Some Stable Monoboron Free Radicals. 2,2′-Bipyridine Stabilization of Unusual Oxidation States of Boron[1]

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Abstract: Treatment of various chloroboranes with lithium 2,2′-bipyridine, dilithium 2,2′-bipyridine, or with mixtures of these two reagents results in the formation of a series of neutral monoboron compounds in which boron is stabilized in unusual oxidation states by chelation with 2,2′-bipyridine. Dimethylaminoboron 2,2′-bipyridine is an even-electron diamagnetic species while 2,2′-biphenyleneboron 2,2′-bipyridine, bis(dimethylamino)boron 2,2′-bipyridine, and boron bis(2,2′-bipyridine) all are odd-electron paramagnetic species. The characterizations of these compounds are discussed along with some of their chemical properties and electron spin resonance spectra of the paramagnetic species.

Reduction of 2,2′-bipyridine with lithium in tetrahydrofuran results in the formation of the deep purple lithium 2,2′-bipyridine. Further reduction with lithium yields the deep green dilithium 2,2′-bipyridine. Using these two reagents, Herzog and Taube have been successful in stabilizing unusual oxidation states of a large number of metals and two metalloids by chelation.[4]

For example, treatment of the 2,2′-bipyridine adduct of silicon tetrachloride in tetrahydrofuran with enough dilithium 2,2′-bipyridine to form 4 moles of lithium chloride per mole of silicon tetrachloride results in the formation of the deep violet silicon tris(2,2′-bipyridine). This air-sensitive compound was isolated in the crystalline state.[4]

In a similar manner, the neutral 2,2′-bipyridine complexes of a number of elements of the periods beginning with sodium, potassium, and rubidium have been prepared. However, among the elements of the period beginning with lithium, only beryllium has been stabilized in a reduced oxidation state with 2,2′-bipyridine.[5,6] Addition of an ether solution of lithium 2,2′-bipyridine to an ether solution of beryllium chloride results in the immediate formation of the intense green beryllium bis(2,2′-bipyridine) according to eq 1.

$$2\mathrm{LiC_{10}H_8N_2} + \mathrm{BeCl_2} \longrightarrow \mathrm{(C_{10}H_8N_2)_2Be} + 2\mathrm{LiCl} \qquad (1)$$

In the present work, lithium 2,2′-bipyridine and dilithium 2,2′-bipyridine have been used in the preparation of a number of organoboron compounds. Reduction and chelation of various boron halides has produced examples of boron in unusual oxidation states.[7]

Results and Discussion

The preparation of a diamagnetic compound by the reaction shown in eq 2 is readily effected in tetrahydrofuran. The product of this reaction, dimethylamino-

$$\mathrm{Li_2C_{10}H_8N_2} + \mathrm{(CH_3)_2NBCl_2} \longrightarrow \mathrm{(CH_3)_2NBC_{10}H_8N_2} + 2\mathrm{LiCl} \qquad (2)$$

boron 2,2′-bipyridine, is a deep red solid that can be obtained in a crystalline state and appears to be stable for an indefinite period at room temperature in the absence of air.

None of the paramagnetic boron 2,2′-bipyridines could be obtained from similar reactions when tetrahydrofuran and dimethoxyethane were used as solvents. In each of the preparations where the expected product is an odd-electron molecule, heterogenous reactions between solid lithium 2,2′-bipyridines and cyclopentane solutions of chloroboranes were required in order to obtain any paramagnetic product.[8]

Thus, a cyclopentane solution of bis(dimethylamino)chloroborane reacts with solid lithium 2,2′-bipyridine to form bis(dimethylamino)boron 2,2′-bipyridine according to eq 3.

$$\mathrm{[(CH_3)_2N]_2BCl} + \mathrm{LiC_{10}H_8N_2} \longrightarrow \mathrm{[(CH_3)_2N]_2BC_{10}H_8N_2} + \mathrm{LiCl} \qquad (3)$$

A similar reaction between 2,2′-biphenylenechloroborane, dissolved in cyclopentane, and lithium 2,2′-bipyridine occurs as shown in eq 4.

$$\mathrm{C_{12}H_8BCl} + \mathrm{LiC_{10}H_8N_2} \longrightarrow \mathrm{C_{12}H_8BC_{10}H_8N_2} + \mathrm{LiCl} \qquad (4)$$

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[2] Taken from the Doctoral Dissertation of M. A. Kuck, Purdue University, Jan. 1965.

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[4] S. Herzog and R. Taube, *Z. Chem.*, **2**, 210 (1962).

[5] A. Gegenfurthner, Thesis, Griefswald, 1962.

[6] J. E. Coates and S. L. E. Green, *J. Chem. Soc.*, 3340 (1962).

[7] The actual oxidation state of boron in all of the compounds reported in the present work is a matter of some speculation. Many resonance forms representing various virtual oxidation states for boron undoubtedly contribute to the stability of this series of compounds. Titration with iodine produced results expected from the formal oxidation state only in the case of dimethylaminoboron 2,2′-bipyridine. This compound also proved to be the least chemically reactive of all the molecules studied and did not appear to undergo reaction with compounds containing active hydrogen. All of the other cases, being free radicals, showed evidence of typical free-radical reactions, such as hydrogen abstraction from molecules possessing active hydrogen, which might be expected to interfere with the iodine titration. The only statement pertaining to the oxidation state of boron in these various compounds which can be made with certainty is that boron bis(2,2′-bipyridine), bis(dimethylamino)boron 2,2′-bipyridine, and 2,2′-biphenyleneboron 2,2′-bipyridine all are odd-electron molecules and as such represent molecules in which boron is in an even oxidation state while dimethylaminoboron 2,2′-bipyridine is an even-electron molecule with boron in an odd oxidation state.

[8] The properties of the odd-electron species produced in the present work appear to differ significantly from the paramagnetic species reported by Koester and co-workers [R. Koester, G. Benedikt, and H. W. Schroetter, *Angew. Chem.*, **76**, 649 (1964)] as resulting from the sodium reduction of the diethylchloroborane–pyridine adduct carried out in ethereal solvents. The radical they obtain, which they describe as the pyridine complex of the diethylboryl radical, displays a truly remarkable stability in ethereal solvents as well as an electron spin resonance spectrum with a hyperfine complexity unusual for boron-containing free radicals.

Boron bis(2,2′-bipyridine) results from the reaction of boron trichloride in cyclopentane with an equimolar mixture of lithium 2,2′-bipyridine and dilithium 2,2′-bipyridine according to the stoichiometry required by eq 5.

$$BCl_3 + LiC_{10}H_8N_2 + Li_2C_{10}H_8N_2 \longrightarrow B(C_{10}H_8N_2)_2 + 3LiCl \quad (5)$$

The diamagnetic dimethylaminoboron 2,2′-bipyridine is an air-sensitive material which can be crystallyzed by distillation of the solvent from a tetramethylsilane solution. It was characterized by elemental analysis, molecular weight determination, and reaction with iodine. The optical spectrum and nmr proton spectrum are consistent with those expected from the proposed species.

Since this compound may be considered to be a 2,2′-bipyridine complex of dimethylaminoborene [$(CH_3)_2NB{:}$], several attempts were made, using aluminum, to effect dissociation according to eq 6. This was done

$$3(CH_3)_2NBC_{10}H_8N_2 + Al(Hg) \longrightarrow 3[(CH_3)_2NB{:}] + Al(C_{10}H_8N_2)_3 \quad (6)$$

with the knowledge that aluminum, activated with mercury metal, reacts directly with 2,2′-bipyridine at 200° to form the brown-yellow aluminum tris(2,2′-bipyridine).[9]

However, mercury-activated aluminum did not displace dimethylaminoborene from dimethylaminoboron 2,2′-bipyridine. Treatment with activated magnesium also failed to effect the displacement reaction.

An attempt to produce simple thermal dissociation according to eq 7 also was unsuccessful. Indeed, the

$$(CH_3)_2NBC_{10}H_8N_2 \not\longrightarrow [(CH_3)_2NB] + C_{10}H_8N_2 \quad (7)$$

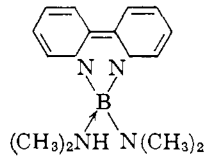
material proved to be very stable *in vacuo* with no observable decomposition below 250°. The stability of this polycyclic system may be attributed in part to resonance stabilization involving the delocalization of charge on the reduced boron atom.

In the course of attempting to synthesize a boron(II) species stabilized by 2,2′-bipyridine, bis(dimethylamino)chloroborane was treated with lithium 2,2′-bipyridine. The products formed in this reaction appear to depend on the solvent used.

With tetrahydrofuran as solvent, a red material is formed which can be handled in a drybox without decomposition. The elemental analysis and apparent molecular weight are virtually identical with those for bis(dimethylamino)boron 2,2′-bipyridine, the expected product. This odd-electron species, if monomeric, as indicated by the molecular weight, would necessarily be paramagnetic. However, the red material obtained from the reaction in tetrahydrofuran is diamagnetic.

When cyclopentane is used as a solvent for bis(dimethylamino)chloroborane, an intense red material is formed, which cannot be handled in a drybox without decomposition. This material is paramagnetic, exhibiting a single broad resonance. The optical spectrum consists of two maxima in the 220–300-mμ region characteristic of chelated 2,2′-bipyridine.

The observed results can be explained by assuming that while the even-electron diamagnetic dimethylaminoboron 2,2′-bipyridine is stable in tetrahydrofuran, odd-electron molecules such as bis(dimethylamino)boron 2,2′-bipyridine possess a high degree of reactivity enabling the abstraction of hydrogen from solvents like tetrahydrofuran to form diamagnetic species. In the present case two likely possibilities exist for the species expected when a hydrogen atom is abstracted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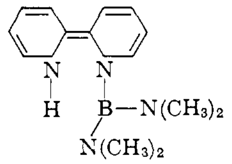
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from tetrahydrofuran. The first structure (I) is the dimethylamine adduct of the compound dimethylaminoboron 2,2′-bipyridine. Since dimethylaminoboron 2,2′-bipyridine did not form an adduct with dimethylamine stable above −45°, it is unlikely that I is the structure of the diamagnetic compound. The optical spectrum of the material formed in tetrahydrofuran consists of a single maximum in the 220–330-mμ region and not the two maxima characteristic of 2,2′-bipyridine chelates.[6]

These facts considered along with the elemental analysis and molecular weight determination would make II the most likely structure for the product of the reaction in tetrahydrofuran.

The apparent reactivity of odd-electron boron 2,2′-bipyridine complexes also makes it impossible to prepare the (2,2′-bipyridine)boron(0) complex in tetrahydrofuran; although the color of the lithium 2,2′-bipyridine is discharged and some solid precipitates, no observable amount of the desired boron bis(2,2′-bipyridine) is formed.

However, in cyclopentane, a very slow heterogenous reaction occurs with the formation of the red boron bis(2,2′-bipyridine) as described in eq 5. This material cannot be handled in a drybox without decomposition. The product, boron bis(2,2′-bipyridine), exhibits the characteristic 2,2′-bipyridine band in the ultraviolet region of the spectrum and is paramagnetic.

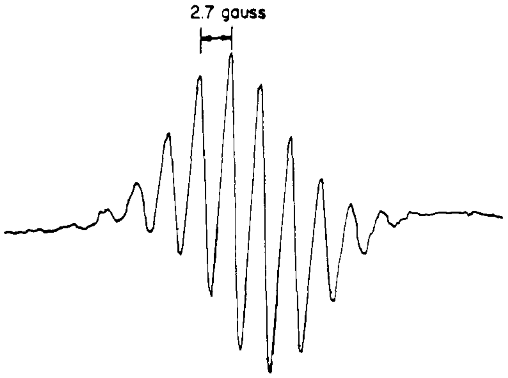

Figure 1. Electron spin resonance spectrum of boron bis(2,2′-bipyridine) (normal gain).

The paramagnetic resonance spectrum for this new species, shown in Figures 1 and 2, has a total breadth of approximately 30 gauss and consists of twelve lines spaced 2.7 gauss apart. The hyperfine structure can be accounted for by assuming equal splittings of the electron spin by the central boron and the four surrounding nitrogens. B^{11} has a nuclear spin of $^3/_2$ while that of

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[9] S. I. Weissman, private communication.

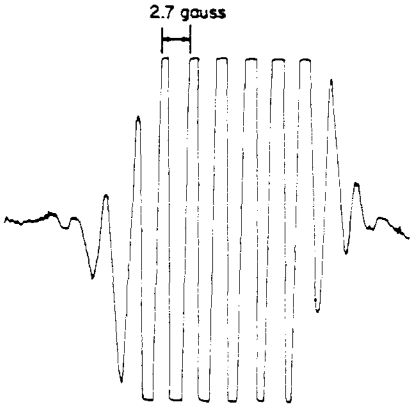

Figure 2. Electron spin resonance spectrum of boron bis(2,2′-bipyridine) (high gain).

N^{14} is 1. The relative intensities of the twelve lines predicted making the aforementioned assumptions would be 1:5:15:31:49:61:61:49:31:15:5:1. These calculated relative intensity values are seen to be in good agreement with the observed hyperfine structure shown in Figure 2, which is a high gain presentation such that the weakest lines are clearly observable.

Coates and Green, in their investigation of beryllium bis(2,2′-bipyridine),[6] report an observed magnetic susceptibility of 2.05 and 2.15 BM for this even-electron compound. In rationalizing this, they propose that this compound does not contain coordinate–covalent bonding analogous to the transition metal 2,2′-bipyridine complexes but rather that the ionic assembly, (2,2′-bipyridine)$^-$Be^{+2}(2,2′-bipyridine)$^-$, best represents the system. Since the magnetic susceptibility should then be 2.8–2.9 BM, they reason that an equilibrium such as in eq. 8 may exist.

$$(C_{10}H_8N_2)^-Be^{+2}(C_{10}H_8N_2)^- \rightleftharpoons (C_{10}H_8N_2)^0Be^{+2}(C_{10}H_8N_2)^{-2} \qquad (8)$$

A model similar to this is not reasonable for boron bis(2,2′-bipyridine) in light of the paramagnetic resonance spectrum. The apparent interaction of the odd electron with the four nitrogens and the boron clearly indicates a covalent bonding between the 2,2′-bipyridine ligands and the boron.

The splitting of the electron spin by the spiro boron atom in this molecule was not expected. In the bis(2,2′-biphenylene)methane uninegative ion radical, while the electron delocalizes over both aromatic systems,[10] the central spiro atom apparently does not interact appreciably with the electron spin when C^{13} is the spiro atom.[11] The dinegative ion of bis(2,2′-biphenylene)methane is paramagnetic and is likely a ground-state triplet with one unpaired electron located in each biphenyl aromatic system.[10] While it has proved impossible as yet to prepare the trinegative ion of bis(2,2′-biphenylene)methane, the boron bis(2,2′-bipyridine) prepared in the present work is isoelectronic with that unobtainable methane ion radical.

One might expect the trinegative bis(2,2′-biphenylene)methane ion to have one unpaired electron with a delocalization of spin similar to that found in the uninegative ion radical of the same species. Thus, the effect upon the paramagnetic resonance spectrum of the spiro boron atom in boron bis(2,2′-bipyridine) would appear to be at odds with the usual intuition exercised in the case of isoelectronic molecules.

It was therefore interesting to prepare a boron species isoelectronic with a known bis(2,2′-biphenylene)methane ion radical in an attempt to see if in a comparable case splittings by the spiro boron atom were observed. Accordingly, the compound, 2,2′-biphenyleneboron 2,2′-bipyridine was synthesized. While the electron spin resonance spectrum of this compound is not conclusive it can be resolved into 22 lines. The even number of lines in this spectrum is consistent with splittings of the unpaired electron with the boron and both nitrogens.

While dimethylaminoboron 2,2′-bipyridine is an even-electron diamagnetic species, when it is treated with methanol *in vacuo* a deep blue-green solution is formed which exhibits a single broad unresolved paramagnetic resonance. After approximately 8 hr, the color of the solution changes to red-brown. The color change is accompanied by a decay in the paramagnetic resonance signal.

Treatment of boron bis(2,2′-bipyridine) with methanol *in vacuo* also results in the formation of a deep green paramagnetic solution. The electron spin resonance examination of this solution gives a twelve-line spectrum identical in features, but possibly slightly narrower than that observed for boron bis(2,2′-bipyridine) in the absence of methanol. The color of the solution changes to pale yellow in approximately 12 hr. Accompanying the color change is a decay in the paramagnetic signal. Other alcohols produce similar results.

It is apparent from the present work that the as yet unexplored chemistry of the very reactive boron 2,2′-bipyridines promises to be quite complex and should prove to be very interesting.

Experimental Section

Methods, Apparatus, and Reagents. All reactions and purifications of materials volatile at room temperature were carried out using standard vacuum techniques. Molecular weight determinations were carried out by a modification of the isopiestic method described by Morton, Campbell, and Ma.[12]

Electron spin resonance spectra were obtained using an Alpha Scientific Laboratories Al-X-10 spectrometer.

Carbon, hydrogen, and nitrogen analyses generally were carried out using conventional organic microtechniques with transfers made in a dry nitrogen atmosphere. Boron was determined by conversion to boric acid and titration of the boric acid–mannitol complex with 0.1 *N* NaOH.

Several materials proved to be so air sensitive that a modification of the procedure described by Brown, Schlesinger, and Burg[13] for the determination of boron, carbon, and hydrogen using vacuum line techniques was required.

Ammonia, commercial grade, was dried over sodium and used without further purification. *Azobenzene*, obtained from Eastman Organic Chemicals, Rochester, N. Y., was used as received. *2,2′-Biphenylenechloroborane* was prepared according to the method of Koester and Benedikt.[14] It was purified by distillation *in vacuo* at 90°. *2,2′-Bipyridine*, secured from the Matheson Coleman

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[10] R. D. Cowell, G. Urry, and S. I. Weissman, *J. Chem. Phys.*, **38**, 2028 (1963).

[11] G. Urry, R. D. Cowell, and S. I. Weissman, unpublished results.

[12] J. E. Morton, A. D. Campbell, and T. S. Ma, *Analyst*, 78, 722 (1953).

[13] H. C. Brown, H. I. Schlesinger, and A. Burg, *J. Am. Chem. Soc.*, **61**, 673 (1939).

[14] R. Koester and G. Benedikt, *Angew. Chem. Intern. Ed. Engl.*, **2**, 323 (1963).

and Bell Co., Norwood, Ohio, exhibited a melting point of 69–70° and was used without further purification. *Bis(dimethylamino)-chloroborane* was prepared from boron trichloride and dimethylamine according to the method of Wiberg.[15] *Boron trichloride*, obtained from the Matheson Co., Joliet, Ill., was distilled through traps maintained at −78, −126, and −196° until the material retained at −126° had an observed vapor tension of 477 mm at 0° and 4.0 mm at −78°. *Boron triethyl* was prepared from boron trifluoride etherate and ethylmagnesium bromide in diethyl ether according to the method of Brown and Pearsall.[16] It was purified by distillation through traps maintained at −45 and −78° until the material retained at −45° had a vapor tension at 0° of 12.5 mm. *2-Bromobiphenyl*, obtained from K and K Laboratories, Inc., Jamaica, N. Y., was used without further purification. *n-Butyllithium* solution in *n*-hexane, secured from the Foote Mineral Co., New Johnsonville, Tenn., was used as received. *Carbon tetrachloride*, Spectroquality reagent, obtained from Matheson Coleman and Bell, was dried over calcium hydride and used without further purification. *Cyclopentane*, secured from the Phillips Petroleum Co., Bartlesville, Okla., was repeatedly shaken with concentrated sulfuric acid until no coloration was observed in the acid layer, washed several times with water, dried over calcium hydride, and distilled from lithium aluminum hydride. *Diborane* was prepared from sodium borohydride and boron trifluoride etherate according to the method of Schlesinger, *et al.*[17] *Diethylchloroborane* was prepared from boron triethyl and boron trichloride according to the method of Buls, Davis, and Thomas.[18] It was purified by repeated distillation through traps maintained at −45 and −78° until the material retained at −45° had a vapor tension of 100 mm at 0°. *Diethyl ether*, Mallinckrodt analytical reagent, was used without further purification. *Dilithium 2,2′-bipyridine* was prepared by stirring the stoichiometric amounts of lithium and 2,2′-bipyridine in dimethoxyethane or tetrahydrofuran for 24 hr. *Dimethoxyethane*, commercial grade, was dried over sodium. *Dimethylamine*, obtained from the Matheson Co., was purified by distillation through traps maintained at −78, −95, and −196° until the material which stopped at −95° had an observed vapor tension of 2.8 mm at −78°. *Dimethylaminodichloroborane* was prepared from boron trichloride and dimethylamine according to the method of Wiberg.[12] *Iodine*, U.S.P., secured from the J. T. Baker Chemical Co., Phillipsburg, N. J., was purified by grinding with potassium iodide and calcium oxide and subliming the iodine from the mixture. *Lithium 2,2′-bipyridine* was prepared by stirring stoichiometric amounts of lithium and 2,2′-bipyridine in tetrahydrofuran for 12 hr at room temperature or in liquid ammonia for 0.5 hr at −30°. *Lithium wire* was obtained from the Lithium Corporation of America. Measured amounts were secured in the following manner. A length of lithium wire, measured and cut under mineral oil, was placed in a 10% solution of ethanol in dry dimethoxyethane for a measured length of time. This clean wire was transferred to the reaction apparatus fitted with an O-ring joint, which then was immediately evacuated. The amount of lithium per unit length was estimated by a determination of the hydrogen evolved from methanolysis of a measured length of lithium wire which had been treated in the same manner. Measured amounts of lithium accurate to the nearest tenth of a mmole could be secured by this procedure. *Methylene chloride*, obtained from Eastman Organic Chemicals, was dried over calcium hydride and distilled through traps maintained at −45, −78, and −196° until the material retained at −78° had a vapor tension of 144.0 mm at 0°. *Methyl alcohol*, reagent grade, obtained commercially, was dried over phosphorus pentoxide and distilled through traps maintained at −30, −45, and −96° until the material retained at −45° had a vapor tension of 30.0 mm at 0°. *Pyridine*, Baker analyzed reagent, was distilled from calcium hydride. *Tetrahydrofuran*, Mallinckrodt analytical reagent, was distilled from lithium aluminum hydride before use. *Tetramethylsilane*, obtained from the Stauffer Chemical Co., Weston, Mich., was dried over calcium hydride and distilled through traps maintained at −78, −95, and −196° until the material which stopped at −95° had a vapor tension of 61.0 mm at −30°. *Trimethylamine*, secured from the Matheson Co., was purified by distillation through traps maintained at −78, −95, and −196° until the fraction which stopped at −95° had a vapor tension of 6.6 mm at −78°.

Preparation and Purification of Dimethylaminoboron 2,2′-Bipyridine. A 50-ml round-bottom flask was equipped with a standard break-off seal, O-ring joint, and constriction. After adding a glass-coated stirring bar, 6.24 mmoles of 2,2′-bipyridine, and 12.5 mmoles of lithium, the apparatus was attached to the vacuum line and cooled to −78°. The vessel then was evacuated and approximately 25 ml of tetrahydrofuran condensed in. Immediately upon warming the bulb to room temperature, the purple color of lithium 2,2′-bipyridine was apparent. The mixture was stirred at room temperature for 24 hr. During this period the color of the solution changed to the deep green color of dilithium 2,2′-bipyridine.

The solution was cooled to −196°, 6.24 mmoles of dimethylaminodichloroborane condensed in, the constriction fused, and the apparatus removed from the vacuum line. Upon warming the bulb to room temperature, an immediate color change from green to deep red was observed. The contents of the bulb was stirred for 8 hr at this temperature. The apparatus then was attached to the vacuum line and cooled to −78°; the break-off seal was opened. After warming the bulb to room temperature, the volatile material, assumed to be pure solvent, was distilled away, the bulb cooled to −196°, and 15 ml of cyclopentane distilled on the nonvolatile residue. The apparatus again was warmed to room temperature, a red material extracted from the insoluble lithium chloride, and the resulting solution filtered. On removal of the solvent from the filtrate by distillation, a viscous red oil resulted. This same material was produced if dimethoxyethane was used as the reaction solvent.

If the red oil is dissolved in tetramethylsilane and the solvent then is distilled from the resulting solution, a red crystalline material is secured which is pure dimethylaminoboron 2,2′-bipyridine. The estimated yield is approximately 75%.

Physical Properties of Dimethylaminoboron 2,2′-Bipyridine. Dimethylaminoboron 2,2′-bipyridine is soluble in tetrahydrofuran, cyclopentane, toluene, and tetramethylsilane. While it is soluble in chlorine-containing solvents such as methylene chloride and carbon tetrachloride, these solutions are unstable as evidenced by a change in color from red to green on standing for several hours at room temperature.

The impure red oil can be distilled *in vacuo* at 80° without decomposition.

Dimethylaminoboron 2,2′-bipyridine was observed to be diamagnetic as expected.

Characterization of Dimethylaminoboron 2,2′-Bipyridine. (a) Molecular Weight Determination. The molecular weight of dimethylaminoboron 2,2′-bipyridine was determined by the isopiestic method. In a typical experiment, 31.53 mmoles of the solvent, cyclopentane, was allowed to equilibrate *in vacuo* between a 0.1235-g sample of dimethylaminoboron 2,2′-bipyridine and a 0.0967-g sample of the standard, azobenzene. After 74 days the amount of solvent in each solution was measured. The reference solution contained 14.68 mmoles of cyclopentane while that of dimethylaminoboron 2,2′-bipyridine contained 16.85 mmoles. The apparent molecular weight determined using these data is 203. For dimethylaminoboron 2,2′-bipyridine, the calculated molecular weight is 210.8.

(b) Analysis. Using the method described in a previous section, we secured the following analysis of the red material.

Anal. Calcd for $C_{12}H_{14}N_3B$: C, 68.3; H, 6.63; B, 5.16; N, 19.9. Found: C, 68.0; H, 6.95; B, 5.06; N, 19.0.

(c) Nuclear Magnetic Resonance. The proton spectrum of a solution of dimethylaminoboron 2,2′-bipyridine in tetramethylsilane was obtained using a Varian A-60 nmr spectrometer. The spectrum consists of a sharp resonance with a chemical shift of −2.9 ppm relative to tetramethylsilane, attributed to the dimethylamino protons and a broad resonance in the −5.6- to −7.4-ppm region attributed to the 2,2′-bipyridine protons. The ratio of intensities of the −5.6- to −7.4-ppm region to that at 2.9 ppm is 1.27; that calculated for dimethylaminoboron 2,2′-bipyridine is 1.33.

(d) Optical Absorption. The spectrum of dimethylaminoboron 2,2′-bipyridine in cyclopentane from 220 to 600 mμ was obtained using a Cary Model 11 spectrophotometer and matched 1.0-cm quartz cells. Strong absorptions were observed at 240 and 284 mμ and a broad absorption in the 370- to 490-mμ region. The broad absorption is responsible for the red color of the solution while the absorptions at 240 and 284 mμ are characteristic of 2,2′-bipyridine chelates.[4]

Chemical Properties of Dimethylaminoboron 2,2′-Bipyridine. (a) Reaction with Iodine. A weighed sample of dimethylamino-

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(15) E. Wiberg, *Z. anorg. allgem. Chem.*, **213** (1933).

(16) H. C. Brown and H. Pearsall, *J. Am. Chem. Soc.*, **67**, 1765 (1945).

(17) H. I. Schlesinger, H. C. Brown, J. R. Gilbraeth, and J. J. Katz, *ibid.*, **75**, 195 (1953).

(18) V. W. Buls, O. L. Davis, and R. L. Thomas, *ibid.*, **79**, 337 (1957).

boron 2,2′-bipyridine was treated *in vacuo* with a standard solution of iodine in pyridine, and the amount of unreacted iodine measured. For five determinations, an average of 1.9 equiv of iodine was consumed per mole of dimethylaminoboron 2,2′-bipyridine.

(b) Treatment with Dimethylamine. A bulb containing 0.742 mmole of dimethylaminoboron 2,2′-bipyridine was cooled to −196° and 4.17 mmoles of dimethylamine was condensed on the material. The solution was warmed to −45° and maintained at that temperature for 0.5 hr after which the material volatile at −45° was distilled away and measured in the vapor phase. A total of 4.12 mmoles of tensiometrically pure dimethylamine was recovered. It is apparent that no adduct is formed with dimethylamine at this temperature.

(c) Treatment with Aluminum. A sample of dimethylaminoboron 2,2′-bipyridine dissolved in tetrahydrofuran was washed into a bulb containing finely divided aluminum activated by mercury metal. After agitating the mixture for 24 hr at room temperature, and for an additionl 24 hr at 60°, visual examination of the aluminum and the solution gave no evidence of chemical reactions.

(d) Treatment with Magnesium. In an experiment similar to that with aluminum, an unweighed sample of magnesium, activated with mercury metal, was treated with a solution of dimethylaminoboron 2,2′-bipyridine in tetrahydrofuran. There was no apparent reaction even at 60°.

(e) Pyrolysis of Dimethylaminoboron 2,2′-Bipyridine. An evacuated tube containing an unweighed sample of dimethylaminoboron 2,2′-bipyridine was placed in an oven and slowly warmed. At temperatures below 250°, the red material appeared to be stable. Above this temperature decomposition was observed as evidenced by the formation of a black solid.

Reaction of Lithium 2,2′-Bipyridine with Bis(dimethylamino)-chloroborane in Tetrahydrofuran. A 50-ml round-bottom flask was equipped with a standard break-off seal, O-ring joint, and constriction. After adding a glass-coated stirring bar, 6.65 mmoles of 2,2′-bipyridine, and 6.7 mmoles of lithium, the apparatus was attached to the vacuum line and cooled to −78°. The vessel then was evacuated, and approximately 25 ml of tetrahydrofuran was condensed into the bulb. The resulting mixture was warmed to room temperature and stirred for 18 hr. The solution of lithium 2,2′-bipyridine which formed was cooled to −196° and 6.65 mmoles of bis(dimethylamino)chloroborane was condensed on the solid. The constriction was fused and the apparatus removed from the vacuum line and warmed to room temperature. After stirring for approximately 10 min, the formation of an intense red material was observed. Stirring was continued for 24 hr. The apparatus was reattached to the vacuum line and cooled to −78°; the break-off seal was opened. After warming the bulb to room temperature, the volatile material, assumed to be the solvent, was distilled away. The bulb was cooled to −196° and 15 ml of cyclopentane was condensed on the red residue. Again the apparatus was warmed to room temperature. The cyclopentane-soluble material was extracted from the insoluble lithium chloride and the resulting solution filtered. After removal of the solvent from the filtrate by distillation, a dark red oil remained.

It was found that this material could be handled in a drybox without decomposition. Using the methods described in a previous section, we secured the following analysis of the red material.

Anal. Calcd for $C_{14}H_{20}N_4B$: C, 65.9; H, 7.84; B, 4.23; N, 22.0. Found: C, 66.5; H, 7.52; B, 4.8; N, 20.3.

The apparent molecular weight of the red oil was determined by the isopiestic method. The solvent, 49.70 mmoles of cyclopentane, was allowed to equilibrate *in vacuo* between a 0.2203-g sample of the red material and a 0.1831-g sample of the reference, azobenzene. After 77 days the amount of solvent in each solution was measured. The reference solution contained 27.35 mmoles of cyclopentane while that of the red material contained 22.35 mmoles. The apparent molecular weight determined using these data is 268. The molecular weight calculated for bis(dimethylamino)boron 2,2′-bipyridine is 254.8.

The optical absorption spectrum of the red oil in cyclopentane from 220 to 600 mμ was secured in the manner previously described. A maximum was observed at 283 mμ with a much less intense broad absorption in the 400- to 480-mμ region. A single maximum in the 220- to 300-mμ region is not typical of 2,2′-bipyridine chelates. The broad absorption is responsible for the red color of the solution.

A cyclopentane solution of the red oil was observed to be diamagnetic.

Reaction of Lithium 2,2′-Bipyridine with Bis(dimethylamino)-chloroborane in Cyclopentane. A 50-ml round-bottom flask was equipped with a standard break-off seal, O-ring joint, and constriction. After addition of a glass-coated sitrring bar, 2.89 mmoles of 2,2′-bipyridine, and 2.9 mmoles of lithium, the apparatus was attached to the vacuum line and cooled to −78°. The vessel was evacuated.

Approximately 20 ml of ammonia was condensed on the solids and the resulting mixture warmed to −45° and stirred for 20 min. The bulb was slowly warmed to room temperature and the solvent distilled away, leaving the deep purple solid, lithium 2,2′-bipyridine.

The bulb was cooled to −196° and approximately 25 ml of cyclopentane and 2.89 mmoles of bis(dimethylamino)chloroborane was condensed onto the solid. After fusing the constriction and removing the apparatus from the vacuum line, the mixture was warmed to 50° and stirred for 72 hr. Filtration of the product solution, followed by removal of the solvent from the filtrate by distillation at room temperature, yielded a viscous red oil. This material could not be handled in a drybox without decomposition.

A cyclopentane solution of the red oil was found to be paramagnetic having a single broad resonance with a breadth between points of extreme slope of 14 gauss and a normal *g* factor. The resonance was observed at various concentrations and temperatures with several field modulations in an unsuccessful attempt to resolve hyperfine structure.

The optical absorption spectrum of a cyclopentane solution of the red oil from 220 to 600 mμ was secured in the manner previously described. Maxima were observed at 245 and 282 mμ. These are characteristic of 2,2′-bipyridine chelates.

Preparation and Purification of Boron Bis(2,2′-bipyridine). A 50-ml round-bottom flask was equipped with a standard break-off seal, O-ring joint, and constriction. After addition of a glass-coated stirring bar, 8.74 mmoles of 2,2′-bipyridine, and 13.1 mmoles of lithium, the apparatus was attached to the vacuum line and cooled to −78°. The vessel then was evacuated and approximately 25 ml of tetrahydrofuran was condensed in the bulb. The resulting mixture was warmed to room temperature and stirred for 24 hr. After the material volatile at room temperature was distilled away and the bulb cooled to −196°, approximately 20 ml of cyclopentane and 4.37 mmoles of BCl_3 were condensed on the solid. The constriction was fused and the apparatus removed from the vacuum line. The bulb then was warmed to 45° at which temperature it was stirred by shaking for 3 days.

The resulting mixture was filtered at room temperature and the solvent distilled from the filtrate, leaving a very air-reactive, viscous red oil and a white solid, 2,2′-bipyridine. By pumping on the mixture for 3 days at 50°, the 2,2′-bipyridine was sublimed away, leaving pure boron bis(2,2′-bipyridine).

Characterization of Boron Bis(2,2′-bipyridine). (a) Molecular Weight Determination. The molecular weight of boron bis(2,2′-bipyridine) was determined by the isopiestic method. The solvent, 51.60 mmoles of cyclopentane, was allowed to equilibrate *in vacuo* between a 0.1621-g sample of boron bis(2,2′-bipyridine) and a 0.1103-g sample of the standard, azobenzene. After 30 days the amount of solvent in each solution was measured. The reference solution contained 28.20 mmoles of cyclopentane while that of boron bis(2,2′-bipyridine) contained 23.40 mmoles. The apparent molecular weight determined using these data is 323. For boron bis(2,2′-bipyridine) the calculated molecular weight is 322.8.

(b) Analysis. This material proved to be too reactive for the usual microanalytical procedures for determination of carbon, hydrogen, nitrogen, and boron. A partial analysis was secured using a modification of the method of Brown, Schlesinger, and Burg.[12]

Anal. Calcd for $C_{20}H_{16}N_4B$: C, 74.4; H, 4.96; B, 3.34. Found: C, 75.0; H, 5.37; B, 3.10.

(c) Optical Absorption. The spectrum of a cyclopentane solution of boron bis(2,2′-bipyridine) from 220 to 600 mμ was determined as previously described. Maxima were observed at 245 and 283 mμ with a broad absorption in the 360- and 450-mμ regions. The broad absorption is responsible for the red color of the solution. The maxima at 245 and 283 mμ are characteristic of 2,2′-bipyridine chelates.

(d) Paramagnetic Resonance. A solution of boron bis(2,2′-bipyridine) in cyclopentane was observed to be paramagnetic. The resonance, having a total breadth of approximately 30 gauss, was resolved into twelve lines spaced 2.7 gauss apart. The electron spin resonance spectra are shown in Figures 1 and 2. In

Figure 1 the weakest lines are barely visible while in Figure 2, a high-gain presentation, all twelve lines are clearly observed.

Reaction of 2,2′-Biphenylenechloroborane with Lithium 2,2′-Bipyridine. A glass ampoule equipped with a standard break-off seal and containing 2.21 mmoles of 2,2′-biphenylenechloroborane was sealed to the side arm of a 50-ml round-bottom flask equipped with a standard break-off seal, O-ring joint, and constriction. After addition of a glass-coated stirring bar, 2.21 mmoles of 2,2′-bipyridine, and 2.2 mmoles of lithium, the apparatus was attached to the vacuum line and cooled to −78°. The apparatus then was evacuated and approximately 20 ml of tetrahydrofuran was condensed on the solids. The resulting mixture was warmed to room temperature and stirred for 10 hr. The solvent then was distilled away leaving the purple solid, lithium 2,2′-bipyridine.

After cooling the bulb to −196°, approximately 25 ml of cyclopentane was condensed in, the constriction fused, and the apparatus removed from the vacuum line. The bulb again was warmed to room temperature. Using a magnetic breaker, the break-off seal to the ampoule was opened and the sample of 2,2′-biphenylenechloroborane transferred to the bulb. The resulting mixture was shaken at room temperature for 3 days, then filtered, and the solvent removed from the filtrate by distillation at room temperature. A very sensitive brown-red residue and a white solid remained. The solid, 2,2′-bipyridine, was removed by pumping on the mixture for 48 hr at room temperature.

The brown-red, cyclopentane-soluble material was observed to decompose slowly *in vacuo* at room temperature as evidenced by the formation of a black solid. This instability made it impossible to secure a good elemental analysis, molecular weight data, and optical absorption data.

A cyclopentane solution of the freshly prepared brown-red oil was found to exhibit paramagnetism. By varying the concentration and temperature of the solution, the paramagnetic resonance was resolved into 22 lines with a total breadth of some 35 gauss.

Methanolysis of Dimethylaminoboron 2,2′-Bipyridine. An evacuated ampoule containing a sample of dimethylaminoboron 2,2′-bipyridine was attached to the vacuum line and cooled to −196° and methanol was condensed on the red material. On warming the bulb to room temperature a vigorous reaction took place as evidenced by boiling and formation of a deep blue-green paramagnetic solution

After allowing the solution to remain at room temperature for 8 hr, the color had changed to red-brown. The color change was accompanied by a decay in the paramagnetic resonance signal.

Methanolysis of Boron Bis(2,2′-bipyridine). When a sample of boron bis(2,2′-bipyridine) was treated with methanol *in vacuo*, a deep blue-green paramagnetic solution was formed having an electron spin resonance spectrum identical in hyperfine structure, but possibly slightly narrower than that of boron bis(2,2′-bipyridine).

The blue-green color changed to pale yellow in approximately 12 hr. Accompanying the color change was a decay in the paramagnetic resonance signal.

Reactions of Halogens with Tris(ethylenediamine)osmium(III) Iodide

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Abstract: The initial product of the interaction of halogens and tris(ethylenediamine)osmium(III) iodide 2-hydrate, $[Os(en)]I_3 \cdot 2H_2O$, is the trihalide. Chlorine, bromine, and iodine were used but only chlorine gave any further reaction involving the complex cation. The ICl_2^- and IBr_2^- anions gave metathesis products upon prolonged standing and the I_3^- species was stable in the solid state but decomposed slowly when dissolved in water or ethanol; the rate constant for the decomposition in ethanol was 8.70×10^{-3} min^{-1}.

Of the possible oxidation states of osmium, those in which osmium is surrounded by nitrogen-containing ligands vary from Os(VI) in $[Os(en\text{-}H)_4]I_2 \cdot 3H_2O$[1] $[(en\text{-}H) = H_2NCH_2CH_2NH^-]$ to Os(0) in $[Os(NH_3)_6]$.[2] Much attention has been directed to the effect of oxidizing agents on $[Os(bipy)_3]^{n+}$ in low oxidation states[3–7] but only qualitative observations have been recorded on oxidation–reduction reactions of Os–en complexes. In view of the ease with which Os(III) is oxidized in $[Os(NH_3)_5X]X_2$ (X = Br or Cl) by bromine water or even air,[8] it was thought that the first reaction of a halogen with the tris(ethylenediamine)osmium(III) complex would be oxidation of osmium. Halogen attack on, or reaction with, the ligand might be involved if elevated temperatures were employed or acido groups were used as donor groups;[9,10] once chlorination begins on the ligand, acido groups (chloroamido groups) would be formed.[10] Rather it was found that the first products of reaction between halogens and $[Os(en)_3]I_3 \cdot 2H_2O$ by "dry" techniques[11,12] were the trihalides. The I_3^- and IBr_2^- compounds appeared to be the terminal products of reaction of $[Os(en)_3]I_3 \cdot 2H_2O$ with I_2 and Br_2, respectively, except for some metathesis of the IBr_2^-. The ICl_2^- compound was found to undergo further reactions involving oxidation of the central metal ion and reaction with the ligands.

Trihalides of ammine complexes are known[13] but are usually limited to triiodides. Of the trihalides, tri-

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