tests on the normalized structure factors as well as the *N*(*z*) test of Howells, Phillips, and Rogers²⁰ unambiguously showed the correct space group to be *Pnma*. The cell dimensions as determined by a least-squares refinement for 12 reflections on a Picker four-circle diffractometer are *a* = 10.80 (2), *b* = 9.77 (2), and *c* = 5.883 (9) Å. The observed density by the flotation method in a benzene-hexane solution is 0.830 (6) g/cm³ and agrees well with a density of 0.826 g/cm³ calculated for four molecules of $\text{LiB}(\text{CH}_3)_4$ per unit cell.

X-Ray Diffraction. A crystal of suitable size was mounted in a glass capillary because of the compounds sensitivity to air and water. A computer-controlled four-circle Picker diffractometer with Mo K α radiation and a highly oriented graphite monochromator were used for all X-ray intensity measurements. Integrated intensities were collected, using the θ - 2θ scan technique at a rate of 1°/min. Each reflection was taken with 10-sec background counts at both sides of the peak. Three forms of data were measured with $2\theta_{\text{max}}$ equal to 40°. The intensities were corrected for background and Lorentz and polarization effects. Equivalent reflections were then averaged to give 513 unique reflections. Non-hydrogen scattering factors were taken from the compilation of Hanson et al.²¹ while the hydrogen atom scattering factor was taken from Stewart et al.²² The data refined to

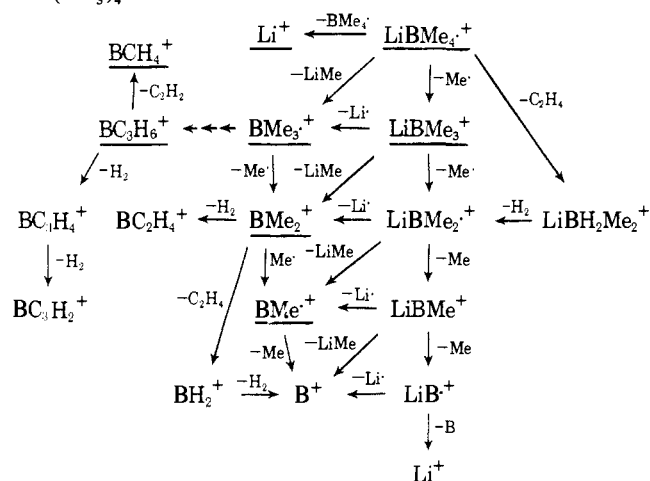
$$R_1 = \sum(|F_o - F_c|) / \sum F_o = 0.049 \text{ (all data)}$$

$$R_1 = \sum|F_o - F_c| / \sum F_o = 0.029 \text{ (observed data only)}$$

$$R_2 = \sum w|F_o - F_c| / \sum w F_o = 0.022 \text{ (all data)}$$

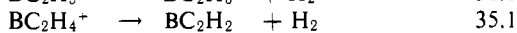
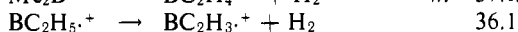
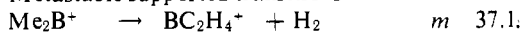
after several cycles of least-squares refinement using anisotropic thermal parameters. Weights were calculated with the expression,

Scheme I. Mass Spectroscopic Fragments Observed for LiB(CH₃)₄

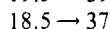


Fragments underlined also appeared in spectrum obtained at 30 eV.

Metastable supported transitions



Multiple charged ions formed at 90°C At 155°



$w = 1/\sigma^2(F)$, where $\sigma(F) = F/2I\{CN + 0.25(TC/TB)^2(B_1 + B_2) + (KI)^2\}^{1/2}$. CN = total counts, TC = total scan time for reflection, TB = total time for background counts, B_1, B_2 = background counts on each side of reflection, I = net counts for reflection, and K = constant = 0.02. The weighting scheme gave no significant variation of $w(F_o - F_c)$ with the magnitude of F_o or $\sin \theta/\lambda$.

Neutron Diffraction. A well-formed crystal with dimensions 4.24 × 2.24 × 0.96 mm grown by slow sublimation was mounted in a lead glass capillary for neutron data collection. Three-dimensional data were collected using an Electronics and Alloys four-circle diffractometer at the CP-5 reactor (Argonne National Laboratory) with a wavelength of 1.142 Å. The fully automated diffractometer operates under remote SIGMA V computer control. Data collection was via the 2θ scan technique, employing 0.1° step intervals, with backgrounds measured on both sides of the peak. Scans of 50 steps were found suitable for data collection. The time spent collecting diffraction intensities at each interval was determined by monitoring the neutron beam, until 50,000 counts had been registered by the monitoring system. This procedure was employed to correct for any deviation in the neutron flux. Data were collected to 2θ_{max} = 72° with one standard reflection being monitored every 20 reflections. The observed intensities were corrected for background, Lorentz, and absorption effects. The calculated linear absorption coefficient of the molecule is 6.424 cm⁻¹ (cross section of hydrogen was taken as 37.5 barns). One form of data, 378 unique reflections (228 reflections observed according to the criterion $I > 3\sigma$), was measured. Refinement was begun using the X-ray positions. After converting to anisotropic temperature parameters R_1 (observed reflections) converged to 0.032 and R_2 (all data) to 0.029 using the above weight expression with $k = 0.02$. No significant variation of $w(F_o - F_c)$ vs. the magnitude of F_o and $\sin \theta/\lambda$ was observed for this weighting scheme.

Discussion

The degree of association of LiB(CH₃)₄ in the gas phase was examined by mass spectroscopy with the results given in Scheme I and Table I. In a spectrum obtained at 70 eV and 90°C, the highest *m/e* value corresponds to the tetrameric species Li₄B₄(CH₃)₁₅⁺ indicating that LiBMe₄ is

Table I. Fragments Observed at Various Excitation Voltages (90°C)

Mass	70 eV	30 eV	18 eV
6	⁶ Li	Li	
7	⁷ Li	Li	Li
10	¹⁰ B		
11	¹¹ B		
12	BH, C		
13	BH ₃ , CH		
14	BH ₃ , CH ₂		
15	BH ₄ , CH ₃		
18	LiB		
26	BCH ₃	BCH ₃	
27	BCH ₃	BCH ₄	
33	LiBCH ₃		
34	LiBCH ₄		
35	BC ₂		
36	BC ₂ H		
37	BC ₂ H ₂		
38	BC ₂ H ₃		
39	BC ₂ H ₄		
40	BC ₂ H ₅		
41	BC ₂ H ₆	BC ₂ H ₆	BC ₂ H ₆
42	BC ₂ Li		
47	BC ₃		
48	BC ₃ H, LiBC ₂ H ₆		
49	BC ₃ H ₂ , LiBC ₂ H ₇		
50	BC ₃ H ₃ , LiBC ₂ H ₈		
51	BC ₃ H ₄		
	(BC ₃ H ₅), ¹⁰ BC ₃ H ₆		
53	BC ₃ H ₆	BC ₃ H ₆	
	(BC ₃ H ₇), ¹⁰ BC ₃ H ₉		
56	BC ₃ H ₉	BC ₃ H ₉	
	Li ¹⁰ BC ₃ H ₉		
63	Li ¹¹ BC ₃ H ₉	LiBC ₃ H ₉	LiBC ₃ H ₉
78	LiBC ₄ H ₁₂	LiBC ₄ H ₁₂	

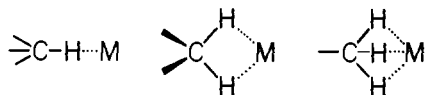
also associated in the gas phase. Most lower *m/e* values observed corresponded to a loss of Me, BMe₃, or LiMe fragments. The spectrum at *m/e* values below 56 closely parallel the mass spectrum reported for trimethylboron.²³ At very high temperatures (250°C), decomposition occurred and the spectrum for LiMe was observed.

At all temperatures and ionization potentials studied, the Me₂B⁺ ion was the most abundant. At 70 eV, the abundance of the MeB⁺ and B⁺ ions was about 2.5 and 0.9%, respectively, and at lower ionization potentials, no B⁺ was observed. The abundance of Li⁺ was 2.1% and a trace of Li⁺ ion was still present in the spectrum obtained at 18 eV. The abundance of LiBMe₃⁺ increased from 18% at 70 eV to almost 50% of the BMe₂⁺ ion at 18 eV.

Fractional *m/e* values were observed at 24.5 and 25.5 at 70 eV. Additional fractional *m/e* values were observed at 26.5, 19.5, and 18.5 when the temperature was increased to 155°C. These *m/e* values correspond to doubly charged ions of mass values of 53, 51, 49, 39, and 37. Doubly charged species usually are found for ions which have unusual stability and these ions may possess a carborane type structure in which the charge can be delocalized.

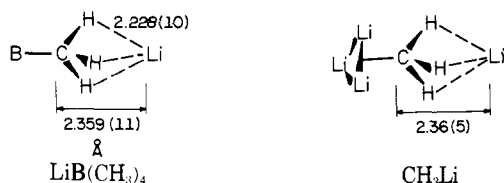
Lithium-Hydrogen-Carbon Interactions. The chemical activation of C-H bonds by early main group and transition metal compounds is a well-established aspect of their organometallic chemistry. For example, alkyl lithium compounds, RCH₂Li, thermally decompose via β hydride elimination at relatively mild temperatures ($T \leq 100^\circ\text{C}$) to give alkenyl derivatives.^{24,25} Similarly, the reversible reaction of organoaluminum hydrides with olefins is fundamental to a number of industrially important catalytic processes.²⁶ Electron deficient metallic sites are also important in high

temperature catalytic cracking processes used in the treatment of hydrocarbons. The stereochemical interaction of a metal atom with a C-H bond can be considered in terms of variations on the three basic structural configurations shown below, i.e., linear monobridged, dibridged, and tri-



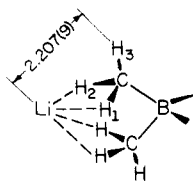
bridged geometries. Two of these arrangements are observed in the molecular structure of $\text{LiB}(\text{CH}_3)_4$. A tribridged configuration exists (Figures 1 and 2) between Li and C(2) and Li and C(3), while the dibridged geometry is observed for Li-C(1) and Li-C'(1). The first coordination sphere of the lithium atom thus consists of ten hydrogen atoms, with six hydrogen atoms at a distance of 2.234 (10) Å and four at a distance of 2.115 (8) Å. The details of these bridging arrangements are discussed below. For completeness, and because only a limited number of examples are known, a brief discussion of the monobridged configuration is also included.

Tribridged Configuration. The structural features (Tables II-VII) associated with the lithium atom in the linear $\text{B}-\text{CH}_3-\text{Li}$ grouping (Figures 1 and 2) are remarkably similar to those found for the intermolecular interaction between tetrameric units in $\text{CH}_3\text{Li}^{15}$ (below), with Li-C distances which are identical within the experimental error. The



H-C-H angles for the linear bridging methyl groups in $\text{LiB}(\text{CH}_3)_4$ average $109.0(2.9)^\circ$. No other examples of the tribridged alkyl-hydrogen atom-metal atom configuration have been reported. However, one can compare the corresponding tribridged borohydride geometry in $\text{Zr}(\text{BH}_4)_4$.²⁷ The zirconium atomic metallic (L12) radius is 1.60 Å while that of lithium is 1.55 Å.²⁸ The zirconium atom-bridging hydrogen atom distance as determined by electron diffraction is 2.21 (2) Å, compared to 2.228 (10) Å for the Li-H distance in $\text{LiB}(\text{CH}_3)_4$. The basicity of the hydrogen atoms in a BH_4^- anion should be greater than that for the hydrogen atoms in the $\text{B}-\text{CH}_3$ fragment, so that a relatively smaller distance for a metal-hydrogen atom approach, would be predicted for a given metal in the former case. The fact that the tribridged metal-hydrogen atom distance in $\text{Zr}(\text{BH}_4)_4$ is equal to that in $\text{LiB}(\text{CH}_3)_4$ when the radii differ by only 0.05 Å suggests that the strength of the bonding interactions in the two systems is quite similar.

Dibridged Configuration. H(1) and H(2) of $\text{LiB}(\text{CH}_3)_4$ participate in the methyl dihydrogen bridge arrangement in a fashion similar to that first proposed by Pitzer and Gutowsky²⁹ for $\{(\text{CH}_3)_3\text{Al}\}_2$.



The Li-H(1) and Li-H(2) distances average 2.116 (8) Å (Figure 2). The H(1)-C-H(2) angle is $108.3(6)^\circ$ while the H(1)-C-H(3) angles and H(2)-C-H(3) angles average

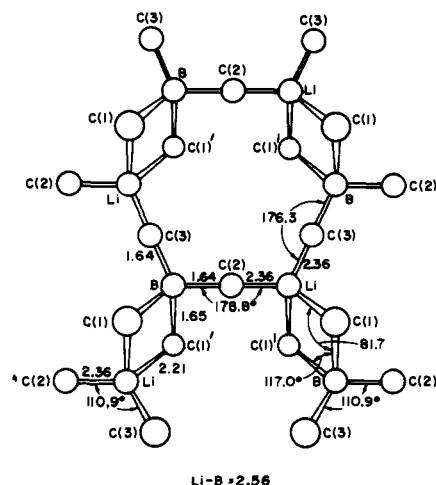


Figure 1. Molecular structures of $\text{LiB}(\text{CH}_3)_4$. All of the atoms except C(1) and C(1') lie in a crystallographic mirror plane which has its normal perpendicular to the plane of the paper. C(1) is related to C(1') by the mirror plane.

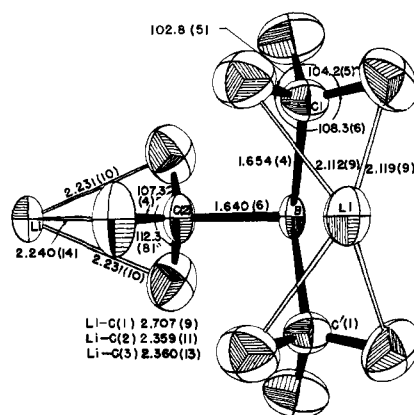


Figure 2. Partial molecular structure of $\text{LiB}(\text{CH}_3)_4$ showing the bridging and linear methyl geometry.

Table II. Positional Parameters for $\text{LiB}(\text{CH}_3)_4^a$

	x	y	z
C(1)	0.1218 (3)	0.3943 (3)	0.2077 (6)
	0.1209 (2)	0.3932 (2)	0.2078 (4)
C(2)	0.3150 (4)	0.25	0.0668 (10)
	0.3133 (3)	0.25	0.0713 (6)
C(3)	0.1046 (5)	0.25	-0.1745 (7)
	0.1052 (3)	0.25	-0.1728 (6)
B	0.1633 (3)	0.25	0.0820 (6)
	0.1622 (2)	0.25	0.0821 (6)
Li	0.0334 (9)	0.25	0.4463 (20)
	0.0331 (4)	0.25	0.4433 (8)
H(1)	0.1594 (6)	0.4103 (6)	0.3732 (13)
	0.162 (1)	0.409 (2)	0.348 (3)
H(2)	0.0214 (6)	0.4146 (5)	0.2148 (10)
	0.030 (1)	0.417 (2)	0.228 (3)
H(3)	0.1558 (5)	0.4791 (7)	0.1104 (10)
	0.148 (1)	0.475 (2)	0.111 (3)
H(4)	0.3468 (5)	0.3393 (7)	-0.0138 (12)
	0.346 (1)	0.332 (1)	-0.011 (3)
H(5)	0.3536 (7)	0.25	0.2439 (19)
	0.352 (2)	0.25	0.231 (5)
H(6)	0.1337 (8)	0.3392 (8)	-0.2690 (13)
	0.135 (2)	0.164 (1)	-0.265 (3)
H(7)	0.0067 (11)	0.25	-0.1717 (16)
	0.018 (2)	0.25	-0.171 (3)

^a Neutron positional parameters are given first and X-ray parameters second for each atom.

Table III. Neutron Temperature Parameters for LiB(CH₃)₄

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0086 (3)	0.0083 (4)	0.0265 (13)	0.0001 (3)	0.0025 (6)	-0.0016 (7)
C(2)	0.0042 (4)	0.01336 (7)	0.0036 (20)	0	0.0000 (7)	0
C(3)	0.0093 (6)	0.0136 (8)	0.0186 (17)	0	-0.0033 (7)	0
B	0.0042 (3)	0.0100 (6)	0.0071 (13)	0	-0.0018 (3)	0
Li	0.0061 (11)	0.0131 (18)	0.0267 (43)	0	0.0041 (18)	0
H(1)	0.0166 (7)	0.0139 (8)	0.0382 (26)	-0.0001 (6)	-0.0034 (11)	-0.0035 (13)
H(2)	0.0109 (6)	0.0172 (8)	0.0521 (26)	0.0037 (6)	0.0083 (9)	0.0016 (14)
H(3)	0.0179 (7)	0.0123 (7)	0.0389 (26)	-0.0022 (7)	0.0073 (10)	-0.0004 (13)
H(4)	0.0095 (6)	0.0200 (11)	0.0539 (31)	-0.0007 (7)	0.0050 (10)	0.0070 (14)
H(5)	0.0076 (8)	0.0278 (17)	0.0485 (42)	0	-0.0037 (14)	0
H(6)	0.0256 (10)	0.0237 (13)	0.0471 (35)	-0.0036 (11)	-0.0114 (15)	0.0074 (17)
H(7)	0.0125 (11)	0.0341 (22)	0.0555 (56)	0	-0.0100 (20)	0

Table IV. Bond Angles (deg) for LiB(CH₃)₄

	X-Ray	Neutron
C(1) Li C(1)	79.5 (2)	79.4 (3)
C(1) Li B	39.7 (2)	39.7 (2)
C(1) Li C(2)	114.2 (2)	114.3 (4)
C(1) Li C(3)	117.4 (2)	117.4 (1)
C(3) Li B	127.7 (2)	127.8 (4)
C(2) Li B	121.2 (3)	121.3 (5)
C(2) Li C(3)	111.1 (2)	110.9 (5)
C(1) B C(1)	116.9 (3)	117.0 (3)
C(1) B C(2)	106.8 (2)	107.1 (2)
C(1) B C(3)	108.1 (2)	107.9 (2)
C(2) B C(3)	110.1 (3)	109.6 (3)
C(1) B Li	58.5 (1)	58.5 (2)
C(2) B Li	125.5 (3)	126.3 (4)
C(3) B Li	124.4 (3)	124.0 (4)
H(1) C(1) H(2)	107.9 (14)	108.3 (6)
H(1) C(1) H(3)	102.6 (13)	104.2 (5)
H(2) C(1) H(3)	99.7 (13)	102.6 (5)
H(1) C(1) B	113.4 (10)	115.5 (4)
H(2) C(1) B	120.7 (9)	115.8 (4)
H(3) C(1) B	110.1 (8)	109.1 (4)
H(1) C(1) Li	75.5 (9)	71.2 (4)
H(2) C(1) Li	69.4 (9)	70.4 (4)
B C(1) Li	81.8 (2)	81.7 (3)
H(4) C(2) H(4)	105.9 (18)	112.3 (8)
H(4) C(2) H(5)	107.3 (11)	107.3 (4)
H(4) C(2) B	112.1 (9)	110.5 (3)
H(4) C(2) Li	67.9 (9)	70.0 (3)
H(5) C(2) B	111.6 (13)	108.7 (5)
H(5) C(2) Li	179.9 (52)	178.8 (6)
H(6) C(3) H(6)	106.2 (18)	107.6 (9)
H(6) C(3) H(7)	108.3 (12)	107.3 (6)
H(6) C(3) B	111.0 (10)	111.9 (6)
H(7) C(3) B	111.7 (16)	111.2 (4)
H(6) C(3) Li	67.3 (10)	66.9 (6)
H(7) C(3) Li	71.6 (16)	71.8 (4)
B C(3) Li	176.7 (3)	176.3 (4)

103.5 (1.0)°. The corresponding B-C-H(1), B-C-H(2), and B-C-H(3) angles are 115.5 (4), 115.8 (4), and 109.1 (4)°, respectively. Using Gillespie's arguments,³⁰ the H-C-H angles in a CH₃⁻ group should be significantly less than 109.5°. This is the case for the H_B-C-H_T angle which involves one terminal and one bridging hydrogen atom. The H_B-C-H_B angles of 108.3 (6) and 109.0 (2.9)° may be, in fact, anomalously large and the result of the bridging nature of the hydrogen atoms. An interesting question is whether or not there are any differences in C-H bond lengths associated with bridging and nonbridging H atoms. Unfortunately, the low frequency rotational amplitudes of the methyl group are apparently such that the motional corrections to the bond lengths (Tables VII) are too large to permit a statistically significant comparison to be made. The thermally corrected C-H bond lengths average 1.13 (3) Å for the nonbridging hydrogen atom. Low temperature neutron diffraction data on complexes of this type will be

Table V. Bond Distances (Å) for LiB(CH₃)₄

	X-Ray	Neutron
C(1)-B	1.642 (4)	1.654 (4)
C(2)-B	1.632 (5)	1.640 (6)
C(3)-B	1.621 (5)	1.636 (6)
C(1)-Li	2.189 (5)	2.207 (9)
C(2)-Li	2.375 (7)	2.359 (11)
C(3)-Li	2.389 (7)	2.360 (13)
Li-B	2.541 (5)	2.561 (12)
C(1)-H(1)	0.954 (15)	1.066 (10)
C(1)-H(2)	1.011 (16)	1.104 (7)
C(1)-H(3)	1.024 (18)	1.071 (9)
C(2)-H(4)	1.005 (16)	1.051 (9)
C(2)-H(5)	1.024 (26)	1.122 (15)
C(3)-H(6)	1.056 (16)	1.080 (10)
C(3)-H(7)	0.939 (20)	1.058 (15)
Li-H(1)	2.158 (15)	2.119 (9)
Li-H(2)	2.064 (15)	2.112 (9)
Li-H(4)	2.204 (15)	2.231 (10)
Li-H(5)	2.210 (21)	2.240 (14)
Li-H(6)	2.208 (17)	2.177 (15)
Li-H(7)	2.274 (25)	2.265 (13)

Table VI. Nonbonding Distances (Å) (neutron results) for LiB(CH₃)₄

C(1)-C(2)	2.650 (6)	H(2)-H(7)	2.435 (9)
C(1)-C(3)	2.661 (6)	H(3)-H(6)	2.579 (8)
C(2)-C(3)	2.678 (8)	H(4)-H(4)'	1.745 (11)
C(1)-C(1)'	2.821 (9)	H(4)-H(5)	1.751 (11)
H(1)-H(3)	1.686 (11)	H(4)-H(1)	2.536 (11)
H(1)-H(2)	1.758 (10)	H(5)-H(2)	2.435 (9)
H(1)-H(6)	2.235 (11)	H(6)-H(7)	1.722 (13)
H(2)-H(3)	1.697 (9)	H(6)-H(6)'	1.743 (16)

Table VII. Neutron Distances (Å) Corrected for Thermal Motion for LiB(CH₃)₄

	Riding model, second riding on first		Riding model, second riding on first
B-C(1)	1.671 (4)	C(1)-H(3)	1.112 (10)
B-C(2)	1.659 (6)	C(2)-H(4)	1.093 (10)
B-C(3)	1.652 (6)	C(2)-H(5)	1.166 (17)
C(1)-H(1)	1.106 (11)	C(3)-H(6)	1.154 (11)
C(1)-H(2)	1.147 (9)	C(3)-H(7)	1.135 (17)

required to evaluate the structural effects on methyl group bond lengths and angles.

Although, it has yet to be confirmed by neutron diffraction studies, a dibridged geometry is also undoubtedly present in LiAl[N-C(*t*-Bu)]₂.³¹ The lithium atom in LiAl[N-C(*t*-Bu)]₂ is coordinated to two bridging nitrogen atoms (Figure 3). In addition, two N=C(α)-C(β)-C(γ) groups are bent toward the lithium atom to form a five-membered planar ring, excluding the hydrogen atoms. The hydrogen atom positions on the γ-carbon atom were not reported or shown in the original figure, however, calculations

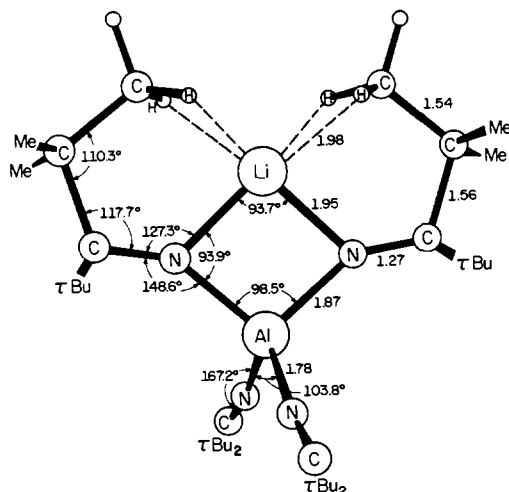


Figure 3. Structure of $\text{LiAl}(\text{N}=\text{C}-t\text{-Bu}_2)_4$; H. M. M. Shearer et al., *Chem. Commun.*, 275 (1971). Hydrogen atom positions were calculated from the data given for $\text{LiAl}(\text{N}=\text{C}-t\text{-Bu}_2)_4$ assuming tetrahedral geometry and C-H distances of 1.09 Å.

show that if a γ -hydrogen atom is in the same plane as the five-membered ring, the Li-H distance would be less than 1.3 Å. The configuration shown in Figure 3 gives a Li-H atom distance of slightly less than 2 Å (1.98 Å), assuming a C-H distance of 1.09 Å. The coordination sphere of the lithium atom then contains four hydrogen atoms at 1.98 Å and two nitrogen atoms at 1.95 Å.

In view of the comparisons made earlier between the Zr-H-B and the Li-H-C structural features, mention should also be made here of the dibridged $\text{Li-H}_2\text{-B}$ geometry observed about the lithium atom in lithium dimethylborohydride bis(dimethoxyethane).³² The Li-H distance (2.06 (4) Å) in this compound is 0.05 Å less than that observed for the CH_2Li in $\text{LiB}(\text{CH}_3)_4$ and, as for the tribridged system, indicates that there is little difference between $>\text{BH}_2\text{M}$ and $>\text{CH}_2\text{M}$ bonding to BH_4^- and $\text{B}(\text{CH}_3)_4^-$ groups.

Monobridged Configurations. The only confirmed example of this for a main group electron deficient center is in hexameric cyclohexyllithium, in which C_6H_{11} groups are rotated in such a way as to result in a short Li α -hydrogen atom distance of 2.00 (4) Å.¹⁷ (The Li-H distance in solid lithium hydride is 2.04 (1) Å, and the sum of the ionic radii, Li^+H^- , is 2.68 Å.) The first coordination sphere of the lithium atom in $\{\text{C}_6\text{H}_{11}\text{Li}\}_6$ is made up of three carbon atoms (two at 2.184 (3) and one at 2.300 (3) Å), and three hydrogen atoms (monobridged at 2.00 (4), 2.09 (1), and 2.33 (1) Å), whereas in methyllithium,¹⁵ the lithium atom achieves coordinative saturation through three carbon atoms at 2.3 (5) Å and three hydrogen atoms tribridging at 2.2 (1) Å.

Two other examples of $\text{M-H}\cdots\text{C}$ monobridged geometries which involve electron deficient coordination sites have been recently reported. A metal-H-C interaction was suggested by Trofiminko³³ from NMR measurements in (diethylidene-1-pyrazolylborato)(η^3 -2-phenylallyl(dicarbonyl)molybdenum). The formally 16 electron molybdenum atom was found to achieve coordinative saturation via a $\text{Mo-H}\cdots\text{C}$ bond with a molybdenum-hydrogen atom distance of 2.15 Å.³⁴ More recent temperature NMR dependent studies have shown an upfield shift of τ 14.3 for the hydrogen atom coordinated to the metal.³⁵ A second example has been suggested from the X-ray data of Maitlis³⁶ for the compound bromobis(triphenylphosphine)-1,2,3,4-tetra(bis-methoxycarbonylbuta-1,3-dienyl)palladium.

Conclusions

In summary, we suggest that a stereochemically impor-

tant mechanism for achieving coordinative saturation at electron deficient metal centers is via a metal-alkane hydrogen interaction. The physical properties of CH_3Li , the gas phase existence of oligomeric units derived from $\text{LiB}(\text{CH}_3)_4$, and the structural properties of these compounds as well as of $\{\text{C}_6\text{H}_{11}\text{Li}\}_6$ and $\{\text{LiAl}(\text{N}=\text{C}(t\text{-Bu})_2)_4\}$ can be considered to be the result of the strong Lewis acidity of the lithium atom toward the weakly basic H atoms in the alkyl groups. Similar structural effects are now known and can be expected for early transition metal centers which are electron deficient. Specific examples of mono-, di- and tribridged $\text{C-H}_n\text{-M}(n = 1, 2, \text{ or } 3)$ configurations have been established and should provide a starting point for understanding metal activation of C-H bonds.

A comparison of the X-ray and neutron diffraction results (Tables IV and V) shows excellent agreement between bond angles and distances involving the heavier atoms. Bond distances for bonds involving hydrogen atoms as determined by neutron diffraction differed from those obtained by X-ray diffraction as expected; however, the bond angles which include hydrogen atoms agree surprisingly well. The largest angle differences are for $\text{H}(4)\text{-C}(2)\text{-H}(4)$ (6.4°), $\text{H}(2)\text{-C}(1)\text{-B}$ (4.9°), and $\text{H}(1)\text{-C}(1)\text{-Li}$ (4.3°). The other 18 bond angles which involve hydrogen atoms differ by 3° or less. Neutron diffraction studies of other compounds containing electron deficient metal-H-C interactions are in progress.

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Supplementary Material Available. Structure factor tables for X-ray and neutron data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 mm, 24 \times reduction, negatives) containing all of the supplementary material for pages in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St. N.W. Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-6401.

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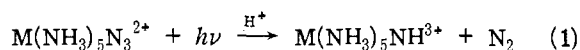
Contrasting Photochemical Processes in Azido- and Isothiocyanatopentaamminecobalt(III) Complexes. Implications for Excited State Processes¹

Guillermo J. Ferraudi, John F. Endicott,* and John R. Barber

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. November 20, 1973

Abstract: Contrasts in the photoreactivity of $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ have been explored in fluid solutions using irradiations in the range $580 \geq \lambda \geq 214$ nm. The predominant product of all irradiations of the azido complex has been established to be $\text{Co}(\text{NH}_3)_4\text{OH}_2\text{N}_3^{2+}$, but the ammonia aquation process was found to be much less important for $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$. In a similar manner, the photoredox modes are less efficient in the isothiocyanato than the azido complex for irradiations with $\lambda \leq 254$ nm. This contrast is attributed to a "heavy atom effect", i.e., to relatively more rapid electronic relaxation and deactivating cascade of photoactive excited states in the isothiocyanato complex. For such ultraviolet irradiations, thermalization of the charge transfer excited states is the postulated mechanism for the observed plateaus in photoredox yield with excitation energy. For deep ultraviolet excitations ($\lambda \leq 254$ nm) a new photoredox process predominates; this new process, postulated to involve direct photooxidation of the solvent, has been found to be common to several pentaammine complexes.

Among the most fundamental concerns in photochemical studies of transition metal complexes are the elucidation of the interdependence of photoreaction mode and efficiency on the electronic structure of the central metal and the coordination environment of the central metal. For the photoredox reactions of prototypical cobalt(III) complexes, efforts to explore such dependencies have often been frustrated by the preponderate observation of a single significant photoreaction mode following excitation of charge transfer to metal (CTTM) absorption bands.² Some useful insights^{2,3} have resulted from the discovery that CTTM bands of ruthenium(III) complexes have very small photoredox efficiencies,^{4,5} similarly the discovery⁶ of a nitrene pathway (eq 1)



following charge transfer excitation of heavy metal azido complexes gives promise of providing an instructive contrast to the photoredox mode reported for first-row transition metal complexes.^{2,7-10} With regard to this latter contrast in reactivities, the change of metal from cobalt to rhodium or iridium in the azidopentaammine complex represents a rather dramatic electronic perturbation. Since $\text{Co}(\text{NH}_3)_5\text{N}_3^{3+}$ actually seems to be one of the most photosensitive cobalt complexes, exhibiting two major photoreaction modes,^{3,8,11} we have chosen to explore relatively small electronic perturbations of the system by contrasting the photoreactivity of azido and isothiocyanato complexes. This alteration in the acido ligand results in some small changes in the relative energies of metal centered excited states¹²⁻¹⁵ but almost no differences in the energies of charge transfer excited states since the reduction potentials^{2c,3,16} of N_3^- and NCS^- are very similar (see Figures 4 and 5, below). Even such a small alteration of the coordination environment and the electronic structure of the complex does dra-

matically alter the photoreactivity of the system, with $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ being relatively photoinsensitive for low energy excitations.

Experimental Section

Materials. The preparations of $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2^{8,17}$ and $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2^{18}$ were performed according to literature descriptions; $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ were available from earlier studies.^{3,19} All complexes were recrystallized until no free NCS^- , N_3^- , etc. could be detected and absorption spectra agreed with literature reports.^{7a,8,17,20}

Water was redistilled from alkaline permanganate in all-glass apparatus. Nitrogen streams were purged of oxygen using scrubbing towers filled with chromous solutions.

The Sephadex C-25 cation exchange resin was used in the sodium form. The Bio-Rad AG-50W-X4 (100-200 mesh) resins were used in the acid form.

Other materials used were reagent grade and used without purification. Spectralquality acetonitrile, glycerol, 2-propanol, and ethylene glycol were used without further purification. The neat alcohols exhibited no significant absorbance in the 200-400 nm region.

Photochemical Apparatuses. The various photochemical apparatuses used in this study have been described previously^{4,8,9,21,22} and will be mentioned only briefly here. Irradiations at $\lambda \geq 285$ nm were performed using a Xenon Model 270 spectral irradiator (Xenon Corporation, Medford, Mass.). The instrument was operated in the monochromator mode with the output of the high intensity grating focused through 0.9×1.5 cm slits onto a sample in a standard cuvet. Irradiation wavelengths and band widths were determined by passing the irradiator output through a Bausch and Lomb high intensity monochromator equipped with a Charles M. Reeder and Co. (Detroit, Mich.) thermopile and microvoltmeter detection systems (band widths at half maximum intensity were ± 20 nm in this system). Irradiations at 254 nm were performed using Ultraviolet Products, Inc., immersion and helical low pressure mercury lamps ($I_0 \approx 8 \times 10^{-4}$ and 3.5×10^{-3} einstein $\text{l}^{-1} \text{min}^{-1}$, respectively) and a Phillips spectral lamp (low pressure mercury; $I_0 \approx 10^{-5}$ einstein $\text{l}^{-1} \text{min}^{-1}$); band widths of the reso-