dimethylformamide and 150 ml. of acetonitrile was added 7.68 g. (0.02 mole) of $Cs_2B_{10}H_{10}$ while cooling in an ice bath. The resulting mixture was stirred at 0° for 30 min. and then at room temperature for 15 min. The mixture was filtered into dilute aqueous sodium acetate and evaporated under reduced pressure to a small volume. The residue was treated with water, and the resulting precipitate was purified by treatment with decolorizing charcoal in refluxing carbon tetrachloride. The resulting solution was evaporated, and the residue was recrystallized from aqueous ethanol to give 645 mg. (11%) of white crystals of II, m.p. 177–186°. Recrystallization from carbon tetrachloride–pentane raised the m.p. to 183–186°. *Anal.* Calcd. for $B_{10}H_{24}C_6N_2Cl_2$: C, 23.8; H, 7.97; B, 35.7; N, 9.25; Cl, 23.4. Found: C, 24.1; H, 7.75; B, 36.3; N, 9.41; Cl, 22.9.

The H^1 n.m.r. spectrum of the product in carbon tetrachloride solution shows two single peaks at τ 5.22 and 7.20 (external $(CH_3)_4Si$) in the ratio 1:3 which can be assigned to the four methylene hydrogens and the twelve methyl hydrogens, respectively.

$(CH_3)_4NB_{12}H_{11}N(CH_3)_2CH_2Cl$ (III).—A solution of 46 g. (0.22 mole) of phosphorus pentachloride in 500 ml. of dry acetonitrile and 36 ml. of dimethylformamide was stirred at room temperature for 15 min. under a nitrogen atmosphere. Then 29 g. (0.1 mole) of $[(CH_3)_4N]_2B_{12}H_{12}$ was added, the resulting mixture was stirred for 4 hr. and filtered into 100 ml. of 1 *M* aqueous sodium acetate, and the resulting solution was evaporated under reduced pressure to a small volume. The residue was treated with water and extracted with 1:1 methylene chloride–benzene. The extract was evaporated, and the residue was recrystallized from ethyl acetate to give 3.71 g. (12%) of white crystals, m.p. 285°. Recrystallization from water, from acetone–water, and finally from water gave crystals of $(CH_3)_4NB_{12}H_{11}N(CH_3)_2CH_2Cl$, m.p. 283–284°. *Anal.* Calcd. for $B_{12}H_{31}C_7N_2Cl$: C, 27.2; H, 10.1; B, 42.1; N, 9.02; Cl, 11.5; 0.5 mol. wt., 154.3. Found: C, 27.4; H, 9.90; B, 41.4; N, 9.17; Cl, 12.9; mol. wt., 161. The infrared spectrum of the product shows no absorption characteristic of N—H or C=N. The H^1 n.m.r. spectrum of the product in trifluoroacetic acid solution shows three single peaks at τ 5.35, 7.05, and 7.3 (external $(CH_3)_4Si$) with relative intensities 1:6:3 which can be assigned to the two hydrogens adjacent to chlorine, the twelve hydrogens of $(CH_3)_4N^-$, and the six hydrogens of the $N(CH_3)_2$ group, respectively.

$B_{12}H_{10}[N(CH_3)_2CH_2Cl]_2$ (IV).—To a solution of 31.25 g. (0.15 mole) of phosphorus pentachloride in 150 ml. of dimethylformamide and 500 ml. of acetonitrile was added 14.5 g. (0.05 mole) of $[(CH_3)_4N]_2B_{12}H_{12}$. The resulting mixture was stirred at room temperature under nitrogen for 22 hr. and then filtered into aqueous sodium acetate and evaporated under reduced pressure. The residue was treated with water and extracted with 1:1 methylene chloride–benzene, and the extracts were evaporated. The oily residue was recrystallized from aqueous acetone to give 950 mg. (6%) of off-white crystals of IV, m.p. 198–226°. Two additional recrystallizations raised the m.p. to 245–248°. *Anal.* Calcd. for $B_{12}H_{26}C_6N_2Cl_2$: C, 22.0; H, 8.01; B, 39.7; N, 8.57; Cl, 21.4. Found: C, 22.4; H, 7.94; B, 39.5; N, 8.58; Cl, 21.5.

The H^1 n.m.r. spectrum of the product in methylene chloride solution shows two single peaks at τ 4.9 and 6.9 (external $(CH_3)_4Si$) with an intensity ratio of 1:3 which can be assigned to the four methylene hydrogens and the twelve methyl hydrogens, respectively.

2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$ (V).—A mixture of 50 ml. of *t*-butyl alcohol, 5 ml. of ethyl alcohol, 587 mg. (1.94 mmoles) of II, and several small pieces of sodium was refluxed for 3 hr. during which time additional sodium was added so that there was undissolved sodium present at all times. The mixture was cooled and treated with 30 ml. of water, and the organic solvents were removed under reduced pressure. Filtration of the resulting slurry gave 405 mg. (90%) of V as a white solid. Recrystallization from aqueous ethanol and then from acetone–ethanol gave crystals of 2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$, m.p. 298–300°. *Anal.* Calcd. for $B_{10}H_{26}C_6N_2$: C, 30.4; H, 11.2; B, 46.1; N, 12.0; mol. wt., 234. Found: C, 30.1; H, 10.7; B, 46.1; N, 11.8; mol. wt., 236 (X-ray).

The H^1 n.m.r. spectrum of the product in chloroform-*d* shows a single peak at τ 7.12 ($N-CH_3$). The B^{11} n.m.r. spectrum of the product (Fig. 2) is consistent with 2,7(8) geometry. The unsymmetrical low-field doublet can be assigned to two substituted equatorial boron atoms (peak at +20.5 p.p.m.) and two unsubstituted apical boron atoms (doublet with high-field half at +26.2 p.p.m. and a low-field half beneath the 20.5 p.p.m. peak, $J \sim 110$ c.p.s.). The +35.8, +42.7, +47.8, and +52.5 p.p.m. peaks can be assigned to the remaining six unsubstituted equatorial boron atoms. On irradiation at 60 Mc., the unsymmetrical low-field doublet can be decoupled to a single, somewhat broad peak centered at +22.4 p.p.m., and the remainder of the peaks can be decoupled more or less independently. The observed intensity ratio of the +22.4 p.p.m. peak to the sum of the +35.8, +42.7, +47.8, and +52.2 p.p.m. peaks of 2:3 is in agreement with theory. The absence of resonance in the vicinity of 0 p.p.m. precludes any apical substitution,[2] and the presence of only a single resonance for both apical boron atoms suggests that their environment is similar and, hence, that each is adjacent to one substituted equatorial boron atom, *i.e.*, the $N(CH_3)_3$ groups are on different equatorial belts. Entirely different results were reported for the B^{11} n.m.r. spectrum of 2,4- and 2,3-$B_{10}H_8[N(CH_3)_3]_2$ in which both substituents are on the same equatorial belt.[2] To the extent which interpretation of the B^{11} n.m.r. spectrum of V has been carried it is not possible to distinguish between 2,7(8) and 2,6(9) substitution, but the latter assignment (substituents on adjacent boron atoms) seems unlikely from steric and electronic considerations.

Contribution No. 954 from the Central Research
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Chemistry of Boranes. XVI.[1] A New Heterocyclic Boron Compound

By N. E. Miller and E. L. Muetterties

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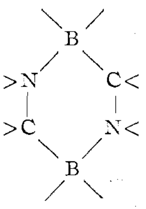
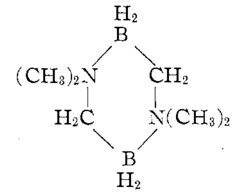
A number of heterocyclic boron compounds have been prepared and characterized in recent years.[2] One of the simpler ring systems yet to be described is the six-membered ring with a repeating BCN sequence, **1**. We have prepared the N-tetramethyl derivative,



1



2

2, in low yield from sodium hydride and $H_2B[N(CH_3)_3]_2Cl$.[3] The stability of **2** is fair. The compound is stable to long exposure to the atmosphere and to thermal degradation to at least 100° but it is rapidly decomposed by strong mineral acids. Bromine does not destroy the ring system but replaces three of the BH hydrogen atoms to give **3**.

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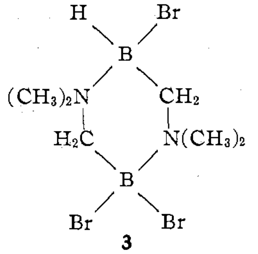
[1] Paper XV: T. A. Ford, G. H. Kalb, A. L. McClelland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1032 (1964).

[2] This subject has been reviewed in some detail by P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962).

[3] N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, in press.



3

Experimental

Synthesis of 2.—The heterogeneous system of sodium hydride (0.58 mole) as a 56% dispersion in mineral oil, $H_2B[N(CH_3)_3]_2^+Cl^-$ (31.3 g., 0.19 mole), and 200 ml. of dimethoxyethane was held at the reflux temperature of the ether for 8 hr. The reaction product was filtered, and the filtrate was subjected to repeated vacuum fractionation through cold traps maintained at −15 and −78°. The material in the −15° trap was a mixture of **2** and trimethylamine borane. Repeated recrystallization from 95% ethanol gave **2** in pure form as transparent crystals with a camphor-like odor, m.p. 89–91°. Yields based on $H_2B[N(CH_3)_3]_2^+Cl^-$ varied from 1 to 5%. *Anal.* Calcd. for $[(CH_3)_2NCH_2BH_2]_2$: C, 50.8; H, 14.2; B, 15.2; N, 19.8; mol. wt., 142. Found: C, 51.1; H, 14.4; B, 15.2; N, 19.8; mol. wt., 130. The infrared spectrum[4] had a multiplet BH absorption at 2300 cm.$^{-1}$ and a large number of long wave length bands, the more intense bands at 1170, 1110, 1090, 990, 965, 910, and 760 cm.$^{-1}$.

The B^{11} spectrum is a 1:2:1 triplet with A_{BH} = 98 c.p.s. and $\delta = +27.4$ p.p.m. (trimethyl borate reference). This establishes that two hydrogen atoms are strongly coupled or directly bonded to the boron atom and that the two boron atoms are spectroscopically equivalent. In the proton n.m.r. spectrum, there are three major peaks. The lowest field peak at −2.51 p.p.m. (tetramethylsilane reference) of relative intensity 3 is ascribed to $N-CH_3$ protons, the −2.01 p.p.m. peak of relative intensity 1 to methylene protons, and the quartet at −1.21 p.p.m. to the BH_2 protons. Assignment of structure as presented for **2** would appear to be unequivocal.

Synthesis of 3.—About 0.1 g. of **2** was dissolved in ~10 ml. of dichloromethane and sodium carbonate (2 g.) was added. This slurry was stirred and bromine was added from a fine pipet until the bromine color persisted. The slurry was filtered and the filtrate was evaporated under reduced pressure to leave a solid which was recrystallized from dichloromethane. *Anal.* Calcd. for $C_6H_{17}B_2N_2Br_3$: C, 19.0; H, 4.5; N, 7.4; B, 5.7; Br, 63.3. Found: C, 19.8; H, 4.9; N, 7.8; B, 5.8; Br, 63.4. The intensity of the infrared BH stretching frequency of **3** was sharply reduced from that of **2**, shifted to 2450 cm.$^{-1}$, and consisted of a single sharp band. These data indicated replacement of BH hydrogen atoms by bromine atoms.

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(4) It was conclusively shown that **2** is not $[(CH_3)_2NBH_2]_3$, which has a similar melting point, by comparison of the infrared and n.m.r. spectra of **2** with those of $[(CH_3)_2NBH_2]_3$. The latter compound is described by G. W. Campbell and L. Johnson, *J. Am. Chem. Soc.*, **81**, 3800 (1959).

CONTRIBUTION FROM THE UNIVERSITY OF MICHIGAN,
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A Specific Synthesis for Bis(bipyridine)ruthenium Compounds

BY CHUI FAN LIU, NORA C. LIU, AND JOHN C. BAILAR, JR.

Received December 9, 1963

As was pointed out by Dwyer and co-workers[1] the bis(bipyridine)ruthenium type of chelate represents an ideal material for a number of fundamental chemical studies due to the accessibility of different oxidation states and the kinetic inertness of the bipyridine–ruthenium linkage. Miller and co-workers[2] concluded that the formation of the tris(bipyridine)ruthenium(II) ion involved the mono(bipyridine) and bis(bipyridine) chelates as intermediates. They were able to isolate the compound $[Ru(bipy)_2(H_2O)_2](ClO_4)_3$. This, however, did not represent a satisfactory method of preparation as a complex mixture of products was obtained. The bis(bipyridine)ruthenium(II) ion was also obtained by heating $[Ru(bipy)_3]Cl_2$ under vacuum over a long period of time[3] and by pyrolysis of bipyridinium tetrachloro(bipyridine)ruthenate(III).[3] In the present investigation a simple method has been devised to produce bis(bipyridine)ruthenium complexes from aqueous solution, in relatively high yields under mild conditions.

Experimental

Oxalatobis(bipyridine)ruthenium(II)-4-Hydrate.—A mixture of 1 g. of potassium pentachloroaquoruthenate(IV), 1.5 g. of potassium oxalate, and 40 ml. of water was heated on a steam bath for 1 hr. A solution of 0.8 g. of bipyridine in 10 ml. of alcohol was then added. Heating was continued for 3 hr. more. On cooling crystals appeared. These were filtered, washed with warm water (~60°) until the washings were pink in color, then washed with ether, and air dried. The yield was 58% of the theoretical. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_2(C_2O_4)]\cdot 4H_2O$: C, 46.01; H, 4.22; N, 9.76. Found: C, 46.00; H, 4.29; N, 9.95. The product was found to be diamagnetic, and therefore involved ruthenium in its +2 state. The compound was found to be insoluble in water but soluble in methanol and ethanol. Recrystallization could be carried out from methanol. The water of crystallization could be driven out easily at 110°. The calculated weight of water was 12.54%; the loss of weight at 110° was found to be 12.51%.

Dichlorobis(bipyridine)ruthenium(III) Perchlorate.—A suspension of 0.2 g. of oxalatobis(bipyridine)ruthenium(II)-4-hydrate in 25 ml. of 2 *N* hydrochloric acid was warmed to 80°. Chlorine was bubbled through the mixture until all the solid material dissolved. The solution turned bright red. After filtering, 4–5 ml. of 7% perchloric acid was added. Upon cooling crystals appeared. These crystals were recrystallized from 180 ml. of water containing about 5 ml. of concentrated hydrochloric acid and a small amount of chlorine. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_2Cl_2]ClO_4$: C, 41.10; H, 2.76; N, 9.59. Found: C, 41.54; H, 2.98; N, 9.69. The magnetic susceptibility of the compound was determined to be 1.82 B.M., which corresponds to that of a ruthenium(III) complex.

Dichlorobis(bipyridine)ruthenium(III) Chloride-2-Hydrate.—A heated suspension of 0.2 g. of oxalatobis(bipyridine)ruthenium(II)-4-hydrate in 20 ml. of 2 *N* hydrochloric acid was treated with excess chlorine gas. After all the crystals dissolved, 5 ml. of concentrated hydrochloric acid was added. On cooling, the desired compound crystallized. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_2Cl_2]Cl\cdot 2H_2O$: C, 43.16; H, 3.62; N, 10.07; residue, 24.3. Found: C, 43.71; H, 3.72, N, 10.14; residue, 23.2.

For comparison purposes, dichlorobis(bipyridine)ruthenium(III) perchlorate was prepared by a different method.

Dichlorobis(bipyridine)ruthenium(II).—Tris(bipyridine)ruthenium(II) chloride (1 g.) was deposited on 50 g. of quartz powder (300 mesh). The mixture was heated at 290° under

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(1) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Australian J. Chem.*, **16**, 42 (1963).

(2) R. R. Miller, W. W. Brandt, and M. Puke, *J. Am. Chem. Soc.*, **77**, 3178 (1955).

(3) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Australian J. Chem.*, **16**, 544 (1963).