

Figure 4.—Ultraviolet and visible spectra of $\text{Fe}(\text{DPM})_3$ (broken line) and $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)]_2$ in cyclohexane solution. ϵ is based on formula weight per iron(III).

d-d transitions (Figure 5). Following Piper and Carlin,¹⁹ these bands are assigned to the d-d transitions ${}^6A_1 \rightarrow {}^4T_1$ and ${}^6A_1 \rightarrow {}^4T_2$, respectively. The somewhat higher energies of the dimer d-d bands as compared to the corresponding monomer could be due to a smaller ligand field strength for bridging alkoxide than for β -diketonate. This conclusion is not firm, however, because small differences in interelectronic repulsions in the two cases could also lead to shifts of the magnitude observed.

It is important to note that there is no evidence in the electronic spectra of the dialkoxo-bridged dimers for

(19) T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

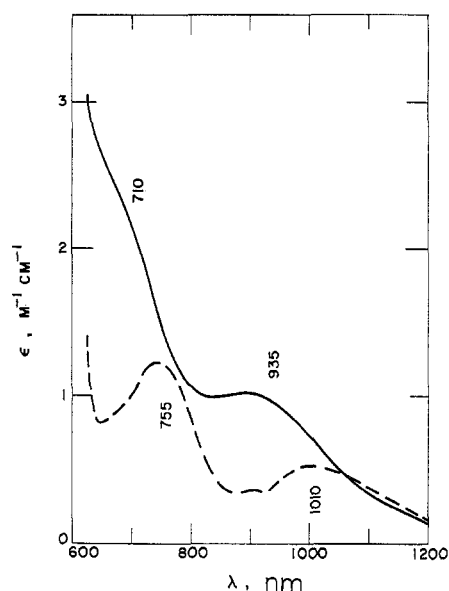


Figure 5.—Near-infrared (ligand field) spectra of $\text{Fe}(\text{DPM})_3$ (broken line) and $[(\text{DPM})_2\text{Fe}(\text{OCH}_3)]_2$ in cyclohexane solution. ϵ is based on formula weight per iron(III).

either substantial intensity enhancements of the spin-forbidden d-d bands or simultaneous pair excitations such as found in certain oxo-bridged Fe(III) dimers.^{14,20} Such special spectral features are apparently properties of antiferromagnetically coupled systems with $-J$ values considerably in excess of 10 cm^{-1} .

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Synthetic Aspects of the Reaction between Azide Ion and $\text{Ru}(\text{bipy})_2(\text{NO})\text{X}^{2+}$ ($\text{X} = \text{Cl}, \text{NO}_2$). Substitution-Induced Nitro-Nitrito Isomerism

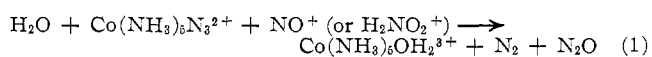
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The reaction $\text{Ru}(\text{bipy})_2(\text{NO})\text{X}^{2+} + \text{N}_3^- + \text{S} \rightarrow \text{Ru}(\text{bipy})_2\text{SX}^+ + \text{N}_2 + \text{N}_2\text{O}$ ($\text{S} = \text{solvent}$; $\text{X} = \text{Cl}, \text{NO}_2$) has been used to prepare a series of solvent complexes. For $\text{X} = \text{NO}_2$, mixtures of nitro and nitrito isomers are obtained as products. Displacement of coordinated acetone in $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{X}^+$ has provided a general route to the cis complexes $\text{Ru}(\text{bipy})_2\text{YX}^{+6}$ ($\text{Y} = \text{neutral or anionic ligand}$). During the substitution reactions of $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{NO}_2^+$, nitrito-nitro interconversion also occurs.

Introduction

Haim and Taube² have shown that coordinated azide can be nitrosated



(1) National Science Foundation undergraduate research participant, summer 1970.

(2) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

In nonaqueous solvents using $\text{NO}^+\text{ClO}_4^-$ as the nitrosating agent, labile solvent complexes are obtained, $\text{Co}(\text{NH}_3)_6\text{S}^{3+}$ ($\text{S} = \text{triethyl phosphate, sulfolane, etc.}$),^{3,4} which are useful synthetic intermediates.³⁻⁵ The intermediates allow synthetic control because un-

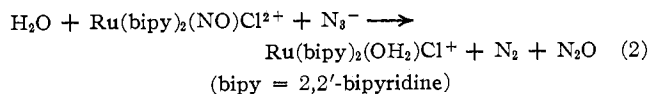
(3) R. B. Jordan, A. M. Sargeson, and H. Taube, *ibid.*, **5**, 1091 (1966).

(4) J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1174 (1968).

(5) J. L. Burmeister and N. J. DeStefano, *Inorg. Chem.*, **9**, 972 (1970).

der mild conditions only the labile solvent molecule is displaced. Examples of other synthetically useful solvent complexes include $\text{Ru}(\text{NH}_3)_5(\text{OH}_2)^{2+}$,⁶ $(\pi\text{-C}_6\text{H}_5)\text{-Fe}(\text{CO})_2(\text{OC}(\text{CH}_3)_2)^+$,⁷ and $(\text{CO})_3\text{Mo}(\text{diglyme})$.⁸

In a recent communication⁹ we reported the reverse of (1), reaction between free azide and coordinated nitrosyl



The coordinated nitrosyl behaves chemically as NO^+ .^{9,10} Reaction 2 also occurs in nonaqueous solvents giving solvent complexes $\text{Ru}(\text{bipy})_2\text{SCl}^+$. We report here some synthetic aspects of this reaction and of the displacement of acetone from $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{Cl}^+$. The products of similar reactions with $\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2^{2+}$ are mixtures of nitro and nitrito isomers.

Experimental Section

Infrared spectra were recorded on Perkin-Elmer 421 or Beckman IR-12 spectrophotometers in KBr pellets. Ultraviolet-visible spectra were obtained using a Cary Model 14 spectrophotometer. Sodium azide was recrystallized from water and then ethanol-water before use. Water was deionized and then distilled from alkaline permanganate. Acetone and methanol (reagent grade) were dried over molecular sieves or magnesium sulfate. The preparations of the nitrosyl complexes $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$ and $[\text{Ru}(\text{bipy})_2(\text{NO})(\text{NO}_2)](\text{PF}_6)_2$ were described previously.¹⁰

Direct Preparation of Solvent Complexes. $\text{Ru}(\text{bipy})_2\text{SX}^+$ ($\text{X} = \text{Cl}, \text{NO}_2$).—The nitrosyl complex was dissolved in the appropriate solvent. A *stoichiometric* amount of either suspended or dissolved NaN_3 was then added. Noticeable gas evolution was observed and the solution color deepened from the yellow-orange color of the nitrosyl complex to the characteristic red-brown color of the solvent complex. The solution was stirred until the reaction was complete and the products were worked up as described below. If an excess of azide was used in either acetone or methanol, an unidentified complex was obtained. The details of this reaction are currently under investigation.

$\text{Ru}(\text{bipy})_2\text{SX}^+$ ($\text{S} = \text{Acetone or Methanol}$).—In a typical experiment 0.397 g (0.51 mmol) of $[\text{Ru}(\text{bipy})_2(\text{NO})(\text{NO}_2)](\text{PF}_6)_2$ was dissolved in 30 ml of acetone and 0.034 g (0.52 mmol) of solid sodium azide was added. The solution was stirred for 1.5 hr and then filtered to remove the precipitated NaPF_6 . The filtrate containing the acetone complex was then used directly to prepare other complexes. The acetone complexes were obtained as solids by adding ether and carefully drying the precipitates *in vacuo*. The solids are both air and moisture sensitive and were manipulated in a glove bag in an atmosphere of dry nitrogen. The methanol complexes were prepared similarly. They also appear to be air and moisture sensitive although less so than the acetone complex.

$\text{Ru}(\text{bipy})_2\text{SX}^+$ ($\text{S} = \text{Water or Acetonitrile}$).— $[\text{Ru}(\text{bipy})_2(\text{NO})(\text{NO}_2)](\text{PF}_6)_2$ (0.780 g, 1.000 mmol) was converted quantitatively into the chloride salt by dissolving it in acetone and adding a nearly saturated solution of tetra-*n*-butylammonium chloride in acetone. The solid was collected, air-dried, and then dissolved in 20 ml of water. Sodium azide was added slowly (0.065 g, 1.000 mmol) and the solution was stirred for 0.5 hr and then filtered. A nearly saturated solution of 1.0 g of NH_4PF_6 in water was added. The precipitated red-brown solid was collected, washed four times with water and twice with ether, air-dried, and dried *in vacuo* over P_2O_{10} . The yield of $[\text{Ru}(\text{bipy})_2(\text{NO}_2)(\text{OH}_2)](\text{PF}_6)$ was 38%. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{18}\text{N}_5\text{O}_3\text{PF}_6$: C, 38.56; H, 3.21; N, 11.25. Found: C, 38.39; H, 2.95; N, 11.11. The acetonitrile complex $[\text{Ru}(\text{bipy})_2(\text{NCCH}_3)(\text{NO}_2)](\text{PF}_6)$ was prepared directly from the PF_6^- salt of the nitrosyl since it is

soluble in acetonitrile. After adding NaN_3 the solution was stirred for 2 hr and filtered. Addition of ether gave a deep orange solid which was collected, washed with ether, and dried *in vacuo* over P_2O_{10} . The yield of $[\text{Ru}(\text{bipy})_2(\text{NCCH}_3)(\text{NO}_2)](\text{PF}_6)$ was 80%. *Anal.* Calcd for $\text{RuC}_{22}\text{H}_{19}\text{N}_5\text{O}_2\text{PF}_6$: C, 40.90; H, 2.94; N, 13.02. Found: C, 39.44; H, 2.95; N, 12.50. In a similar reaction the chloroacetonitrile complex $\text{Ru}(\text{bipy})_2(\text{NCCH}_3)\text{Cl}^+$ was obtained in 95% yield as determined spectrophotometrically at 478 nm (ϵ 5160) and 342 nm (ϵ 4890).¹¹

Preparation of Complexes by Displacement of Coordinated Acetone.—A solution of the acetone complex in acetone was prepared as described above. An acetone solution of the appropriate ligand in excess was then added. The solution was stirred at room temperature until the reaction appeared to be complete and the product was isolated as described below. The methanol complexes appear to be equally useful synthetic intermediates. The existence of lattice water in several of the complexes was verified by elemental and infrared analyses.¹²

$\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{X}\cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{I}$).—In a typical experiment, a solution of $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)(\text{NO}_2)^+$ in acetone {0.5 mmol calculated from the weight of $[\text{Ru}(\text{bipy})_2(\text{NO})(\text{NO}_2)](\text{PF}_6)_2$ used to prepare the acetone complex} was added slowly to 2.0 g (7.2 mmol) of tetra-*n*-butylammonium chloride dissolved in acetone. The red-brown solid which rapidly precipitated was collected and washed several times with acetone and three times with ether and air-dried. The complex was recrystallized from dichloromethane-ether and dried *in vacuo* over P_2O_{10} . The yield of $\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl}\cdot\text{H}_2\text{O}$ was 60%. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{18}\text{N}_5\text{O}_3\text{Cl}$: C, 47.70; H, 3.74; Cl, 6.94. Found: C, 46.90; H, 3.51; Cl, 6.92. $\text{Ru}(\text{bipy})_2\text{NO}_2\text{I}\cdot 2\text{H}_2\text{O}$ was prepared similarly. An 81% yield of the red-brown solid was obtained. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{20}\text{N}_5\text{O}_4\text{I}$: C, 38.60; H, 3.21; N, 11.30; I, 20.30. Found: C, 38.02; H, 2.65; N, 11.10; I, 20.23.

$\text{Ru}(\text{bipy})_2\text{XCl}\cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{I}, \text{Cl}$).—To a solution of $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{Cl}^+$ (0.26 mmol) was added a saturated solution of tetra-*n*-butylammonium iodide (2.0 g, 5.43 mmol) in acetone. The mixture was stirred for 15 min. Ether was added to the deep purple solution precipitating the chloroiodo complex and excess $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{I}^-$. The complex was separated from the iodide salt by washing the combined solids four times with boiling benzene. The deep purple solid which remained on the frit was washed twice with ether and dried *in vacuo* over P_2O_{10} . The yield of $\text{Ru}(\text{bipy})_2\text{Cl}\cdot 2\text{H}_2\text{O}$ was 56%. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{20}\text{N}_5\text{O}_2\text{ClI}$: C, 39.20; H, 2.94; N, 9.15; Cl, 5.81; I, 20.79. Found: C, 40.35; H, 3.12; N, 9.59; Cl, 6.10; I, 20.89. $\text{Ru}(\text{bipy})_2\text{Cl}_2$ was prepared on a small scale by adding an acetone solution of $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Cl}^-$ to $\text{Ru}(\text{bipy})_2(\text{OCMe}_2)\text{Cl}^+$. The solution was evaporated to a purple oil by heating. The oil was dissolved in dichloromethane and the dichloromethane solution was washed several times with water in a separatory funnel. The complex was present in 41% yield in the dichloromethane as shown spectrophotometrically using ϵ 7760 at 554 nm and ϵ 8130 at 375 nm.

$\text{Ru}(\text{bipy})_2(\text{py})\text{X}^+$ ($\text{X} = \text{Cl}, \text{NO}_2$; $\text{py} = \text{Pyridine}$).—Pyridine (0.5 ml) was added to 0.26 mmol of $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{NO}_2^+$ in acetone. The solution was stirred for 15 min and a nearly saturated solution of sodium tetraphenylboron (0.5 g) in water was added. The red-brown solid which appeared was collected and recrystallized from dichloromethane-ether. It was washed three times with ether and dried *in vacuo* over P_2O_{10} . The salt $[\text{Ru}(\text{bipy})_2(\text{NO}_2)(\text{py})]\text{B}(\text{C}_6\text{H}_5)_4$ was obtained in 71% yield. *Anal.* Calcd for $\text{RuC}_{48}\text{H}_{40}\text{N}_6\text{O}_2\text{B}$: C, 68.60; H, 4.79; N, 9.81. Found: C, 68.37; H, 4.68; N, 10.03. The chloropyridine complex was prepared similarly but isolated as the hexafluorophosphate salt $[\text{Ru}(\text{bipy})_2(\text{py})\text{Cl}](\text{PF}_6)$ (40% yield). *Anal.* Calcd for $\text{RuC}_{25}\text{H}_{21}\text{N}_5\text{ClPF}_6$: C, 44.61; H, 3.15; Cl, 5.25; F, 16.95. Found: C, 44.36; H, 3.27; Cl, 5.80; F, 17.26. The solvent complexes $[\text{Ru}(\text{bipy})_2(\text{OH}_2)(\text{NO}_2)](\text{PF}_6)$ and $[\text{Ru}(\text{bipy})_2(\text{NCCH}_3)(\text{NO}_2)](\text{PF}_6)$ were prepared similarly.

Preparation of $[\text{Ru}(\text{bipy})_2(\text{NO})(\text{OH}_2)](\text{PF}_6)_3$.— $[\text{Ru}(\text{bipy})_2(\text{NO}_2)(\text{OH}_2)](\text{PF}_6)$ (0.315 g, 0.218 mmol) was suspended in 75 ml of methanol. The suspension was stirred vigorously while 5 ml of 75% HPF₆ was added slowly. The solution was stirred for 1 hr and filtered. Ether was added to the filtrate giving a light gray solid which was collected on a frit, washed three times with ether, and air-dried. The solid was recrystallized from acetone-ether (49% yield). *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{18}\text{N}_5\text{O}_2\text{P}_3\text{F}_{18}$: C, 26.80;

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(8) R. P. M. Werner and T. H. Coffield, *Chem. Ind. (London)*, 936 (1960).

(9) F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, **93**, 1294 (1971).

(10) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).

(11) N. Winterton and T. J. Meyer, unpublished results.

(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 156.

H, 2.01; N, 7.82. Found: C, 26.61; H, 2.09; N, 7.75. The infrared spectrum of the complex has a very strong $\nu(\text{N-O})$ band at 1939 cm^{-1} (KBr pellet).

Results

For the complexes reported here which contain coordinated nitrite, $\nu(\text{N-O})$ bands are given in Table I.

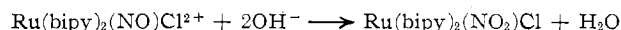
TABLE I
 $\nu(\text{N-O})$ BANDS FOR THE NITRITE COMPLEXES^a

Complex	$\nu(\text{N-O}), \text{cm}^{-1}$	
	Nitro	Nitrito
[Ru(bipy) ₂ (NCCH ₃)NO ₂](PF ₆)	1337 vs, 1292 vs	
[Ru(bipy) ₂ (OH ₂)NO ₂](PF ₆)	1338 s, 1294 s	1394 sh, 1134 s, br
[Ru(bipy) ₂ (HOCH ₃)NO ₂](PF ₆)	1337 s, 1291 s	1397 sh, 1133 s, br
[Ru(bipy) ₂ (OC(CH ₃) ₂)NO ₂](PF ₆)	1340 sh, 1297 w	1394 sh, 1131 s, br
[Ru(bipy) ₂ (py)NO ₂](PF ₆) ^b	1340 s, 1299 s	1394 sh, 1130 s, br
Ru(bipy) ₂ NO ₂ Cl·H ₂ O	1338 s, 1298 s	1396 sh, 1133 s, br
Ru(bipy) ₂ NO ₂ ·2H ₂ O	1339 s, 1297 s	1395 sh, 1134 s, br

^a In KBr pellets; $\pm 4\text{ cm}^{-1}$ except for the 1394–1396- cm^{-1} bands which are $\pm 8\text{ cm}^{-1}$. Abbreviations: very strong, vs; strong, s; weak, w; broad, br. ^b py = pyridine.

In all of the preparations the products are presumably cis isomers.^{10,13}

From the infrared data most of the samples contain mixtures of nitro and nitrito isomers, e.g., Ru(bipy)₂(NO₂)Cl·H₂O and Ru(bipy)₂(ONO)Cl·H₂O. Shifts in $\nu(\text{N-O})$ between free and coordinated nitrite have been used to distinguish between nitro and nitrito isomers.^{14,15} From the earlier work of Nakamoto and Goodgame and coworkers we assign the bands at 1291–1299 and 1337–1340 cm^{-1} to the symmetric and anti-symmetric N-O stretching vibrations of nitrogen-bound nitrite and the bands at 1130–1134 and 1394–1397 cm^{-1} to the same vibrations for oxygen-bound nitrite. In most spectra the 1394–1397- cm^{-1} band appears as an indistinct shoulder on a higher energy 2,2'-bipyridine band. Two of the complexes in Table I, [Ru(bipy)₂(py)NO₂](PF₆) and Ru(bipy)₂(NO₂)Cl·H₂O, were prepared in earlier work¹⁶ as pure nitro isomers by reaction with OH⁻



The $\nu(\text{N-O})$ bands of samples made by this reaction agree well with the values for the nitro isomers in Table I.

Pure nitro isomers are obtained by heating samples of nitro-nitrito mixtures. For example, if a sample containing Ru(bipy)₂(NO₂)Cl·H₂O and Ru(bipy)₂(ONO)Cl·H₂O is heated under nitrogen above 200° for several hours or refluxed in methanol under nitrogen for 12 hr, complete conversion to Ru(bipy)₂(NO₂)Cl is observed. The spectra of a sample of (bipy)₂RuI(NO₂(ONO))·H₂O in a KBr pellet before and after heating at 225° for 24 hr are shown in Figure 1.

The nitro and nitrito bands are indicated in Figure 1. The bands at 1422, 1311, 1270, 1243, 1156, and 1122 cm^{-1} have been identified as bipy bands by comparisons with the spectra of Ru(bipy)₂X₂·2H₂O (X = Cl, Br, I, NCS).

From this and previous work¹⁶ several synthetic routes are available for the preparation of nitrite complexes. In Table II are given some complexes, their

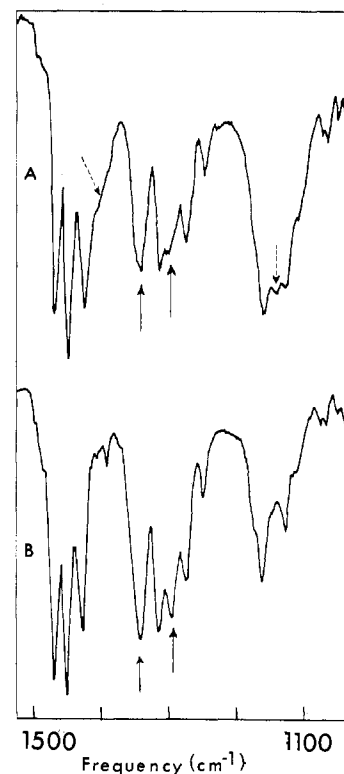


Figure 1.—Infrared spectrum of (bipy)₂RuI(NO₂(ONO)); A, in a KBr pellet before heating; B, after heating under nitrogen at 225° for 24 hr. Nitro bands are indicated by full arrows and nitrito bands by broken arrows.

methods of preparation, and the per cent of nitro isomer in the sample. In all cases the reactions were carried out and solid samples isolated as described in the Experimental Section or as described previously.¹⁶ Infrared spectra were recorded on the solid samples. The percentage values were estimated from the relative areas of a bipy band at $\sim 1600\text{ cm}^{-1}$ and the nitrite band at $\sim 1340\text{ cm}^{-1}$ and are probably good to $\pm 10\%$. The areas were measured using a planimeter.

Isomeric mixtures are obtained as products of methods 1 and 2 (in Table II) only. Nitrite in the parent complex Ru(bipy)₂(NO)NO₂²⁺ is completely nitrogen bound.¹⁰ Partial isomerization to oxygen-bound nitrite accompanies the formation of solvent complexes in the reactions between Ru(bipy)₂(NO)NO₂²⁺ and N₃⁻. The preparation of the acetone complex Ru(bipy)₂(OC(CH₃)₂)NO₂⁺ by reaction 1 in Table II gives greater than 95% of the nitrito isomer. Displacement of the coordinated acetone (reaction 2 in Table II) is also accompanied by partial isomerization. We have not been able to separate the two isomers from a mixture nor to prepare a pure sample of a nitrito isomer. The nitro:nitrito ratios for the complexes Ru(bipy)₂(NCCH₃)NO₂⁺ and Ru(bipy)₂(OH₂)NO₂⁺ are dependent on the method of preparation (reactions 1 and 2 in Table II). This is apparently a consequence of the different media in which the reactions were carried out.

Except for the acetone and methanol cases, the complexes once formed appear to be stable to further substitution or isomerization under the mild conditions of the reactions. Conversion of nitrito to nitro isomers occurs only at elevated temperatures, implying that the isomerizations observed here take place during substitu-

(13) F. P. Dwyer, H. A. Goodwin, and E. C. Gyrfas, *Aust. J. Chem.*, **16**, 42 (1963); B. Bosnich and F. P. Dwyer, *ibid.*, **19**, 2229 (1966).

(14) Reference 12, pp 151–155.

(15) D. M. L. Goodgame, M. A. Hitchman, D. F. Marsham, and C. E. Souter, *J. Chem. Soc. A*, 2464 (1969), and references therein.

(16) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 2150 (1971).

TABLE II

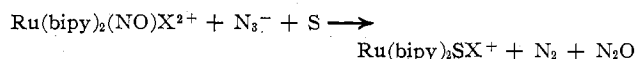
Methods of preparation	Products	% nitro
1. $(\text{bipy})_2\text{Ru} \begin{matrix} \text{NO}^{2+} \\ \text{NO}_2 \end{matrix} + \text{N}_3^- \xrightarrow{\text{S}}$	$\text{Ru}(\text{bipy})_2(\text{NCCH}_3)\text{NO}_2^+ (\text{S} = \text{CH}_3\text{CN})$ $\text{Ru}(\text{bipy})_2(\text{OH}_2)\text{NO}_2^+ (\text{S} = \text{H}_2\text{O})$ $\text{Ru}(\text{bipy})_2(\text{HOCH}_3)\text{NO}_2^+ (\text{S} = \text{CH}_3\text{OH})$ $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{NO}_2^+ (\text{S} = (\text{CH}_3)_2\text{CO})$	100 90 35 <5
2. $(\text{bipy})_2\text{Ru} \begin{matrix} \text{OC}(\text{CH}_3)_2^+ \\ \text{ONO} \end{matrix} + \text{Y} \xrightarrow{(\text{CH}_3)_2\text{CO}}$	$\text{Ru}(\text{bipy})_2(\text{NCCH}_3)\text{NO}_2^+ (\text{Y} = \text{CH}_3\text{CN})$ $\text{Ru}(\text{bipy})_2(\text{OH}_2)\text{NO}_2^+ (\text{Y} = \text{OH}_2)$ $\text{Ru}(\text{bipy})_2(\text{py})\text{NO}_2^+ (\text{Y} = \text{py})$ $\text{Ru}(\text{bipy})_2\text{NO}_2\text{Cl} (\text{Y}^- = \text{Cl}^-)$ $\text{Ru}(\text{bipy})_2\text{NO}_2\text{I} (\text{Y}^- = \text{I}^-)$	90 35 50 40 50
3. $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{Cl}^+ + \text{NO}_2^- \xrightarrow{(\text{CH}_3)_2\text{CO}}$	$\text{Ru}(\text{bipy})_2\text{NO}_2\text{Cl}$	100
4. $\text{Ru}(\text{bipy})_2(\text{NO})\text{Y}^{n+} + 2\text{OH}^- \xrightarrow{\text{H}_2\text{O}}$	$\text{Ru}(\text{bipy})_2\text{NO}_2\text{Cl} (\text{Y}^- = \text{Cl}^-)$ $\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{py}^+ (\text{Y} = \text{py})$ $\text{Ru}(\text{bipy})_2\text{NO}_2\text{NO}_2 (\text{Y}^- = \text{NO}_2^-)$	100 100 100

tion. We have not found evidence for light catalysis, at least by ordinary room lighting.

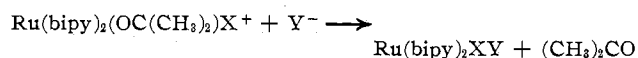
λ_{max} values for $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{Cl}^+$ in acetone (from 1000 to 300 nm) are at 511 nm (ϵ 7250) and 359 nm (ϵ 7850) and for $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{NO}_2^+$ at 450 nm (ϵ 6500). In acetone the aquo complexes $\text{Ru}(\text{bipy})_2(\text{OH}_2)\text{Cl}^+$ and $\text{Ru}(\text{bipy})_2(\text{OH}_2)\text{NO}_2^+$ (90% nitro isomer, 10% nitrito; see Table II) have λ_{max} values at 483 and \sim 350 nm and at 460 nm, respectively. The acetone complexes were generated *in situ* by reaction between N_3^- and $\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^+$ or $\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2^+$ and ϵ values were calculated from the weight of the nitrosyl complexes used assuming a quantitative reaction. To obtain solid-state infrared spectra, ether was added to solutions of the complexes and the solids obtained were carefully dried *in vacuo*. The solids so obtained were handled in an atmosphere of dry nitrogen in a glove bag because of their air and moisture sensitivity. In addition to the usual bands in infrared spectra, a new weak band appears for both complexes at 1690–1700 cm^{-1} . The band may be $\nu(\text{C}-\text{O})$ for acetone coordinated to ruthenium. The shift in frequency from free acetone ($\Delta\nu(\text{C}-\text{O}) \approx -25 \text{ cm}^{-1}$) is small but consistent with coordination of ruthenium to the carbonyl oxygen.¹⁷ A recent crystal structure¹⁸ shows that acetone is bound to zinc in the anion $[\text{ZnCl}_3(\text{OC}(\text{CH}_3)_2)]^-$.

Discussion

Preparations.—The synthetic aspects of the work presented here parallel the earlier work of Sargenson, Jordan, and Taube³ and Hurst and Taube⁴ using $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$. The solvent complexes $\text{Ru}(\text{bipy})_2\text{SX}^+$ ($\text{X} = \text{NO}_2$; $\text{S} = \text{CH}_3\text{CN}, \text{H}_2\text{O}, \text{CH}_3\text{OH}, (\text{CH}_3)_2\text{CO}$. $\text{X} = \text{Cl}$; $\text{S} = \text{CH}_3\text{CN}, (\text{CH}_3)_2\text{CO}$) have been isolated as products of the reaction



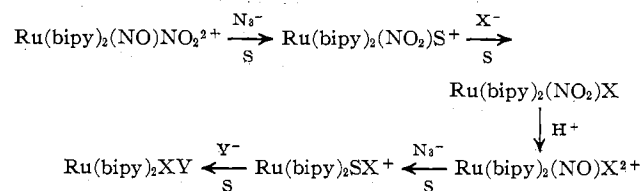
Displacement of the weakly bound acetone molecule in $\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{X}^+$ by added L or X^- gives $\text{Ru}(\text{bipy})_2\text{LX}^+$ ($\text{X} = \text{NO}_2$; $\text{L} = \text{py}, \text{CH}_3\text{CN}, \text{H}_2\text{O}$; $\text{X} = \text{Cl}$; $\text{L} = \text{py}$) or $\text{Ru}(\text{bipy})_2\text{XY}$ ($\text{X} = \text{NO}_2$; $\text{Y} = \text{Cl}, \text{I}$. $\text{X} = \text{Cl}$; $\text{Y} = \text{Cl}, \text{I}, \text{NO}_2$)



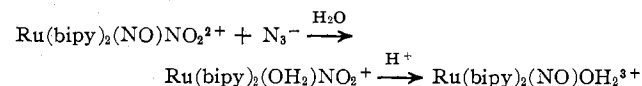
(17) F. R. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968).

(18) V. C. Adam, V. A. Gregory, and B. T. Kilbourn, *Chem. Commun.*, 1400 (1970).

The reactions represent a general method for the preparation of mixed cis complexes. The procedures described here should be useful for the series of nitrosyl complexes $\text{Ru}(\text{AA})_2(\text{NO})\text{X}^{2+}$ and $\text{Ru}(\text{AA})_2(\text{NO})\text{py}^{3+}$ ($\text{AA} = 2,2'$ -bipy, 1,10-phen; $\text{X} = \text{Cl}, \text{Br}, \text{NO}_2$)¹⁰ and should also be useful for other ligands including CN^- , NCS^- , etc. Using $\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2^+$, two coordination sites are potentially available for substitution using sequential reactions (where $\text{S} = \text{solvent}$)



and as reported here, otherwise unknown nitrosyl complexes can be prepared by



No attempt was made to exhaust the synthetic possibilities of the two reactions.

Nitro-Nitrito Isomerism.—Goodgame, Hitchman, and coworkers have investigated the mode of coordination of NO_2^- in complexes of $\text{Ni}(\text{II})$,¹⁹ $\text{Co}(\text{II})$,¹⁵ and $\text{Zn}(\text{II})$.²¹ Examples of chelating^{20,21} and bridging^{22,23} nitrite as well as unidentate nitro and nitrito coordination have been found. The complexes are labile and in some cases the mode of coordination is not the same in solution as in the solid state.¹⁹

Nitrito complexes have been prepared in less labile systems by reaction between NO_2^- and aquopentaamine complexes, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ ²⁴ or $\text{M}(\text{NH}_3)_5\text{OH}_2^{n+}$ [$\text{M} = \text{Rh}(\text{III}), \text{Ir}(\text{III}), \text{and Pt}(\text{IV})$],²⁵ in acidic solution. A common rate law is observed for all cases and nitrosation of coordinated oxygen has been proposed. In acidic solution $\text{Co}-\text{O}$ bond rupture is known not to

(19) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chim. Acta*, **3**, 319 (1969), and references therein.

(20) D. M. L. Goodgame, M. A. Hitchman, and D. F. Marsham, *J. Chem. Soc. A*, 1933 (1970), and references therein.

(21) M. G. B. Drew and D. Rogers, *Chem. Commun.*, 476 (1965).

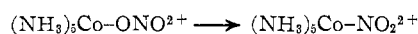
(22) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **6**, 813 (1967).

(23) M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Chem. Commun.*, 477 (1965).

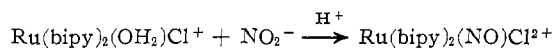
(24) R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Amer. Chem. Soc.*, **76**, 5920 (1954).

(25) F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

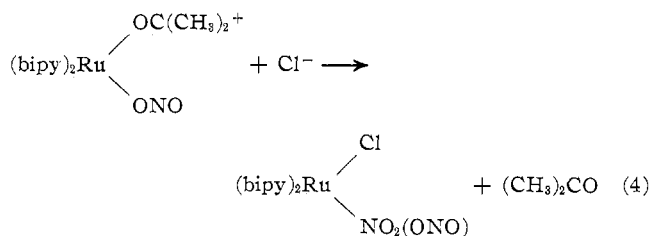
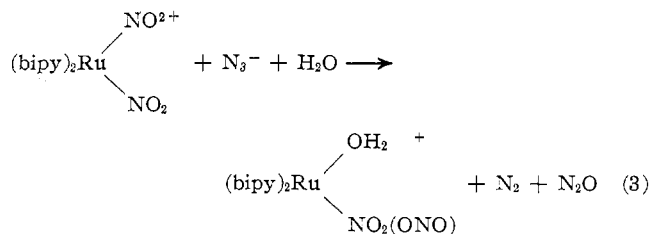
occur.²⁶ The nitrito isomers once formed slowly rearrange to the more stable nitro isomers



This path to nitrito coordination is not available for the bipy-Ru complexes. Under the conditions of the reaction nitrosyl complexes are known to form¹⁰

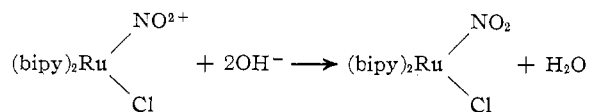


In the ruthenium chemistry presented here, mixtures of nitrito and nitro isomers are obtained as products of two reactions, *e.g.*



The nitrito isomers are converted into the more stable nitro isomers only by prolonged heating either in solution or in the solid state. Exceptions are the acetone and methanol complexes $(\text{bipy})_2\text{RuS}(\text{NO}_2(\text{ONO}))^+$. They are labile, which should provide a path for isomerization, and yet each retains a constant nitro to nitrito ratio for several hours in solution. Apparently the nitro and nitrito isomers are of comparable stability with the nitrito slightly favored (see Table II).

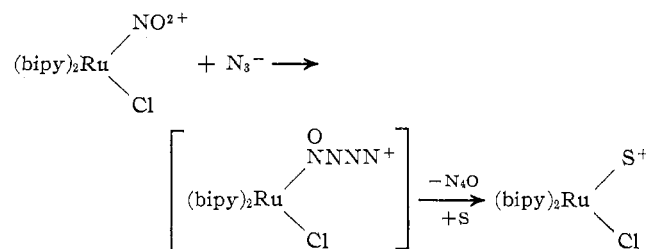
The conversion of pure nitro or nitrito isomers into mixtures of the two is induced by net substitution at ruthenium (reactions 3 and 4). Reaction of OH^- with nitrosyl proceeds by attack at the nitrogen atom,¹⁶ no net substitution occurs, and the products are pure nitro isomers



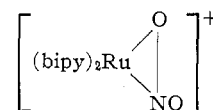
The nitro-nitrito interconversion is potentially a sensitive probe into the detailed nature of the substitution reactions. The rate law for the reaction of the chloro-nitrosyl complex with N_3^- is

$$-\frac{d[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}]}{dt} = k[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}][\text{N}_3^-]$$

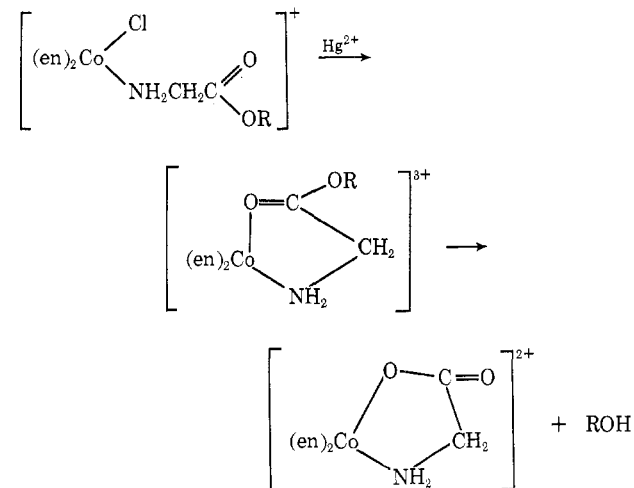
and no evidence for N_2 , N_2O , or N_4O intermediates has been found.⁹ The reaction may take the same course as nitrosation of $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$,²⁷ *i.e.*



Loss of the good leaving group N_4O (or N_2 or N_2O) would leave a reactive five-coordinate intermediate $(\text{bipy})_2\text{Ru}-\text{Cl}^+$ analogous to $\text{Co}(\text{NH}_3)_5^{3+}$.²⁷ For the nitro complex partial nitrito conversion can be accounted for by rearrangement of an intermediate like $(\text{bipy})_2\text{Ru}-\text{NO}_2^+$ to



If nitrite remains bound during substitution, an intermediate or activated complex with ruthenium bonded simultaneously to both oxygen and nitrogen must exist. The capture of lower coordinate intermediates by chelation has been observed in cobalt-ammine chemistry²⁸



Acetone is also a good leaving group (reaction 4). In substitution reactions of $(\text{bipy})_2\text{RuONO}(\text{OC}(\text{CH}_3)_2)^+$ partial conversion to nitro isomers can similarly be accounted for by rearrangement of an intermediate $(\text{bipy})_2\text{Ru}-\text{ONO}^+$. For $\text{Ru}(\text{bipy})_2(\text{NCCH}_3)\text{NO}_2^+$ and $\text{Ru}(\text{bipy})_2(\text{OH}_2)\text{NO}_2^+$ the nitro:nitrito ratios are somewhat dependent on the method of preparation (see Table II). This may be a medium effect [reaction 3 is carried out in pure solvent and reaction 4 in acetone with the solvent added as a nucleophile], or in one of the reactions (either (3) or (4)) more than one intermediate may be important in giving the final products.

Our attempts to study reactions 3 and 4 quantitatively have been frustrated by three factors. (1) We have been unable to isolate a pure sample of a nitrito isomer. (2) The infrared method of analyzing for the nitro and nitrito isomers is only approximate. (3) In cases where less than quantitative yields are obtained, selective separation of one of the isomers may have occurred. Nitro-nitrito interconversion may be a

(26) R. K. Murmann and H. Taube, *J. Amer. Chem. Soc.*, **78**, 4886 (1956).

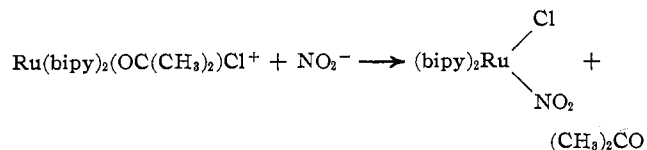
(27) A. M. Sargeson, I. I. Olsen, and D. A. Buckingham, *Aust. J. Chem.*, **20**, 597 (1967).

(28) M. D. Alexander and D. H. Busch, *J. Amer. Chem. Soc.*, **88**, 1130 (1966).

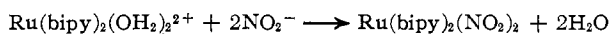
common feature for complexes containing both coordinated nitrite and a good leaving group and being otherwise substitution inert.

In light of the known complexes *trans*-Ru(das)₂(N₂)Cl⁺ [das = *o*-phenylenebis(dimethylarsine)],²⁹ Ru(NH₃)₅N₂²⁺,³⁰ and Ru(NH₃)₅N₂O²⁺,³¹ it is somewhat surprising that N₂ or N₂O complexes are not formed as products of reaction 3 in acetone. Earlier attempts³ to coordinate dinitrogen to ruthenium in bipyridine complexes were also unsuccessful. Ruthenium may be considerably less capable of back-bonding to dinitrogen in bipyridine and 1,10-phenanthroline complexes.¹⁰

In the reaction



nitrite must attack through the nitrogen atom. The product is the pure nitro isomer and under the mild conditions of the reaction the nitrito isomer once formed is stable. By contrast it has been suggested that in the reaction of NO₂⁻ with Ru(bipy)₂(OH)₂²⁺ in aqueous solution³²



a nitrito isomer is formed initially.

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(29) P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, **93**, 84 (1971).

(30) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

(31) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **91**, 6876 (1969).

(32) N. R. Davies and T. L. Mullins, *Aust. J. Chem.*, **21**, 915 (1968).

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Synthesis of *cis*-Dihalotetrapyridineruthenium(II) Complexes (Halide = Chloride, Bromide, Iodide) and Verification of Their *Cis* Stereochemistry

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The syntheses of *cis*-Ru(py)₄Cl₂, *cis*-Ru(py)₄Br₂ and *cis*-Ru(py)₄I₂ are reported. Also reported is the synthesis of *cis*-Ru(py)₄ox·H₂O which is the key intermediate in the synthesis of these complexes. Far-infrared, Raman, and proton nmr spectral data are presented for both the *cis* and *trans* isomers of these pyridine-halogen-ruthenium(II) complexes, and this evidence is used to assign the stereochemistry of the geometrical isomers.

In our investigation of the electronic and proton nmr spectral properties of pyridine complexes of Ru(II), we have synthesized both the *cis* and *trans* isomers of Ru(py)₄X₂ (X⁻ = Cl⁻, Br⁻, I⁻; py = pyridine). The *trans* isomers have been previously synthesized.¹⁻⁶ We now report the synthesis of the *cis* isomers and give evidence to support our assignment of the stereochemistry of these geometrical isomers.

Experimental Section

Reagents.—Ruthenium trichloride hydrate (RuCl₃·xH₂O, 38.95% Ru) was used as supplied by Engelhard Industries. Water was doubly distilled, the second distillation being from an alkaline potassium permanganate solution. Argon was bubbled through two chromous solution-zinc amalgam reducers⁷ in series to remove any oxygen present. All other chemicals were reagent grade and were used without further purification.

Instruments and Techniques.—Proton nmr spectra were obtained on the Varian T-60 spectrometer. Far-infrared spectra

were obtained with the Beckman IR-11 spectrophotometer (350–70 cm⁻¹) using Nujol mulls between polyethylene plates and with the Perkin-Elmer 457 spectrophotometer (600–250 cm⁻¹) using CsI pellets. Raman spectra were obtained with the Spex Industries Ramalog laser-Raman system, using a Spectra Physics He-Ne laser (exciting wavelength 6328 Å). The spectra were obtained from solid samples in capillary tubes.

Preparation of *cis*-Dichlorotetrapyridineruthenium(II).—The preparation of *cis*-Ru(py)₄Cl₂ involved three steps: (1) synthesis of a form⁸⁻¹⁰ of potassium tris(oxalato)ruthenate(III) hydrate, (2) synthesis of *cis*-Ru(py)₄ox·H₂O (ox = C₂O₄²⁻),¹¹ and (3) synthesis of *cis*-Ru(py)₄Cl₂.

Step 1.—RuCl₃·xH₂O (1.0 g) and potassium oxalate monohydrate (2.7 g) were dissolved in 30 ml of water. Absolute ethanol (5 ml) was added and the solution was refluxed for 4 hr. Ethanol was quickly added to the resulting hot, brown solution until a brown oil formed and sank to the bottom of the beaker. The cloudy yellow supernate was decanted and the oil was cooled in a refrigerator for 5 min to give a brown solid (2.0 g). The infrared spectrum indicated this solid to be K₃Ru(ox)₃·xH₂O.⁸

Step 2.—The substance K₃Ru(ox)₃·xH₂O (2.0 g) was dissolved in 20 ml of water, and 6 ml of pyridine was added to this solution. The mixture was then refluxed for 1 hr. During this time, the solution exhibited a color change from an initial dark brown to a

(8) The composition of potassium tris(oxalato)ruthenate(III) hydrate varies with the method and conditions of synthesis.⁹ The method given is an adaptation of an already existing method.¹⁰

(9) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, pp 158–159.

(10) C. Creutz, Ph.D. Thesis, Stanford University, 1970, pp 23–24.

(11) *cis*-Oxalatotetrapyridineruthenium(II) has also been synthesized from the hexapyridineruthenium(II) cation.⁶

(1) V. I. Goremykin and T. D. Avtokratova, *Izv. Sekt. Platiny Drugikh Blagorod. Metal Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR*, **25**, 117 (1950).

(2) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

(3) J. Soucek and J. Vrestal, *Collect. Czech. Chem. Commun.*, **26**, 1931 (1961).

(4) J. Lewis, F. E. Mabbs, and R. A. Walton, *J. Chem. Soc. A*, 1366 (1967).

(5) J. D. Gilbert, D. Rose and G. Wilkinson, *ibid.*, 2765 (1970).

(6) Barry Loescher, private communication, University of Toronto.

(7) R. G. Gaunter, Ph.D. Thesis, Stanford University, 1969, p 8.