The values of $\Delta H^{\ddagger}$ for the acid-independent and acid-dependent paths, 24.9 and 22.9 kcal, are consistent with breaking relatively strong bonds, while the negative $\Delta S^{\ddagger}$ values, −9 and −14 eu for acid-independent and dependent, respectively, are appropriate for an activated complex in which solvent molecules participate.[21]

While the data do not differentiate the order of the bond breaking between carbon-chromium and carbon-fluorine, the experimental evidence does suggest a mechanism involving concerted action in breaking these two bonds. The data also suggest the involvement of a solvent molecule, H_2O, or other ions such as H^+ or Al^{3+} in the activated complex. These molecules or ions most probably form a bond with the fluorine in CF_3 and thereby affect the lability of the carbon-fluorine bond.

The aquation of $CrCF_3^{2+}$ increased in rate as the reaction proceeded, indicating that a product of the initial reaction was acting as a catalyst. This autocatalyst was identified as fluoride ion since the rate also increased when NaF was added. A pink +1 chromium species, $FCrCF_3^+$, was isolated from solutions of NaF and $CrCF_3^{2+}$, and this same species was also separated from solutions with low $[H^+]$ which originally contained only $CrCF_3^{2+}$. The $FCrCF_3^+$ ion is a possible means by which fluoride affects the aquation reaction. The following sequence is consistent with the data if the Cr–C bond in $FCrCF_3^+$ is more labile than that in $CrCF_3^{2+}$

$$CrCF_3^{2+} + HF \rightleftarrows FCrCF_3^+ + H^+ \tag{7}$$

$$FCrCF_3^+ + H_2O \xrightarrow{H^+} FCr^{2+} + CO + 3HF \tag{8}$$

where (7) is an equilibrium reaction which is rapidly established relative to the rate of aquation. The Cr–C bond could then be labilized by the fluoride ion in $FCrCF_3^+$. A similar mechanism has been postulated by Kochi[22] in his study of the aquation of benzylpentaaquochromium(III) ion. There are a number of reports that ligands such as iodide[23] and hydroxide[24] ion affect substitution rates in chromium complexes, although no similar studies have been done with fluoride ion.

The formation of $FCrCF_3^+$ is not sufficient to explain the kinetic data with added fluoride ion. The aquation rates in the presence of added F^- more than double for a twofold increase in fluoride, and zero-charged chromium species were detected in solutions containing higher amounts of added fluoride. This indicates that species such as F_2CrCF_3 might be formed and participate in the increase in aquation rate. However, species like F_2CrCF_3 are not likely to be important in the aquation of $CrCF_3^{2+}$ in the absence of added fluoride since the concentration of fluoride remained low (maximum of three times the original concentration of $CrCF_3^{2+}$).

The $FCrCF_3^+$ ion is rapidly formed when fluoride is added to solutions containing $CrCF_3^{2+}$. Rapid color changes are also noted when azide and thiocyanate ions are added to $CrCF_3^{2+}$. The CF_3 moiety must therefore exhibit a very pronounced labilizing effect on the other ligands in the inner coordination sphere of chromium(III). The labilization does not appear to be a trans effect since zero-charged species, F_2CrCF_3, are also rapidly formed. Observations on other organochromium(III) complexes indicate that the labilizing ability is a general property of the Cr–C bond and is not restricted to $CrCF_3^{2+}$. A study of the substitution rates in organochromium(III) complexes is now being made.

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Registry No. $Cr(OH_2)_5CF_3^{2+}$, 51652-63-2; $Cr(OH_2)_4FCF_3^+$, 51652-64-3; $Cr(OH_2)_6^{3+}$, 14873-01-9; HF, 7664-39-3.

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Reduction of Coordinated Nitrosyls. III. Alternative Routes to Chromium(III) Dimers and Evidence for Coordinated Hydroxylamine[1,2]

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The kinetics and mechanism of reduction of $Cr(NH_3)_5NO^{2+}$ by Cr^{2+} have been investigated. The reduction consumes 2 mol of Cr^{2+}/mol of $Cr(NH_3)_5NO^{2+}$, resulting in 1 mol of NH_3OH^+/mol of $Cr(NH_3)_5NO^{2+}$ consumed. However, the rate of reduction of $Cr(NH_3)_5NO^{2+}$ is only first order in the $[Cr^{2+}]$ and $[Cr(NH_3)_5NO^{2+}]$. The stoichiometry and the rate law are similar to those observed for the Cr^{2+} reduction of $Cr(H_2O)_5NO^{2+}$. Greater than 78% of the products consist of three different polymeric Cr(III) complexes. Some $[Cr(H_2O)_4OH]_2^{4+}$ is observed in the product mixture, but the use of the pentaammine in place of the pentaaquo complex produces two new additional polymeric products, which we suggest may be represented by the formula $(NH_3)_5Cr\text{-}X\text{-}Cr(H_2O)_4Y^{n+}$, $X = OH^-$ or NH_2OH, $Y = H_2O$ or NH_2OH. Hydroxylamine analysis of each of the eluents from the ion exchange of the product mixture indicates that at least 50% of the NH_2OH is initially held up in the highly charged fractions. This leads us to propose a metal complex containing coordinated hydroxylamine. These products demonstrate the existence of at least two separate paths for chromium dimer formation upon reduction of a chromium nitrosyl.

Introduction

Some efforts have been made to study the reduction of ligands containing nitrogen atom centers. Mukaida[3] and

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Griffith[4] studied the Sn^{2+} reduction of ruthenium nitrosyls. In the high-chloride medium, they obtained nitrido complexes of ruthenium. Later, Griffith investigated[4] the stoichiometric ratios of Cr^{2+}:Z (where Z = NO_3^-, NO_2^-, $Co(NH_3)_5ONO^{2+}$, $Co(NH_3)_5NO_2^{2+}$, and $Co(NH_3)_5NO^{2+}$) and obtained values of 5:1, 3:1, 3:1, 3:1, and 1:1, respectively. Fraser[5] further investigated the reduction of nitropentaammine complexes of Co(III) and Cr(III) by Cr^{2+}. With the Co(III) center, he observed that the consumption of the reactant was irregular.

We have been investigating the reduction of coordinated nitrosyls by a variety of reductants.[1,2,6,7] In an earlier paper, we discussed the reduction of $(H_2O)_5CrNO^{2+}$ by Cr^{2+} to yield >95% of a polymeric Cr(III) species which appeared to be the dimer $[Cr(H_2O)_4OH]_2^{4+}$ (I) with the quantitative production of hydroxylamine. A recent paper by Ogino, Tsukahara, and Tanaka[8] discussed the use of Sp-Sephadex C-25 for ion exchanging Cr(III) complexes. We now wish to discuss the products of the pentaaquochromium(III) system utilizing this improved separation technique. In addition, we shall discuss the reduction of a similar complex, $Cr(NH_3)_5NO^{2+}$, by Cr^{2+}. A comparison of the two systems indicates that several parallels exist in the reduction of the nitrosyl which now permit some further discussion about the mechanism of the reduction.

Experimental Section

Reagents. Solutions of $LiClO_4$, $HClO_4$, and $Cr(H_2O)_6^{3+}$ were prepared and/or standardized as outlined in a previous report.[1] Solid $[Cr(NH_3)_5NO](ClO_4)_2$ was prepared and twice recrystallized according to the procedure of Mori.[9]

Analysis. Hydroxylamine was analyzed spectrophotometrically (λ_M 368, ϵ 1.4 × 10^4 M^{-1} cm^{-1})[10] after forming the *p*-nitrobenzaldoxime. Neither chromium(III) nor $Cr(NH_3)_5NO^{2+}$ was found to interfere with this analytical method. Ammonium ion was analyzed after separating it from the product mixture *via* ion exchange on Dowex 50W-X8 (200–400 mesh).[11] Spectrophotometric analysis for NH_3 by the formation of the indophenol[12] (λ_M 628, ϵ ~6.6 × 10^{-4} M^{-1} cm^{-1}) was performed using NH_3-free water (distilled water was redistilled once from alkaline permanganate and then again from acidic dichromate). The analysis is very sensitive to impurities and the time intervals between addition of the various reagents. Standard NH_4^+ solutions were prepared by weighing a sample of NH_4Cl to the nearest milligram and preparing a solution of ~0.06 *M* NH_4^+. Aliquots of this stock solution were ion-exchanged in the same manner as the unknown solutions. The results of the analysis of the standard NH_4^+ solutions were used to prepare a curve of absorbance (628 nm) *vs.* $[NH_4^+]$. Chlorine water was prepared fresh before each analysis by saturating redistilled water with $Cl_2(g)$. Enough unknown solution to contain *ca.* 6 μmol of NH_4^+ (at pH 4–7) was added to 12.5 ml of saturated boric acid in a 25-ml volumetric flask. While swirling the solution, 2.5 ml of Cl_2 water was added, followed by the addition of 2.5 ml of the 8% phenol solution. The volumetric flasks were placed inside a stream bath and heated for exactly 3 minutes and then rapidly cooled in ice. After 5 min in the ice bath, 2.5 ml of 3 *M* NaOH was added with swirling and the solutions were diluted to 25.0 ml. A period of 5 minutes was allowed for the reaction to proceed to completion. Chromium was analyzed spectrophotometrically (λ_M 372, ϵ 4815 M^{-1} cm^{-1})[13] after oxidation in alkaline peroxide.

Kinetics. Most kinetic studies were performed under pseudo-first-order conditions. Although $Cr(NH_3)_5NO^{2+}$ is fairly stable (hours) with respect to decomposition at 25°, precautions were taken to minimize any secondary reactions due to decomposition products. The reaction medium containing H^+ and/or Li^+ was degassed with nitrogen in a Zwickel flask.[14,15] The Zwickel flask contained one neck which was stoppered with a heavy-wall septum cap. In this manner, the flask, the solution, and a 5-cm cell (connected to the exit of the gas flow from the flask) were degassed with nitrogen (Cr^{2+} scrubbed through an all-glass apparatus)[14] for 30 min. After quickly removing the septum cap, a weighed amount of $[Cr(NH_3)_5NO](ClO_4)_2$ was added driectly to the flask, and the solution was degassed for another 20 min. A known volume of Cr^{2+} was then injected into the solution (*via* a platinum needle), and the solution was transferred into the 5-cm cell by rotation of the four-way stopcock on the Zwickel flask. The cell was disconnected from the Zwickel flask, removed from the temperature bath, and transferred to the thermostated cell compartment of a Cary 14 recording spectrophotometer. A minimum of 30 sec was required from the initiation of the reaction until absorbance data could be collected. The rate constants obtained from the above procedure were the same as those obtained by degassing the $[Cr(NH_3)_5NO](ClO_4)_2$ in a glass side arm on the Zwickel flask. The side arm could be rotated 180°, thereby dumping the solid into the reaction medium, and the reaction was initiated upon the immediate addition of Cr^{2+}. The decay of $Cr(NH_3)_5NO^{2+}$ was followed at 470 nm using a fixed chart speed. All reactions were followed for $>10\tau_{1/2}$. Plots of ln $(A - A_\infty)$ *vs.* time were linear beyond $3\tau_{1/2}$ (A = absorbance at time t; A_∞ = final absorbance). Ionic strength was maintained with $LiClO_4$ and $HClO_4$. The acidity was maintained with $HClO_4$. A few reactions were also performed under second-order conditions where $[Cr^{2+}] = 2[Cr(NH_3)_5NO^{2+}]$. Most of our ion-exchange work was originally done using the Dowex resin. During the reviewing of the original manuscript, we uncovered the report discussing the use of a Sephadex ion-exchange resin. Product analyses were performed using both of these results.

Product Analysis. Two stages were detected in the development of the products of the reaction. (Refer to Figure 1.) Most of the product studies were done within a time period corresponding to $3\tau_{1/2}$ (2.5 hr at 10^{-2} *M* Cr^{2+}). An aliquot of the product solution was diluted and placed onto an ion-exchange column (Dowex 50W-X8, 200–400 mesh). The solution passing directly through the column (hereafter referred to as the "rinse") and the 0.8 *M* $HClO_4$ eluent (both containing little or no chromium) were used for NH_4^+ analyses. A solution of 2 *M* $HClO_4$ was used to separate a gray band from a pink band. The pink band (together with a small, blue-gray band) was eluted with 2.5 *M* $HClO_4$. Acidic (~0.01 *M* $HClO_4$) 2 *M* NaCl was used to separate a green band, and acidic, saturated NaCl was used to elute a rose-colored product. The spectra of the various eluents were compared with those previously reported for aquo and/or amine complexes of chromium.[1,16-18] All eluents except the saturated NaCl eluent could be characterized in this manner. Using Sp-Sephadex C-25 as our ion-exchange material, we were able to separate and isolate all the Cr(III) product without using NaCl eluents or [cation] > 2 *M*. Using columns of ~1.5 in. of Sephadex (~1 cm in diameter), we were able to isolate $CrNO^{2+}$ (with 0.1 *M* $HClO_4$–0.1 *M* $NaClO_4$), $Cr(H_2O)_6^{3+}$ (with 0.5 *M* $NaClO_4$–0.1 *M* $HClO_4$), the blue-violet Cr(III) dimer[19] (with 0.9 *M* $NaClO_4$–0.1 *M* $HClO_4$), and a green Cr(III) trimer[19] (with 1.5 *M* $NaClO_4$–0.1 *M* $HClO_4$) as reported earlier.[8] The additional bands observed on our Dowex resin were separated using different volumes of these eluents and a 2 *M* $NaClO_4$–0.1 *M* $HClO_4$ eluent to elute the rose-colored product observed above.

Analyses for NH_3OH^+ were performed on every one of the eluents. In an effort to characterize further the chromium product in the saturated NaCl eluent, the solution was treated with an equal volume of concentrated HCl. Upon ion exchange, the decomposition products could be identified. Attempts to isolate a solid product from the reaction mixture were only successful after allowing the solution (0.03 *M* Cr^{2+}, 0.015 *M* $Cr(NH_3)_5NO^{2+}$) to stand overnight (in the

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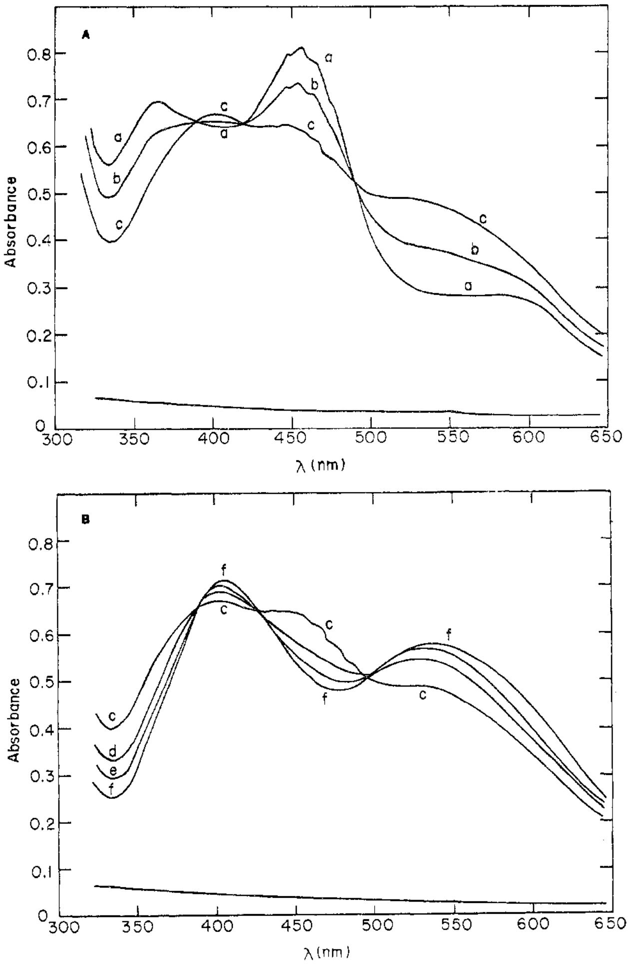

Figure 1. Reduction of 0.012 *M* $Cr(NH_3)_5NO^{2+}$ by 0.024 *M* Cr^{2+} ($[H^+] = 0.3$ *M*) in a glass-stopped 1 cm cell; $T = 25°$, $\mu = 1.3$: (A) first stage of reaction, a = 2.0 min, b = 7.0 min, and c = 23 min from the addition of Cr^{2+}; (B) second stage of reaction, c = 23 min, d = 55 min, e = 1.5 hr, and f = 2.3 hr from the addition of Cr^{2+}.

dark) in ~3 *M* $HClO_4$ saturated with $NaClO_4$. A 15% yield of $[Cr(NH_3)_5OH_2](ClO_4)_3$ (identified by its distinct visible spectrum)[16] was recovered from the product mixture. Room light did not appear to affect either the kinetics or the product distribution.

Results

The addition of Cr^{2+} to acidic solutions of $Cr(NH_3)_5NO^{2+}$ results in the slow decay of the nitrosyl complex as evidenced by the decay of the absorption of the nitrosyl at 450 and 330 nm. This is coupled with an increase in absorbance at ~400 and 530 nm (see Figure 1A). After this stage of the reaction appears to reach completion, a secondary reaction becomes more apparent, resulting in a shift in the absorbance at 530 nm (sh) into a band at 500 nm and a shoulder at 400 nm into a maximum at 410 nm. Isosbestic points are apparent at 675, ~490, 420, and 380 nm for the first stage of the reaction and 670, 500, 425, and 390 nm for the second stage of the reaction.

Ion exchange of product solutions of Cr^{2+}-$Cr(NH_3)_5NO^{2+}$ in ratios of 1:2, 1:1, 1.5:1, 2:1, and 2.5:1 at the end of the first stage of the reaction indicated a uniform reduction of the metal nitrosyl with complete reduction occurring at a ratio of 2:1 (using Dowex resin). Analysis of the product solutions for total NH_3OH^+ indicated that 1 mol of NH_3OH^+ was produced for every mole of $Cr(NH_3)_5NO^{2+}$ consumed. Further, the production of NH_3OH^+ was essentially quantitative within the first stage of the reaction in either 0.05 or 1.0 *M* $HClO_4$. Ion exchange of the product solution at $[Cr^{2+}] = 1.23 \times 10^{-2}$ *M* and $[Cr(NH_3)_5NO^{2+}] = 6.1 \times 10^{-3}$ *M* indicated that approximately half of the NH_3OH^+ was retained in the higher charged chromium(III) fractions. The bulk of this retained NH_3OH^+ was tied up in the saturated NaCl rinse. However, if the ion exchange is repeated 1 day later (well into the second stage of the reaction), essentially all the NH_3OH^+ is recovered in the rinse and/or 0.8 *M* $HClO_4$ eluent. The holdback of NH_3OH^+ appears unrelated to the pH of the solution. Similar behavior reflecting free and coordinated NH_2OH was noted using a Sephadex column with most of the retained NH_3OH^+ appearing in the 2 *M* $NaClO_4$-0.1 *M* $HClO_4$ eluent.

Table I. Ion-Exchange Separation of the Products from $Cr^{2+} + Cr(NH_3)_5NO^{2+\,a}$ on Dowex Resin

	% total Cr at various reacn times				
	2.5 hr	4.3 hr	21 hr	2 days	4 days
Rinse[b]	0	0	0	0	0
0.8 *M* $HClO_4$[c]	0.3	1	0.5	0.7	0.7
2.0 *M* $HClO_4$[c]	10	10	16	18	18
2.5 *M* $HClO_4$[c]	10	10	20	18	21
2 *M* NaCl[c]	18[e]	13[e]	20[e]	15[e]	20[e]
Sat NaCl[c,d]	54[e]	59[e]	45[e]	45[e]	40[e]
Total recovered	92	93	98	98	100

[a] $T = 25°$, $\mu = 1.3$, $[Cr^{2+}] = 1.23 \times 10^{-2}$ *M*, $[Cr(NH_3)_5NO^{2+}] = 6.1 \times 10^{-3}$ *M*, $[H^+] = 1.0$ *M*. [b] Reaction medium diluted and transferred onto column (50.0 ml). [c] 25.0 ml of eluent. [d] ~8 *M* NaCl. [e] These bands are very close, and the separation cannot be regarded to better than ±3%.

Table I describes the distribution of Cr (using the Dowex resin) in the product solution. In the initial stage of the reaction, some Cr is held in a small residue at the top of the column. However, the aged product solutions no longer display a residue at the top of the column, and all the Cr can be recovered.

From a knowledge of the elution[1,18-20] properties and visible spectra[1,15] of a variety of aquo and ammine complexes of chromium(III), the species rapidly removed with 2 *M* $HClO_4$ can be identified as $Cr(H_2O)_6^{3+}$. The pink 2.5 *M* $HClO_4$ eluent appears to have the features of $Cr(NH_3)_5OH_2^{3+}$ (contaminated with an unidentified blue-gray species). The light green species in the 2 *M* NaCl eluent has a spectrum similar to the primary product isolated from the $Cr(H_2O)_5NO^{2+} + Cr^{2+}$ reaction 1 and identified as the Cr dimer I. The spectrum of the saturated NaCl rinse (λ_M ~540 nm, ϵ 21 M^{-1} cm^{-1}; λ_M 410 nm, ϵ 24 M^{-1} cm^{-1}) does not appear to resemble any previously characterized chromium complex. Its elution with saturated NaCl suggests that it is more highly charged than the symmetrical aquo dimer in the 2 *M* NaCl eluent. We shall return to a study of this product using the Sephadex resin.

In 0.05 *M* $HClO_4$, ion exchange of the product solution at the end of the first stage of the reaction indicates the following approximate product distribution: residue:rose species: I:$Cr(NH_3)_5OH_2^{3+}$ + blue-gray species:$Cr(H_2O)_6^{3+}$ = 2:10:2:1:1. As compared to the product analysis at 1 *M* $HClO_4$, the larger ratio of the Cr in the saturated NaCl fraction to that in the 2 *M* NaCl fraction arises primarily out of a decrease in the yield of I. The yield of NH_3OH^+ displays the same behavior as noted in the more acidic medium.

When the rose-colored, saturated NaCl fraction is treated with concentrated HCl, a distinct color change from rose to gray occurs. Upon heating with HCl, the solution acquires a green tinge. Table II summarizes experiments for the decay

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Table II. Decay of Chromium Species in Saturated NaCl Rinse

	% total Cr[a,b]	
	No heating	Heat at 60° for 5 min
Rinse	15	32
0.5 *M* $HClO_4$	1	9
1.0 *M* $HClO_4$	5	9
2.5 *M* $HClO_4$	23	41
Sat NaCl	50	8

[a] ~10^{-2} *M* Cr(III); in 5 *M* HCl and ~4 *M* NaCl. [b] Separated on Dowex resin.

of the rose-colored chromium species in acidic chloride media. It is apparent that the complex decomposes into a variety of complexes. However, definite trends are noted: (1) the rinse and 0.5 *M* $HClO_4$ eluents are green (characteristic of chlorochromium complexes),[16] (2) the 2.5 *M* rinse is pink with a spectrum similar to that of $Cr(NH_3)_5Cl^{2+}$, and (3) the ratio of the sum of chromium in the rinse, the 0.5 *M* $HClO_4$, and the 1.0 *M* $HClO_4$ eluents to the chromium in the 2.5 *M* eluent is approximately 1:1.

Returning to Table I, it is apparent that the second stage of the reaction results in the decay of the rose-colored chromium complex. While the symmetrical Cr(III) dimer, I, remains almost unchanged, the yields of chromium in the 2 *M* rinse ($Cr(H_2O)_6{}^{3+}$) and the 2.5 *M* rinse ($Cr(NH_3)_5OH_2{}^{3+}$) increase equally with their sum corresponding to the decrease in chromium in the saturated NaCl rinse.

The use of the Sephadex ion-exchange resin to separate our product mixture (in 1.0 *M* $HClO_4$) confirmed the presence of multiple products as indicated already by our analysis with the Dowex resin. The 0.5 *M* $NaClO_4$-0.1 *M* $HClO_4$ rinse first moved a light blue band off followed closely by a light pink band. The separation of these two products is difficult. A small volume of the 0.9 *M* $NaClO_4$-0.1 *M* $HClO_4$ rinse can be used to obtain most of the pink material. Once the pink material is isolated, more of the 0.9 *M* $NaClO_4$ rinse can be used to isolate a blue-green species (λ_M 575 nm, ϵ 17; λ_M 418 nm, ϵ 21) with, perhaps, a trace of light green above the blue-green band. This leaves a broad lavender band halfway down the Sephadex column with a rose-colored band at the very top. The lavender band (λ_M 553 nm, ϵ 21; λ_M 410 nm, ϵ 26) was not observed on the Dowex resin, and it probably was obscured by the rose-colored band. The 1.5 *M* $NaClO_4$-0.1 *M* $HClO_4$ rinse separates most of the lavender band from the rose-colored band, although the separation is difficult. The 2 *M* $NaClO_4$-0.1 *M* $HClO_4$ rinse then removes the remaining rose-colored Cr product (λ_M 515 nm, ϵ 22; λ_M 398 nm, ϵ 23). Thus, at least five different products can be isolated. The Sephadex column is capable of separating the last band which remained on the Dowex resin (prior to the 8 *M* NaCl rinse). In general it appears that the Sephadex resin is not suitable for clearly separating the lower charged bands (as is the Dowex resin), but it is superior to the Dowex resin in separating highly charged (and/or polymeric) Cr(III) species. Table III describes the separation of the Cr(III) products (on Sephadex) with time. Note that the amounts of the blue-green species (*e.g.*, the 2 *M* NaCl rinse on Dowex and the 0.9 *M* $NaClO_4$-0.1 *M* $HClO_4$ rinse on Sephadex) correspond fairly well. From the color on the resin, the elution behavior of the blue-green band, and spectral comparisons with the blue-green dimer produced *via* $O_2 + Cr^{2+}$, we conclude that these rinses correspond to the symmetrical Cr(III) dimer I. The sum of the Cr in the 1.5 *M*-0.1 *M* $NaClO_4$ and 2.0 *M* $NaClO_4$-0.1 *M* $HClO_4$ eluents (on Sephadex) corresponds to the Cr in the saturated NaCl rinse (on Dowex). The slow decay of the species observed (upon elution with saturated NaCl) using the Dowex resin appears primarily associated with the 2.0 *M* $NaClO_4$-0.1 *M* $HClO_4$ rinse on the Sephadex column. The lavender species observed on the Sephadex column does not appear to decay appreciably with time in comparison with the rose-colored species.

Table III. Separation of Cr(III) Products on Sephadex[a]

	% total[b] Cr at various reacn times			
	2.5 hr	4 hr	24 hr	5 days
Rinse	0.4	0.1	0.2	0.1
0.5 *M* $NaClO_4$	3.3[c]	6.1[c]	14.4[c]	25.0[c]
0.9 *M* $NaClO_4$	8.4[c]	10.4[c]	10.0[c]	12.0[c]
0.9 *M* $NaClO_4$-II	17.7	15.9	19.2	27.0
1.5 *M* $NaClO_4$	36.9[c]	41.4[c]	36.8[c]	35.7
2.0 *M* $NaClO_4$	33.4[c]	26.0[c]	19.4[c]	*d*

[a] $T = 25°$, $\mu = 1.3$, $[Cr^{2+}] = 1.9 \times 10^{-2}$ *M*, $[Cr(NH_3)_5NO^{2+}] = 9.5 \times 10^{-3}$ *M*, $[H^+] = 1.0$ *M*. [b] Total recovery of Cr is 95–100%; volume each eluent is 15 ml diluted to 25.0 ml for analysis. [c] These bands are very close to one another, and the separation is only approximate. [d] No band observed.

As noted earlier, the Sephadex resin indicated that the NH_2OH in the highly charged Cr(III) products (early in the reaction) is concentrated primarily in the rose-colored 2.0 *M* $NaClO_4$-0.1 *M* $HClO_4$ fraction—not the lavender 1.5 *M* $NaClO_4$-0.1 *M* $HClO_4$ fraction. Thus, the decay of the Cr(III) product in the 2.0 *M* $NaClO_4$-0.1 *M* $HClO_4$ fraction parallels the decrease of coordinated NH_2OH in the highly charged Cr(III) products (or the added increase in free NH_2OH) with time.

Analysis of the product solution (from the Cr^{2+} reduction of $Cr(NH_3)_5NO^{2+}$) for the presence of free NH_4^+ indicated that 70 ± 10 μmol of NH_4^+ was released upon treatment of 61 μmole of $Cr(NH_3)_5NO^{2+}$ with 123 μmol of Cr^{2+} (during the first stage of the reaction). Further, the release of NH_4^+ was not markedly enhanced well into the second stage of the reaction. The results are similar in both 1.0 and 0.05 *M* $HClO_4$.

Product Analysis on $Cr(H_2O)_5NO^{2+} + Cr^{2+}$. Repeating the reaction between Cr^{2+} and $Cr(H_2O)_5NO^{2+}$ and separating the products on a Sephadex column, we observed both a blue-green product and a green product (a green product was reported by Ogino, *et al.*[8]). The amount of blue-green material increases from 4% at 90% into (30 min) the reaction to 24% of the total Cr(III) after 24 hr. The blue-green material has elution characteristics of the Cr dimer[19] I. The green polymeric material (λ_M 585 nm, 19; λ_M 423 nm, ϵ 27) formed initially in the reaction has a visible spectrum similar to (but not identical with) the "chromium trimer" reported earlier by Laswick and Plane.[19] However, it cannot be exactly the same since ~50% of NH_2OH is retained in the 0.9 *M* $NaClO_4$-0.1 *M* $HClO_4$ and 1.5 *M* $NaClO_4$-0.1 *M* $HClO_4$ rinses after 90% reaction. However, no significant amount of NH_2OH is retained on the column after 5 hr, and it appears that coordinated NH_2OH from the reduction of $Cr(H_2O)_5NO^{2+}$ by Cr^{2+} is retained somewhat less tightly than that from the $Cr(NH_3)_5NO^{3+}$ reduction. Our earlier report on the products of Cr^{2+} reduction of $Cr(H_2O)_5NO^{2+}$ dealt with the products obtained after at least 0.5 day of reaction [as opposed to the 40 min (90% into the reaction) discussed above]. Thus, it appears that with $Cr(H_2O)_5NO^{2+}$ as the reactant, some coordinated NH_2OH is produced but it readily decomposes to yield the Cr dimer, $Cr(H_2O)_6{}^{3+}$, and free NH_3OH^+. However, large amounts of this green polymeric product are not observed in the $Cr(NH_3)_5NO^{2+}$ reaction.

Table IV. Kinetics of the $Cr^{2+} + Cr(NH_3)_5NO^{2+}$ Reaction

$[Cr^{2+}]$,[a] M	$[H^+]$, M	No. of runs	10^2k,[b] M^{-1} sec^{-1}
0.204	0.0550	6	6.0 ± 0.5
0.204	0.0524	3	6.2 ± 0.4[c]
0.0408	1.02	4	5.3 ± 0.2
0.0408	0.540	4	5.8 ± 0.3
0.0408	0.114	3	6.5 ± 0.2
0.0408	0.0574	6	7.0 ± 0.5
0.0408	0.0339	2	7.6 ± 0.1
0.0408	0.0205	2	7.9 ± 0.1
0.0408	0.0165	3	8.3 ± 0.2
0.0144	1.18	2	6.4 ± 0.2[d]
0.0144	0.108	5	7.8 ± 0.6
0.0144	0.0345	2	7.8 ± 0.2[d]
0.0144	0.0170	2	8.0 ± 0.4
0.0144	0.0086	2	8.8 ± 0.1
0.0408	1.03	3	1.6 ± 0.1[e]
0.0408	0.0339	3	2.7 ± 0.2[e]
0.0408	0.0165	3	3.1 ± 0.2[e]
0.0408	1.03	3	1.10 ± 0.05[f]
0.0408	0.0339	3	1.44 ± 0.09[f]
0.0408	0.0165	3	1.69 ± 0.02[f]

[a] $[Cr(NH_3)_5NO^{2+}] \approx 7 \times 10^{-4}$ M, $\mu = 1.3$, λ 470 nm, and $T = 24.8°$, unless otherwise specified. [b] Second-order rate obtained from the observed pseudo-first-order rate constant divided by $[Cr^{2+}]$. If $\leqslant 3$ runs, the ± values represent the range of data points around the mean; otherwise, ±1σ. [c] Also at $[Cr(NH_3)_5NO^{2+}] = 1.3 \times 10^{-2}$ M. [d] Also at $[Cr(NH_3)_5NO^{2+}] = 7.2 \times 10^{-3}$ M (second-order reaction). [e] 10.3°. [f] 35.0°.

Table V. Values of k_1 and k_2 as a Function of Temperature[a]

T, °K	10^2k_1,[b] M^{-1} sec^{-1}	10^4k_2,[b] sec^{-1}
283.5	1.7 ± 0.1	2.7 ± 0.3
298.0	5.7 ± 0.1	4.8 ± 0.4
308.2	11.2 ± 0.4	9.1 ± 0.9

[a] At $[Cr^{2+}] = 0.0408$ and 0.0144 M. [b] Errors are reported within ±1 standard deviation. The slope and intercept were obtained from a linear, least-squares fit of the data.

Kinetics. Table IV summarizes the rate constants for the decay of $Cr(NH_3)_5NO^{2+}$ at 470 nm. All rates were measured at $\mu = 1.3$. Within the error limits attached to our rate constants (±8%), the rate law is first order in $Cr(NH_3)_5NO^{2+}$ and Cr^{2+}. The Cr^{2+} dependence was established under both pseudo-first-order and second-order conditions. The rate constants determined under second-order conditions (24.8°, $[Cr^{2+}] = 2[Cr(NH_3)_5NO^{2+}] = 3.8 \times 10^{-3}$ M, $[H^+] = 1.2$-0.030 M) were consistent with the values in Table IV. At very high levels of Cr^{2+}, the second-order rate constants were not exactly the same as those reported at 0.04 and 0.01 M Cr^{2+}, but the former values lie closely within the error limits associated with the other rates reported in Table IV. Unfortunately at 0.20 M Cr^{2+}, we were observing relatively fast reactions on the Cary 14 with very small absorbance changes ($\Delta A \leqslant 0.1$). Considering the size of the Cr^{2+} ion (and the Zn^{2+}), part of the difference in rate constants at high and low levels of Cr^{2+} may be attributed to the inappropriate substitution[21] of Li^+ for Zn^{2+} to maintain $\mu = 1.3$. We did try some runs at low Cr^{2+} with Zn^{2+} in place of Li^+ ($\mu = 1.3$). Apparent differences in second-order rate constants were within our error limits. Because of the limitations of ionic strength and the aquation of $Cr(NH_3)_5NO^{2+}$ at very low Cr^{2+}, we were unable to test adequately for a more complicated dependence of our rate law upon Cr^{2+}. Thus, the spectrum of the product solutions and the similarity of the rate constants under both limiting and excess Cr^{2+} concentrations establish the following general rate law indicated as the major path for reduction of the nitrosyl. The rate studies were further complicated by a small, but significant, dependence of the reaction upon $1/[H^+]$. Between 0.0165 and 1.18 M $HClO_4$, the rate of decay of $Cr(NH_3)_5NO^{2+}$ (at 0.04 or 0.01 M Cr^{2+}) displays an inverse acid behavior. Thus the total rate law for the Cr^{2+} reduction of $Cr(NH_3)_5NO^{2+}$ can be best represented by

$$\frac{-d[Cr(NH_3)_5NO^{2+}]}{dt} = [k_1 + k_2/[H^+]][Cr^{2+}][Cr(NH_3)_5NO^{2+}]$$

The values of k_1 and k_2 as a function of temperature are listed in Table V. The plots of k_{obsd}, M^{-1} sec^{-1}, *vs.* $1/[H^+]$ are very similar to those obtained in our earlier report.[1] A few experiments at λ 330 nm ($T = 24.8°$), following the decay of $Cr(NH_3)_5NO^{2+}$, indicate a similar second-order rate constant of 6×10^{-1} M^{-1} sec^{-1} (1 M H^+). The rate of formation of the initial product at λ 530 nm was slightly faster, 8×10^{-2} M^{-1} sec^{-1} ($T = 24.8°$, 1 M H^+).

The Eyring plots for each of the reaction paths indicate $\Delta H_1^{\ddagger} = 12.7 \pm 0.8$ kcal/mol (the errors are assigned assuming the two most extreme alternatives for plotting the values of ln (k/T) *vs.* $1/T$), $\Delta S_1^{\ddagger} = -22 \pm 3$ eu, $\Delta H_2^{\ddagger} = 7.6 \pm 1.5$ kcal/mol, and $\Delta S_2^{\ddagger} = -48 \pm 5$ eu.

Discussion

The kinetics of the decay of $Cr(NH_3)_5NO^{2+}$ at 470 nm suggest two paths for the reduction of the coordinated nitrosyl. Both paths are first order in the reductant and the nitrosyl, despite an overall two-electron reduction of the metal nitrosyl. The inverse acid path only contributes about 1% to the product at 1 M $HClO_4$. For simplicity, we will discuss the product distribution and the mechanism of the reaction without regard to this path; however, we will return to it at the end of the Discussion.

The kinetics of the reaction followed at 530, 470, or 330 nm correspond to the first stage of the reaction as illustrated in Figure 1A. The ion-exchange data of Table I and Figure 1B correspond to the very slow second stage of the reaction.

The 2:1 stoichiometry of the Cr^{2+}-$Cr(NH_3)_5NO^{2+}$ reaction suggests that the further reduction of hydroxylamine is not significant. Taube and coworkers[22] have studied the reduction of free NH_3OH^+ by Cr^{2+} and observed a much slower rate (1.5×10^{-2} M^{-1} sec^{-1}, 25°, $\mu = 1.3$) than we report for the reduction of the coordinated nitrosyl. Thus, in excess Cr^{2+}, we would expect a further, slower reduction of NH_3OH^+ to NH_4^+. Our studies have not been directed to this point, since we are concerned with the reduction of the coordinated nitrosyl.

To a first approximation, the ν_{NO} frequency[23] at 1730 cm^{-1} and the characteristic d-d spectrum of the $Cr(NH_3)_5NO^{2+}$ complex are consistent with the charge assignment Cr^{III}-(NO^-). For the sake of argument, we will view the complex in this form of the valence tautomer, although Cr^I-(NO^+) cannot be ruled out. Viewed in this way, a 2 e$^-$ reduction of Cr^{III}-(NO^-) should result in Cr(III) and NH_3OH^+, which corresponds to our gross product distribution.

From the results of the ion-exchange behavior, the spectra, the decomposition in concentrated HCl, the slow decay into $Cr(H_2O)_6^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$, the small amounts of NH_4^+ produced in the first stage of the reaction, and the separation of the products using both Dowex and Sephadex resins,

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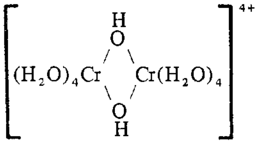
$$Cr^{2+} + Cr(NH_3)_5NO^{2+} \xrightarrow{H^+} NH_3OH^+ + NH_4^+ +$$

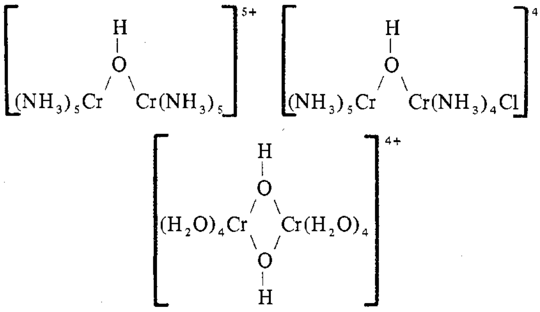
2 : 1



$$\text{polymer I} + \text{polymer II }(NH_2OH) + \left[(H_2O)_4Cr\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\;}}Cr(H_2O)_4\right]^{4+} + Cr(H_2O)_6^{3+} + Cr(NH_3)_5OH_2^{3+} \qquad (1)$$

approximate Cr ratio: 4 : 4 : 2 : 1–0.5 : 0.5–1

the rose-colored chromium complex in the saturated NaCl fraction can best be described as a mixture of two Cr(III) polymers, one polymer containing coordinated NH_2OH. The small amounts of free NH_4^+ produced in the reaction and the decomposition of the rose-colored (Dowex eluent) fraction in Cl^- suggest that these polymers may be unsymmetrical dimers, *e.g.*, $(NH_3)_5Cr\text{-}X\text{-}Cr(H_2O)_4Y^{n+}$, $X = OH^-$ or $NHOH^-$ and $Y = H_2O$ or NH_2OH. A variety of Cr(III) dimers have been prepared including[15,24]



$$\left[(NH_3)_5Cr\overset{\overset{H}{O}}{\;}Cr(NH_3)_5\right]^{5+} \quad \left[(NH_3)_5Cr\overset{\overset{H}{O}}{\;}Cr(NH_3)_4Cl\right]^{4+} \quad \left[(H_2O)_4Cr\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\;}}Cr(H_2O)_4\right]^{4+}$$

However, our products may also be trimeric species since the "Cr trimer" readily moves off a Sephadex resin with 1.5 *M* $NaClO_4$-0.1 *M* $HClO_4$.

While we cannot precisely discriminate between tetraammine (oxo- or μ-hydroxy-bridged dimer) and pentaammine forms of our polymeric products, one should recall that we only observed a small amount of free NH_4^+ in our product mixture. Even this small amount can be envisioned as arising from the aquation of one of our products which ultimately yields "Cr dimer" and/or $Cr(H_2O)_6^{3+}$. While hydroxylamine complexes of Cr(III) have not been observed in the past, NH_2OH is a sufficiently good Lewis base, and it should be capable of remaining bonded to the substitution-inert Cr(III) center following the electron-transfer process. The rates of aquation of other nitrogen-containing ligands on aquochromium(III) centers are somewhat slower than the apparent rate of aquation of our hydroxylamine complex above [$Cr(H_2O)_5NH_3^{3+}$, $\tau_{1/2}(45°, 0.005\ M\ HNO_3) \approx 4 \times 10^3$ hr;[25] $Cr(H_2O)_5py^{3+}$, $\tau_{1/2}(25°, 1\ M\ HClO_4) = 1.5 \times 10^4$ hr[26]]. Our polymeric, hydroxylamine product may appear to aquate faster because (1) it may be O-bonded NH_2OH, (2) the NH_2OH complex may be inherently unstable (recall that no stable complex of NH_2OH was obtained in the Cr^{2+}-$Cr(H_2O)_5NO^{2+}$ system), or (3) the small amounts of Cr^{2+} (unconsumed in the latter stages of the stoichiometry studies) may serve to catalyze the aquation of coordinated NH_2OH.[25]

The appearance of at least five chromium-containing products complicates a precise description of the stoichiometry of the reduction of the metal nitrosyl by Cr^{2+} (reaction 1). However, recalling that >75% of the chromium(III) exists initially in the form of "dimers" helps to simplify the arguments. Further, Cr^{2+} and/or H^+ are known to catalyze the cleavage of chromium-ammine dimers.[27] Thus, even at low concentrations of Cr^{2+} present in a product study, Cr^{2+} may be capable of catalyzing the aquation of the unsymmetrical dimer. This would explain the production of the small but comparable amounts of $Cr(H_2O)_6^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$.

The observation that the redox reaction consumes 2 equiv of Cr^{2+}/ equiv of the metal nitrosyl but requires only 1 equiv of Cr^{2+} in the rate-determining step (RDS) has also been obtained for the reaction

$$4Cr^{2+} + 2Cr(H_2O)_5NO^{2+} \xrightarrow{H^+} \text{polymer III} + 2NH_3OH^+ \qquad (2)$$

The rate law for reaction 2 is very similar to that observed for reaction 1 with even similar activation parameters (reaction 2 is about twice as fast as reaction 1). It now appears that our original suggestion[1] of polymer III as possibly the Cr(III) dimer was incorrect. The elution properties of polymer III on the white Sephadex resin and the uv-vis spectrum of polymer(III) resemble more closely the Cr trimer.[19] (We have prepared the Cr trimer as described by Laswick and Plane[19] and observed its elution with 1.5 *M* $NaClO_4$-0.1 *M* $HClO_4$ on a Sephadex resin.) As noted earlier, polymer III cannot be identical with the Cr trimer, but perhaps polymer III resembles the Cr trimer differing only by the presence of coordinated hydroxylamine.

Recall that $Cr(H_2O)_5NO^{2+}$ gave only one polymeric product, yet $Cr(NH_3)_5NO^{2+}$ gave three different polymeric products. The difficulties encountered in explaining both the rate laws and the product distributions for both reactions may be linked to the fact that after the rate-determining step several different pathways exist for producing the polymeric Cr(III) product. The use of $Cr(NH_3)_5NO^{2+}$ as the reactant provides a "label" for the original nitrosyl chromium atom. Thus, one can possibly view the production of unsymmetrical amineaquo dimers as resulting from the attack of Cr^{2+} upon the complex formed in the RDS. This trimeric species must have a very short lifetime and actually can be viewed as resulting from Cr^{2+} attack upon the dimer (from the RDS) at several possible sites—thus providing an explanation for the alternative polymeric products which we obtain (see eq 3). Alternatively, the polymeric species thus produced may undergo hydrolysis by several different paths in order to account for numerous dimeric products. Momentarily viewing one of the chromium atoms in III as Cr^{IV} also enables one to explain the $\overset{H}{-O-}$ bridge product formed in both reactions 1 and 2. The assignment of the oxidation states on II as +4 and +2 is purely hypothetical. One could view the oxidation states as +3 and +3. The use of a +4 chromium center permits us to draw a parallel to the early work on the reaction between O_2 and Cr^{2+}. The production of I in reaction 3 is thought to proceed *via* the attack of Cr^{2+} upon Cr(IV).[18]

If one takes the view that Cr^{2+} reduction of $Cr(H_2O)_5NO^{2+}$

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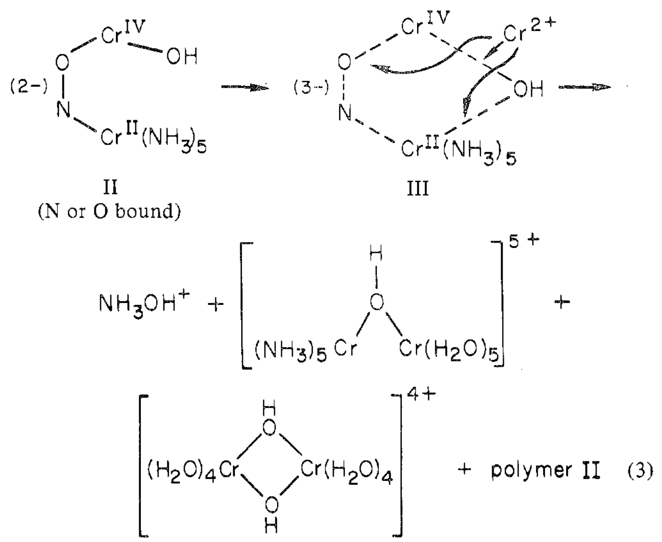

II (N or O bound)

III

(3)

or $Cr(NH_3)_5NO^{2+}$ should proceed by similar mechanisms (based on similar rate behavior and the large yields of dimer), then no satisfactory conclusion can be made about the mechanism beyond the rate-determining step. However both reactions produce primarily Cr(III) polymers and give rise to unstable, coordinated NH_2OH complexes.

One possible explanation for the small contribution which the $1/[H^+]$ term in the rate law makes to the overall reaction may be a preequilibrium involving a protonated nitrosyl

$$(NH_3)_5CrNOH^{3+} \rightleftharpoons (NH_3)_5CrNO^{2+} + H^+ \qquad (4)$$

While we have no spectrophotometric evidence to indicate protonation of the nitrosyl, reaction 4 cannot be ruled out on the basis of the Lewis basicity of NO^-.[28] If reaction 4 is important, it predicts that a substantial amount of the nitrosyl is protonated at 1 *M* $HClO_4$, while the unprotonated form becomes important beyond pH 2.

Unlike the reduction of coordinated nitro complexes, the reduction of the nitrosyls appears to be cleanly controlled with relation to the overall stoichiometry. Although the sequence of reactions occuring after the rate-determining step has not been solved, one can conclude that (1) large amounts of polymeric chromium(III) species are produced upon reduction of the chromium nitrosyls and (2) there is more than one pathway to dimer (or trimer) formation. A dramatic difference is observed for the products of the Cr^{2+} reduction of ruthenium nitrosyls[6] (NH_3) as compared with the chromium nitrosyls (NH_2OH), and this emphasizes the control that the metal center has on the extent of the reduction of the nitrosyl ligand.

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Registry No. Cr^{2+}, 22541-79-3; $Cr(NH_3)_5NO^{2+}$, 14951-33-8.

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Contribution from the "Groupe d'Etude et d'Application des Complexes metalliques,"
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Dinuclear-Bridged d^8 Metal Complexes. III. Behavior of the $[RhCl(CO)(C_2H_4)]_2$ Compound toward Amines[1]

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The complex $[RhCl(CO)(C_2H_4)]_2$ provides an excellent starting material for the preparation of $[RhCl(CO)L]_2$ complexes where L = diethylamine, *n*-propylamine, pyridine, and 3,5-lutidine. The $RhCl(CO)(\alpha\text{-pic})_2$ and $RhCl(CO)(C_2H_4)(2,6\text{-lut})$ (pic = picoline; lut = lutidine) compounds are also prepared and the role of steric requirements of entering ligands is shown. The $RhCl(CO)(PR_3)(2,6\text{-lut})$ derivatives are obtained from $RhCl(CO)(C_2H_4)(2,6\text{-lut})$ or $[RhCl(CO)PR_3]_2$ complexes by action of PR_3 or 2,6-lutidine, respectively. Isolation of the $[RhCl(CO)(C_2H_4)(NHEt_2)]_2$ compound affords strong evidence for the general scheme of reaction mechanisms previously suggested. A rationalization of results obtained with phosphine and amine ligands is proposed.

Introduction

Di-μ-chloro-tetracarbonyldirhodium undergoes chloro-bridge splitting by amines L to give the mononuclear species *cis*-$RhCl(CO)_2L$.[2,3] Any attempt to obtain further direct substitution of a carbonyl group was unsuccessful and, in the particular case of $L = NC_5H_5$,[3] excess of ligand leads to the $RhCl(CO)_2L_2$ compound. Dinitrogen-containing ligands not only brought about the splitting but also acted as bridges between the two dicarbonylrhodium(I) moieties.[3-6] In addition, the reactivity of amines toward di-μ-chloro-di-η-1,5-cyclooctadienedirhodium has been extensively studied;[7-10] splitting of the bridge occurs to form $C_8H_{12}RhClL$,[7,8] and further addition of ligand leads to cationic species $[C_8H_{12}RhL_2]^+$.[8,10] By carbonylation $[Rh(CO)_2L_2]^+$ complexes

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