tra (0 and 25°)[9] $B_6H_{11}^-$ would go undetected, since we have found that it decomposes above −15° to form similar decomposition products as $B_5H_8^-$.

Experimental Section

A conventional vacuum line system was used in handling air-sensitive materials. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. X-Ray powder patterns were obtained using a Debye–Scherrer camera and Cu Kα radiation. Boron-11 nmr spectra were obtained on a Varian Associates HA-100 spectrometer with a 32.1-MHz probe.

Materials.—Potassium hydride was obtained from ROC/RIC as a 50% suspension in mineral oil. The mineral oil was removed by washing with pentane. Pentaborane(9) was obtained from Callery Chemical Co. Hexaborane(10) was prepared according to the literature.[11] Tetra-*n*-butylammonium iodide was obtained from Matheson Coleman and Bell.

Preparation of $(n\text{-}C_4H_9)_4B_5H_8$ and $(n\text{-}C_4H_9)_4B_6H_9$.—In a standard drybox 2.00 mmol (0.738 g) of $(n\text{-}C_4H_9)_4NI$ and 2.00 mmol (0.08 g) of KH were weighed in a reaction vessel containing a Teflon-covered magnetic stir bar. The vessel was attached to the vacuum line and approximately 3 ml of dry THF was condensed in and KB_5H_8 or KB_6H_9 was prepared as described elsewhere.[3] The reaction mixture was frozen and 6 ml of methylene chloride was condensed in. The mixture was stirred and allowed to warm to −22.5° at which temperature it was kept for 30 min. Diethyl ether was added to precipitate the salt. The mixture was frozen and transferred under nitrogen to an extractor and filtered at −78°. Under nitrogen a new vessel was placed under the extractor and the precipitate was washed with CH_2Cl_2 dissolving the borate salt. The product on the frit was identified by its X-ray powder pattern as KI. A portion of the solution was tipped into an nmr tube side arm attached to the vessel, which was sealed and removed. The remainder of the compound was precipitated with ether and filtered. The infrared spectrum of $(n\text{-}C_4H_9)_4NB_5H_8$ showed an absorption in the B–H terminal region at 2500 cm^{-1} and a very weak, very broad peak in the B–H–B stretching region centered at 1780 cm^{-1}.

Analyses.—Boron and hydrolyzable hydrogen analyses for $(n\text{-}C_4H_9)_4NB_5H_8$ and $(n\text{-}C_4H_9)_4NB_6H_9$ were carried out by acid hydrolysis. *Anal.* Calcd for $(n\text{-}C_4H_9)_4NB_5H_8$: B, 17.76%; H, 12.00 mol/mol of sample. Found: B, 17.14%; H, 11.64 mol/mol of sample. Calcd for $(n\text{-}C_4H_9)_4NB_6H_9$: B, 20.49%; H, 14.00 mol/mol of sample. Found: B, 20.37%; H, 13.37 mol/mol of sample.

X-Ray Powder Patterns.—$(n\text{-}C_4H_9)_4NB_5H_8$: *d* (Å) = 10.8 (s), 8.63 (m), 7.46 (m), 6.71 (m), 5.38 (m), 5.01 (w), 4.75 (m), 4.47 (w), 4.29 (s), 4.15 (w), 3.78 (w). $(n\text{-}C_4H_9)_4NB_6H_9$: *d* (Å) = 10.0 (m), 9.12 (m), 8.22 (m), 7.70 (m), 7.16 (m), 6.79 (s), 6.19 (w), 5.82 (vw), 5.31 (m), 4.77 (s), 4.53 (s), 4.29 (m), 4.05 (m), 3.79 (m), 3.49 (w), 3.39 (w).

Regeneration of B_5H_9 and B_6H_{10}.—Into a test tube type vessel was placed 0.154 g (0.505 mmol) of $(n\text{-}C_4H_9)_4NB_5H_8$. Approximately 1 ml of liquid HCl was condensed in at −196°. The vessel was warmed to −111° and the solution was stirred for 45 min. The mixture was fractionated and 0.485 mmol (96%) of B_5H_9 was recovered.

Reaction of $(n\text{-}C_4H_9)_4NB_6H_9$ with liquid HCl was carried out using a similar procedure. Regeneration of B_6H_{10} was also attempted in $(CH_3)_2O$. In a vessel 0.321 g (1.52 mmol) of $(n\text{-}C_4H_9)_4NB_6H_9$ was weighed. About 3 ml of dimethyl ether and 1.55 mmol of HCl passed through P_2O_5 were condensed in at −196°. The vessel was warmed to −78° and stirred overnight. Fractionation of the volatiles yielded B_5H_9 and B_6H_{10} in both procedures. B_5H_9 and B_6H_{10} were condensed in on excess KH in $(CH_3)_2O$ at −78°. The H_2 evolved was collected and measured as 0.785 mmol representing 52% of the original $B_6H_9^-$. The solid residue in the vessel was dissolved in CH_2Cl_2 and the ^{11}B nmr showed the presence of $B_6H_9^-$ and $B_5H_8^-$.

Decomposition of $B_5H_8^-$ and $B_6H_9^-$.—A solution of KB_5H_8[3,4] in tetrahydrofuran (*ca.* 0.5 *M*) was stirred at room temperature for 2 days. The solution was filtered and the solid on the frit was identified as BH_4^- by its infrared spectrum and X-ray powder pattern. As much tetrahydrofuran as possible was removed under vacuum. The vessel was removed from the vacuum line and a solution containing excess $(CH_3)_4NCl$ in water was added to the gummy residue. The solution was stirred and filtered. The solid isolated was identified as $(CH_3)_4NB_9H_{14}$ by its ^{11}B nmr spectrum[8] and comparison of its infrared spectrum and X-ray powder pattern with those of an authentic sample. The yield of $(CH_3)_4NB_9H_{14}$ ranged from 0.15 to 0.20 mmol/mmol of KB_5H_8. The X-ray powder pattern of $(CH_3)_4NB_9H_{14}$ has the following *d* (Å) values: 7.18 (vw), 6.03 (w), 5.04 (vs), 4.12 (vw), 4.00 (vw), 3.56 (w), 3.19 (m). Concentration of the solution yielded another precipitate which was identified as $B_3H_8^-$ by its infrared spectrum and ^{11}B nmr spectrum.

Solutions of KB_6H_9 in tetrahydrofuran (*ca.* 1 *M*) were allowed to stir at room temperature for 2 weeks. Filtration of the solution and identification of the solid product by its infrared spectrum and X-ray powder pattern showed KBH_4. The boron-11 nmr spectrum of the resulting solution showed a doublet at 16.2 ppm (J = 138 Hz) which compares favorably with the literature value for $B_{11}H_{14}$.[12,13] Addition of dioxane to the solution precipitated a solid which exhibited the same infrared spectrum and X-ray powder pattern as an authentic sample of $KB_{11}H_{14}$ prepared in dioxane by the method previously reported for $B_{11}H_{14}^-$ salts.[12] The X-ray powder pattern of $KB_{11}H_{14}$ which has not been previously reported contains the following *d* (Å) values: 8.39 (m), 6.37 (m), 5.56 (m), 5.07 (s), 4.32 (m), 4.20 (s), 3.58 (m), 3.10 (vw), 2.98 (w), 2.80 (m), 2.70 (w), 2.56 (m), 2.49 (w), 2.41 (w), 2.36 (w).

Solutions of the tetrabutylammonium salts of these boranes in methylene chloride were monitored by ^{11}B nmr. The $B_5H_8^-$ salt was completely decomposed in 30 hr. The $B_6H_9^-$ species was completely decomposed after 2 weeks. The ^{11}B nmr spectra of the decomposition products of these salts appeared identical with those of their potassium counterparts.

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Preparation of *B*-Tris(cyclopentadienyl)-*N*-trimethylborazines and *B*-Tris(methylcyclopentadienyl)-*N*-trimethylborazines

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Two reports have previously appeared concerning cyclopentadienyl reactions with borazines.[1,2] In view of their brevity, it was of interest to investigate the reactions of certain cyclopentadienides and methylcyclopentadienides with both *B*-trichloro-*N*-trimethylborazine and *B*-trichloroborazine in order to develop a preparative technique for obtaining cyclopentadienyl-substituted borazines. We were able to prepare methylcyclopentadienyl and cyclopentadienyl derivatives of *B*-trichloro-*N*-trimethylborazine while we were unsuccessful in similar attempts with *B*-trichloroborazine.

Experimental Section

General Information.—All preparations involved standard drybox and high-vacuum procedures with particular care being

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taken to exclude atmospheric oxygen from the alkali metal cyclopentadienides. Solvents were refluxed over $LiAlH_4$ and distilled *in vacuo*. All chloroborazines were purified by sublimation immediately before use. Both cyclopentadiene and methylcyclopentadiene were prepared by cracking their respective dimers[3] employing reflux and distillation using a 20-cm Vigreux column.

Microanalyses were obtained from the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Nuclear magnetic resonance spectra were recorded on a Bruker HFX-90 spectrometer using vacuum-sealed samples internally referenced to TMS (sweep time 10^3 sec). Infrared mull spectra were recorded on a Perkin-Elmer Model 521 grating infrared spectrometer using 0.05-mm polystyrene film for calibration. High-resolution mass spectral data were obtained on an AEI MS 902 mass spectrometer internally referenced to perfluorokerosene using a DEC PDP-8/I computer. Melting points were determined with a Buchi melting point apparatus using capillaries sealed under nitrogen.

Preparation of *B*-Tris(cyclopentadienyl)-*N*-trimethylborazine ($Cp_3B_3N_3Me_3$).—A suspension of potassium cyclopentadienide in benzene was prepared using standard methods[3] by allowing 2.58 g of potassium (0.066 mol) to react with a slight excess of freshly cracked cyclopentadiene under nitrogen. Initially the reaction took place in 100 ml of 1,2-dimethoxyethane which, after removal by vacuum distillation, yielded the dry potassium salt. Benzene (100 ml) was added to the salt *in vacuo* and the resulting suspension was stored under nitrogen. A solution of 4.52 g (0.020 mol) of *B*-trichloro-*N*-trimethylborazine in 100 ml of benzene was placed in a pressure-equalized dropping funnel and rapidly connected to the flask containing the cyclopentadienide. The entire system was purged with nitrogen for several minutes and the borazine solution was added dropwise (30 min). Upon completion of the addition, a reflux condenser was quickly substituted for the dropping funnel and flushed with nitrogen, and the mixture was heated to reflux for 8 hr. After cooling, the reaction mixture was rapidly transferred to the drybox and suction filtered, and the filtrate was dried under high vacuum. The slightly pink solid remaining was sublimed (180° at 10^{-4} Torr) overnight yielding 2.46 g (38.5%) of white crystalline solid, mp 215–219°. *Anal.* Calcd for $C_{18}H_{24}B_3N_3$: C, 68.67; H, 13.35; N, 7.68. Found: C, 66.50; H, 13.53; N, 8.02; mol wt (mass spectrum) 315.2253 (calcd 315.2248).

Preparation of *B*-Tris(methylcyclopentadienyl)-*N*-trimethylborazine [$(MeCp)_3B_3N_3Me_3$].—Preparation of this compound was analogous to that of $Cp_3B_3N_3Me_3$ except that the potassium salt of methylcyclopentadiene was used. Upon working up the reaction mixture, a reddish solid was obtained and sublimed (100° at 10^{-4} Torr) to yield 1.38 g (19.3%) of a white crystalline solid, mp 130–133°. *Anal.* Calcd for $C_{21}H_{30}B_3N_3$: C, 70.67; H, 8.47; N, 11.77. Found: C, 70.46; H, 8.63; N, 11.59; mol wt (mass spectrum) 357.2733 (calcd 357.2719).

Reactions Involving *B*-Trichloroborazine.—Many attempts were made to prepare both the cyclopentadienyl and methylcyclopentadienyl derivatives of *B*-trichloroborazine. Procedures identical with the preceding, as well as variations with respect to reaction times and temperatures, resulted only in the isolation of translucent, yellow, film-like materials. These substances were insoluble in typical organic solvents, were nonsublimable, and gave green flame tests. Various other cyclopentadienyl reagents were also used in related reactions with similar results.[4]

Infrared Spectral Data (cm^{-1}).—$Cp_3B_3N_3Me_3$, in HCBD: 3100 (vw), 3068 (vw), 3042 (vw), 2943–2926 (w), 2896 (w), 2876 (w), 2851 (w), 2824 (w), 2782 (w), 2729 (vw), 2262 (vw), 1511 (m), 1463 (sh, m), 1440 (s), 1399 (vs), 1367 (m), 1341 (m), 1334 (sh, m), 1296 (w), 1241 (w), 1221 (w), 1086 (m), 1055 (vw), 1034 (w), 732 (m), 722 (m), 704 (w); in Nujol: 1580 (m), 1511 (m), 1399 (vs), 1367 (m), 1086 (m), 1055 (vw), 993 (w), 983 (w), 961 (w), 943 (w), 930 (w), 895 (m), 866 (w), 851 (w), 815 (w), 684 (m). $(MeCp)_3B_3N_3Me_3$, in HCBD: 3063–3057 (vw), 3040–3036 (vw), 2954 (m), 2932 (sh, m), 2913 (m), 2871 (sh, w), 2856 (w), 2824 (vw), 2777 (vw), 2734 (vw), 2259 (vw), 1468 (m), 1465 (m), 1444 (s), 1399 (vs), 1372 (m), 1351 (vw), 1339 (w), 1308 (w), 1270 (vw), 1232 (m), 1100 (m), 733 (w), 693 (m); in Nujol: 1599 (vw), 1399 (vs), 1300 (w), 1198 (w), 1100 (w).

Nuclear Magnetic Resonance Spectral Data (δ in ppm).—$Cp_3B_3N_3Me_3$ ($CDCl_3$): 6.70–6.33 (m, 3), 3.17–2.94 (m, 2), 2.69 (t, 3, J = 3.6 Hz) (See Figure 1.) $(MeCp)_3B_3N_3Me_3$ ($CDCl_3$): 6.61–5.94 (m, 2), 3.17–2.83 (m, 2), 2.66 (m, 3), 2.07 (m, 3). (See Figure 2.)

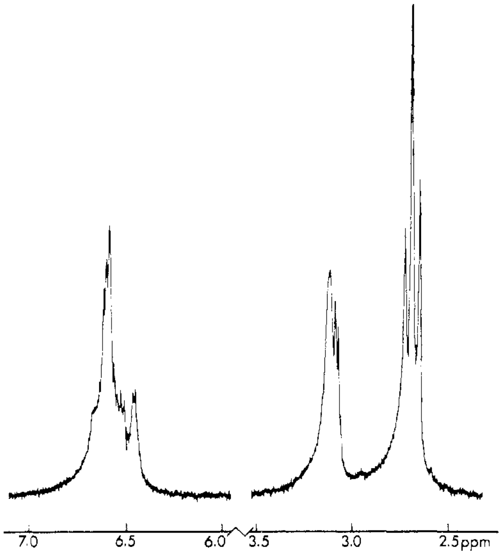

Figure 1.—The 90-MHz proton nmr spectrum of $Cp_3B_3N_3Me_3$.

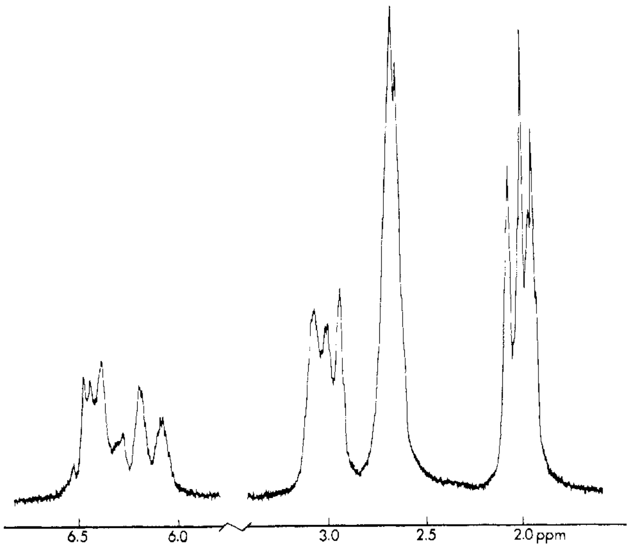

Figure 2.—The 90-MHz proton nmr spectrum of $(MeCp)_3B_3N_3Me_3$.

Discussion

The cyclopentadienyl and methylcyclopentadienyl derivatives of *B*-trichloro-*N*-trimethylborazine were readily isolated while those of *B*-trichloroborazine were not. Although the products obtained from attempts to prepare *B*-tris(cyclopentadienyl)borazine were not analyzed, their insolubility, appearances, and lack of volatility suggest polymerization.[5] Reddish insoluble films also remained after sublimation of $Cp_3B_3N_3Me_3$ and $(MeCp)_3B_3N_3Me_3$, particularly when sublimation temperatures were allowed to reach or exceed the melting points.

When a cyclopentadienide ion and a borazine react, hydrogen migration may lead to one of the three bonding situations I–III [where β = borazine ring (attachment

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(3) "Dicyclopentadiene and Methylcyclopentadiene Dimer," Enjay Chemical Corp., New York, N. Y., and references contained therein.

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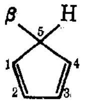
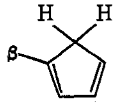
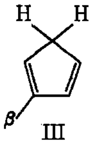
(5) M. Neuenschwander and H. Schaltegger, *Helv. Chim. Acta*, **50**, 1775 (1967), have reported similar polymerization for cyclopentadienyl derivatives of *s*-triazine.



I



II



III

through boron)]. For a methylcyclopentadienide ion, more isomers may result. Studies have shown that an equilibrium distribution of methylcyclopentadiene contains 95–99% of the 1- and 2-substituted isomers.[6,7] However, even with boron attachment limited to C-1 or C-2, there are four possible isomers in $Cp_3B_3N_3Me_3$ resulting from the three different boron atoms in each molecule. For $(MeCp)_3B_3N_3Me_3$, there are 56 such isomeric possibilities. Since it has been shown that a base such as NaC_5H_5 dramatically accelerates rearrangement in substituted cyclopentadienes,[8] our reaction conditions should have yielded an equilibrium mixture of products. The spectroscopic data obtained tend to confirm this.

Through chemical shift comparisons with the literature,[9] absorption intensities, and indor data, the nmr spectrum of $Cp_3B_3N_3Me_3$ has been assigned as follows: the downfield multiplet (3H), vinyl protons; the absorption at *ca.* δ 3.06 (2H), methylene protons; the absorption at δ 2.69 (3H), methyl protons.[10] Broad-band irradiation of the vinyl multiplet led to simplification of the methylene region into two lorentzian singlets at δ 3.11 and 3.07 with relative intensities of *ca.* 58:42, respectively (shapes and area percentages obtained using a Du Pont 310 curve resolver). This result is indicative of two different groups of methylene hydrogens corresponding to 58% borazine substitution at C-2 and 42% substitution at C-1. The peak positions are in agreement with relative positions of the methylene absorptions reported for 1-methyl- and 2-methylcyclopentadiene[9] and the peak intensities compare well with the equilibrium distribution of cyclopentadiene isomers generally observed.[6,7] Reverse decoupling led to changes in the vinyl multiplet, but no simple interpretations could be made.

Similarly for $(MeCp)_3B_3N_3Me_3$ the four absorptions are assigned to vinyl protons (δ *ca.* 6.28 (2)), to methylene protons (δ *ca.* 3.06 (2)), and to two groups of methyl protons (δ 2.66 (3) and 2.07 (3)). Indor data and chemical shift comparisons with the $Cp_3B_3N_3Me_3$ methyl group support assignment of the absorption at δ 2.66 to the methyl protons on the borazine nitrogen. Double-resonance experiments led to spectral changes which did not yield useful information.

Infrared data for both products compared favorably with that reported for cyclopentadiene,[11] indicating the presence of methylene and vinyl protons. Both products exhibited their strongest ir absorption at 1399 cm^{-1} indicative of the presence of a borazine ring.

Our nmr data clearly indicate a mixture of 1- and 2-cyclopentadienylborazines, with little if any 5-cyclopentadienyl material. The physical characteristics of the components of such a mixture should be similar and their separation difficult. Since the usual method for establishing the positions of substituents in cyclopentadienyl compounds consists of preparing Diels–Alder adducts for nmr comparison, we attempted such a preparation using tetracyanoethylene (TCNE) as the dienophile. Reactions involving $Cp_3B_3N_3Me_3$ and TCNE in chloroform–benzene yielded only dark flocculent suspensions, probably arising from TCNE coordination with the boron atoms in the borazine ring itself.[12] Since our primary interest in these compounds lies with their sodium and potassium salts as reaction intermediates, no further attempts at isomer separation were made.

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Some Anionic Tetrahalo(2,4-pentanedionato)stannate(IV) Complexes

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Several studies of the interaction of the tin tetrahalides with 2,4-pentanedione have been reported.[1–10] Thus far, two types of complexes have been isolated: (1) disubstituted six-coordinate oxygen-chelated enolate derivatives, $X_2Sn(C_5H_7O_2)_2$, where X = F, Cl, Br, and I, and (2) a Lewis acid–base adduct $Cl_4Sn(C_5H_8O_2)$. This paper reports studies on the interaction of 2,4-pentanedione and SnX_4 (X = Cl, Br, I) in the presence of an amine to form a new series of anionic β-diketonate–tin complexes.

Experimental Section

Reagents.—Tin tetrachloride (Fisher Scientific Co.), tin tetrabromide, and tin tetraiodide (Ventron Corp.) were used without further purification. 2,4-Pentanedione (Eastman Organic Chemicals) was distilled prior to use. Pyridine (Fisher Scientific Co.) and triethylamine (J. T. Baker Co.) were distilled from P_2O_5 and stored over Linde Molecular Sieves, Type 4A. All

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