Boron–Carbon Coupling Constants.[1] III. Determination and Calculation of J_{BC} in Some Simple Organoboranes

L. W. HALL,[2] D. W. LOWMAN,[2a] P. D. ELLIS,* and J. D. ODOM*

Directly bonded boron–carbon coupling constants have been determined for eleven organoboranes. Some experimental values have been compared to those predicted by an INDO SCF finite perturbation theory of nuclear spin coupling constants. In these calculations only the Fermi contact contribution to J_{BC} was computed. The overall agreement between theory and experiment was good.

Introduction

Since the first direct experimental determination of a ^{11}B–^{11}B spin coupling constant in our laboratory,[3] qualitative and semiquantitative information concerning the factors which influence boron–boron spin coupling constants has been presented for three-center two-electron BHB bonds[4] in diborane(6) and tetraborane(10) and partial two-center two-electron BB bonds[5,6] in pentaborane(9). In connection with these studies, examination of boron–carbon coupling constants and ^{13}C chemical shifts in organoboranes became of interest.[7] Due to the paucity of experimental data,[8-10] little is known about the ^{13}C nmr parameters of organoboranes. Weigert and Roberts[8] presented the first example of a boron–carbon coupling constant in the tetraphenylborate anion ($J_{BC} = 49.5$ Hz). A boron–carbon coupling constant has also been obtained for 1-methylpentaborane(9).[7] Recently Weigert and Roberts[9] have reported ^{13}C chemical shifts of tri-*n*-propylborane and triisopropylborane. These authors were unable to observe boron–carbon coupling presumably due to partial decoupling by boron quadrupolar relaxation effects.

The ultimate aim of our studies of the nmr parameters of boron-containing compounds is an understanding of the factors which influence these parameters and their relative importance. With this end in mind, it is imperative that we not only be able to measure these values experimentally but also be able to predict chemical shifts and coupling constants. In this way, the level of understanding will hopefully move from an empirical knowledge to a semiquantitative one. At the present time, there is no systematic theoretical interpretation of boron magnetic resonance parameters. Therefore, it would seem reasonable to investigate the nmr properties of compounds containing boron and other nuclei for which semiquantitative theories have been developed.

The rapidly increasing interest and activity in ^{13}C magnetic resonance[11] has focused attention on the need and desirability of reliable theories of ^{13}C magnetic resonance parameters. Recently, semiempirical and *ab initio* SCF perturbation methods[12] have been applied to ^{13}C spin coupling constants[13] and chemical shifts.[14] The overall success of these methods has been promising. To document further the performance of these methods it is important to test these theories against experimental information for a variety of molecules. It is also necessary, however, that the experimental systems chosen for the initial studies be inherently simple with respect to their structure and number of atoms. Furthermore, these systems should exhibit the major types of substituent effects on shielding and spin coupling at the nuclei of interest. Organoboranes are such a class of compounds.

A general theoretical treatment of second-order properties has been introduced by Pople, McIver, and Ostlund[12] and applied to the calculation of indirect spin coupling constants. Briefly, their method involves the calculation of an unrestricted[15] MO wave function in the presence of the contact perturbation. If the MO calculation is performed at the INDO

level[16] of approximation, the contact perturbation takes the form

$$h_B = (8\pi/3)\beta\mu_B s^2{}_B(0) \tag{1}$$

where β is the Bohr magneton, μ_B is the nuclear moment of atom B, and $s^2{}_B(0)$ is the value of the valence s-orbital electron density at the nucleus B. Under the constraints of these MO approximations and with the use of the Hellman–Feynmann theorem,[17] Pople and coworkers[12] demonstrated that the Fermi contact contribution to the indirect spin coupling constant between atoms A and B is

$$J_{AB} = (4/3)^2 h\beta^2 \gamma_A \gamma_B s^2{}_A(0) s^2{}_B(0)[\partial \rho_{s_A s_A}(h_B)/\partial h_B]_{h_B=0} \tag{2}$$

Here, γ_A is the magnetogyric ratio of nucleus A and $\rho_{s_A s_A}(h_B)$ is the diagonal element of the induced spin density matrix which denotes the induced spin density in the s orbital of atom A due to the contact perturbation on atom B.

Presented herein are the experimentally determined ^{13}C chemical shifts and directly bonded boron–carbon couplings of nine simple organoboranes: 1-CH$_3$B$_5$H$_8$, 1-C$_2$H$_5$B$_5$H$_8$, 1-CH(CH$_3$)$_2$B$_5$H$_8$, B(CH$_3$)$_3$, B(C$_2$H$_5$)$_3$, B(C$_2$H$_3$)$_3$, 1,1-(CH$_3$)$_2$B$_2$H$_4$, BH$_3$·CO, and BH$_3$CN$^-$. In addition we also present SCF INDO perturbation theory calculations of the Fermi contact contribution to the boron–carbon coupling constant in these compounds.

Experimental Section

Instrumental Work. Carbon-13 nmr measurements were obtained on a Varian Associates XL-100-15 nmr spectrometer operating in the Fourier transform mode at 25.2 MHz. Field–frequency lock was employed by locking to either ^2H or ^{19}F. Proton noise decoupling was accomplished using the Varian Gyrocode decoupler. For those experiments employing ^{19}F lock and ^1H noise decoupling, a combline band-pass filter was used to prevent the decoupler from interfering with the lock channel.[18,19] Standard variable-temperature accessories were employed. Chemical shifts, reported in ppm with respect to CS$_2$, were obtained with respect to either internal C$_6$D$_6$ (δ(CS$_2$) = δ(C$_6$D$_6$) + 64.7) or acetone-d_6 (δ(CS$_2$) = 159.3 + δ(CD$_3$)) or external CS$_2$. A positive sign for the chemical shift denotes a resonance to higher shielding. The estimated maximum error in the measurement of the chemical shifts is 0.1 ppm. The concentration of the samples varied from 50 to <100% by volume except for tetra-*n*-butylammonium tetraphenylborane (*ca.* 0.15 *M*). The samples were run in 5- or 12-mm o.d. nmr tubes. All spectra were obtained at 28° unless otherwise stated. Spectra of trimethylborane and triethylborane were also obtained at 65 and 85°, respectively.

Computational Methods. All calculations are based on eq 2. The computations were performed on a CDC 6600 computer. In contrast to previous work[12] the convergence requirement for all the SCF calculations was such that the largest element of the difference matrix formed between two successive density matrices was less than or equal to 10^{-9}. The only parameters used in the calculations, other than those used in the INDO MO theory, were the $s^2(0)$ values as given by Pople, *et al.*[12]

Synthesis of Compounds. Standard high-vacuum techniques were employed throughout this investigation.[20] All vacuum systems were equipped with greaseless stopcocks. Trimethylborane, triethylborane, and sodium cyanoborohydride were obtained from Alfa Inorganics,

Table I. Experimental and Calculated Boron–Carbon Coupling Constants for Some Organoboranes[a]

Compd	J_{BC} Exptl	Calcd	$P^2 s_C s_B$	δ_{C_α}	δ_{C_β}
1-CH(CH$_3$)$_2$B$_5$H$_8$[b]	75.0 ± 0.5	71.6	0.0974	187.1	166.2
1-CH$_3$B$_5$H$_8$[b]	72.7 ± 0.2	72.6	0.1050	205.0	
1-CH$_3$CH$_2$B$_5$H$_8$[b]	72.1 ± 0.5	72.8	0.1017	195.7	176.0
B(C$_2$H$_3$)$_3$[c]	<65	65.8	0.1166	51.3	54.8
1,1-(CH$_3$)$_2$B$_2$H$_4$[d]	61.3	51.0	0.0952	183.1	
BH$_3$CN$^-$[e]	53.0	51.7	0.1143	47.4	
B(C$_2$H$_5$)$_3$[f]	<52	44.8	0.0788	173.0	184.5
Na$^+$B(C$_6$H$_5$)$_4^-$[g]	49.4 ± 1.0				
(n-Bu)$_4$N$^+$B(C$_6$H$_5$)$_4^-$[g]	48.8 ± 1.0				
B(CH$_3$)$_3$[f]	46.7	42.1	0.0964	179.0	
BH$_3$·CO[h]	30.2 ± 0.4	29.3	0.1027	36.0	

[a] Coupling constants are reported in Hz; chemical shifts are reported in ppm with respect to CS$_2$. A positive value of the chemical shift denotes shifts to higher shieldings. [b] A combination of the B$_5$H$_9$ structural data from K. Hedberg, M. E. Jones, and V. Schomaker, *J. Amer. Chem. Soc.*, 73, 3538 (1951), and H. J. Hrostowski and R. J. Myers, *J. Chem. Phys.*, 22, 262 (1954). The geometry of the alkyl group was synthesized from the standard geometrical model of Pople and Gordon.[34] [c] Planar structure; bond angles and distances are those from the standard model. [d] Standard methyl groups attached to the diborane framework of K. Hedberg and V. Schomaker, *J. Amer. Chem. Soc.*, 73, 1482 (1951). [e] The BH$_3$–C geometry is that used for BH$_3$·CO and the CN bond distance is that employed in the standard geometrical model. [f] Standard geometrical model. [g] For Na$^+$B(C$_6$H$_5$)$_4^-$: $^2J_{BC} = 1.5 ± 0.05$ Hz, $^3J_{BC} = 2.7 ± 0.05$ Hz, $^4J_{BC} = 0.5 ± 0.1$ Hz. For (n-Bu)$_4$N$^+$B(C$_6$H$_5$)$_4^-$: $^2J_{BC} = 1.4 ± 0.05$ Hz, $^3J_{BC} = 2.8 ± 0.05$ Hz, $^4J_{BC} = 0.6 ± 0.1$ Hz (data from ref 1). [h] See ref 35.

and pentaborane(9) was obtained from Callery Chemical Co. 1-Methyl-,[21] 1-ethyl-,[22] and 1-isopropylpentaborane(9)[22] derivatives, 1,1-dimethyldiborane,[23] and borane–carbonyl[24,25] were prepared by previously published procedures. 2-Isopropylpentaborane(9) was obtained as a minor product in the 1-isopropylpentaborane(9) synthesis.[22] Tetra-*n*-butylammonium tetraphenylborane was obtained from a laboratory supply.

Trivinylborane samples were obtained *via* two different synthetic routes, one of which has been previously described in detail.[26] The second method involved the reaction of boron tribromide with tetravinyltin (both obtained commercially from Columbia Organic Chemicals Co., Inc.). Boron tribromide was purified by trap-to-trap fractionation until its vapor pressure was 19 mm at 0°.[20] Equimolar amounts of BBr$_3$ and Sn(C$_2$H$_3$)$_4$ were condensed, at –196°, from the vacuum system into a 500-ml bulb, equipped with a break-seal, and allowed to stand at room temperature for approximately 24 hr. Volatile products obtained from the reaction of 33.5 mmol of each reactant were separated, with considerable difficulty, by low-temperature column fractionation.[27] In this manner three fractions were obtained: (1) B(C$_2$H$_3$)$_3$, 10.7 mmol (31.9%); (2) a mixture of predominantly B(C$_2$H$_3$)$_3$, with some BrB(C$_2$H$_3$)$_2$, 6.4 mmol; (3) BrB(C$_2$H$_3$)$_2$, 9.6 mmol (28.7%). Trivinylborane was characterized by its infrared spectrum,[26] mass spectrum,[28] and ^{11}B nmr spectrum.[28]

Results and Discussion

Qualitative Observations. A tabulation of ^{13}C nmr parameters for the organoboranes studied is presented in Table I. Well-defined quartets were obtained for the 1-alkylpentaborane(9) derivatives, BH$_3$·CO, and the tetraphenylborate anion. For the other compounds studied, the line shape of the ^{13}C resonance varied considerably. This is undoubtedly due to the different spin–lattice relaxation times of the boron atoms which are coupled to the carbon nucleus under observation. A study of boron T_1's in boron hydrides and organoboranes is currently in progress in our laboratories in order to further our understanding of the factors which govern these relaxation times. Theoretical considerations of the line shape of the quartet obtained for a species coupled to a quadrupolar nucleus[29-31] shows that, upon collapse, the two central resonances move outward only very slightly while the outer two resonances collapse inward. Greater change in the outer
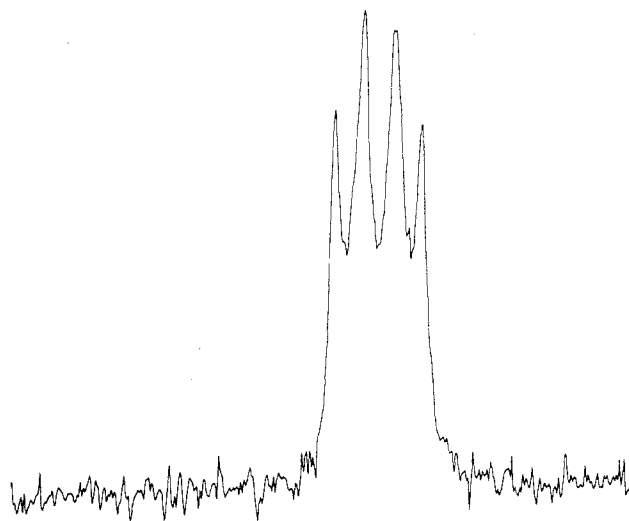

Figure 1. ^{1}H noise-decoupled ^{13}C FT spectrum of neat B(CH$_3$)$_3$. This is a result of 68,000 pulses with an acquisition time of 0.4 sec and no pulse delay.
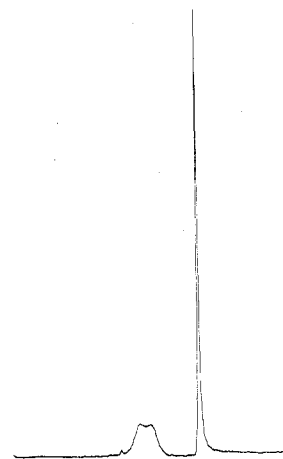

Figure 2. ^{1}H noise-decoupled ^{13}C FT spectrum of B(C$_2$H$_5$)$_3$. The most shielded resonance is that of the methyl group. The partially resolved multiplet (least shielded) is that of the methylene carbons. This is the result of 31,000 pulses with an acquisition time of 0.8 sec and no pulse delay.

resonance separations takes place than in the central resonance separation. Thus, the separation between the two central resonances is a good indicator of an upper limit to J_{BC} in partially collapsed quartets. The ^{13}C spectra obtained for trimethylborane and triethylborane are presented in Figures 1 and 2, respectively. The spectrum of B(CH$_3$)$_3$ (Figure 1) shows an example of a quartet with minimal collapse while that of B(C$_2$H$_5$)$_3$ (Figure 2) shows an example of severe collapse. Even though the outer two resonances in Figure 2 are collapsed into the central two resonances, it is still possible to obtain a value for the separation between the two inner resonances, *i.e.*, an upper limit to the value of J_{BC}.

Two species of special interest in Table I are BH$_3$·CO and BH$_3$CN$^-$. These systems are of interest because they are isoelectronic with each other and furthermore they are isoelectronic with the acylium ion, CH$_3$CO$^+$. This, then, allows a comparison between J_{CC} and J_{BC} for isoelectronic molecules. Rearrangement of eq 2 and use of the $s^2(0)$ values of Pople and coworkers[12] yield

$$J_{BC}/J_{CC} = \gamma_B s^2_B(0)/\gamma_C s^2_C(0) \tag{3}$$

$$J_{BC} = 0.72 J_{CC} \tag{4}$$

In arriving at eq 3 we have assumed that for isoelectronic species the derivatives of the induced spin density matrix
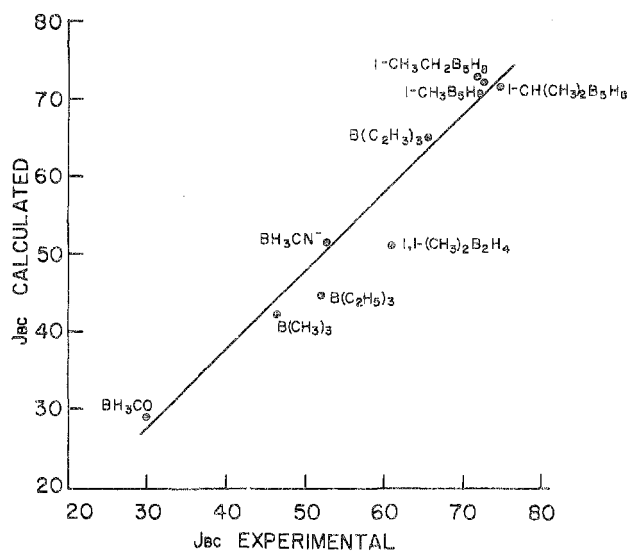
Figure 3. A plot of J_{BC} experimental *vs.* the calculated value of J_{BC}. The calculated couplings resulted from an INDO SCF perturbation theory of the Fermi contact contribution to the coupling constant. The solid line is of unit slope.

element $\rho_{s_A s_A}(h_B)$ will be approximately equal for a carbon–carbon coupling and a boron–carbon coupling.

Using the value[32] of J_{CC} for CH_3CO^+ of 46.5 Hz and comparing the experimental values of J_{BC} for $BH_3 \cdot CO$ and BH_3CN^- we find that eq 4 is valid for CH_3CO^+ and $BH_3 \cdot CO$ but not for the comparison of CH_3CO^+ and BH_3CN^-. From these results it appears not only that $BH_3 \cdot CO$ and CH_3CO^+ are isoelectronic but also that the bonding between the boron and carbon in $BH_3 \cdot CO$ is very similar to the carbon–carbon bonding in CH_3CO^+. However, this is apparently not the case when one compares BH_3CN^- to CH_3CO^+. Even though the molecules are isoelectronic the charge distribution in the respective molecules and, hence, their solution structures must be different. These results underscore the problems that can be encountered in making predictions of properties of molecules solely on the basis of their being isoelectronic with one another.

Comparison between Experimental and Predicted Values of J_{BC}. Presented in Table I and depicted graphically in Figure 3 are the experimental and predicted values for J_{BC}. The overall pattern of agreement between the limited number of calculated coupling constants and the experimental values is encouraging. Except when there are small experimental differences, there exists a monotonic trend between the calculated couplings and the experimental data. Beginning with the 1-substituted pentaborane(9) compounds ($-CH_3$, $-C_2H_5$, $-CH(CH_3)_2$), the finite perturbation theory predicted that the experimental couplings would show very little change upon substitution. For the trisubstituted boranes the theory again predicted the correct order for J_{BC} in going from trivinyl- to triethyl- to trimethylborane. Furthermore, even though the molecules BH_3CN^- and $BH_3 \cdot CO$ are isoelectronic, they do not have similar values for J_{BC}, the difference being approximately 23 Hz. The theoretical prediction for this difference is about 22 Hz.

From the data presented in Figure 3 it is apparent that there are two points which dramatically deviate from the unit slope line, $1,1-(CH_3)_2B_2H_4$ and $B(C_2H_5)_3$. These large differences may be, in part, due to the approximate geometries used for these compounds. The alkyl fragments used in these calculations were assumed to be tetrahedral.[34] In preliminary calculations on $BH_3 \cdot CO$ and BH_3CN^-, it was assumed that the BH_3- fragment was also tetrahedral. The calculated results using these geometries were 65.6 and 46.8 Hz for BH_3CN^- and $BH_3 \cdot CO$, respectively. These values differ significantly

from the experimental data. Use of the published structural data for $BH_3 \cdot CO$[35] dramatically improves the agreement between theory and experiment. Hence, the boron–carbon coupling constant calculation is sensitive to the structural data used in the calculation.

Three points are apparent from the data obtained in this study. First, it appears that the finite perturbation theory of spin couplings (Fermi contact contribution) can successfully account for the major patterns of substituent effects on boron–carbon coupling constants. This level of agreement suggests that the amount of orbital–dipole contribution[33] to J_{BC} is approximately constant in the series of molecules investigated here. Second, if one makes the corresponding plot of $P^2_{2s_B 2s_C}$ (fractional s character) *vs.* the experimental values for J_{BC} there is *no* correlation. Hence, for the limited number of calculations presented here, there is *no* apparent trend between fractional s character in the carbon–boron bond and the experimental value of J_{BC}. Finally, it is also apparent that more comparisons between theory and experiment are needed before any definitive conclusions can be drawn. These comparisons should be made over a wider range of substituents and work toward that end is currently in progress in our laboratories.

Registry No. 1-$CH(CH_3)_2B_5H_8$, 37838-05-4; 1-$CH_3B_5H_8$, 19495-55-7; 1-$CH_3CH_2B_5H_8$, 23753-61-9; $B(C_2H_3)_3$, 7217-01-8; 1,1-$(CH_3)_2B_2H_4$, 16924-32-6; BH_3CN^-, 33195-00-5; $B(C_2H_5)_3$, 97-94-9; $Na^+B(C_6H_5)_4^-$, 143-66-8; $(n\text{-}Bu)_4N^+B(C_6H_5)_4^-$, 15522-59-5; $B(CH_3)_3$, 593-90-8; $BH_3 \cdot CO$, 13205-44-2; ^{13}C, 14762-74-4.

References and Notes

(1) Part II: J. D. Odom, L. W. Hall, and P. D. Ellis, *Org. Magn. Resonance*, 6, 360 (1974).

(2) (a) Taken in part from the Ph.D. thesis of L. W. Hall and the M.S. thesis of D. W. Lowman submitted to the Department of Chemistry in partial fulfillment of their respective degrees. (b) Tennessee Eastman Fellow, 1974–1975.

(3) J. D. Odom, P. D. Ellis, and H. C. Walsh, *J. Amer. Chem. Soc.*, 93, 3529 (1971).

(4) J. D. Odom, P. D. Ellis, D. W. Lowman, and M. H. Gross, *Inorg. Chem.*, 12, 95 (1973).

(5) D. W. Lowman, P. D. Ellis, and J. D. Odom, *Inorg. Chem.*, 12, 681 (1973).

(6) D. W. Lowman, P. D. Ellis, and J. D. Odom, *J. Magn. Resonance*, 8, 289 (1972).

(7) P. D. Ellis, J. D. Odom, D. W. Lowman, and A. D. Cardin, *J. Amer. Chem. Soc.*, 93, 6704 (1971).

(8) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 91, 4940 (1969).

(9) F. J. Weigert and J. D. Roberts, *Inorg. Chem.*, 12, 313 (1973).

(10) D. E. Axelson, A. J. Oliver, and C. E. Holloway, *Org. Magn. Resonance*, 5, 255 (1973).

(11) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N.Y., 1972: J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N.Y., 1972.

(12) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, 49, 2960, 2965 (1968).

(13) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 92, 1, 11, 4151, 4497, 4506 (1970); reference 33.

(14) P. D. Ellis, G. E. Maciel, and J. W. McIver, Jr., *J. Amer. Chem. Soc.*, 94, 4069 (1972); R. Ditchfield, *Chem. Phys. Lett.*, 15, 203 (1972); R. Ditchfield, *J. Chem. Phys.*, 56, 5688 (1972); R. Ditchfield and P. D. Ellis, *Chem. Phys. Lett.*, 17, 342 (1972); A. P. Zens, P. D. Ellis, and R. Ditchfield, *J. Amer. Chem. Soc.*, 96, 1309 (1974); R. Ditchfield and P. D. Ellis in "Topics in Carbon-13 NMR Spectroscopy," Chapter 1, G. C. Levy, Ed., Interscience, New York, N.Y.

(15) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 22, 571 (1954).

(16) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967).

(17) H. Hellman, "Einfuhring in die Quartenchemie," Franz Deutiche, Leipzig, Germany, 1937; R. P. Feynman, *Phys. Rev.*, 56, 340 (1939).

(18) A 146-MHz filter was used as in R. E. Fisher, *QST*, 52, 44 (1968).

(19) V. J. Bartuska, T. T. Nakashima, and G. E. Maciel, *Rev. Sci. Instrum.*, **41**, 1458 (1972).
(20) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N.Y., 1969.
(21) T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, **1**, 742 (1962).
(22) G. E. Ryschkewitsch, S. W. Harris, E. J. Mezey, H. H. Sisler, E. A. Weilmuenster, and A. B. Garrett, *Inorg. Chem.*, **2**, 890 (1963).
(23) H. I. Schlesinger and A. O. Walker, *J. Amer. Chem. Soc.*, **57**, 621 (1935).
(24) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **59**, 780 (1937).
(25) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).
(26) J. D. Odom, L. W. Hall, S. Riethmiller, and J. R. Durig, *Inorg. Chem.*, **13**, 170 (1974).

(27) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).
(28) C. D. Good and D. M. Ritter, *J. Amer. Chem. Soc.*, **84**, 1162 (1962); *J. Chem. Eng. Data*, **7**, 416 (1962).
(29) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).
(30) J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, **41**, 3063 (1963).
(31) M. Suzuki and R. Kubo, *Mol. Phys.*, **7**, 201 (1963).
(32) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 11 (1970).
(33) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).
(34) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).
(35) W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.*, **78**, 512 (1950).

Contribution from the Department of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

Existence of Complexes of LiAlH₄ and AlH₃ in Ether Solvents and in the Solid State
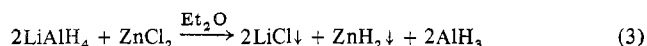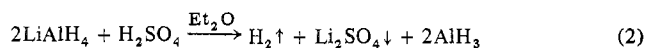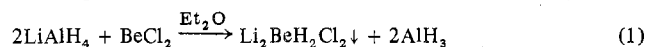
E. C. ASHBY,* JOHN J. WATKINS, and H. S. PRASAD

The reaction between LiAlH₄ and AlH₃ in 1:1, 1:2, 1:3, and 1:4 molar ratios in both diethyl ether and THF has been investigated by infrared spectroscopy. Also solutions of LiAlH₄ and AlH₃ in diethyl ether were evaporated to dryness and the resulting solids were examined by dta–tga and X-ray powder diffraction methods. Previous reports claiming the preparation of LiAl₂H₇ and LiAl₃H₁₀ by the reaction of LiAlH₄ with BeCl₂ in ether and also the reaction of LiH with AlH₃ were studied in detail and attempts were made to prepare the complexes by exactly the same procedure reported. Contrary to previous reports, in no case was any evidence found to indicate the existence of LiAl₂H₇, LiAl₃H₁₀, or any complex between LiAlH₄ and AlH₃ in ether or THF solution or in the solid state as products in the reactions studied.

Introduction

Recently we found that diethyl ether soluble aluminum hydride can be prepared by a number of different methods.[1,2] (See eq 1–3.) This finding allows a convenient study of the

$$2LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2\downarrow + 2AlH_3 \quad (1)$$

$$2LiAlH_4 + H_2SO_4 \xrightarrow{Et_2O} H_2\uparrow + Li_2SO_4\downarrow + 2AlH_3 \quad (2)$$

$$2LiAlH_4 + ZnCl_2 \xrightarrow{Et_2O} 2LiCl\downarrow + ZnH_2\downarrow + 2AlH_3 \quad (3)$$

interaction between LiAlH₄ and AlH₃ in diethyl ether which has been reported by a number of laboratories to be strong enough so as to produce stable complexes (LiAlH₄·nAlH₃, where n = 1–4). Although aluminum hydride can be prepared in tetrahydrofuran,[3] complexes between LiAlH₄ and AlH₃ would not be expected to be stable due to the strong aluminum–oxygen bond in H₃Al–OC₄H₈.

Recent Russian work[4] claims the preparation of LiAl₂H₇ (LiAlH₄·AlH₃) and LiAl₃H₁₀ (LiAlH₄·2AlH₃) in diethyl ether; however, the compounds were reported to be more stable in the solid state than in ether solution. Also a recent study concerning the structure and properties of LiAl₂H₇ has appeared in the French literature.[5] These workers reported LiAl₂H₇ to be stable in the solid state but unstable in diethyl ether solution. In addition, other French workers[6] have reported the preparation of the compound LiAl₄H₁₃ (LiAlH₄·3AlH₃) by the reaction of LiH with AlH₃ in ether solvent. In each case the reports claim solid-state stability of the complexes but report diethyl ether solutions as being unstable.

On the other hand, several reports have appeared that claim the formation of complexes of the type LiAlH₄·nAlH₃ in ether solvent. It has been reported that the electrical conductivity of solutions of LiAlH₄ and AlH₃ in diethyl ether indicates the formation of ions alternate to those arising from LiAlH₄ and AlH₃ separately.[7,8] Because of these reports and because of the analogy to the MAlH₄·nAlR₃ systems,[9] further claims for the existence of MAlH₄·nAlH₃ complexes have been made, in particular, LiAl₂H₇.[10]

We have been evaluating new hydrides as stereoselective reducing agents and felt that LiAlH₄·AlH₃ compounds would

behave differently from either LiAlH₄ or AlH₃. Reduction studies in this laboratory have shown that a mixture of LiAlH₄ and AlH₃ in ether solvent gives the same stereochemistry of reduction of 4-*tert*-butylcyclohexanone and 3,3,5-trimethyl-cyclohexanone as would be expected for a simple physical mixture of LiAlH₄ and AlH₃. At this point we decided to take a closer look at the so-called complexes "LiAlH₄·nAlH₃" both in ether solution by infrared spectroscopy and in the solid state by dta–tga and powder diffraction.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[11] Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide columns to remove oxygen and Dry Ice–acetone traps to remove solvent vapors.[12]

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solids were run as Nujol mulls between CsI plates. Solutions were run in matched 0.10-mm path length NaCl cells. X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually. Dta–tga data were obtained under vacuum with a modified Mettler thermoanalyzer, Model II. A more detailed description of this apparatus has been given elsewhere.[13,14]

Analytical Work. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[11] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration.

Materials. LiAlH₄ was obtained as gray, lumpy solids from Ventron, Metal Hydrides Division. Solutions of LiAlH₄ in diethyl ether and THF were prepared by stirring the solid hydride for 24 hr with freshly distilled solvent, followed by filtration, to yield a clear, colorless solution. Lithium hydride was prepared by the hydrogenation of *tert*-butyllithium at room temperature at 3000 psi for 24 hr. A slurry of LiH in diethyl ether was used. Aluminum hydride in diethyl ether was prepared by the reaction of LiAlH₄ with BeCl₂ in a 2:1 molar ratio.[1,2] The white solid was removed by filtration leaving a nearly lithium-free clear solution of aluminum hydride. The molar ratios of Al to H to Li in this solution were 1.00:3.13:0.043. Aluminum hydride in THF was prepared by the reaction of 100% H₂SO₄ with LiAlH₄ in THF according to the procedure of Brown.[3] Li₂SO₄ was