3. Preparation of Tris(3-phthalimidopropyl)amine (4) and 1-Tetrapicrate (5). Treatment of **1** with a mixture of sodium acetate, acetic acid, and phthalic anhydride[5b] afforded the tris(phthalimido) derivative (**4**) only in poor yield. However, an adaptation of a more forcing procedure used to prepare *N*-alkylphthalimido derivatives for peptide syntheses[6] allowed **4** to be obtained in good yield. A melt of 8.0 g (0.054 mol) of phthalic anhydride, 1.2 g (0.0146 mol) of sodium acetate, and 1.0 g (0.0029 mol) of **1** was maintained at ~200 °C for 15 min, cooled, and then transferred to a beaker containing 400 mL of water. The resulting suspension was heated to boiling and neutralized to pH ~8 by the addition of 10 g of sodium bicarbonate. A tan solid was separated from the aqueous phase by filtration, washed with water, and dried in air. This crude tris(phthalimido) derivative was obtained in 71% yield (1.2 g) and melted at 140–145 °C (lit.[2] mp 150–151 °C). Two recrystallizations from a mixture of 20 mL of dimethylformamide, 8 mL of water, and ~2 g of activated charcoal afforded colorless needles which melted at 150–152 °C. Anal. Calcd for $C_{33}H_{30}N_4O_6$ (**4**): C, 68.51; H, 5.19; N, 9.69. Found: C, 68.28; H, 5.15; N, 9.82.

Addition of a solution of 0.34 g (0.001 mol) of **1** in 100 mL of water to a warm solution of 1.6 g (0.007 mol) of picric acid in 225 mL of water resulted in the immediate precipitation of a yellow solid. A nearly saturated solution of this yellow material was obtained by adding an additional 300 mL of water and heating the mixture to boiling. The hot solution was filtered and stored overnight at 5 °C. The filtrate deposited yellow needles (0.88 g, 79%) which were collected by filtration and dried in a vacuum oven (aspirator pressure, 85 °C). The product melted (with decomposition to a red liquid) in a sealed capillary at 223–224 °C (lit.[2] mp 222 °C). Anal. Calcd for $C_{33}H_{38}N_{16}O_{29}$ (**5**): C, 35.29; H, 3.39; N, 19.96. Found: C, 34.88; H, 3.35; N, 19.95.

Acknowledgment. This work was supported by the National Institutes of Health (Grant AM-16412 to H.J.S.).

Registry No. **1**, 66322-79-0; **3**, 7528-78-1; **4**, 66322-78-9; **5**, 66322-77-8; phthalic anhydride, 85-44-9; picric acid, 88-89-1.

References and Notes

(1) A. Dei, P. Paoletti, and A. Vacca, *Inorg. Chem.*, **7**, 865 (1968).
(2) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 489 (1926).
(3) J. L. Van Winkle, J. D. McClure, and P. H. Williams, *J. Org. Chem.*, **31**, 3300 (1966).
(4) F. E. Gould, G. S. Johnson, and A. F. Ferris, *J. Org. Chem.*, **25**, 1658 (1960).
(5) A. I. Vogel, "Practical Organic Chemistry", 3rd ed, Longman Group Ltd., London, 1974: (a) pp 870–871; (b) p 423.
(6) J. C. Sheehan, D. W. Chapman, and R. W. Roth, *J. Am. Chem. Soc.*, **74**, 3822 (1952).

Contribution from the Paul M. Gross Chemical Laboratory,
Duke University, Durham, North Carolina 27706,
and the Department of Chemistry, North Carolina State
University, Raleigh, North Carolina 27607

Stability and Stereochemistry of Some Amino(bis(trimethylsilyl)amino)boranes[1a]

David M. Graham,[1b] James R. Bowser,[1c] Charles G. Moreland,[1d] Robert H. Neilson,[1e] and Richard L. Wells*[1e]

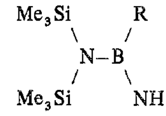
Received January 18, 1978

The thermal instability of most primary aminoboranes is illustrated by the results reported by Mikhailov[2] (eq 1) and Neilson[3] (eq 2).

$$\mathrm{PhBCl_2} \xrightarrow[-2\mathrm{NH_4Cl}]{4\mathrm{NH_3}} [\mathrm{PhB(NH_2)_2}] \xrightarrow{-\mathrm{NH_3}} {}^1/_3(\mathrm{PhBNH})_3 \qquad (1)$$

$$\mathrm{PhB(Cl)NMe_2} \xrightarrow[-\mathrm{NH_4Cl}]{2\mathrm{NH_3}} [\mathrm{PhB(NH_2)NMe_2}] \xrightarrow{-\mathrm{Me_2NH}} {}^1/_3(\mathrm{PhBNH})_3 \qquad (2)$$

While reactions of this type are fairly well documented,[4] it has also been found that when large groups are attached to boron such condensation reactions are less likely to occur. In particular, we have observed that primary aminoboranes which contain the bis(trimethylsilyl)amino substituent,

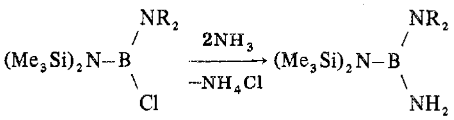


$$(\mathrm{Me_3Si})_2\mathrm{N{-}B(R)NH_2}$$

R = Ph, NHSiMe$_3$, NMe$_2$

are indeed quite stable.[5-8]

This paper reports the preparation (eq 3) of three compounds (**4–6**) in this class and offers an explanation of their thermal stability which is consistent with the observation of high rotational barriers about the B–NR$_2$ bonds in all of the (bis(trimethylsilyl)amino)(dialkylamino)boranes (**1–6**).



$$(\mathrm{Me_3Si})_2\mathrm{N{-}B(NR_2)Cl} \xrightarrow[-\mathrm{NH_4Cl}]{2\mathrm{NH_3}} (\mathrm{Me_3Si})_2\mathrm{N{-}B(NR_2)NH_2} \qquad (3)$$

1, R = Me **4**, R = Me
2, R = Et **5**, R = Et
3, R = *i*-Pr **6**, R = *i*-Pr

Experimental Section

Materials. (Bis(trimethylsilyl)amino)chloro(dimethylamino)borane (**1**) was prepared according to the method reported by Paige and Wells.[9] Synthesis of the other *B*-chloro compounds (**2** and **3**) has been previously described by Geymayer and Rochow.[10] These compounds were converted to the corresponding B–NH$_2$ derivatives (**4–6**) by their reactions with an excess of ammonia according to the following procedures.

Amino(bis(trimethylsilyl)amino)(dimethylamino)borane (4).[5] Compound **1** (18.2 g, 0.073 mol) was dissolved in dry pentane (300 mL) in a flask equipped with a magnetic stirrer. The flask was attached to a vacuum system, cooled to −78 °C, and evacuated. Ammonia (2.5 g, 0.15 mol) was measured at −78 °C and allowed to condense into the reaction flask. The mixture was allowed to warm to room temperature and was stirred overnight. Ammonium chloride (3.9 g, 100% yield) was filtered from the mixture and identified by comparison of its infrared spectrum to that of an authentic sample. Solvent was removed from the filtrate and the liquid residue was distilled to yield compound **4** as a colorless liquid (16.4 g, 97% yield, bp 56–58 °C (2.0 Torr)). The infrared spectrum of the product had two bands between 3450 and 3550 cm^{-1} and a strong band at 1600 cm^{-1}, all indicative of a primary amino function. The proton NMR spectrum of a neat sample gave Me$_3$Si (δ −0.10):Me$_2$N (δ 2.38):NH$_2$ (δ 1.77) = 61:20:6 (calcd 18:6:2). Anal.[11] Calcd for $C_8H_{26}BN_3Si_2$: C, 41.54; H, 11.33; B, 4.67; N, 18.17; Si, 24.29; mol wt, 231. Found: C, 41.67; H, 11.32; B, 4.53; N, 18.05; Si, 24.55; mol wt, 231 (mass spectrum).

Amino(bis(trimethylsilyl)amino)(diethylamino)borane (5).[1b] The procedure used for the preparation of **4** was modified to allow the use of larger quantities of reactants. Thus, compound **2** (25.0 mL, 0.098 mol) and dry hexane (200 mL) were placed in a flask equipped with a cold finger condenser, a gas inlet tube and a magnetic stirrer. Both the condenser and the reaction vessel were cooled to −78 °C. Excess liquid ammonia (6.1 mL, 0.29 mol) was condensed into a graduated tube maintained at −78 °C. The ammonia container was attached to the gas inlet tube of the reaction flask and the ammonia was allowed to evaporate and condense into the cold reaction flask. The cold bath surrounding the flask was removed while maintaining the condenser at −78 °C. After 1 h the condenser was allowed to warm to room temperature and excess ammonia was allowed to escape. Workup of the reaction mixture proceeded as described in the preparation of **4**. Compound **5** was obtained as a colorless liquid (20.1 g, 79% yield, bp 86 °C (2.0 Torr)). The proton NMR spectrum of a neat sample gave Me$_3$Si (δ −0.03):CH$_2$ (δ 2.85):CH$_3$ (δ 0.90):NH$_2$ (δ 1.88) = 12.0:3.3:6.0:2.0 (calcd 18:4:6:2). The mass spectrum[12] contained a molecular ion at *m/e* 259.2078 (calcd for $^{12}C_{10}{}^{1}H_{30}{}^{11}B^{14}N_3{}^{28}Si_2$, 259.2071).

Amino(bis(trimethylsilyl)amino)(diisopropylamino)borane (6).[1b] Compound **6** was prepared by the same method described for **5**. In a typical preparation **3** (202 mL, 0.566 mol) was allowed to react with a 50% excess of ammonia (35.4 mL, 1.69 mol) in hexane (200 mL). Compound **6** was obtained as a colorless liquid (126 g, 77% yield, bp 78 °C (1.0 Torr)). The proton NMR spectrum of a neat sample gave Me_3Si (δ −0.03):CH_3 (δ 0.98):CH (δ 3.05 and 3.92):NH_2 (δ 1.87) = 17.4:12.0:2.2:1.6 (calcd 18:12:2:2). The mass spectrum[12] contained a molecular ion at m/e 287.2390 (calcd for $^{12}C_{12}{}^{1}H_{34}{}^{11}B^{14}N_3{}^{28}Si_2$, 287.2384).

Proton NMR Studies. For compounds **2**–**4** and **6** samples of sufficient purity were obtained by fractional distillation. In the case of **5**, however, purification on an Aerograph Autoprep Model A-70 gas chromatograph equipped with an SE-30 column was required to separate **5** from unidentified impurities. Samples in benzene and chloroform were prepared in Fisher spectrograde solvents with a concentration of 50% (v/v).

All spectra were recorded on a Varian HA-100 high-resolution spectrometer. Temperatures were controlled to an estimated ±2 °C with a Varian variable-temperature control unit. A precalibrated thermocouple insert was used to monitor probe temperatures. For each sample, spectra were recorded over a temperature range of 25–40 °C at ca. 5 °C intervals in the vicinity of the coalescence temperature.

Because the line-shape equation[13] used to analyze the proton NMR data is useful only for exchange between uncoupled sites, decoupling of the observed signals was necessary for compounds **2**, **3**, **5**, and **6**. For **2** and **5** the methyl protons of the ethyl group were saturated and the temperature dependence of the decoupled methylene signal was observed. Similarly the decoupled methine signal was observed for compounds **3** and **6**. Broad-band decoupling was accomplished with two external frequency generators, the first (Hewlett-Packard Model 3310A) operating at the central frequency of the multiplet to be saturated and the second (Hewlett-Packard Model 200 AB) to modulate the frequency of the first over the desired frequency range.

A program using the NMR line-shape equation of Gutowsky, McCall, and Slichter,[13] written for an IBM 360 Model 75 computer, was used to calculate line shapes for the observed protons. Input parameters included $\Delta\nu$, the chemical shift differences between the observed signals under conditions of no observable exchange, T_2, an estimate of the transverse relaxation time which was determined from the line width at no observable exchange, and an educated guess of τ, the mean lifetime of the observed protons. By an iterative process the computer then calcualted a value of τ which corresponds to the best match, by the least-squares criterion, of the experimental and calculated line shapes. From this calculated τ value, the free energy of activation ($\Delta G^\ddagger$) was evaluated by use of the Eyring equation.[14] The free energies of activation ($\Delta G^\ddagger$) for compounds **1**–**6** (Table I) were calculated at a common temperature of 50 °C which is approximately the average coalescence temperature of the compounds studied. These $\Delta G^\ddagger$ values are in excellent agreement (±0.5 kcal/mol) with those calculated using the approximate method of Gutowsky and Holm.[15]

Results and Discussion

When the (bis(trimethylsilyl)amino)(dialkylamino)chloroboranes **1**–**3** were allowed to react with an excess of ammonia, the primary aminoboranes **4**–**6** were obtained in high yields (>75%) according to eq 3. Like their chloroborane precursors, compounds **4**–**6** are colorless liquids which showed no evidence of decomposition even when heated at 150–200 °C for several hours under an inert atmosphere.

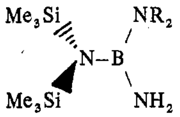
In the ^1H NMR spectra of the aminoboranes **1**–**6** the dialkylamino resonance exhibited a temperature dependence as a result of hindered rotation about the $B–NR_2$ bond. Activation parameters for the rotational process were evaluated using standard line-shape analysis procedures. The calculated free energies of activation ($\Delta G^\ddagger$) are listed in Table I. Although we have previously reported[16] the observation of hindered rotation about the $B–NMe_2$ bond of compound **1**, the results are included here for comparative purposes.

The relatively high $\Delta G^\ddagger$ values obtained for compounds **1**–**3** indicate that only the dialkylamino nitrogen is strongly π bonded to boron[16] in these compounds since bis(amino)boranes typically have much lower rotational barriers (ca. 10–11 kcal/mol).[17–19] This conclusion is supported by the results of a recent study[19] which demonstrated that in related compounds such as $(Me_3Si)_2NB(Ph)NMe_2$, "the bulky bis(trimethylsilyl)amino group is rotated out of the plane of the $B–NMe_2$ moiety and thus is not an effective π-donor to boron." The high $\Delta G^\ddagger$ values also observed for compounds **4**–**6**, therefore, lead one to conclude that, even in these tris(amino)boranes the bis(trimethylsilyl)amino substituent is twisted (ca. 90°) out of the plane defined by the three bonds to boron.

Table I. Rotational Barriers[a] about the $B–NR_2$ Bond in the Aminoboranes $(Me_3Si)_2NB(NR_2)X$

No.	R	X	Solvent	T_c, °C	$\Delta G^\ddagger$, kcal/mol
1[b]	Me	Cl	Neat	53	17.5
			$CHCl_3$	57	17.5
			C_6H_6	67	17.6
2	Et	Cl	C_6H_6	53	17.5
3	*i*-Pr	Cl	$CHCl_3$	80	16.4
			C_6H_6	77	16.5
~~**4**~~	Me	NH_2	Neat	20	16.1
			$CHCl_3$	21	16.0
			C_6H_6	30	15.6
5	Et	NH_2	C_6H_6	59	16.6
6	*i*-Pr	NH_2	$CHCl_3$	64	16.0
			C_6H_6	62	15.5

[a] Estimated experimental precision: T_c, ±2 °C; $\Delta G^\ddagger$, ±0.5 kcal/mol. Tabulated values are the average of two independent measurements. [b] Data taken from ref 16.



Molecular models arranged in this configuration indicate that the boron atom is remarkably "protected"; that is, nucleophilic attack either within the molecular plane or perpendicular to it is effectively blocked. Thus, the apparent stereochemistry of these primary aminoboranes (**4**–**6**) seems to account for their unusual stability by preventing the type of intermolecular interaction necessary for their thermal decomposition.

A final point concerns two recent reports by Curry and Gilje[20] in which some tris(amino)boranes containing diisopropylamino substituents were suggested to have helically chiral ground states. While our NMR data do not preclude the possibility that compounds **4**–**6** may adopt similar configurations, their chemical and thermal stability seems most consistent with the "twisted" structure that we have proposed here and elsewhere.[19]

Registry No. 1, 32882-72-7; **2**, 6591-24-8; **3**, 6663-30-5; **4**, 66322-82-5; **5**, 66322-81-4; **6**, 66322-80-3.

References and Notes

(1) (a) This work was supported in part by grants from the Research Triangle Foundation and the National Science Foundation. (b) Results abstracted from the Ph.D. Dissertation of D. M. Graham, Duke University, Durham, N.C., 1972. (c) Discussion abstracted from the Ph.D. Dissertation of J. R. Bowser, Duke University, Durham, N.C., 1976. (d) North Carolina State University. (e) Duke University.
(2) B. M. Mikhailov and P. M. Aronovich, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1123 (1957).
(3) R. H. Neilson, Ph.D. Dissertation, Duke University, Durham, N.C., 1973.
(4) K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds", Springer-Verlag, West Berlin, 1965.
(5) H. L. Paige, Ph.D. Dissertation, Duke University, Durham, N.C. 1969.
(6) R. L. Wells and A. L. Collins, *Inorg. Nucl. Chem. Lett.*, **2**, 201 (1966).
(7) R. L. Wells and A. L. Collins, *Inorg. Chem.*, **7**, 419 (1968).
(8) R. L. Wells and R. H. Neilson, *Synth. Inorg. Met.-Org. Chem.*, **3**, 137 (1973).
(9) H. L. Paige and R. L. Wells, *Inorg. Chem.*, **10**, 1526 (1971).
(10) P. Geymayer and E. G. Rochow, *Monatsh. Chem.*, **97**, 437 (1966).
(11) Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.
(12) High-resolution mass spectra were obtained on an MS-902 spectrometer located at the RTI Center for Mass Spectrometry supported by NIH under Grant PR-330.
(13) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21** 279 (1953).

(14) K. J. Laidler, "Theories of Chemical Reaction Rates", McGraw-Hill, New York, N.Y., 1969.
(15) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
(16) R. L. Wells, H. L. Paige, and C. G. Moreland, *Inorg. Nucl. Chem. Lett.*, **7**, 177 (1971).
(17) M. J. S. Dewar and P. Rona, *J. Am. Chem. Soc.*, **91**, 2259 (1969).
(18) D. Imbrey, A. Jaeschke, and H. Friebolin, *Org. Magn. Reson.*, **2**, 271 (1970).
(19) R. H. Neilson and R. L. Wells, *Inorg. Chem.*, **16**, 7 (1977).
(20) (a) K. K. Curry and J. W. Gilje, *J. Am. Chem. Soc.*, **98**, 8262 (1976); (b) *ibid.*, **100**, 1442 (1978).

Contribution from the Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650

A Paramagnetic Oxygen Adduct Compound of Rhodium(III)

Horia Caldararu,[1] Keith DeArmond,* and Kenneth Hanck

Received October 10, 1977

Solutions of $[Rh(bpy)_2]^+$ produced by chemical[2a] or electrochemical reduction[2b,3] in acetonitrile are extremely sensitive to air; furthermore, the purple Rh(I) solid when isolated changes to a yellow-brown mixture upon exposure to air. The chemical redox studies of Martin et al.[2a] in water and the work of Miller and Oliver[4] suggest that the yellow-brown solution contains as the dominant product a diamagnetic Rh(III) compound, likely a $[Rh(bpy)_2(H_2O)_2]^{3+}$ species. However, we have observed that chlorine gas bubbled through an acetonitrile solution of $[Rh(bpy)_2]^+$ produces a deep red solution that gives a strong and persistent electron spin resonance signal at room and liquid nitrogen temperature.

Oxygen adduct compounds of Rh(I) with diphosphine ligands are reported by Vaska and co-workers[5] and Gray and co-workers,[6] but in all cases the materials produced are diamagnetic. Alternatively, rather than formation of an O_2 adduct with Rh(I), Rh(II) complexes can be produced by exposure to air. However, Rh(II) typically forms dimer species in solution as for $Rh_2(OAc)_4$ in water.[7,8] Examples of stable monomeric Rh(II) complexes are few—a phosphine adduct[9,10] of Rh whose ESR spectra has been reported and a unique square-planar complex of Rh(II) with the bidentate maleonitrile ligand.[11] Pulse radiolysis[12] in water solvent of a series of $[Rh(NH_3)_5X]^{n+}$ complexes, where X = Cl^-, Br^-, or H_2O and $n = 2$ or 3, produces a monomeric Rh(II) complex that is very reactive in water to ligand displacement and disproportion reactions.

In contrast, monomeric d^7 cobalt(II) compounds are known and a number of Co(II) compounds have been observed to produce paramagnetic oxygen adducts[13–15] in which the unpaired spin is localized on the oxygen. Such an oxygen species is best considered as a superoxide with the $Co^{III}\cdot O_2^-$ moiety then resulting from an intramolecular redox process.[14] Dimeric oxygen adduct compounds of cobalt(III)[16–20] containing two cobalt ions per oxygen molecule are well-known and can be formulated as containing oxygen as a peroxide, i.e., O_2^{2-}. Such materials when oxidized by a one-electron oxidizing agent as Cl_2 also produce a paramagnetic complex best formulated as containing a superoxide species, O_2^-.[19,20]

Therefore, we undertook characterization of the paramagnetic material resulting from the Cl_2 oxidation of the diamagnetic product produced by air oxidation of $[Rh(bpy)_2]^+$ to determine if Rh(II) or superoxo complexes had been produced. The synthesis, analysis, and spectral and some chemical properties of the brown diamagnetic precursor and the bright red paramagnetic complex are reported, and a simple reaction sequence is proposed to rationalize these data.

Experimental Section

Materials. The complexes were synthesized from $RhCl_3\cdot 3H_2O$ (Engelhard) and 2,2′-bipyridine (Aldrich) used as received. The acetonitrile (Fisher reagent grade) and tetraethylammonium perchlorate (Eastman White Label) were further purified and dried by methods reported previously.[2b]

Syntheses. Preparation of $[Rh(bpy)_3](ClO_4)_3\cdot 2H_2O$[21] and of $[Rh(bpy)_2]ClO_4\cdot 3H_2O$[1] have been described elsewhere. The diamagnetic rhodium dimer, I, was prepared as follows: 1.2 g of $[Rh(bpy)_2]ClO_4\cdot 3H_2O$ was dissolved in 50 mL of acetonitrile, and the solution was left in the presence of dry air for 24 h while it turned completely from purple-violet as it was initially to a yellow-brown color. (*Caution*! Too rapid exposure to air or pure O_2 results in a fire and occasionally an explosion.) After air evaporation, the solution was decanted from the yellow insoluble Rh(III) complex which was discarded. This process was repeated until no more yellow solid was produced from the solution. The brown solution remaining was then slowly evaporated to dryness to obtain ~0.2 g of the brown compound (I). This compound (I) was further purified on a polyamide column using acetonitrile as eluent. Analysis indicated some residual impurity.

Anal. (Galbraith Laboratories, Knoxville, Tenn.) Calcd for $[Rh_2(bpy)_4(CH_3CN)_2][ClO_4]_4$: C, 40.31; H, 2.90; N, 10.69; Cl, 10.82; O, 19.53; Rh, 15.71. Found: C, 41.60; H, 3.50; N, 9.63; Cl, 11.79; O, 21.23.

The red paramagnetic rhodium dimer (II) was prepared by one of the following methods.

A. Chemical Preparation. One-tenth gram of I dissolved in acetonitrile was treated with chlorine gas in the presence of air for 10 min, forming a deep red solution. After the acetonitrile was evaporated, a red crystalline compound (II) was obtained. This material (II) is sensitive to traces of water and base. It was further purified by bidimensional TLC using acetonitrile eluent. Some decomposition occurred as a result of the water in the plate substrate.

Anal. (Galbraith Laboratories, Knoxville, Tenn.) Calcd for $[Rh_2(bpy)_4Cl_2O_2][ClO_4]_3$: C, 39.00; H, 2.60; N, 9.10; Cl, 14.40; O, 18.18; Rh, 16.71. Found: C, 38.84; H, 2.99; N, 9.29; Cl, 14.08; O, 20.96.

Attempts to obtain I and II from $[Rh(bpy)_2]^+$ materials produced by reduction of $[Rh(bpy)_2Cl_2]X$ (where $X^- = Cl^-$, NO_3^-, or BF_4^-) were unsuccessful.

B. Electrochemical Preparation. A 5×10^{-3} M $[Rh(bpy)_3](ClO_4)_2\cdot 2H_2O$ solution in acetonitrile (supporting electrolyte 2.5×10^{-1} M) was completely electrolyzed at −1.2 V, where both cyclic voltammetry[3] and coulometric measurements ($n = 1.9$ electrons) indicated the formation of $[Rh(bpy)_2]^+$. This solution left in dry air turns from deep purple-violet to yellow-brown. Subsequently, Cl_2 gas was bubbled through the solution for 10 min, producing a bright red solution. The ESR spectrum is identical with that obtained from the red complex (in acetonitrile) prepared chemically.

Results

Neither the solution of the starting material $[Rh(bpy)_2]^+$ nor the solution of the brown rhodium dimer, I, gave an ESR signal at room or liquid nitrogen temperatures.

The red rhodium dimer, II, obtained from either the chemical or the electrochemical preparation gave a signal at room temperature and an anisotropic spectrum at 77 K (Figure 1). Pure solid samples of II gave g factors identical with those of the solution. Solution samples allowed to stand in air give in addition to the spectrum of II a superimposed spectrum (IIa) due to a second species (Figure 1). Subsequent addition of water to dry samples of II verified that IIa results from reaction of water with II. Addition of large quantities of H_2O, NH_3, or pyridine causes destruction of II and loss of the paramagnetism. The dry red paramagnetic complex, II, is stable in solution or as a solid indefinitely since the characteristic ESR signal can be measured after a period of months.

The experimental **g** tensor values are tabulated in Table I along with g_{iso} calculated from eq 1. The analysis of the 77

$$g_{iso} = {}^1/_3(g_1 + g_2 + g_3) \qquad (1)$$