Stereochemistry of Polynuclear Compounds of the Main-Group Elements.[1,2] A Four-Center and Linear Three-Center Methyl-Bridged Electron-Deficient Boron Compound

Sir:

The characterization of stable electron-deficient organometallic species such as $[(CH_3)_3Al]_2$[3,4a] and $[(CH_3)_5Al_2N(C_6H_5)_2]$[4b] has provided a direct analogy for bonding in isoelectronic nonclassical carbonium ion systems[5] and has suggested the possibility of the formation of electron-deficient intermediates in a variety of organometallic reactions. The conditions which promote bridge bonding by an alkyl group are, however, still not completely resolved.[6] For example, boron and zinc are noted for their inability to form methyl-bridged species such as $[B(CH_3)_3]_2$ and $[Zn(CH_3)_2]_n$,[7] while the closely related metals aluminum, beryllium, and magnesium readily form electron-deficient compounds with a number of hydrocarbon groups. In this communication, we wish to present the first structural example of a hydrocarbon-bridged system in which one of the metal atoms is boron. The structure also contains unusual linear metal–methyl–metal bridge groups.

$LiB(CH_3)_4$ was prepared by previously published procedures.[7–9] This compound has the physical properties which one might expect for a covalent material. It is soluble in benzene and toluene, can be readily sublimed at 140° under vacuum, and has a melting point of 189°. It has an association number in cineole of approximately one[10] and is reported to spontaneously ignite in moist air.[9]

The proton magnetic resonance spectrum of $LiB(CH_3)_4$ in diethyl ether and the association measurements in cineole[8,10] suggest that an associated species, $LiB(CH_3)_4$, exists in these solvents. We have examined the proton magnetic resonance spectrum of $LiB(CH_3)_4$ in toluene and observed a temperature-dependent spectrum very similar to that reported previously in diethyl ether.[8,10] A broad doublet at 40° is resolved into a quartet (J_{B-CH_3} = 3.5 cps) at 100°. The corresponding features in diethyl ether are found at −2 and 37° with J_{B-CH_3} = 3.4 cps.

At an ionization potential of 18 eV and a temperature of 150°, the two most intense peaks in the mass spectrum correspond to $LiB(CH_3)_3^+$ and $B(CH_3)_2^+$. A small amount of Li^+ is also present. At 25 eV the above as well as peaks corresponding to $B(CH_3)_3^+$ and $LiB(CH_3)_4^+$ can be identified. The tetrameric species $[Li_4B_4(CH_3)_{15}]^+$ appeared in a 70-eV spectrum.

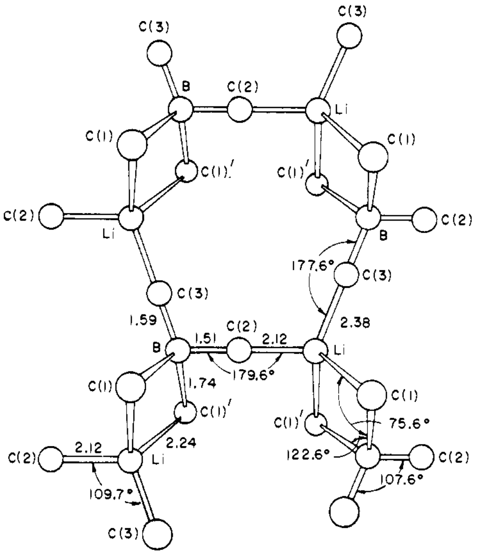

Figure 1. Molecular structure of $LiB(CH_3)_4$. All of the atoms except C(1) and C(1)′ lie in a crystallographic mirror plane which has its normal perpendicular to the plane of the paper. C(1) is related to C(1)′ by the mirror plane.

A single crystal of $LiB(CH_3)_4$ was grown by slow sublimation. It was mounted in a thin-walled glass capillary and sealed under an argon atmosphere. X-Ray precession photographs revealed that the crystal system is orthorhombic and belongs to one of the space groups, *Pnma* or $Pn2_1a$. Statistical tests on the normalized structure factors[11] as well as the $N(z)$ test of Howells, Phillips, and Rogers[12] unambiguously showed the correct space group to be *Pnma*. The cell dimensions as determined by a least-squares refinement of sin θ/λ values for 12 reflections measured on a Picker four-circle diffractometer are a = 9.77 (2), b = 10.80 (2), c = 5.883 (9). The observed density measured 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 $LiB(CH_3)_4$ per unit cell. Crystals grown from benzene have the same unit cell parameters and space group as those obtained by sublimation. Three-dimensional intensity data were collected on the above diffractometer using Mo Kα radiation and a 2θ scanning technique; 310 independent reflections, 217 of which had an integrated intensity greater than two standard deviations, were used in the subsequent analysis.

The crystal and molecular structure of $LiB(CH_3)_4$ was solved by Patterson and Fourier techniques. Full-matrix least-squares refinement of all parameters including positional and isotropic thermal parameters for hydrogen atoms has given a weighted R factor of 0.050 for all reflections and 0.043 for observed reflections only. The hydrogen atom parameters refined smoothly with final values for the isotropic thermal parameters lying between 3 and 5 Å².

The structure is shown in Figure 1 as viewed approximately along the normal to a crystallographic mirror plane. C(1) and C(1)′ are related to each other by the mirror plane; the remaining atoms are in the mirror plane. All the lithium atoms in the plane are related

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(1) The previous paper in the series is J. Toney and G. D. Stucky, *J. Organometal. Chem.*, in press.

(2) This work was supported by the National Science Foundation and by the Advanced Research Projects Agency under Contract No. SD-131.

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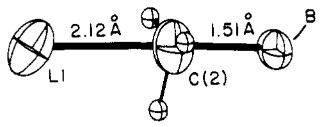


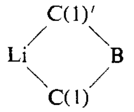
Figure 2. Linear bridge portion B–C(2)–Li illustrating the approximate stereochemistry of C(2).

to each other by symmetry operations of the space group *Pnma*. The same is true of the boron atoms, the methyl carbon atoms C(2), and the methyl carbon atoms C(3), *i.e.*, there are three structurally distinct carbon atoms, one lithium atom, and one boron atom.

The Li–C(1)–B bridge angle (75.6°) and Li–B distance (2.47 Å) are consistent with the corresponding parameters in electron-deficient compounds.[4b] It should also be noted that a completely dissimilar configuration is found for $\mathrm{Li_2Be(CH_3)_4}$,[13] in which the Li–Be approach is 3.67 Å and Li–C distances are 2.52 Å.

The B–C(2)–Li and B–C(3)–Li groups (angles 179.6 and 177.6°) are a surprising and completely unexpected feature of the structure. The only other linear metal–methyl carbon–metal grouping which has been reported is in $\mathrm{(CH_3)_3In}$[14] and apparently involves at most a very weak interaction with unsymmetrical In–$\mathrm{CH_3}$ distances of 2.15 and 3.10 Å. In contrast, the short boron–carbon distance (B–C(2)) of 1.51 Å and lithium–carbon distance (Li–C(2)) of 2.12 Å suggest strongly coordinated linearly bridged groups. In fact, these values represent the shortest known metal–methyl carbon distances for boron and lithium and are to be compared with values of 1.590 (3) and 1.578 (1) reported for $\mathrm{[(CH_3)_2BH]_2}$[15] and $\mathrm{B(CH_3)_3}$[16] and 2.30 and 2.31 Å reported for $\mathrm{LiAl(C_2H_5)_4}$[17] and $\mathrm{CH_3Li}$.[18]

If the



moiety is considered to be a four-electron, four-center electron-deficient group, then the linear groups are two-electron, three-center systems. Because of the heteronuclear nature of the compound, this is undoubtedly an oversimplified view of the charge distribution. The present hydrogen atom positions, which must be regarded as somewhat tentative, are also of interest. The average HCH angles for C(1) and C(2) are 98 and 117°. The average B–C–H angle for C(2) is 102°. In short, the geometry of the methyl groups C(1) suggests a significant amount of carbanion character, while that of the five-coordinate C(2) is approaching a trigonal-bipyramidal configuration (Figure 2). The implications of the above to the stereochemistries of related boron compounds of representative and transition metal elements are currently being investigated.

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Interception of an Intermediate in the Addition of Diphenylcarbene to Acetylenes[1]

Sir:

Two-step addition of triplet carbenes to olefins has been demonstrated several times through the observation of nonstereospecificity in the reaction.[2] Examples typical of the known cases include methylene[3] and biscarbomethoxycarbene,[4] which give a mixture of cyclopropanes independent of the starting olefin and appropriate for product determined by the stereochemical preferences of an intermediate diradical. However, the stereochemistry of the reaction of triplet diphenylcarbene with olefins has not been determined in a system free from abstraction. Thus the stepwise nature of the addition reaction of triplet diphenylcarbene can only be presumed at this time.[5–7]

Acetylenes, which generally form cyclopropenes on reaction with carbenes,[8] lack a stereochemical "handle" through which two-step addition can be observed. Nevertheless it seemed to us that the intermediate diradical might reveal itself, provided an appropriate intramolecular trap were available. Diphenylcarbene provided the necessary triplet nature and the trap at the same time. It was hoped that the initially formed diradical **1** would attack one of the benzene rings to give the intermediate **2** which would suffer hydrogen shift to the indene **3**. With the three monosubstituted acetylenes shown, this is the course the reaction takes.[9]

No more than traces of the cyclopropenes could be formed, as nmr spectra of the crude reaction products do not show appropriate signals. Indenes **3a** and **3c** are known,[10] and were identified by a comparison of spectra. Compound **3b** is new and was identified by elemental analysis and an examination of its spectra, which closely resemble those of **3a** and **3c**.

One must now ask if the cyclopropenes could be serving as the sources of **3a–c**. Both thermal[11] and

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(1) Financial support from the National Science Foundation through Grant No. GP-12759 is gratefully acknowledged.

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(7) The small amount of cyclopropane produced in the reaction of diphenylcarbene with *cis*- or *trans*-2-butene is formed in a largely stereospecific fashion. The cyclopropanes may well be formed largely by singlet carbene and thus not reflect the properties of the triplet.

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