doubtful that this cation could be formed from the reactions which provided its isolation and identification.

The isolation of $H_2B(NH_2CH_3)_2BH_4$ provides another example in the growing list of reactions which initiate the unsymmetrical cleavage of diborane. The relative thermodynamic stability of $H_2B(NH_2CH_3)_2BH_4$ and $H_2B(NH_3)_2BH_4$ compared to the corresponding amine borane might be indicative of the probability of the occurrence of similar reactions with other donor systems. Ammonia borane, H_3B-NH_3, decomposes to form the more stable $H_2B(NH_3)_2BH_4$. However, methylamine borane is more stable than $H_2B(NH_2-CH_3)_2BH_4$, as $H_2B(NH_2CH_3)_2BH_4$ slowly forms $H_3B-NH_2CH_3$ upon standing. Therefore, dimethylamine,[3] trimethylamine, and other donor molecules (DR'_3) might also initiate the unsymmetrical cleavage of diborane. Compounds of the type $H_2B(DR'_3)_2BH_4$ might be capable of isolation only at low temperatures because they will probably rapidly rearrange to corresponding compounds of the type $H_3B-DR'_3$ at room temperature. Thus, there might be only one type of reaction of donor systems with diborane, unsymmetrical cleavage. The compounds observed at room temperature would depend on the relative stabilities of the two systems, $H_2B(DR'_3)_2BH_4$ and $H_3B-DR'_3$, instead of the occurrence of symmetrical and unsymmetrical cleavage of diborane.

Acknowledgments.—The author wishes to thank Professor A. W. Laubengayer for his cooperation in making his research facilities available.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE
STATE UNIVERSITY, DETROIT 2, MICHIGAN

Prediction of Stabilities of Trialkylgallium Addition Compounds

BY ALLAN LEIB,[1] MERLE T. EMERSON, AND JOHN P. OLIVER

The ability of group III derivatives to form addition compounds and the stability of these has been recognized as indicative of their chemical reactivity.[2] In the case of many of these compounds either direct gas phase dissociation measurements or calorimetric determinations provide the desired information; however, these standard techniques are not readily applicable to triethylgallium addition compounds because of their low volatility, small heat of formation, and tendency to undergo decomposition. Therefore, another suitable measure of stability is needed.

It has been shown that the chemical shift of the methyl group and the internal chemical shift of the ethyl group in CH_3X and CH_3CH_2X compounds have a direct dependence on the electronegativity of the attached group.[3,4] When considering the formation of an addition compound between a Lewis acid and base, a shift in electron density must take place upon formation of the coordinate bond. One would suppose that a large shift in electron density would correspond to the formation of a strong bond. This shift in electron density will be reflected in the chemical shift of neighboring protons in the moieties attached to the donor and acceptor. Therefore, the change in chemical shift of neighboring protons should reflect the stability of the addition compound. Studies of n.m.r. chemical shifts have been correlated with the stability of addition compounds of boron trihalides,[5] trimethylboron,[6] triethylboron,[7] and triethylaluminum.[8] Good agreements between chemical shift changes and independently determined stabilities were found. In this note we report a study of the change in chemical shift for a series of trimethyl- and triethylgallium addition compounds. The data are then used to obtain relative stabilities for these adducts.

Experimental

Trimethyl- and triethylgallium were prepared by reaction of the corresponding mercury compound with gallium metal[9] and were purified by repeated vacuum distillation or gas chromatography. Samples were prepared by distilling the gallium alkyl directly into the n.m.r. sample tube, adding excess base, and allowing the mixtures to warm to 0°. After standing for several hours to ensure complete reaction, the excess base was removed by low-temperature distillation. Alternately, to ensure the formation of 1:1 addition compounds a second series of samples was prepared by reaction of equimolar quantities of base with either trimethyl- or triethylgallium (determined by weight or gas volume). The samples were then dissolved in sufficient Freon 11 or Freon 113 to make a 20 to 30% solution and 1% of an internal standard was added. 1,1,1-Trichloroethane was used as an internal standard in the first experiments but was discarded because it underwent reaction in this system. Benzene or cyclopentane was used thereafter as internal standard. All reported line positions and chemical shifts were computed relative to cyclopentane with the results from the two series of samples within experimental error of each other. N.m.r. spectra were taken on a Varian D.P. 60 spectrometer and were calibrated by the audiofrequency side-band technique. Line frequencies were obtained by averaging the interpolated line positions from four or more spectra. The average deviation of line positions was ±0.2 c.p.s. The observed spectra of the addition compounds were analyzed as A_3B_2 systems,[10–12] and the resulting spectral parameters were used to calculate the theoretical line positions and intensities. These were then compared to the experimental spectra to check the validity of these parameters.

Discussion

The resulting chemical shifts, internal chemical shifts, and coupling constants are listed in Table I.

(3) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).
(4) C. R. McCoy and A. L. Allred, *J. Inorg. Nucl. Chem.*, **25**, 1219 (1963).
(5) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).
(6) T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).
(7) R. R. Holmes and R. P. Carter, Jr., *Inorg. Chem.*, **2**, 1146 (1963).
(8) H. E. Swift, C. P. Poole, Jr., and J. F. Itzel, Jr., *J. Phys. Chem.*, **68**, 2509 (1964).
(9) L. M. Dennis and W. Patnode, *J. Am. Chem. Soc.*, **54**, 182 (1932).
(10) P. T. Narasimhan and M. T. Rogers, *ibid.*, **82**, 34 (1960).
(11) P. T. Narasimhan and M. T. Rogers, *ibid.*, **82**, 5983 (1960).
(12) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

Table I

Chemical Shifts, Internal Chemical Shifts, Coupling Constants, and Heats of Dissociation of Alkylgallium Derivatives

Compound	δ_{CH_3}, p.p.m.	ΔH,[a] kcal./mole
$(CH_3)_3Ga$ (20%)	1.495	
$(CH_3)_3Ga:S(CH_3)_2$	1.899	8[b]
$(CH_3)_3Ga:O(CH_3)_2$	1.965	9.5[b]
$(CH_3)_3Ga:NH_2CH_3$	2.082	(17.1)
$(CH_3)_3Ga:P(CH_3)_3$	2.085	18[b]
$(CH_3)_3Ga:NH_3$	2.108	(18.5)
$(CH_3)_3Ga:N(CH_3)_3$	2.161	21[b,c]
$(CH_3)_3Ga:NH(CH_3)_2$	2.215	(24.0)

Compound	$\delta_{CH_2} - \delta_{CH_3}$, p.p.m.	J, c.p.s.	
$(C_2H_5)_3Ga$ (5%)	0.486	8.02	
$(C_2H_5)_3Ga$ (25%)	0.494	8.04	
$(C_2H_5)_3Ga$ (100%)	0.497	8.07	
$(C_2H_5)_3Ga:S(CH_3)_2$	0.726	8.32	6[d]
$(C_2H_5)_3Ga:O(CH_3)_2$	0.765	8.10	(9.0)
$(C_2H_5)_3Ga:P(CH_3)_3$	0.840	8.15	(14.5)
$(C_2H_5)_3Ga:N(CH_3)_3$	0.872	8.15	17[d]
$(C_2H_5)_3Ga:NH(CH_3)_2$	0.895	8.28	(18.8)
$(C_2H_5)_3Ga:NH_3$	0.903	7.98	(19.2)
$(C_2H_5)_3Ga:NH_2CH_3$	0.909	8.09	(19.8)

[a] Values in parentheses are taken from Figure 1. [b] G. E. Coates, *J. Chem. Soc.*, 2003 (1951). [c] G. E. Coates and R. G. Hayter, *ibid.*, 2519 (1953). [d] L. G. Stevens, B. Park, and J. P. Oliver, *J. Inorg. Nucl. Chem.*, **26**, 97 (1964).

It has been shown that in ethyl derivatives the internal shift is more nearly dependent on the electronegativity[3,13,14] of the attached substituent than the chemical shifts of either the CH_2 or CH_3 protons. The same rationale that applies in this case would be expected to apply to triethylgallium and its adducts. Therefore, the internal shift is used in preference to the individual CH_2 and CH_3 shifts to obtain an estimate of the adduct bond strength. The free acid, triethylgallium, was studied at three different concentrations to determine if there is any dependence of the internal shift on concentration. No significant change was observed in going from a 5% to a neat sample, and the spectral parameters obtained were in good agreement with those previously determined.[11,15] Upon formation of an addition compound an increase in the internal shift was observed. As one would expect, there was no significant change in the coupling constant upon coordination.

If the arguments relating chemical shifts and bond strengths apply, then the relative stabilities should be in the following order, for triethylgallium: $NH_2CH_3 >$ $NH_3 > NH(CH_3)_2 > N(CH_3)_3 > P(CH_3)_3 > O(CH_3)_2 >$ $S(CH_3)_2$. In two cases, $(C_2H_5)_3Ga:N(CH_3)_3$ and $(C_2H_5)_3Ga:S(CH_3)_2$, dissociation data are available.[16] For these we find that this correlation holds: the internal chemical shift is greater for the more stable addition compound. This can be seen graphically in Figure 1. As a further test of this, the chemical shifts of a
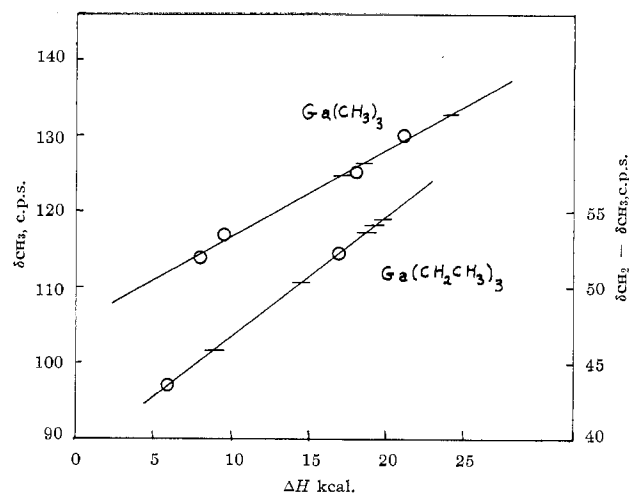
(13) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
(14) J. R. Cavanaugh and B. P. Dailey, *ibid.*, **34**, 1099 (1961).
(15) S. Brownstein, B. C. Smith, G. Ehrlich, and A. W. Laubengayer, *J. Am. Chem. Soc.*, **81**, 3826 (1959).
(16) L. G. Stevens, B. Park, and J. P. Oliver, *J. Inorg. Nucl. Chem.*, **26**, 97 (1964).

Figure 1.—The chemical shift, δ_{CH_3}, of trimethylgallium and the internal chemical shift, $\delta_{CH_2} - \delta_{CH_3}$, of triethylgallium are plotted *vs.* the heat of dissociation, ΔH, for the addition compounds listed in Table I. O represents points for which both δ and ΔH are known.

number of trimethylgallium addition compounds were measured and may also be found in Table I along with the dissociation energies determined by other means, where available.[17,18] It can be seen that the chemical shifts of the methyl protons on the gallium fragment (Figure 1) again correlate well with the bond dissociation energies: $NH(CH_3)_2 > N(CH_3)_3$ (21 kcal.) $>$ $NH_3 > P(CH_3)_3$ (18 kcal.) $> NH_2(CH_3) > O(CH_3)_2$ (9.5 kcal.) $> S(CH_3)_2$ (8 kcal.). On this basis it is felt that a reliable prediction of the relative stabilities may be made for alkylgallium addition compounds based either upon the internal chemical shift of the ethyl group on triethylgallium or on the chemical shift of the methyl group on trimethylgallium. This method of estimating the relative stabilities of addition compounds has the advantage that the measurements are easily performed on systems in which it would otherwise be difficult to obtain this information.

Since it is known that several factors contribute to the chemical shift parameter,[13,14] the magnitude of the change in chemical shift upon coordination should not be assumed to give a quantitative measure of electron density change and hence of bond strength. Nevertheless, chemical shifts have been found to give essentially linear correlations with electronegativity in many cases[3,4] and recently with bond strength in BX_3 addition compounds.[5] In view of this we have shown in Figure 1 experimental chemical shifts *vs.* bond strength for those adducts whose stability has been determined by other means. In the case of the $Ga(CH_3)_3$ adducts a reasonably linear correlation was obtained. The remaining chemical shift values were then placed on this line to give estimates of the bond strength for the corresponding addition compounds. An analogous plot has been made for the ethyl derivatives using the internal chemical shift.

(17) G. E. Coates, *J. Chem. Soc.*, 2003 (1951).
(18) G. E. Coates and R. G. Hayter, *ibid.*, 2519 (1953).