Acknowledgments. We wish to thank C. Herndon Williams, Jr., for helpful discussions and D. F. Shriver and B. G. Ramsey for enlightening comments on the manuscript prior to submission for publication. Also, we are grateful to the Instituto de Física, Universidade de São Paulo for free computer time and to the Fundação de Amparo à Pesquisa de Estado de São Paulo for financial support.

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Reactions between Nitrosylpentaammineruthenium(II) and Hydroxylamine or Hydrazine. Formation of (Dinitrogen oxide)pentaammineruthenium(II)

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Abstract: $[Ru^{II}(NH_3)_5NO]X_3\cdot H_2O$ and hydroxylamine formed $[Ru^{II}(NH_3)_5N_2O]X_2$ (X = Cl, Br, I). The products showed a strong infrared band in the 1160-cm^{-1} region (ν_1 of N_2O) and a weak band in the 2250-cm^{-1} region (ν_3 of N_2O). The bromide salt was face-centered cubic, a = 10.32 Å. $[Ru^{II}(NH_3)_5NO]X_3$ and hydrazine hydrate formed, at room temperature, $[Ru^{II}(NH_3)_5N_2]X_2$ only. At −23° or below a mixture of $[Ru^{II}(NH_3)_5N_2]X_2$ and $[Ru^{II}(NH_3)_5N_2O]X_2$ was obtained. The same mixture was obtained from reaction of OH^- with a solution of $[Ru^{II}(NH_3)_5NO]I_3\cdot H_2O$ and $N_2H_6I_2$ at room temperature. The properties of $[Ru^{II}(NH_3)_5N_2O]^{2+}$ are reported and mechanisms for the reactions of $[Ru^{II}(NH_3)_5NO]^{3+}$ with hydroxylamine or hydrazine suggested.

Nucleophilic attack at the nitrosyl ligand has been demonstrated for a variety of ruthenium complexes.[1–9] Particularly noteworthy are the reactions of $[Ru^{II}Cl(das)_2NO]^{2+}$ (das = *o*-phenylenebisdimethylarsine) with hydrazine, forming $[Ru^{II}ClN_3(das)_2]$,[1] and with azide ion, forming $[Ru^{II}ClN_3(das)_2]$, N_2O, and N_2.[2] A similar reaction was also found for $[Ru^{II}Cl(dipy)_2NO]^{2+}$ (dipy = 2,2′-dipyridine).[3] We have investigated reactions of nitrosylpentaammineruthenium(II), $[Ru^{II}(NH_3)_5NO]^{3+}$,[4–6] and present here the results of investigations of reactions of $[Ru^{II}(NH_3)_5NO]^{3+}$ with hydroxylamine and hydrazine which give (dinitrogen oxide)pentaammineruthenium(II), $[Ru^{II}(NH_3)_5N_2O]^{2+}$. N_2O complexes of pentaammineruthenium(II) were prepared previously from N_2O and $[Ru^{II}(NH_3)_5H_2O]^{2+}$.[10–12]

Results

$[Ru^{II}(NH_3)_5NO]X_3\cdot H_2O$ and hydroxylamine reacted rapidly, at room temperature, forming pale yellow, diamagnetic $[Ru^{II}(NH_3)_5N_2O]X_2$ (X = Cl, Br, I). Because of rapid decomposition, precipitation of the complexes as they formed was a necessity (see Experimental Section). Addition of a precipitating anion to increase yields of the more soluble salts gave products contaminated with $[Ru^{II}(NH_3)_5N_2]^{2+}$ and $[Ru^{III}(NH_3)_5OH]^{2+}$. The stability of the N_2O complexes was dependent on the anion ($I^- > Br^- > Cl^-$). The iodide salt was stable for several weeks in dry air, but the chloride salt decomposed in a few days. The rate of decomposition may be an inverse function of the sample purity, since the very soluble chloride salt was difficult to obtain pure.

The complexes had properties similar to $[Ru^{II}(NH_3)_5N_2O](BF_4)_2$ prepared from $[Ru^{II}(NH_3)_5H_2O]^{2+}$ and N_2O.[12] The bromide and iodide salts evolved N_2O on oxidation with ceric(IV) and N_2O, N_2, and H_2O on dry heating. N_2O, 82% (±5%; mean of six determinations) of the theoretical amount, was obtained on treatment of the iodide salt with Ce^{4+}. Treatment of the complex prepared from $[Ru^{II}(NH_3)_5{}^{15}NO]I_3\cdot H_2O$ and $^{14}NH_2OH$ with Ce^{4+} gave $^{29}N_2O$ whose cracking pattern in the mass spectrum showed almost exclusively $^{14}NO^+$. It was concluded the product was $[Ru^{II}(NH_3)_5{}^{15}N^{14}NO]I_2$ (assuming N_2O is coordinated *via* nitrogen rather than oxygen (see below)).

The infrared spectra of the complexes (Table I) showed a very strong band in the 1160-cm^{-1} region (ν_1 of N_2O) and a very weak band in the 2250-cm^{-1} region (ν_3 of N_2O), as observed for $[Ru^{II}(NH_3)_5N_2O](BF_4)_2$.[12] No bands were observed in the 700–400 cm^{-1} region where metal–ammonia, metal–N_2O, or ν_2 of N_2O might be expected. The frequencies of the N_2O vibrations were anion dependent, and the intensity of $\nu_3(N_2O)$ was also markedly anion dependent ($I^- >$

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Table I. Infrared Spectra of $[Ru^{II}(NH_3)_5N_2O]X_2$[a]

X = Cl	X = Br	X = I: $^{28}N_2O$	X = I: $^{15}N^{14}NO$	Assignment
3310 s, br	3305	3295	3295	ν (NH)
	3240 s, br	3233	3230	
3180 s, br	3180	3174	3170	
2306 vw	2312	2352	2325	$2\nu_1$ (N_2O)
2230 vw	2236 vw	2248 w	2223 w	ν_3 (N_2O)
1627 m	1612	1618	1620	δ_{deg} (NH_3)
	1310 sh	1302	1300	δ_{sym} (NH_3)
1273 s	1271	1273	1273	
1256 sh		1253		
1152 vs, br	1157	1175	1160	ν_1 (N_2O)
798 m	792	779	780	ρ_r (NH_3)

[a] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad.

$Br^- > Cl^-$). Attempts to obtain Raman spectra of the complexes were unsuccessful because of decomposition in the laser beam. The infrared spectrum of $[Ru^{II}(NH_3)_5{}^{15}N^{14}NO]I_2$ had $\nu_3(N_2O)$ of greater intensity than the analogous $^{28}N_2O$ complex and $\Delta\nu_3$ was 25 cm^{-1} ($\Delta\nu_3 = \nu_3(^{28}N_2O) - \nu_3(^{29}N_2O)$). $\Delta\nu_1$ was 15 cm^{-1}. The analogous values for gaseous $^{15}N^{14}NO$ are $\Delta\nu_3 = 21$ cm^{-1} and $\Delta\nu_1 = 15$ cm^{-1}.[13]

The electronic spectra of air- or argon-saturated aqueous solutions of $[Ru^{II}(NH_3)_5N_2O]^{2+}$ showed one band, λ_{max} 233 nm, $\epsilon > 10^3$. Decomposition of such solutions was rapid however. $[Ru^{III}(NH_3)_5OH]^{2+}$ was produced in air-saturated solution and $[Ru^{II}(NH_3)_5H_2O]^{2+}$ in argon-saturated solution; in both cases conversion being essentially quantitative within 4 min. Spectra of the bromide salt in N_2O saturated water taken within 1 min of mixing showed a band, λ_{max} 234 nm, ϵ 5.3×10^3. Using the value of 7.0^{10} for the equilibrium constant for the reaction

$$[Ru^{II}(NH_3)_5N_2O]^{2+} \rightleftarrows [Ru^{II}(NH_3)_5H_2O]^{2+} + N_2O$$

the measured extinction coefficient corresponds to a value of ϵ of 1.9×10^4 for $[Ru^{II}(NH_3)_5N_2O]^{2+}$. Armor and Taube obtained a value of $(1.7 \pm 0.2) \times 10^4$ at 238 nm by extrapolation from the above equilibrium.[10] The reason for the difference in λ_{max} between this work and the literature[10,12] is not clear.

X-Ray powder photographs of the bromide salt (attempts to obtain single crystals were unsuccessful due to decomposition in solution) showed this salt to be face-centered cubic, $a = 10.32$ Å (uncalibrated film). The calculated density for four molecules per unit cell is 2.36 and the observed 2.26 g/cm^3 (by flotation in $CHCl_3 \cdot CHBr_3$). The cell dimension was found to be the same as for $[Ru^{II}(NH_3)_5N_2]Br_2$ (*cf.*, $a = 10.41$ Å from a single crystal[14]), for which the calculated density ($a = 10.32$ Å) is 2.26 and observed 2.21 g/cm^3. Intensities of the powder lines from the N_2O and N_2 complexes were closely similar (14 lines observed).

$[Ru^{II}(NH_3)_5N_2O]Br_2$ reacted with O_2 and HBr giving an essentially quantitative yield of $[Ru^{III}(NH_3)_5Br]Br_2$. With ammonia, in an argon atmosphere, $[Ru^{II}(NH_3)_6]^{2+}$ was obtained by isolation of the iodide salt (64% yield); no other product could be isolated from the reaction.

At room temperature $[Ru^{II}(NH_3)_5NO]Cl_3$ and hydrazine hydrate gave $[Ru^{II}(NH_3)_5N_2]Cl_2$[15] only. A mixture of $[Ru^{II}(NH_3)_5N_2]^{2+}$ and $[Ru^{II}(NH_3)_5N_2O]^{2+}$ was obtained by two methods: (a) conducting the reaction between $[Ru^{II}(NH_3)_5NO]X_3 \cdot H_2O$ (X = Cl, Br, I) and hydrazine hydrate at temperatures from −40 to −23° and precipitating the mixed product within 30 sec, and (b) precipitating the products from solution as they formed by adding OH^- to a saturated solution of $N_2H_6I_2$ and $[Ru^{II}(NH_3)_5NO]I_3 \cdot H_2O$ at room temperature. When the low-temperature reaction was allowed to proceed for a longer period (approx 3 min) some $[Ru^{III}(NH_3)_5N_3]X_2$[15] (X = Cl, I) was obtained, in addition to the above products. The reaction between $[Ru^{II}(NH_3)_5{}^{15}NO]I_3 \cdot H_2O$ and $^{28}N_2H_4$, using method b gave a mixture containing $[Ru^{II}(NH_3)_5{}^{29}N_2]I_2$ and $[Ru^{II}(NH_3)_5{}^{14}N^{15}NO]I_2$ as determined from infrared spectroscopy ($\nu_3(N_2O)$ 2220 cm^{-1}, $\nu_1(N_2O)$ 1165 cm^{-1}, and $\nu(N_2)$ 2075 cm^{-1} [16]) and mass spectral analysis.

Discussion

(Dinitrogen oxide)pentaammineruthenium(II) Salts. The infrared spectra of the complexes in the NH_3 regions (Table I) were not unusual though no bands were observed between 700 and 400 cm^{-1}, where Ru–N vibrations would be expected. The reason for this is not clear. The N_2O vibrations are of some interest. The ν_1 vibration was shifted to lower energy on coordination (gaseous N_2O, $\nu_1 = 1286$ cm^{-1} [13]) and ν_3 was shifted to higher energy (ν_3 N_2O = 2224 cm^{-1} [13]). In addition, marked changes in the relative intensity of the bands were observed. For gaseous N_2O the relative intensity falls in the order $\nu_3 > \nu_1 > \nu_2$ but for coordinated N_2O, $\nu_1 \gg \nu_3 > \nu_2$ (ν_2 (589 cm^{-1} in gaseous N_2O[13]) was not observed for the complexes). Frequency shifts for ν_1 and ν_3 in the same direction as observed here were found in the infrared spectra of N_2O adsorbed on alkali-halide films,[18] and on α-Cr_2O_3,[19] but in both cases the relative intensities were the same as for gaseous N_2O. The bands were assigned to N_2O adsorbed *via* the oxygen atom.[18,19] Bands for which both ν_1 and ν_3 increased over the gaseous N_2O values were assigned to N_2O adsorbed on α-Cr_2O_3 *via* the nitrogen atom.[19] In the present work four modes of coordination of N_2O may be considered: N bonded, O bonded, and N,O-dimer formation[11] (all involving perpendicular N_2O coordination) and parallel coordination from the N_2O π bonds. The crystal symmetry effectively rules out N,O-dimer formation, and, while not conclusive, strongly favors a linear RuNNO group over the bent RuONN or parallel situations. The linear RuNNO group implies the $N{\equiv}N^+{-}O^-$ canonical form predominates in coordinated N_2O, and this is consistent with the frequency shifts on coordination. From the infrared spectra it appears unlikely there is extensive π-electron donation from ruthenium to N_2O, and this

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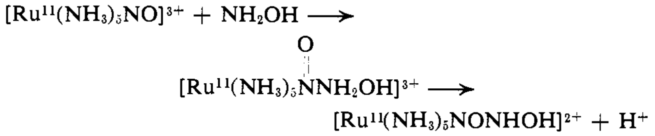
is borne out by the ease of displacement of N_2O in solution.

Mechanism of the Reaction between $[Ru^{II}(NH_3)_5NO]^{3+}$ and Hydroxylamine. $[Ru^{II}(NH_3)_5NO]^{3+}$ and $[Ru^{II}(NH_3)_5NO_2]^{+}$ coexist in equilibrium in aqueous alkaline solution.[4] Reductions of NO_2^- generally proceed through equilibrium amounts of NO^+ ions. For example, the reaction between nitrous acid and hydroxylamine

$$HNO_2 + NH_2OH \longrightarrow N_2O + 2H_2O$$

involves, as the first step, nitrosation of hydroxylamine by NO^+ giving $ONNH_2OH^+$.[20] By analogy the reaction of $[Ru^{II}(NH_3)_5NO]^{3+}$ with NH_2OH may be formulated as



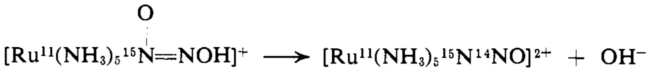
$$[Ru^{II}(NH_3)_5NO]^{3+} + NH_2OH \longrightarrow [Ru^{II}(NH_3)_5\overset{O}{\overset{\vdots}{N}}NH_2OH]^{3+} \longrightarrow [Ru^{II}(NH_3)_5NONHOH]^{2+} + H^+$$

$[Ru^{II}(NH_3)_5(NONHOH)]^{2+}$ may be compared to the intermediate π-$C_5H_5Fe(CO)_2(CONHNH_2)$ in the reaction of N_2H_4 and π-$C_5H_5Fe(CO)_3^+$. This, by loss of NH_3 and rearrangement, formed π-$C_5H_5Fe(CO)_2NCO$.[21] Such a rearrangement (with loss of H_2O) can be written for $[Ru^{II}(NH_3)_5(NONHOH)]^{2+}$, but clearly predicts $[Ru^{II}(NH_3)_5{}^{15}NO]^{3+}$ and ${}^{14}NH_2OH$ will give $[Ru^{II}(NH_3)_5{}^{14}N^{15}NO]^{2+}$

$$[Ru^{II}(NH_3)_5{}^{15}NONHOH]^{2+} \longrightarrow [Ru^{II}(NH_3)_5{}^{14}N^{15}NO]^{2+} + H_2O$$

whereas the major product was $[Ru^{II}(NH_3)_5{}^{15}N^{14}NO]^{2+}$.

Hughes and Stedman[20] suggest ONNHOH may give, by proton transfer, hyponitrous acid, HON=NOH. This corresponds (with loss of a proton) to $[Ru^{II}(NH_3)_5N({-}O){=}NOH]^{+}$, which may be compared to $[Ru^{II}Cl(das)_2N({-}O){=}NNH_2]$, believed to be intermediate in the formation of $[Ru^{II}ClN_3(das)_2]$ from $[Ru^{II}Cl(das)_2NO]^{2+}$ and N_2H_4.[1] $[Ru^{II}(NH_3)_5N_2O]^{2+}$ probably is formed by an analogous route



$$[Ru^{II}(NH_3)_5{}^{15}\overset{O}{\overset{\vdots}{N}}{=}NOH]^{+} \longrightarrow [Ru^{II}(NH_3)_5{}^{15}N^{14}NO]^{2+} + OH^-$$

Attempts to isolate an intermediate by reaction of $[Ru^{II}(NH_3)_5NO]^{3+}$ with CH_3NHOH, NH_2OCH_3, or CH_3NHOCH_3 were unsuccessful. In each case the only products were those expected for attack by OH^- on $[Ru^{II}(NH_3)_5NO]^{3+}$.[4]

Mechanism of the Reaction between $[Ru^{II}(NH_3)_5NO]^{3+}$ and Hydrazine. Using similar arguments to those for the hydroxylamine reaction, the probable first intermediate for the hydrazine reaction is $[Ru^{II}(NH_3)_5NONHNH_2]^{2+}$. This may lose NH_3 and rearrange to $[Ru^{II}(NH_3)_5N_2O]^{2+}$ or, by proton loss, give $[Ru^{II}(NH_3)_5N({-}O){=}NNH_2]^{+}$ and then $[Ru^{II}(NH_3)_5N_3]^{2+}$. $[Ru^{II}(NH_3)_5N_2O]^{2+}$ was observed, and, as predicted by the rearrangement mechanism, $[Ru^{II}(NH_3)_5{}^{15}NO]^{3+}$ and ${}^{28}N_2H_4$ gave $[Ru^{II}(NH_3)_5{}^{14}N^{15}NO]^{2+}$. $[Ru^{II}(NH_3)_5N_3]^{+}$ was not observed, though $[Ru^{III}(NH_3)_5N_3]^{2+}$ was. The latter could arise from oxidation of $[Ru^{II}(NH_3)_5N_3]^{+}$ by hydrazine.[22] $[Ru^{II}(NH_3)_5{}^{29}N_2]^{2+}$ was obtained from $[Ru^{II}(NH_3)_5{}^{15}NO]^{3+}$ and ${}^{28}N_2H_4$. This indicates the source of $[Ru^{II}(NH_3)_5N_2]^{2+}$ was a coordinated ligand, but whether NO^+, N_3^-, or N_2O was involved is unknown.

Experimental Section

Ruthenium trichloride hydrate was obtained from Johnson, Matthey and Mallory, Montreal. It was converted into $[Ru^{III}(NH_3)_6]^{3+}$ [23] and then to $[Ru^{II}(NH_3)_5NO]X_3 \cdot H_2O$[24] by the methods cited. ${}^{15}NO$ was purchased from Merck Sharp and Dohme. NH_3OHBr, NH_3OHI, $N_2H_6Br_2$, and $N_2H_6I_2$ were prepared by recrystallizing NH_3OHCl or $N_2H_6Cl_2$ from the appropriate hydrohalic acid. All other materials were reagent grade.

(Dinitrogen oxide)pentaammineruthenium(II) Dihalide, $[Ru^{II}(NH_3)_5N_2O]X_2$ (X = Cl, Br, I). To a solution of NH_3OHBr (1.0 g) and $[Ru^{II}(NH_3)_5NO]Br_3 \cdot H_2O$ (0.094 g) in water (9 ml) were added 5 pellets (1.0 g) NaOH. A pale yellow precipitate of $[Ru^{II}(NH_3)_5N_2O]Br_2$ formed as the NaOH dissolved, and as soon as NaOH dissolution was complete the precipitate was removed by filtration, washed with alcohol and ether, and dried *in vacuo* over P_2O_5, yield 0.057 g, 74%.

The chloride and iodide salts were prepared using the appropriate nitrosyl and hydroxylamine salts. Yields: chloride salt, 29%; iodide, 83%. Analyses are collected in Table II.

Table II. Analytical Data for $[Ru^{II}(NH_3)_5N_2O]X_2$

	Calcd, %			Found, %		
	H	N	X	H	N	X
$[Ru^{II}(NH_3)_5N_2O]Cl_2$	5.02	32.55	23.54	5.10	31.90	22.92
$[Ru^{II}(NH_3)_5N_2O]Br_2$	3.87	25.13	40.97	3.87	25.87	41.04
$[Ru^{II}(NH_3)_5N_2O]I_2$	3.12	20.26	52.43	3.14	20.84	52.10

Reaction of $[Ru^{II}(NH_3)_5N_2O]Br_2$ with O_2–HBr. $[Ru^{II}(NH_3)_5N_2O]Br_2$ (0.0105 g) was added to an O_2 saturated solution of HBr (48%, 1 ml) in water (20 ml). The mixture was gently heated, giving a bright yellow solution, which was diluted to 100 ml. The electronic spectrum of the solution (λ_{max} 398 nm, ϵ 1809; lit. λ_{max} 398 nm, ϵ 1920[25]) indicated a 94% yield of $[Ru^{III}(NH_3)_5Br]Br_2$. Evaporation of the solution gave orange crystals of $[Ru^{III}(NH_3)_5Br]Br_2$, whose spectra were in good agreement with the literature.[25,26] *Anal.* Calcd for $Br_3H_{15}N_5Ru$: N, 16.44. Found: N, 16.34.

Reaction of $[Ru^{II}(NH_3)_5N_2O]Br_2$ with NH_3. $[Ru^{II}(NH_3)_5N_2O]Br_2$ (0.0307 g) was added (with stirring) to degassed 0.880 NH_3 (5 ml). The resultant yellow solution was diluted to 100 ml with water. The electronic spectrum showed a band at 275 nm (lit. for $[Ru^{II}(NH_3)_6]^{2+}$, λ_{max} 275 nm, ϵ 624[27]); intrusion of a high-energy tail into this region made accurate determination of an extinction coefficient impossible. Addition of potassium iodide to the solution gave $[Ru^{II}(NH_3)_6]I_2$ (0.0230 g, 64%), whose infrared spectrum was in good agreement with the literature.[26] *Anal.* Calcd for $H_{18}I_2N_6Ru$: N, 18.39. Found: N, 18.30.

Reaction of $[Ru^{II}(NH_3)_5NO]^{3+}$ with Hydrazine. (a) With Hydrazine Hydrate at Room Temperature. $[Ru^{II}(NH_3)_5NO]Cl_3 \cdot H_2O$ (0.124 g) was dissolved in water (2 ml) and hydrazine hydrate (85%, 5 ml) added. The solution was stirred for 5 min and NH_4Cl added until precipitation of $[Ru^{II}(NH_3)_5N_2]Cl_2$ was complete. The precipitate was collected by filtration, purified by reprecipitating twice from water, washed with alcohol and ether, and dried *in vacuo* over P_2O_5, yield 0.045 g, 46%. The spectral properties of the product were in good agreement with the literature.[15] *Anal.* Calcd for $Cl_2H_{15}N_7Ru$: H, 5.30; N, 34.38. Found: H, 5.61; N, 34.12.

(b) With Hydrazine Hydrate at −23°. To a solution of hydrazine hydrate (85%, 4.5 ml) which had been cooled to −23° (CCl_4–liquid nitrogen) was added rapidly an ice-cold solution of $[Ru^{II}(NH_3)_5NO]Cl_3 \cdot H_2O$ (0.28 g) in water (10 ml). The solution was stirred for 10 sec and NH_4Cl added until precipitation was complete. The product was removed by filtration, washed with alcohol and ether, and dried *in vacuo* over P_2O_5, yield 0.19 g. The

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iodide and bromide salts were prepared by addition of NH_4Br or KI instead of NH_4Cl. The products were shown by spectroscopy {$\nu_1(N_2O)$, 1155 (Cl^- salt), 1160 (Br^-), 1175 cm^{-1} (I^-); $\nu_3(N_2O)$, 2235 (Br^-), 2250 cm^{-1} (I^-), unobservable for Cl^- salt; $\nu(N_2)$, 2100 (Cl^-), 2110 (Br^-), 2120 cm^{-1} (I^-);[15] $\nu_1(N_2O)$ and $\nu(N_2)$ were of comparable intensity, λ_{max} 221 ($[Ru^{II}(NH_3)_5N_2]^{2+}$) and 235 nm ($[Ru^{II}(NH_3)_5N_2O]^{2+}$); the latter band decreased rapidly and a new band appeared at 299 nm, due to $[Ru^{III}(NH_3)_5OH]^{2+}$ [28]} and analysis (Table III) to be mixtures of $[Ru^{II}(NH_3)_5N_2]X_2$ and $[Ru^{II}(NH_3)_5N_2O]X_2$, with the latter complex comprising, at maximum, 70% of the product.

Table III. Analytical Data for Mixed $[Ru^{II}NH_3)_5N_2O]X_2$–$[Ru^{II}(NH_3)_5N_2]X_2$ Product

	Calcd, %[a]			Found, %		
	H	N	X	H	N	X
$[Ru^{II}(NH_3)_5N_2]Cl_2$	5.30	34.38	24.86		33.80	23.55
$[Ru^{II}(NH_3)_5N_2]Br_2$	4.04	26.21	42.72	3.98	25.87	40.42
$[Ru^{II}(NH_3)_5N_2]I_2$	3.23	20.95	54.22	3.23	21.62	52.70

[a] The calculated percentages for $[Ru^{II}(NH_3)_5N_2O]X_2$ are given in Table II.

By a similar method, but stirring the cold solution for approximately 3 min before precipitating, brick red (Cl^-) or purple (I^-) salts were obtained. These salts, which showed paramagnetism, became pale yellow on setting aside. The infrared spectra showed a band at 2020 cm^{-1} in addition to those of $[Ru^{II}(NH_3)_5N_2]X_2$ and $[Ru^{II}(NH_3)_5N_2O]X_2$. The electronic spectrum showed a band at 460 nm which decreased with time. These properties indicated the presence of $[Ru^{III}(NH_3)_5N_3]^{2+}$.[15]

(c) **With $N_2H_6^{2+}$ and OH^- at Room Temperature.** To a solution of $[Ru^{II}(NH_3)_5NO]I_3 \cdot H_2O$ (0.089 g) and $N_2H_6I_2$ (1.0 g) in water (7 ml) were added four pellets (0.8 g) of NaOH. The precipitate which formed on dissolution of the NaOH was removed by filtration, washed with alcohol and ether, and dried *in vacuo* over P_2O_5, yield 0.040 g. The product was a mixture of $[Ru^{II}(NH_3)_5N_2O]I_2$ and $[Ru^{II}(NH_3)_5N_2]I_2$ in similar proportion to that obtained by method b above.

Electronic spectra were measured on a Hitachi-Perkin-Elmer EPS-3T instrument; infrared spectra (as Nujol or hexachlorobutadiene mulls between KBr plates) on a Beckman IR 12 instrument. Mass spectra were obtained, at ionizing voltages of 30 and 70 V, on a Hitachi-Perkin-Elmer RMU-6D instrument. Magnetic moments were by the Gouy method. Microanalyses were by A. Bernhardt, West Germany, and Chemalytics, Tempe, Ariz.

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Ground States of Molecules. XIX.[1] Carbene and Its Reactions[2]

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Abstract: MINDO/2 calculations are reported for singlet and triplet carbene and for their reactions with methane and ethylene. The energies of the various states of carbene have been calculated as a function of HCH bond angle. The results lead to the prediction that for small bond angles the singlet state becomes progressively favored. This prediction has been tested by calculations for cyclopropylidene, cyclopropenylidene, and vinylidene.

The divalent carbon compounds known variously as methylenes or carbenes have long fascinated organic chemists,[4] and numerous theoretical studies of them have been reported.[5]

It is now recognized that compounds of this kind can exist in both singlet and triplet states, and carbene itself has been shown[6–8] to have a triplet ground state, in agreement with recent *ab initio* SCF calculations.[5]

The reactions of singlet and triplet carbene have also aroused much interest, particular attention being paid to the mechanism and stereochemistry of insertion and addition reactions. Here the only detailed calculations are those recently reported by Hoffmann, *et al.*;[9] these, however, were carried out by a procedure ("extended Hückel" method) which is known to give very poor estimates of molecular energies.

Here we report calculations for singlet and triplet carbene and their addition and insertion reactions, using a procedure (MINDO/2[10]) which has been shown to

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