# SOME BIS-AMINE COMPLEXES OF BORONIUM IONS WITH BULKY SUBSTITUENTS OF BORON

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The reaction of iodine with amine-boranes has proven to be a convenient method for the synthesis of boron cations of the type, $R_2B(amine)_2^+$, according to eqn. (1)[1]. The reaction is quite general and usually affords the bisamine complex salt

$$R_2BH \cdot amine + I_2 + 2 \text{ amine} \rightarrow R_2B(amine)_2^+ I^- + amine \cdot HI \qquad (1)$$
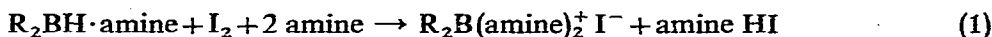
in good yield. In order to further test the generality of the reaction, and to demonstrate the usefulness of the hydroboration reaction as a convenient procedure for making certain intermediate boranes, the reaction was attempted with two quite sterically hindered organoboranes, *viz.,* (1,1,2-trimethylpropyl)borane (thexylborane) and dicyclohexylborane.

Thexylborane and dicyclohexylborane were prepared by the hydroboration of 2,3-dimethyl-2-butene and cyclohexene, respectively, using the procedures developed by Brown and co-workers[2]. As further alkylation proceeds at much diminished rates in both cases, these compounds reportedly are not contaminated to any significant degree with more highly alkylated boranes. However, to remove any possible ambiguity concerning the nature of the organoboranes which, as will be discussed below, were formed and consumed without ever being isolated, it was deemed prudent to convert them into stable derivatives which could be isolated and characterized. Suitable derivatives of thexylborane and dicyclohexylborane proved to be those formed by their reaction with o-phenylenediamine[3] and 8-quinolinol,[4] respectively, as given by eqns. (2) and (3). Both the 2-thexyl-1,3,2-benzodiazaborole and the 8-

$$C_6H_{13} = thexyl \equiv 1,1,2-trimethylpropyl$$
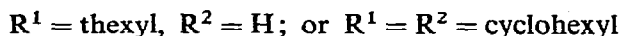
(2)

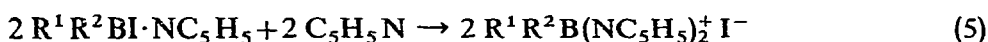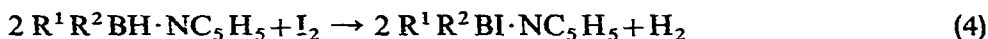$$C_6H_{11} = cyclohexyl$$

(3)
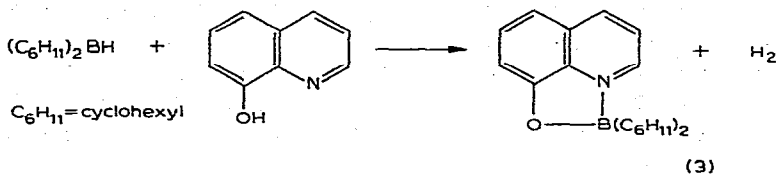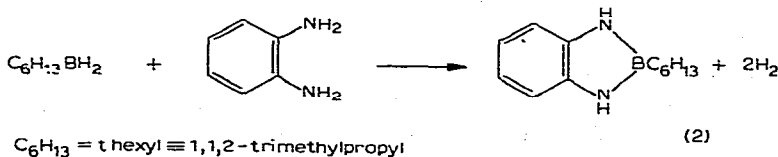
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quinolinyl dicyclohexylborinate were isolated as stable solids in yields of 95–97%
and were adequately characterized, so that there was no doubt as to the structure
of the organoboranes involved—aside from the well-documented dimeric nature
boron hydrides.

In previous work[1], the pyridine (or other tertiary amine) complex of the borane
was used as the starting material as indicated by eqn. (1), and in each case was a
relatively stable compound which could be handled without difficulty in air. All
efforts to find tertiary amine complexes of thexylborane and dicyclohexylborane of
comparable stability were unsuccessful. (In agreement with the report of Brown and
Klender[2], it was found that thexylborane does form a white, solid complex with
trimethylamine which is stable at room temperature in the absence of air; however,
the material rapidly decomposes in air.) Consequently, the pyridine organoboranes
used in this work were prepared *in situ*.

It came as some surprise to find that neither thexylborane nor dicyclohexyl-
borane react with iodine in the presence of excess pyridine according to the stoichi-
ometry given by eqn. (1). Much less than one mole of iodine was decolorized per mole
of borane, and the reaction gave rise to a mixture of products from which only pyri-
dinium iodide could be isolated in a pure state. After considerable experimentation
suitable conditions were found for effecting the conversion of these organoboranes
to their bis-amine complexes. The two-step sequence which was developed for
carrying out the transformation is shown by eqns. (4) and (5). As the intermediate

$$2\ R^1 R^2 BH \cdot NC_5 H_5 + I_2\ \rightarrow\ 2\ R^1 R^2 BI \cdot NC_5 H_5 + H_2 \tag{4}$$

$$2\ R^1 R^2 BI \cdot NC_5 H_5 + 2\ C_5 H_5 N\ \rightarrow\ 2\ R^1 R^2 B(NC_5 H_5)_2^+\ I^- \tag{5}$$

$$R^1 = \text{thexyl},\ R^2 = H;\ \text{or}\ R^1 = R^2 = \text{cyclohexyl}$$

iodoboranes proved to be rather unstable, it was deemed expedient to convert them
into the complex ions without any attempt at isolation. The overall reaction, (eqn. 6)
involves two moles of borane per mole of iodine, and hydrogen, rather than pyridinium

$$2\ R^1 R^2 BH \cdot NC_5 H_5 + I_2 + 2\ C_5 H_5 N\ \rightarrow\ 2\ R^1 R^2 B(NC_5 H_5)_2^+\ I^- + H_2 \tag{6}$$
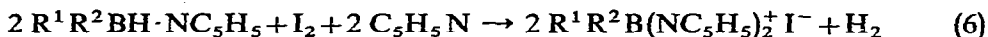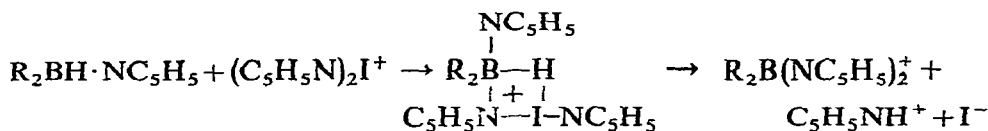
iodide, is the principle by-product. It must be pointed out, however, that in practice
the reaction was not as clean-cut as indicated by eqn. (6). First of all, a significant
amount of pyridinium iodide was always formed, and secondly, only about 80% of
the theoretical amount of iodine was decolorized.

The chemical behavior of the thexylhydridobis(pyridine)boron(III) cation is
consistent with that previously reported[1,5,6] for complex ions of this type: (1) it is
resistant to further oxidation by iodine and (2) it is resistant to hydrolysis under both
basic and acidic conditions. The dicyclohexylbis(pyridine)boron(III) cation, on the
other hand, is not nearly so stable. In fact, the iodide salt of the complex ion proved
to be so unstable in air as to prevent its adequate characterization, although the
perchlorate formed by metathesis with silver perchlorate is a stable crystalline com-
pound which was unambiguously identified. An interesting transformation occurred,
however, when the material was heated for several hours in chloroform solution:
it underwent *dehydroboration* to yield cyclohexylhydridobis(pyridine)boron(III)
perchlorate. Dehydroboration, of course, is known to be involved in the thermal
isomerization of alkylboranes[7]. The driving force for this reaction is very probably

the relief of steric crowding in the cation.

The question arises as to why the two amine boranes under discussion should fail to react with iodine in the presence of excess amine as does pyridine phenylborane and a number of other amine boranes. As there should be no significant electronic differences about the boron atom in these compounds, one might suspect that a steric factor is responsible for the observed differences in reactivity. This effect would become even more prominent if the iodine-containing species which attacked the boron–hydrogen bond were also of considerable size. As suggested previously[8], it is quite possible that the oxidizing agent is $(C_5H_5N)_2I^+$, a species which would certainly possess considerable bulk. We propose as a working hypothesis the following mechanism for the reaction shown by eqn. (1). It is evident that the energy of the

$$R_2BH \cdot NC_5H_5 + (C_5H_5N)_2I^+ \rightarrow R_2\overset{\overset{NC_5H_5}{|}}{B}\!\!-\!\!H \rightarrow R_2B(NC_5H_5)_2^+ +$$
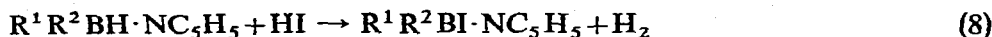$$\underset{C_5H_5\overset{+}{N}\!\!-\!\!I\!\!-\!\!NC_5H_5}{} \qquad C_5H_5NH^+ + I^-$$

transition state depicted would be quite sensitive to the size of the R groups. The mechanism also provides for the direct conversion of the amine borane into the bis-amine boronium ion as opposed to a previously proposed[1] two-step mechanism involving the amine iodoborane as an intermediate. However, there is presently in hand no evidence which permits a distinction to be made between the one-step and two-step mechanisms.

TABLE 1

SPECTRAL DATA FOR $R^1R^2(C_5H_5N)_2B^+$ PERCHLORATES

Compound	IR bands $(cm^{-1})^a$		NMR peaks $(\delta, ppm)^b$	
	B–H	N–B–N	^1H (intensity)	^{11}B (J, c/sec.)
$C_6H_{13}BH(NC_5H_5)_2$	2430 m	1460 s	0.75^c (7) 8.39 (5)	−5 (95±15)
$(C_6H_{11})_2B(NC_5H_5)_2$		1455 s	0.95 (21) 8.48 (10)	

^{a} In KBr pellets. ^{b} ^1H and ^{11}B with respect to TMS and $BF_3 \cdot O(C_2H_5)_2$, respectively. c All values in this column represent the centers of complex multiplets.

In the absence of added pyridine, iodine must of necessity function as the oxidizing agent, although it is decolorized at a somewhat slower rate than it is when pyridine is present. A reasonable mechanism which accounts for the reaction shown by eqn. (4) is given by eqns. (7) and (8). The latter reaction is a known method for

$$R^1R^2BH \cdot NC_5H_5 + I_2 \rightarrow R^1R^2BI \cdot NC_5H_5 + HI \qquad (7)$$

$$R^1R^2BH \cdot NC_5H_5 + HI \rightarrow R^1R^2BI \cdot NC_5H_5 + H_2 \qquad (8)$$

the preparation of amine monohaloboranes[9]. It is also clear that under such circumstances the formation of pyridinium iodide would not be unexpected.

EXPERIMENTAL

Elementary analyses were performed by Drs. Weiler and Strauss, Oxford, England, and by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Infrared spectra were recorded using a Perkin–Elmer Model 21 spectrophotometer and NMR spectra were determined using a Varian HR-60 or A-60A spectrometer. Melting points were measured on a calibrated Fisher-Johns block.

Diglyme and boron trifluoride etherate were distilled *in vacuo* from calcium hydride shortly before use; tetrahydrofuran was distilled from lithium aluminum hydride. 2,3-Dimethyl-2-butene (99.5%) was used as received from Phillips Petroleum Company. All other chemicals were of reagent grade. All reactions were carried out under an atmosphere of pre-purified nitrogen.

2-Thexyl-1,3,2-benzodiazaborole

Diborane was generated by the dropwise addition of a solution of 0.81 g (21 mmoles) of sodium borohydride in 90 ml of diglyme to a stirred solution of 3.50 g (24 mmoles) of boron trifluoride etherate in 10 ml of diglyme. The gas was swept by a slow stream of nitrogen through a cold trap $(-20°)$ into a solution of 1.56 g (18.7 mmoles) of 2,3-dimethyl-2-butene in 100 ml of tetrahydrofuran. After the addition of borohydride solution was complete, the generator flask was heated to 100° in order to expel any dissolved diborane.

Freshly recrystallized *o*-phenylenediamine (1.56 g, 14.8 mmoles) was added to the tetrahydrofuran solution, and the resulting solution was distilled to near dryness at near room temperature under reduced pressure. After taking up the residue in 75 ml of dry benzene, the mixture was refluxed for 2 h, or until no further evolution of hydrogen was observed. The solution was reduced to about one-third its original volume and an equal volume of pentane was added. The crystals which formed upon cooling were collected on a filter, washed with a small amount of cold benzene/pentane, and sucked dry; wt. 1.38 g, m.p. 75–77°. After two vacuum sublimations the derivative melted at 78°. (Found: C, 71.49; H, 9.57; N, 13.92. $C_{12}H_{19}BN_2$ calcd.: C, 71.32; H, 9.48; N, 13.86%.)

8-Quinolinyl dicyclohexylborinate

Dicyclohexylborane was prepared by adding diborane (prepared from 0.99 g of sodium borohydride and 4.7 g of boron trifluoride etherate) to a solution of 4.1 g (50 mmoles) of cyclohexene in 50 ml of tetrahydrofuran, followed by stirring for 30 min. After adding 3.62 g (25 mmoles) of 8-quinolinol, the mixture was refluxed for 1 h, by which time the solution had taken on an intense green fluorescence. The solvent was stripped off on a rotary evaporator and the residue was recrystallized twice from 95% ethanol to afford yellowish-green needles, m.p. 119–120°. (Found: C, 78.12; H, 8.68; N, 4.32. $C_{21}H_{28}BNO$ calcd.: C, 78.48; H, 8.80; N, 4.36%.)

Thexylhydridobis(pyridine)boron(III) salts

To a reaction flask equipped with a reflux condenser, dropping funnel and a magnetic stirring bar was added a solution of 0.10 mole of thexylborane in 100 ml of ether along with 7.90 g (0.10 mole) of dry pyridine. To this refluxing solution was added a solution of 25.4 g (0.10 mole) of iodine dissolved in 300 ml of benzene at

such a rate that the iodine was decolorized rapidly. When about 80% of this solution had been added (about 2 h), decolorization had become very sluggish; no additional solution was added beyond this point. The reaction mixture was heated until all of the iodine had been decolorized. Throughout the course of the reaction, the evolution of gas was apparent.

Pyridine (15.8 g, 0.20 mole) was added to the reaction mixture and heating under reflux was continued for 1 h. The pale yellow precipitate which formed was filtered off, dried, and then triturated with 50 ml of warm chloroform. The solid which remained proved to be pyridinium iodide. The chloroform solution was reduced to about one-third its original volume, and upon adding an equal volume of pentane and cooling, pale yellow crystals formed which were collected on a filter and dried. Two crystallizations from chloroform/carbon tetrachloride (1 : 1) gave 11.7 g of pale yellow flakes, m.p. 160–162° (decomp.). (Found: C, 50.41; H, 6.33; B, 2.42; N, 7.10. $C_{16}H_{24}BIN_2$: C, 50.25; H, 6.29; B, 2.83; N, 7.33%.)

One mmole each of the iodide salt and anhydrous silver perchlorate were stirred together as a slurry in 50 ml of chloroform at room temperature for 3 h, after which time the silver iodide was filtered off. Thexyl(bispyridine)boron(III) perchlorate was precipitated from the filtrate by the addition of an equal volume of carbon tetrachloride. Recrystallization from chloroform/carbon tetrachloride gave fine white needles, m.p. 272–274°. (Found: C, 54.36; H, 6.90; N, 8.08. $C_{16}H_{24}BClN_2O_4$: C, 54.19; H, 6.79; N, 7.92%.)

The perchlorate salt burns with near explosive violence and should be prepared only in small quantities.

Dicyclohexylbis(pyridine)boron(III) salts

Using the apparatus and procedure described above, a solution of 25.4 g (0.10 mole) of iodine in 300 ml of benzene was added dropwise to a refluxing solution of 0.10 mole of dicyclohexylborane and 0.10 mole of pyridine in 100 ml of ether. The iodine was decolorized at a much slower rate than in the experiment with thexyl-borane; furthermore, only about 75% of the theoretical amount of iodine was decolorized even after a prolonged period of heating. The total reaction time was about 6 h. Pyridine (0.20 mole) was added and the mixture was heated under reflux for an additional 3 h. The resulting yellowish precipitate was filtered off, dried and then triturated with 60 ml of warm chloroform. The undissolved material was identified as pyridinium iodide. Evaporation of the solvent from the filtrate left 17.3 g of a pale yellow solid which turned dark quite rapidly in air. Efforts to obtain satisfactory elemental analyses on this material were unsuccessful.

Equimolar amounts of the freshly prepared iodide salt and finely powdered anhydrous silver perchlorate were stirred together as a slurry in chloroform at room temperature for 3 h. After filtering off the silver iodide, carbon tetrachloride was added to the filtrate until no further precipitation occurred. Recrystallization of the dicyclohexylbis(pyridine)boron(III) perchlorate from methanol yielded white needles, m.p. 136–138° (decomp.).

Dehydroboration of dicyclohexylbis(pyridine)boron(III) perchlorate

Two g of the perchlorate salt was dissolved in 75 ml of chloroform and resulting solution was refluxed for 6 h. After allowing about one-half of the solvent to evaporate,

the addition of an equal volume of hexane caused the immediate precipitation of a white solid. Two recrystallizations of the material from acetonitrile gave white needles, m.p. 220–221°; reported[1] m.p. for cyclohexylhydridobis(pyridine)boron(III) perchlorate, 220–222°. The mixture m.p. was undepressed.

Bromine in carbon tetrachloride was added to the filtrate of the original reaction mixture until no further decolorization occurred. After allowing the solvent to evaporate, the oily residue was distilled to give a liquid whose infrared spectrum was indistinguishable from that of authentic *trans*-1,2-dibromocyclohexane.

SUMMARY

The reaction of iodine with pyridine(1,1,3-trimethylpropyl)borane and pyridinedicyclohexylborane in the presence of excess pyridine is anomalous when compared with previous work with the reaction involving less bulky substituents on boron: a mixture of products was obtained from which the complex ion, R_2bis(pyridine)-boron(III)$^+$, could not be isolated. However, in the absence of excess pyridine iodine reacts with the pyridine boranes to afford the unstable pyridine iodoboranes, which react with pyridine to afford the bis-amine complexes. The dicyclohexylbis-(pyridine)boron(III) cation was found to dehydroborate under relatively mild conditions to give the cyclohexylhydridobis(pyridine)boron(III) cation.

REFERENCES

1 J. E. DOUGLASS, *J. Am. Chem. Soc.*, 86 (1964) 5431.
2 H. C. BROWN AND G. J. KLENDER, *Inorg. Chem.*, 1 (1962) 204.
3 M. F. HAWTHORNE, *J. Am. Chem. Soc.*, 83 (1961) 831.
4 J. E. DOUGLASS, *J. Org. Chem.*, 26 (1961) 1312.
5 N. E. MILLER AND E. L. MUETTERTIES, *J. Am. Chem. Soc.*, 86 (1964) 1033.
6 H. NÖTH, H. BEYER AND H. -V. VETTER, *Chem. Ber.*, 97 (1964) 110.
7 H. C. BROWN, *Hydroboration*, Benjamin, New York, 1962, p. 136 ff.
8 O. HASSEL AND H. HOPE, *Acta Chem. Scand.*, 15 (1961) 407.
9 A. B. BURG AND H. I. SCHLESINGER, *J. Am. Chem. Soc.*, 59 (1937) 780; H. NÖTH AND H. BEYER, *Chem. Ber.*, 93 (1960) 2251.