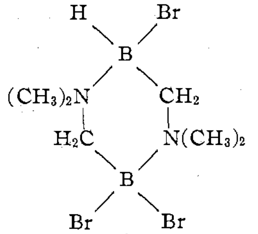

3

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).

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A Specific Synthesis for Bis(bipyridine)ruthenium Compounds

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

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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).

vacuum for 2 hr. The mixture was extracted with ethanol until the ethanol washings became violet. Then it was washed with chloroform until the washings were colorless. The combined chloroform washings were evaporated to dryness to obtain black crystals. These were recrystallized from chloroform. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_2Cl_2]\cdot CHCl_3$: C, 41.73; H, 2.83; N, 9.27. Found: C, 42.15; H, 3.11; N, 9.17.

Dichlorobis(bipyridine)ruthenium(III) Perchlorate.—The above compound (0.1 g.) was suspended in 50 ml. of water containing a few drops of concentrated hydrochloric acid. Chlorine was bubbled through the mixture until the crystals dissolved. Upon addition of 5 ml. of 7% perchloric acid, crystals formed. These were filtered, washed with cold water, then with ether, and air dried. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_2Cl_2]ClO_4$: C, 41.10; H, 2.76; N, 9.59. Found: C, 41.08; H, 2.79; N, 9.62. The infrared spectrum of this compound was identical with that of the perchlorate obtained from the chlorination of oxalatobis(bipyridine)ruthenium(II).

Discussion

The present study describes a convenient method of preparation for bis(bipyridine)ruthenium compounds. Since the oxalato group is very easily oxidized off with chlorine the other compounds can be easily obtained from the dichloro derivative through substitution reactions. From the method of preparation the compounds are most likely of the *cis* configuration.

The oxalate ions serve the dual purpose of occupying two coordination positions and of reducing the ruthenium to the +2 state. The intermediate in the preparation is not known but it is quite likely that a bis- or even tris(oxalato)ruthenate is involved.[4]

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The Low Temperature Reaction of Sulfur Hexafluoride with Solutions of Sodium[1]

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Sulfur hexafluoride, SF_6, is a chemically unreactive material; it is not attacked by aqueous or fused alkali[2] and it does not react appreciably with sodium below 200°.[3] The lowest temperature at which SF_6 has previously been reported to undergo reaction is 180–250°. During 25 hr. at this temperature, it is incompletely decomposed by Al_2Cl_6 and also by SO_3 with the formation of sulfur chlorides and oxyfluorides, respectively.[4] Because of its lack of chemical reactivity, SF_6, and also some of its derivatives containing an SF_5 group, is difficult to analyze.

In the present study, it was found that SF_6 underwent rapid reaction with a solution of sodium in liquid NH_3 at $-64°$. The products were not identified. If, instead, a solution of sodium in a diphenyl–ethylene glycol dimethyl ether solution was used, complete reaction was found to occur within 15 hr. between -64 and $-10°$; at room temperature, quantitative reaction occurred within a few minutes according to the equation

$$8Na + SF_6 \rightarrow Na_2S + 6NaF$$

Both S^{-2} and F^- present in the resulting mixture could be determined quantitatively by standard procedures. It appears that this reaction offers a convenient method for analyzing SF_6 and it would probably be equally successful for quantitative sulfur and fluorine analyses of many species containing the relatively unreactive SF_5 group.

In view of the usual inertness of SF_6 to both nucleophilic and electrophilic reagents it appears that the rapidity of the above low-temperature reaction may be due to an electron transfer from a diphenyl radical-ion[5] to an SF_6 molecule as the first (and rate-controlling) step in the reaction. The relatively low-energy, empty, 3d orbitals of sulfur would be available to accommodate the added electron. It may be presumed that the resulting SF_6^- ion would be unstable since no compound containing this ion has been isolated. It could eliminate F^-, and the $\cdot SF_5$ species so formed would be expected to be sufficiently labile to react further with the sodium "solution" by one of several different mechanisms. It would seem likely that an analogous type of reaction could occur with a solution of sodium in liquid NH_3.

Experimental

All work was carried out using standard vacuum system techniques. Commercial SF_6 (minimum purity, 95%) was purified by repeated distillations through traps held at $-134°$ in which it partially condensed. Pure material was obtained as a condensate in the $-134°$ traps (mol. wt. found 146.8, calcd. 146.06; vapor pressure at $-96.2°$ found 63.19 mm., calcd.[6] 62.80 mm.; at $-112.0°$ found 13.53 mm., calcd.[6] 13.40 mm.; confirmed by infrared spectrum[7]). The approximately 1.5 *M* solution of sodium in the diphenyl–ethylene glycol dimethyl ether mixture, which also contained some added toluene, was prepared according to the method described by Ligget.[8]

Reaction of SF_6 with a Solution of Sodium in NH_3.—An excess of SF_6 was condensed into a flask containing a solution of sodium in predried NH_3. When the flask was placed in a $-64°$ bath and gently shaken for a few minutes, the characteristic blue color of the sodium solution was completely discharged.

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[1] This report is based on portions of a thesis to be submitted by Gregory C. Demitras, F.S.C., to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense.

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