Cadmium Derivatives of Decaborane

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Diethylcadmium (Et_2Cd) reacts with decaborane ($B_{10}H_{14}$) in ether solvents to form $CdB_{10}H_{12},2S$ (where S is diethyl ether or tetrahydrofuran). This compound is thought to be the first example of a neutral, 6,9-internally-bridged derivative of $B_{10}H_{14}$ (2802 topology) and contains direct Cd–B bonds. The cadmium borane reacts quantitatively with ethereal hydrogen chloride to give decaborane and cadmium chloride, and ionises in aqueous solution to yield the novel dianion $[(B_{10}H_{12})_2Cd]^{2-}$. The properties and structures of these compounds are discussed.

DIALKYL- and DIARYL-CADMIUMS are known to metalate compounds containing acidic hydrogen,[1] and, since decaborane can behave as a protic species,[2] the reaction of diethylcadmium with decaborane was investigated.[3]

Diethylcadmium reacted slowly with an equimolar amount of decaborane, in diethyl ether, at room temperature; a white crystalline solid—$CdB_{10}H_{12},2Et_2O$—was precipitated with evolution of ethane, and the reaction can be represented by:

$$Et_2Cd + B_{10}H_{14} + 2Et_2O = 2EtH + CdB_{10}H_{12},2Et_2O \qquad (1)$$

The compound $CdB_{10}H_{12},2Et_2O$ was stable for comparatively long periods (3—4 months) in an atmosphere of pure, dry nitrogen. It lost one molecule of co-ordinated ether when pumped under vacuum at room temperature, but decomposed *in vacuo* at 140° to yield all the co-ordinated ether and some decaborane.

The infrared spectrum of the bisetherate is complex (see Experimental section). A large number of the peaks can be assigned to co-ordinated diethyl ether.[4] The intense terminal B–H stretching band is split into two peaks at 2531 and 2455 cm.$^{-1}$, but the separation is too small to be indicative of a BH_2 group in the molecule; the B–H–B stretch is represented by two very weak bands at 1934 and 1899 cm.$^{-1}$. Other bands attributed to the $B_{10}H_{12}$ cage [4] lie at 740(m) and 719(m) cm.$^{-1}$.

The proton nuclear magnetic resonance spectrum of $CdB_{10}H_{12},2Et_2O$ was simply that of co-ordinated diethyl ether, superimposed on the weak, broad spectrum of the $B_{10}H_{12}$ cage and the peak positions are recorded in the Experimental section. Solutions could not be made sufficiently concentrated to record ^{11}B n.m.r. spectra.

Hydrogen chloride in diethyl ether converted $CdB_{10}H_{12},2Et_2O$ smoothly and quantitatively into cadmium chloride and decaborane; the reaction is formulated as

$$CdB_{10}H_{12},2Et_2O + 2HCl = CdCl_2 + B_{10}H_{14} + 2Et_2O \qquad (2)$$

The cadmium borane bisetherate was soluble without apparent reaction in water, ethanol, acetonitrile, methylene chloride, ethylene dichloride, and benzene although, especially in water, degradation to lower borane anions with evolution of hydrogen and deposition of metallic cadmium began after about 1 hr. The fresh aqueous and ethanolic solutions were yellow and had a well-defined ultraviolet maximum at 295 mμ. On addition of an aqueous solution of tetramethylammonium chloride to these solutions, a yellow precipitate of $(Me_4N)_2[(B_{10}H_{12})_2Cd]$ ($\lambda_{max.}$ 295 mμ) was formed together with a colourless solution containing cadmium ions. The overall reaction stoicheiometry indicated that the solution of $CdB_{10}H_{12},2Et_2O$ in water, or ethanol, must be represented by the equation:

$$2CdB_{10}H_{12},2Et_2O = Cd^{2+} + [(B_{10}H_{12})_2Cd]^{2-} + 4Et_2O \qquad (3)$$

The infrared spectrum of $(Me_4N)_2[(B_{10}H_{12})_2Cd]$ is quite simple, and the absorptions in the range 4000—400 cm.$^{-1}$ are recorded in the Experimental section. The terminal B–H stretch absorption occurs at 2493 cm.$^{-1}$ and the bridge B–H–B band is perceptible at 1900 cm.$^{-1}$; other bands are attributed to cage vibrations and to the tetramethylammonium cation.

The structure of $CdB_{10}H_{12},2Et_2O$ was investigated by measuring its conductance, in certain solvents, and the results are shown in the Table together with those obtained on the tetrahydrofuranate to be discussed below. In this Table Λ_M ohm^{-1} cm.^{2} mole^{-1} is the molar conductance, assuming a molecular formula ($CdB_{10}H_{12},2S$), Λ_{2M} ohm^{-1} cm.^{2} mole^{-1} is the molar conductance, assuming a molecular formula $(CdB_{10}H_{12},2S)_2$ and Λ ohm^{-1} cm.^{2} mole^{-1} is the molar conductance to be expected for a 2 : 2 electrolyte (at 10^{-3}M) assuming this to be approximately double that of the known conductance of a 1 : 1 electrolyte (at 10^{-3}M) in the same solvent. The molar conductance of a 2 : 2 electrolyte (at 10^{-3}M) in water is known.[5]

Conductance of $CdB_{10}H_{12},2S$

S	Solvent	Molar conc. $\times 10^3$	Λ_M	Λ_{2M}	Λ
Et_2O	CH_2Cl_2	1·0	0·3	—	—
Et_2O	H_2O	1·2	137	274	200—300
Et_2O	EtOH	0·8	29	58	60—100
THF	EtOH	0·8	29	58	60—100
Et_2O	MeCN	0·7	146	292	220—300
THF	MeCN	0·7	134	268	220—300

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[1] G. E. Coates and A. Lauder, *J. Chem. Soc.* (*A*), 1966, 264; F. Schindler, H. Schmidbaur, and U. Krüger, *Angew. Chem. Internat. Edn.*, 1965, **4**, 876; A. G. Davies and J. E. Packer, *J. Chem. Soc.*, 1959, 3164; J. Chenault and F. Tatibouët, *Compt. rend.*, 1966, **262**, *C*, 499; N. S. Vyazankin, G. A. Razuvaev, and V. T. Bychkov, *Proc. Acad. Sci.* (*U.S.S.R.*), 1964, **158**, 877; R. Nast and C. Richers, *Z. anorg. Chem.*, 1963, **319**, 320.

[2] G. Guter and R. Schaeffer, *J. Amer. Chem. Soc.*, 1956, **78**, 3546.

[3] N. N. Greenwood and N. F. Travers, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 169.

[4] N. J. Blay, R. J. Pace, and R. L. Williams, *J. Chem. Soc.*, 1962, 3416.

[5] R. A. Robinson and R. H. Stokes, " Electrolyte Solutions," Butterworths, London, 1955, pp. 160, 452.

The results indicate that $CdB_{10}H_{12},2Et_2O$ dissolves as a molecular nonelectrolyte in methylene chloride. The compound ionises in aqueous solution according to (3) and this equation apparently also holds in other solvents of high dielectric constant, such as acetonitrile, since the ultraviolet spectrum of a necessarily dilute solution of $CdB_{10}H_{12},2Et_2O$ in acetonitrile is identical to that of $(Me_4N)_2[(B_{10}H_{12})_2Cd]$ in the same solvent. Thus, the molar conductances should be calculated using $(CdB_{10}H_{12},2Et_2O)_2$, as the molecular formula and the values of Λ_{2M} so obtained show that, as expected, the compound behaves as a strong 2 : 2 electrolyte in water and in other solvents of high dielectric constant.

So as to acquire more information regarding the ionic nature of $CdB_{10}H_{12},2Et_2O$, attempts were made to measure its molecular weight in ethanol solution, but these failed (see Experimental section). Measurements in ethylene dichloride and in benzene showed that $CdB_{10}H_{12},2Et_2O$ is probably tetrameric in these solvents.

In a parallel series of experiments it was found that diethylcadmium reacted quite rapidly with an equimolar amount of decaborane, in tetrahydrofuran (THF), at room temperature; a pale yellow crystalline solid, $CdB_{10}H_{12},2THF$, was precipitated with evolution of ethane. The reaction is represented by:

$$Et_2Cd + B_{10}H_{14} + 2C_4H_8O = 2EtH + CdB_{10}H_{12},2C_4H_8O \quad (4)$$

The compound $CdB_{10}H_{12},2THF$ was stable under pure dry nitrogen for comparatively long periods (4 months). It was soluble in water, ethanol, and acetonitrile and these solutions were stable for short periods (approx. $\frac{1}{2}$ hr.). The cadmium borane bistetrahydrofuranate was insoluble in methylene chloride, ethylene dichloride, and benzene, thus precluding the possibility of determining molecular weights or investigating nuclear magnetic resonance spectra in these solvents.

The infrared spectrum of the bistetrahydrofuranate consisted of absorptions assignable to the $B_{10}H_{12}$ cage, and to co-ordinated tetrahydrofuran. The infrared absorptions of $CdB_{10}H_{12},2THF$ in the range 4000—400 cm.$^{-1}$ are recorded in the Experimental section.

The cadmium borane bistetrahydrofuranate behaved analogously to the bisetherate in its chemical reactions. It reacted smoothly with hydrogen chloride in tetrahydrofuran according to equation (2) above (in which Et_2O is replaced by THF). The dissolution of $CdB_{10}H_{12},2THF$ in water or ethanol occurred according to equation (3) above (where Et_2O is replaced by THF).

Ionic conductance data for $CdB_{10}H_{12},2THF$ in ethanol and in acetonitrile are given in the Table and show that, like the bisetherate previously discussed, the bistetrahydrofuranate behaves as a strong 2 : 2 electrolyte in solvents of high dielectric constant.

DISCUSSION

The structure of $CdB_{10}H_{12},2S$ and the probable mechanism of its formation, will now be considered. The compound $CdB_{10}H_{12},2S$ is thought to be a single species, for the following reasons. It is usual in polymer-forming reactions for the chain length to vary both with the dilution and the rate of addition of the reactants; such variations in conditions were tried but in all cases the yields of the solvated cadmium borane and its analytical composition remained unchanged. Another argument against a polymeric product is the absence of end-group hydrolysis products, such as ethane. Molecular-weight data indicate that $CdB_{10}H_{12},2Et_2O$ is not a high polymer in either benzene or in ethylene dichloride solution, though it appears to be associated to some extent in these solvents.

It is clear that the boron skeleton of the solvated cadmium borane is similar to that in decaborane, since the preparative conditions are mild, and decaborane is readily regenerated from the cadmium borane by reaction with anhydrous hydrogen chloride.

No investigations have been carried out on the nature of alkylcadmiums in solvating media, but, by analogy with the alkylzincs,[6] the following equilibrium would be expected to occur:

$$2R_2Cd \rightleftharpoons RCd^+ + R_3Cd^- \quad (5)$$

That this equation probably applies to solutions of diphenyl cadmium, in similar solvents is consistent with the fact that the anion Ph_3Cd^- is known.[7] The first step, in the reaction of diethylcadmium with decaborane, in an ether solvent, will be basic attack by Et_3Cd^- on an acidic bridge hydrogen, preferably that which lies between the 5- and 6-positions of decaborane (cf. reaction of methylmagnesium iodide with decaborane [8]) to form a transient $B_{10}H_{13}^-$ anion. In this intermediate, the position of highest reactivity towards an electrophile is the 6-position,[8] and it is here that the $EtCd^+$ moiety is likely to attack, with formation of $EtCdB_{10}H_{13}$, which loses a molecule of alkane with consequent production of $CdB_{10}H_{12}$ *via* attack of the electrophilic cadmium atom on the BH_2 group (which would accommodate negative charge) at the 9-position of the boron cage. These reactions are summarised below, transient intermediates being shown in brackets:

$$[Et_3Cd^-] + B_{10}H_{14} \longrightarrow EtH + [B_{10}H_{13}^-] + Et_2Cd \quad (6)$$

$$[EtCd^+] + [B_{10}H_{13}^-] \longrightarrow [EtCdB_{10}H_{13}] \quad 7)$$

$$[EtCdB_{10}H_{13}] \longrightarrow EtH + CdB_{10}H_{12} \quad (8)$$

$CdB_{10}H_{12}$ is represented as (I) using the system previously described.[9] Structure (I) can be regarded as a derivative of decaborane in its nontypical topology 2802.[10] This form has two B–H–B bridges and two

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[6] E. G. Rochow, D. T. Hurd, and R. N. Lewis, "Chemistry of Organometallic Compounds," Wiley, New York, 1957, p. 102; G. Jander and L. Fischer, *Z. Elektrochem.*, 1958, **62**, 965.

[7] G. Wittig, F. J. Meyer, and G. Lange, *Annalen*, 1951, **571**, 167.

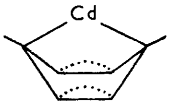
[8] I. Dunstan, N. J. Blay, and R. L. Williams, *J. Chem. Soc.*, 1960, 5016.

[9] N. N. Greenwood and J. A. McGinnety, *J. Chem. Soc.* (*A*), 1966, 1090.

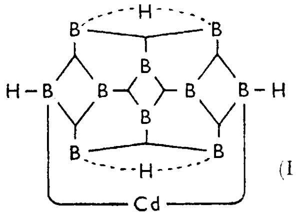
[10] W. N. Lipscomb, "Boron Hydrides," Benjamin, New York, 1963, p. 45.

BH_2 groups and, as shown in (II) it is these BH_2 groups which are substituted by a bridging bivalent cadmium atom. The compound provides the first example of a neutral 6,9-bridged derivative of decaborane and also the first example of a molecule containing direct cadmium–boron bonds. It seems likely that the two molecules of ether solvate the cadmium making it four-co-ordinate.

The covalent radii of boron and cadmium are 0·88 and 1·41 Å, respectively, so that the B–Cd bond length should be about 2·3 Å. The distance between the 6- and 9-positions of the boron framework is between 2·8 and 3·2 Å, and consequently, the B–Cd–B bond angle could be approximately 80°.



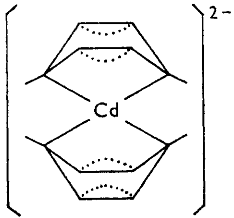
(I)



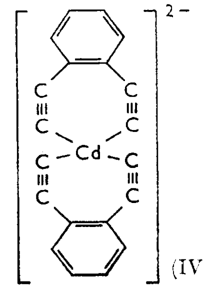
(II)

The ether solvent, required for the reaction of diethylcadmium with decaborane plays a dual role. Equilibrium (5) will be influenced by the solvent, for if the solvent is able to solvate the $EtCd^+$ cation the latter will be stabilised and its formation will be favoured, as in the analogous organozinc compounds.[11] Thus, the greater the solvating power of the reaction medium, the greater will be the dissociation of the alkylcadmium (into ions) in that medium and consequently reaction of a dialkylcadmium with decaborane would be predicted to be faster in strongly solvating media. This prediction was verified, since the reaction rate was greater with tetrahydrofuran as solvent than it was when diethyl ether was used. It is known that the acidity of the bridge hydrogens in decaborane is increased in presence of a basic solvent,[12] and it is anticipated that steps (6) and (8) would only take place if a basic solvent were the reaction medium. Thus, the solvent in which a dialkylcadmium reacts with decaborane must be both solvating and basic. Solvation of the product is also required to give a favourable B–Cd–B bond angle.

The dissolution of $CdB_{10}H_{12},2S$ in water is a less simple process than might be anticipated for equal proportions of Cd^{2+} and $B_{10}H_{12}{}^{2-}$ ions are not obtained the reaction being represented instead by equation (3). The reason for this may be that the $B_{10}H_{12}{}^{2-}$ anion[13] is unstable in such an environment and immediately reacts with a molecule of $CdB_{10}H_{12}$ to form the energetically more favourable anion $[(B_{10}H_{12})_2Cd]^{2-}$ (III) which would contain four-co-ordinate, tetrahedral cadmium; moreover if decaborane is considered to be analogous to the diprotic acid *o*-diethynylbenzene, $HC\vdots C\cdot C_6H_4\cdot C\vdots CH,(H_2od)$ then $[(B_{10}H_{12})_2Cd]^{2-}$ would be a boron analogue of the recently reported[14] $(od)_2Cd^{2-}$ (IV).



(III)



(IV)

EXPERIMENTAL

All manipulations were carried out either *in vacuo*, or in an atmosphere of pure, dry nitrogen. Ether solvents were distilled from lithium aluminium hydride immediately before use; other solvents were purified by conventional methods.

Intermediates.—Decaborane was purified by vacuum sublimation.

Diethylcadmium prepared by the method of Krause,[15] was purified by repeated condensation at −78° *in vacuo* until its infrared spectrum (as a liquid film) corresponded to that reported by Kaesz and Stone.[16] The pure diethylcadmium was then sealed in ampoules which were subsequently stored at −196°. Prior to reaction with decaborane, samples of stock purified diethylcadmium were distilled into a calibrated tube, cooled to −78°, the volume of diethylcadmium measured at room temperature, and its weight determined.[15]

Reaction of Diethylcadmium with Decaborane in Diethyl Ether.—In a typical experiment, diethylcadmium (0·18 ml., 1·8 mmoles) and decaborane (0·23 g., 1·88 mmoles), in anhydrous diethyl ether (15 ml.), were allowed to react in a sealed tube at room temperature for 3 days during which time ethane (2·78 mmoles, 77%) was evolved and a white crystalline solid, *cadmium decaboranate bis(diethyl ether)*, contaminated with a little metallic cadmium was deposited. The crude solid (0·5 g.) was recrystallised twice from methylene chloride–ether to give fine, white needles dried under nitrogen, and analysed (Found: C, 24·8; H, 8·15; B, 28·4; Cd, 28·9. $CdB_{10}H_{12},2Et_2O$ requires C, 25·2; H, 8·5; B, 28·4; Cd, 29·5%). When heated in a sealed nitrogen filled tube, the compound did not melt but appeared to shrink at 126°, to swell at 136°, and to blacken at 146°; there was no further change up to 160°.

Stepwise Desolvation of $CdB_{10}H_{12},2Et_2O$.—$CdB_{10}H_{12},2Et_2O$ (0·458 g., 1·20 mmoles) lost diethyl ether (0·09 g., 1·20 mmoles) *in vacuo* at room temperature to leave a pale yellow crystalline residue (0·370 g., 1·20 mmoles) which was analysed (Found: C, 16·0; H, 7·2; B, 34·7

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[11] O. Yu. Okhlobystin and L. I. Zakharkin, *J. Organometallic Chem.*, 1965, **3**, 257.

[12] M. F. Hawthorne and J. J. Miller, *J. Amer. Chem. Soc.*, 1958, **80**, 754.

[13] P. H. Wilks and J. C. Carter, *J. Amer. Chem. Soc.*, 1966, **88**, 3441.

[14] R. Nast, M. Ohlinger, and G. Wallenwein, Abstracts of the Proceedings of the Second International Symposium on Organometallic Chemistry, Madison, Wisconsin, Sept. 1965, p. 5.

[15] E. Krause, *Ber.*, 1917, **50**, 1813.

[16] H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, 1959, **15**, 360.

$CdB_{10}H_{12},Et_2O$ requires C, 15·65; H, 7·2; B, 35·2%). Complete desolvation was effected by heating $CdB_{10}H_{12},2Et_2O$ (0·454 g., 1·19 mmoles) at 140° *in vacuo* over a period of 12 hr. to yield diethyl ether (0·167 g., 2·26 mmoles) decaborane (0·038 g.) and an amorphous residue (0·256 g.).

Infrared Spectrum of $CdB_{10}H_{12},2Et_2O$.—The position (in cm.$^{-1}$) and a partial assignment of the bands in the infrared spectrum of $CdB_{10}H_{12},2Et_2O$ is as follows. Co-ordinated diethyl ether: 2975(s), 2925(m), 2894(m), 2865(w), 1466(m), 1446(m), 1383(s), 1351(w), 1321(vw), 1284(w), 1184(ms), 1147(ms), 1119(w), 1089(ms), 1044(ms), 993(ms), 894(m), 826(m), 774(s). B–H stretches: 2531(vs), 2455(ms). B–H–B bridge modes: 1934(vw), 1899(w). $B_{10}H_{12}$ cage: 740(m), 719(m). Unassigned bands: 927(w), 912(w), 859(w), 694(w), 644(m), 581(m), 549(m), 529(w), 484(w), 444(m).

Proton Nuclear Magnetic Resonance Spectrum of $CdB_{10}H_{12},2Et_2O$.—The peak positions in p.p.m. upfield from methylene chloride were as follows: CH_2 quartet (two main peaks): 1·55, 1·68; CH_3 triplet: 3·90, 4·05, 4·15.

Reaction of $CdB_{10}H_{12},2Et_2O$ *with Hydrogen Chloride in Diethyl Ether.*—Diethyl ether (50 ml.) saturated with dry hydrogen chloride was allowed to react for 1 hr. at room temperature with $CdB_{10}H_{12},2Et_2O$ (0·49 g., 1·29 mmoles) in a weighed, evacuated flask, fitted with a cold finger of known weight; a white solid was formed, but no hydrogen was evolved. The hydrogen chloride–ether mixture was pumped off, the cold finger filled with acetone–carbon dioxide (−78°), the reaction flask gently warmed, and decaborane sublimed out of the residue to leave a white involatile solid. The weight of decaborane was 0·156 g. (1·28 mmoles, 99%) and the weight of the involatile solid (Found: Cd, 61·1. Calc. for $CdCl_2$: 61·3%) was 0·233 g. (1·27 mmoles, 98·5%).

Solution of $CdB_{10}H_{12},2Et_2O$ *in Water.*—Water (10 ml.) was added *in vacuo* to $CdB_{10}H_{12},2Et_2O$ (0·49 g. 1·29 mg. atom Cd, 12·9 mg. atom B); a clear yellow solution was formed, which, after being stirred for 15 min., had evolved no hydrogen. On addition of a concentrated aqueous solution of tetramethylammonium chloride to the yellow solution a yellow precipitate (0·32 g.) of $(Me_4N)_2B_{20}H_{24}Cd$ was obobtained (Found: C, 19·3; H, 9·5; B, 42·4; Cd, 21·9. $(Me_4N)_2B_{20}H_{24}Cd$ requires C, 19·15; H, 9·6; B, 43·2; Cd, 22·4%). The weight of cadmium in the colourless, aqueous filtrate was found to be 0·07 g. (0·62 mg. ions Cd^{2+}), and—from above—the tetramethylammonium salt contains 0·07 g. cadmium (0·62 mg. atom) and 0·136 g. boron (12·6 mg. atom).

Solution of $CdB_{10}H_{12},2Et_2O$ *in Ethanol.*—$CdB_{10}H_{12},2Et_2O$ (0·42 g., 1·1 mg. atom Cd, 11·1 mg. atom B) dissolved in ethanol (10 ml.) to yield a clear, yellow solution from which a precipitate (0·278 g.) of $(Me_4N)_2B_{20}H_{24}Cd$ was obtained (Found: C, 19·4; H, 9·3; B, 42·5; Cd, 22·0. $(Me_4N)_2B_{20}H_{24}Cd$ requires C, 19·15; H, 9·6; B, 43·2; Cd, 22·45%). Cadmium (0·059 g., 0·53 mg. ion Cd^{2+}) remained in the aqueous alcoholic filtrate. The tetramethylammonium salt contained 0·061 g. cadmium (0·54 mg. atom Cd) and 0·118 g. boron (10·9 mg. atom B).

Infrared spectrum of $(Me_4N)_2B_{20}H_{24}Cd$.—The position (in cm.$^{-1}$) and a partial assignment of the bands in the infrared spectrum of $(Me_4N)_2B_{20}H_{24}Cd$ is as follows; Me_4N^+: 3013(w), 1478(s), 1403(w), 943(s). $B_{20}H_{24}Cd^{2-}$: 2493(vs), 2323(sh), 1900(vw), 1088(m), 1053(m), 1008(ms), 998(sh), 918(sh), 788(m), 723(sh), 714(m).

Molecular Weight of $CdB_{10}H_{12},2Et_2O$.—All measurements were carried out using a Mechrolab osmometer. Ethanol solutions of $CdB_{10}H_{12},2Et_2O$ gave inconsistent results for the molecular weight, probably because unco-ordinated diethyl ether was evaporating from the thermistor, at the same time as the pure solvent, ethanol. When benzene was used as solvent, the molecular weight was found to be 1550 and when ethylene dichloride was used the molecular weight was 1440. $(CdB_{10}H_{12},2Et_2O)_4$ would have a molecular weight of 1524.

Reaction of Diethylcadmium with Decaborane in Tetrahydrofuran.—Diethylcadmium (1·4 ml., 13·6 mmoles) was reacted with a solution of decaborane (1·71 g., 15·8 mmoles) in anhydrous tetrahydrofuran (60 ml.) for 1 day in a break-seal vessel; ethane (23·2 mmoles, 85%) was evolved, and a pale yellow, crystalline solid (4·33 g. ,11·5 mmoles of $CdB_{10}H_{12},2C_4H_8O$) was deposited, which, after being thoroughly washed with tetrahydrofuran then with pentane, was dried under nitrogen and analysed (Found: C, 25·4; H, 7·3; B, 28·5; Cd, 29·8. $CdB_{10}H_{12},2C_4H_8O$ requires C, 25·5; H, 7·5; B, 28·7; Cd, 29·8%). When heated in a sealed nitrogen-filled tube the compound did not melt but began to swell at 138° and to blacken at 140°. No metallic cadmium was formed when diethylcadmium reacted with decaborane in tetrahydrofuran at room temperature, presumably because the rate of this reaction is considerably faster than the rate of decomposition of diethylcadmium in tetrahydrofuran at room temperature (cf. reaction of diethylcadmium and decaborane in diethyl ether).

Infrared Spectrum of $CdB_{10}H_{12},2THF$.—The position (in cm.$^{-1}$) and a partial assignment [4,17] of the bands in the infrared spectrum of $CdB_{10}H_{12},2THF$ is as follows. Co-ordinated tetrahydrofuran: 2986(s), 2888(ms), 1481(w), 1456(ms), 1416(w), 1364(w), 1340(m), 1291(w), 1242(m), 1165(m), 1120(w), 1055(ms), 1028(s), 1005(m), 915(m), 865(s), 810(w), 785(w), 770(w). $B_{10}H_{12}$ cage: 2528(vs), 2458(s), 1920(w), 738(ms), 720(m). Unassigned bands: 690(w), 670(w), 645(m), 578(m), 548(m), 525(w), 445(w).

Reaction of $CdB_{10}H_{12},2THF$ *with Hydrogen Chloride in Tetrahydrofuran.*—$CdB_{10}H_{12},2THF$ (0·58 g., 1·54 mmoles) was reacted for 1½ hr. with anhydrous tetrahydrofuran (60 ml.) saturated with dry hydrogen chloride using the method already described for the analogous reaction of $CdB_{10}H_{12},2Et_2O$ to yield cadmium chloride (0·278 g., 1·52 mmoles, 99%) and decaborane (0·187 g., 1·53 mmoles, 99·5%). No hydrogen was evolved.

Solution of $CdB_{10}H_{12},2THF$ *in Water.*—Water (10 ml.) was added to $CdB_{10}H_{12},2THF$ (0·51 g., 1·35 mg. atom Cd, 13·5 mg. atom B) and, although most of the solid dissolved, there was also a small amount of insoluble material (0·024 g.) indicating that the solution of $CdB_{10}H_{12},2THF$ in water was a less "clean" process than that of $CdB_{10}H_{12},2Et_2O$. After 15 min. no hydrogen had been evolved and to the clear, yellow, filtered solution of $CdB_{10}H_{12},2THF$ was added a strong aqueous solution of tetramethylammonium chloride. The yellow precipitate (0·31 g.) so obtained was analysed [Found: C, 19·4; H, 9·6; B, 42·6; Cd, 21·8. $(Me_4N)_2B_{20}H_{24}Cd$ requires C, 19·15; H, 9·6; B, 43·2; Cd, 22·4%]. The weight of cadmium in the colourless aqueous filtrate was found to be 0·07 g.

[17] J. Lewis, J. R. Miller, R. L. Richards, and A. Thompson, *J. Chem. Soc.*, 1965, 5850.

(0·62 mg. ion Cd^{2+}) and from the above, the tetramethylammonium salt contains 0·068 g. cadmium (0·605 mg. atom) and 0·133 g. boron (12·3 mg. atom).

Analytical and Instrumental Techniques.—All compounds were decomposed by the Parr procedure;[18] the boron cage was degraded to borate and this was acidified to boric acid which was titrated in the presence of solid mannitol from pH 6·3 to 8·0 with 0·05M-sodium hydroxide. Cadmium, after conversion into cadmium oxide and dissolution of this in dilute hydrochloric acid, was determined by EDTA titration according to the procedures outlined by Schwarzenbach.[19] Cadmium in the aqueous filtrates (from the dissolution experiments) was determined by direct EDTA titration using Xylenol Orange as indicator.[19] Carbon and hydrogen analyses were performed by Beller, Mikroanalytisches Laboratorium, 34 Gottingen, Germany.

Ethane was identified by its mass spectrum as measured on an A.E.I. M.S.3 instrument by Mr. P. Kelly.

Infrared spectra were recorded on a Perkin-Elmer 125 grating infared spectrophotometer using mulls in Nujol or hexachlorobutadiene.

Proton nuclear magnetic resonance spectra were measured at 60 Mc./sec. on a Perkin-Elmer R10 spectrometer; methylene chloride was used as solvent.

Conductances of solutions of the compounds were measured at 25°, using a Wayne-Kerr Universal Bridge B221.

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[18] Parr Manual No. 121, Parr Instrument Co., Moline, Illinois, U.S.A.

[19] G. Schwarzenbach, " Complexometric Titrations," Methuen, London, 1960.