to the methylene and methyl protons, respectively (Table III). The complex *trans*-$RhCl_3(CH_3CH_2CN)_3$ in CD_3CN exhibited a set of two quartets centered at 2.96 and 2.90 ppm in a ratio of approximately 2:1 and a lone triplet centered at 1.32 ppm. The ratio of the quartets to the lone triplet was 2:3 as in the free ligand. Thus the assignment of the trans structure to this species on the basis of its optical spectra is confirmed. It is interesting to observe that the difference in ligands does not extend to the nitrile methyl group or that the difference is very small and cannot be resolved, since a single triplet is observed for the terminal methyl group. However, the triplet has been shifted downfield by 0.14 ppm from its position in the free ligand as compared to 0.62 and 0.56 ppm for the two methylene quartets, respectively.

The proton nmr spectrum of $RhBr_3(CH_3CN)_2H_2O$ contained two peaks of equal intensity from the coordinated acetonitrile, thus indicating that this complex could have only an even number of bonded nitriles. Again the nmr spectrum confirms the proposed stoichiometry for this species.

Electronic Spectra.—The electronic spectra of the rhodium–nitrile complexes reported in this study are presented in Table IV. The various assignments were made with the aid of previous reports.[8] The assignment of the transitions in the bromide complexes is not completely clear, because of the large magnitude of the molar absorptivities of some of the d–d bands. Schmidtke assigned such bands with molar absorptivities as high as 1000 to d–d transitions, which are spin allowed and Laporte forbidden.[8b] The unusually high values are probably due to the overlap of these transitions with strong charge-transfer bands.

Conclusion

A final word is needed with regard to the geometric configurations of the complexes in this report. The complexes $RhX_4(RCN)_2^-$ can be assigned the trans configuration on the basis of their visible spectra by comparison with the spectra of the geometrical isomers of the analogous pyridine complexes.[18a] This assignment is further substantiated by the number of Rh–X stretching bands observed in their far-infrared spectra since theoretically four such stretches would be expected for the less symmetrical cis configuration.[2c] The trans assignment for the $RhCl_4(C_6H_5CN)_2^-$ species would indicate that in the reaction of the bridged species $Rh_2Cl_9^{3-}$ with benzonitrile, the size of the ligand necessitates a rearrangement.

The formation and structure of the complex $RhBr_3(CH_3CN)_2H_2O$ is of interest. The infrared spectrum of the complex indicated the presence of coordinated water and suggested a low symmetry, and the nmr spectrum confirmed the presence of an even number of nonequivalent acetonitrile molecules. On the basis of this information the two nitrile ligands cannot be bonded trans to each other and in addition one nitrile would have to be bonded across a bromide ion, whereas the other nitrile would lie across the lone water molecule.

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Synthesis of *N*-Trialkylborazines from Phenyl Borate, Aluminum, Hydrogen, and Primary Amines

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N-Trialkylborazines have received considerable attention in recent years and presently are utilized as synthetic intermediates[2,3] and as reducing agents.[4] Previously reported synthetic procedures involve reaction of diborane with primary amines[5] (eq 1), diborane with alkyl cyanides[6] (eq 2), and reaction of lithium borohydride and the appropriate monoalkylammonium halide[7] (eq 3).

$$B_2H_6 + 2H_2NR \xrightarrow{\Delta} {}^2/_3(HBNR)_3 + 4H_2 \tag{1}$$

$$B_2H_6 + 2RCN \xrightarrow{\Delta} {}^2/_3(HBNCH_2R)_3 \tag{2}$$

$$LiBH_4 + RNH_3^+Cl^- \xrightarrow{\Delta} LiCl + {}^1/_3(HBNR)_3 + 3H_2 \tag{3}$$

We have previously reported on the preparation of B–H compounds by the reduction of borate esters with aluminum and hydrogen. In this way amine–boranes[8] (eq 4) and aminoboranes[9] (equation 5) have been prepared in high yield. By analogy it would appear that reduction of phenyl borate with aluminum and hydrogen in the presence of a primary amine might produce borazines according to eq 6. In order to test this

$$B(OC_6H_5)_3 + Al + R_3N \xrightarrow[\Delta,\text{pressure}]{H_2} H_3BNR_3 + Al(OC_6H_5)_3 \tag{4}$$

$$B(OC_6H_5)_3 + Al + R_2NH \xrightarrow[\Delta,\text{pressure}]{H_2} HB(NR_2)_2 + Al(OC_6H_5)_3 \tag{5}$$

$$B(OC_6H_5)_3 + Al + RNH_2 \xrightarrow[\Delta,\text{pressure}]{H_2} {}^1/_3(HBNR)_3 + Al(OC_6H_5)_3 \tag{6}$$

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[1] To whom correspondence should be addressed.

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idea phenyl borate was allowed to react with aluminum and hydrogen in the presence of primary amines under mild conditions of temperature and pressure. The success of this economic route to *N*-trialkylborazines should increase interest in this class of compounds considerably.

Experimental Section

Equipment and Materials.—Manipulation of air-sensitive materials was accomplished by the use of standard Schlenk-tube techniques or by use of a drybox equipped with an atmosphere purification system for removal of oxygen and moisture.[10] Infrared spectral measurements were obtained using a Perkin-Elmer 621 automatic grating spectrophotometer. Samples were prepared for analysis in the drybox. Spectra of liquid samples were obtained from analysis of the neat material between KBr salt plates while spectra of solid samples were obtained as the Nujol mull. Proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance spectrometer using solvent signals (either benzene or methylene dichloride) as the internal standard. Mass spectra were obtained from analysis of the neat material using a Varian MS-66 instrument.

Hydrogenation reactions were performed using a 300-ml Magnedrive autoclave unit obtained from Autoclave Engineers, Inc. The chamber was charged in the drybox, and the contents heated with stirring under hydrogen pressure for a predetermined period of time. A hydrogen pressure of 3000 psig was utilized since previous studies[9] have established the suitability of this reaction condition in the direct preparation of aminoborane compounds. After sufficient cooling the chamber was vented and soluble products were filtered from excess unreacted aluminum and aluminum phenoxide in the drybox.

Benzene, used as the solvent in the hydrogenation reactions, was purchased from Fisher Chemical Co. (Certified ACS grade) and distilled from $NaAlH_4$ prior to use. Monoethyl-, isopropyl-, and *tert*-butylamines were purchased from Eastman Chemical and dried over active molecular sieves, Type 4-A. Aluminum powder (600 mesh) was obtained from the Alcan Aluminum Corp. The aluminum was "activated" prior to use by a modification of the Ziegler activation process.[11] Boric acid and phenol, used to prepare phenyl borate,[12] were obtained from Fisher Chemical and used without further purification.

Reaction of Ethylamine, Phenyl Borate, Aluminum, and Hydrogen.—Aluminum (5 g, 0.18 g-atom), ethylamine (6.5 ml, 0.1 mol), phenyl borate (30 g, 0.1 mol), and benzene (100 ml) were heated at 150° under 3000 psig of hydrogen for 5 hr (reaction 1, Table I). The chamber was allowed to cool and was vented, and the benzene-soluble material was separated from unreacted aluminum by filtration in the drybox. Removal of solvent *in vacuo* left a white solid of low volatility. The infrared spectrum of this material (Nujol mull) revealed ν(B–H) (2490 cm^{-1}) and aromatic ν(C–H) ($\sim$>3000 cm^{-1}) in addition to "normal" alkyl C–C and N–C vibrations. *N*-Triethylborazine was collected in a Schlenk tube (cooled in a Dry Ice–acetone slurry) by heating at 200° under vacuum (0.25 mm). This left an undetermined amount of aluminum phenoxide (identified by comparison of infrared spectral data) as a residue. The borazine was purified by vacuum distillation (21° at 2.5 mm compared to the literature value[6] of 20° and 2.5 mm); yield 4.5 g, 82%. The purity and identity of the *N*-triethylborazine product were established by infrared, proton magnetic resonance, and mass spectral techniques. These data are compiled in Tables II–IV, respectively. The data are in good agreement with literature values. The infrared spectrum of *N*-triethylborazine was reported in ref 9. Literature values for the proton magnetic resonance spectrum of *N*-triethylborazine[13] are listed in Table III for comparison with the values obtained in this study. Significantly, no other resonances except those listed in Table III and the solvent signal were observed. The mass spectrum of this material revealed a molecular ion at *m/e* 165 (the molecular weight of $(H^{11}BNC_2H_5)_3$ is 165) and a base peak at *m/e* 150 (M − 15) due to the loss of one methyl group. The molecular ion and the M − 15 fragment exhibit a typical isotopic cluster pattern expected for fragments which contain three boron atoms. A simple calculation based on the natural relative isotopic abundances for ^{10}B and ^{11}B of 19.91 and 80.09%, respectively, reveals a cluster pattern of four peaks separated by a single *m/e* unit in the ratio 1.5 (all three boron atoms ^{10}B): 18.5 ($2^{10}B + {}^{11}B$):74.5 ($^{10}B + 2^{11}B$):100% (all three boron atoms ^{11}B). The relative ratio of the observed isotopic cluster for the M − 15 fragment (relative ratio of *m/e* 147, 148, 149, and 150) was 3.2:25.0:73.5:100.0.

TABLE I

PREPARATION OF *N*-TRIALKYLBORAZINES BY REDUCTION OF PHENYL BORATE WITH ALUMINUM AND HYDROGEN IN THE PRESENCE OF MONOALKYLAMINES

Reaction no.	R	Reaction time, hr	Reaction temp, °C	Product	Yield, %
1	C_2H_5	5	150	$(HBNC_2H_5)_3$	82
2	*i*-C_3H_7	12	150	(HBN-*i*-$C_3H_7)_3$	93
3	*tert*-C_4H_9	12	120	(HBN-*tert*-$C_4H_9)_3$	86

TABLE II

N-TRIALKYLBORAZINE INFRARED SPECTRAL DATA

$(HBNC_2H_5)_3$[a]	(HBN-*i*-$C_3H_7)_3$[a]	(HBN-*tert*-$C_4H_9)_3$[b]
2970 s	2972 s	
2935 w	2930 m	
2895 m	2872 m	
2494 s	2520 m	2631 s
1474 s	2478 s	2560 s
1439 vs	1468 s	2480 s
1376 m	1440 vs	1600 w
1354 m	1380 m	1420 s, b
1326 m	1364 m	1360 s
1110 w	1348 m	1200 s
1088 m	1262 w	1081 s
1071 m	1220 w	1029 w
925 w	1170 m	873 s
900 w	1145 w	752 w
880 s	1130 w	740 w
791 w	1111 w	719 w
672 w	1100 w	688 w
	881 s	502 m
		472 w

[a] Neat liquid between KBr salt plates. As Nujol mull between KBr salt plates.

Reaction of Isopropylamine, Phenyl Borate, Aluminum, and Hydrogen.—Aluminum (5 g, 0.18 g-atom), isopropylamine (0.1 mol, 8.55 ml), phenyl borate (30 g, 0.1 mol), and benzene (100 ml) were heated at 150° under 3000 psig of hydrogen for 12 hr (reaction 2, Table I). The chamber was allowed to cool and was vented; the benzene-soluble material was separated from unreacted aluminum by filtration in the drybox. Removal of solvent *in vacuo* left a white solid of low volatility. The infrared spectrum of this material (Nujol mull) exhibited aromatic ν(C–H) (>300 cm^{-1}) and ν(B–H) (strong absorption at 2475 cm^{-1}) in addition to other normal C–C and N–C frequencies. *N*-Triisopropylborazine was collected in a Schlenk tube (cooled to −120°) by heating this material at 200° under vacuum (0.25 mm). Aluminum phenoxide remained as the residue. The borazine was purified by vacuum distillation (44° at 0.1 mm compared to the literature value[14] of 46° at 1.1 mm) and the yield was found to be 6.4 g, 93%. Purity and identity were established by infrared, proton magnetic, and mass spectral techniques. These data are compiled in Tables II–IV, respectively. The mass spectrum of this material exhibited a weak molecular ion at *m/e* 207 (mol wt of (H^{11}BN-*i*-$C_3H_7)_3$ 207) and a strong M − 15 fragment at *m/e* 192 (due to loss of one methyl group). The isotopic cluster pattern for the M − 15 fragment (relative intensity of *m/e* 189, 190, 191, and 192) was found to be 6:22:70.5:100.

Reaction of *tert*-Butylamine, Aluminum, Phenyl Borate, and Hydrogen.—Aluminum (5 g, 0.18 g-atom), phenyl borate (30 g, 0.1 mol), *tert*-butylamine (10.5 ml, 0.1 mol), and benzene (100

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TABLE III

N-TRIALKYLBORAZINE NMR DATA

Compd	τ^c	Area ratio	Multiplicity	J^c	Assignment
$(HBNC_2H_5)_3$[a]	6.64 (6.66)	2.0	Quartet	7.0 (7.1)	N-C_2H_5 (methylene)
	8.90 (8.86)	3.0	Triplet	7.0 (7.1)	N-C_2H_5 (methyl)
(HBN-*i*-$C_3H_7)_3$[a]	6.13 (6.33)	1.0	Septet	7.0 (7.0)	N-*i*-C_3H_7 (methyne)
	8.63 (8.77)	6.0	Doublet	7.0 (6.8)	N-*i*-C_3H_7 (methyl)
(HBN-*tert*-$C_4H_9)_3$[b]	8.64 (8.63)	. . .	Singlet	. . . (. . .)	N-*tert*-C_4H_9

[a] Neat material (trace benzene as internal standard). [b] Concentrated solution in CH_2Cl_2 (CH_2Cl_2 standard). [c] Literature values are included in parentheses for comparison. Data from ref 13.

TABLE IV

MASS SPECTRAL DATA FOR N-TRIALKYLBORAZINES

$(HBNC_2H_5)_3$		(HBN-*i*-$C_3H_7)_3$		(HBN-*tert*-$C_4H_9)_3$	
m/e	Rel intens	*m/e*	Rel intens	*m/e*	Rel intens
165	8.9	207	1.25	249	1.29
164	11.2	192	93.7	234	100.0
163	4.9	191	66.2	233	70.5
162	2.3	190	20.6	232	10.2
150	100.0	189	5.63	231	1.29
149	73.5	165	6.25	178	42.3
148	25.0	164	7.50	177	28.6
147	3.2	150	92.6	176	5.13
93	4.5	149	70.0	100	18.0
79	6.6	148	20.0	93	25.8
78	27.4	147	4.38	92	3.84
77	10.9	79	16.3	58	88.5
63	4.9	78	100.0	57	25.8
52	9.9	77	27.5	53	1.29
51	9.2			52	2.56
50	8.2			51	1.29
39	4.3			50	1.29
38	6.0			44	25.8
37	3.3			42	25.8
				41	32.0
				39	12.8
				32	25.8
				28	60.4

ml) were heated at 120° under 3000 psi of hydrogen for 12 hr (reaction 3, Table I). The chamber was allowed to cool and was vented; the benzene-soluble material was separated from excess, unreacted aluminum by filtration in the drybox. Removal of solvent *in vacuo* left a white solid. The infrared spectrum of this material (Nujol mull) revealed ν(B–H) (2560 cm^{-1}), aromatic ν(C–H) (3100 cm^{-1}), weak ν(N–H) (3650 cm^{-1}), and other "fingerprint" frequencies. The weak ν(N–H) band indicates the presence of $H_nBN(H_{n-1})$-*tert*-C_4H_9 (n = 1 or 2) compounds in admixture with the expected N-tri-*tert*-butylborazine. This mixture was therefore heated at 200° for 2 hr to pyrolize any primary aminoborane contaminant. The infrared spectrum of the heated material did not exhibit a band in the 3650-cm^{-1} region, indicating complete pyrolysis. N-tri-*tert*-butylborazine was sublimed by heating the mixture at 80° (0.25 mm). It was difficult to obtain complete isolation of the borazine due presumably to its relatively low volatility under these conditions. Complete isolation required several sublimation attempts which involved mechanically "breaking up" the solid residue repeatedly in the drybox. The sublimed material obtained in these steps was combined and resublimed at 80° (0.25 mm); yield 7.15 g, 86%. The purity and identity of this product was determined by its melting point of 93° (lit.[15] mp 94°) and by infrared, proton magnetic resonance, and mass spectral analyses (Tables II–IV, respectively). The spectral data compare well with the literature values.[13,15] The mass spectrum of this solid revealed a weak molecular ion at *m/e* 249 and an intense M − 15 peak at *m/e* 234. The isotopic cluster for the M − 15 peak (relative intensities of *m/e* 231, 232, 233, and 234) was found to be 1.9:17.1:70.3:100.0.

Results and Discussion

The reaction of primary, secondary, and tertiary monoalkylamines (alkyl = ethyl, isopropyl, and *tert*-butyl) with phenyl borate, aluminum, and hydrogen (3000 psig) in benzene solution proceeds to give the corresponding N-trialkylborazine in high yield (82–93%) according to the equation

$$B(OC_6H_5)_3 + Al + RNH_2 \xrightarrow[\Delta,\text{pressure}]{H_2} {}^1/_3(HBNR)_3 + Al(OC_6H_5)_3 \quad (7)$$

where R = C_2H_5, *i*-C_3H_7, and *tert*-C_4H_9.

The exact reaction conditions and product yields are summarized in Table I. According to this study, heating equimolar mixtures of phenyl borate and monoalkylamine with excess aluminum and hydrogen gives 82% yield of N-triethylborazine after 5 hr (reaction 1), 93% yield of N-triisopropylborazine, and 86% yield of N-tri-*tert*-butylborazine after 12 hr (reactions 2 and 3, respectively). The adopted procedure involves filtration of the reaction products (to remove excess, unreacted aluminum metal) followed by removal of the reaction solvent under vacuum and distillation (in the case of the ethyl and isopropyl compounds) or sublimation (in the case of the *tert*-butyl derivative) of the borazine product from by-product aluminum phenoxide. Although this by-product is normally insoluble in hydrocarbon solvents, it was found to be largely soluble in hydrocarbon solutions of a N-trialkylborazine.

A high-temperature digestion step was found necessary for synthesis of N-tri-*tert*-butylborazine prior to sublimation of this product (see Experimental Section for details) due to the presence of trace primary amine–borane impurities ($H_nBN(H_{n-1})$-*tert*-C_4H_9, n = 2 or 3) which persisted under conditions of the direct preparation reaction (120° for 12 hr). That these species are pyrolized only slowly to the borazine at these temperatures was demonstrated by direct pyrolysis of *tert*-butylamine–borane at ~100°.[15]

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The Preparation of Bis(trimethylsilyl)aminochlorodimethylaminoborane[1]

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The dehydrohalogenation reaction between triethylamine–trichloroborane and hexamethyldisilazane was

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(1) (a) Presented at the Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968. (b) Taken from the Ph.D. dissertation of H. L. Paige, Duke University, Durham, N. C., 1969.