Notes

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Coordinated Benzyl Radical Derivatives: Reaction of Chromium(II) with Complexes of Pentaamminecobalt(III) and 4-Cyano- and 4-Carbamoylbenzyl Bromide

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Previous work[2-4] indicates that derivatives of the benzyl radical coordinated to cobalt(III) can be generated by the pathways shown in Scheme I. The upper reaction is based on the original preparation[2] of $(H_2O)_5CrCH_2C_6H_5^{2+}$ and involves initial halogen atom abstraction. The lower reaction is homolysis of the $Cr-CH_2$ bond, which has been studied in some detail.[3,4] In the present work these reactions have been explored for the systems Y ≡ 4-NC– (I) and Y ≡ 4-NHC(OH)– (II).
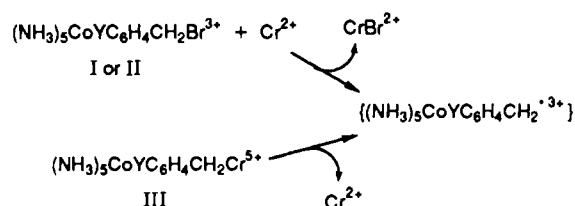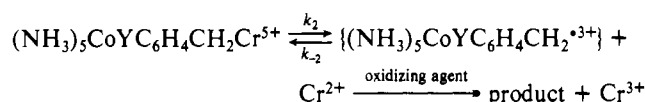
Aside from the previously described decomposition modes of the benzyl radical,[3,4] the radical coordinated to cobalt(III) may undergo intramolecular electron transfer to produce cobalt(II). This process has been observed in radiolysis studies of nitrophenyl derivatives,[5] imidazole,[6] and pyridinyl derivatives.[7] In the latter case, the reaction may be intra- or intermolecular depending on the structure of the ligand. Reactions of radicals with their pentaamminecobalt(III) parents have been observed by Gould[8] and Balahura[9] and co-workers. The intermolecular pathway is unlikely with benzyl systems because Nohr and Espenson[4] found that the benzyl radical dimerizes in preference to reacting with $Co(en)_3^{3+}$ or $Co(NH_3)_5Cl^{2+}$.

Results

Kinetics of Reactions with Cr(II). When 5×10^{-5} M I and 5 $\times 10^{-3}$ M Cr(II) react in aqueous acid under an argon atmosphere, the solution changes from pale yellow to reddish yellow in a few minutes. In the electronic spectrum, new peaks appear at 320, ~420 (shoulder), and 580 nm with final absorbance ratios of 6:1:0.3, respectively. These changes are consistent with formation of the $CrCH_2C_6H_4–$ chromophore.[10,11] If only the cobalt(III) were being reduced, the absorbance should decrease throughout the 300–500-nm region.

The reaction kinetics were monitored at 320 and 420 nm at 25 °C in 1.0 M $NaClO_4/HClO_4$ with [Cr(II)] ≫ [Co(III)]. The rate is first order in [Cr(II)] $((1.6–8.0) \times 10^{-3}$ M) and independent of [H⁺] (0.11–0.80 M). The rate constant (M^{-1} s^{-1}) is 2.4 ± 0.1 for I and 1.2 ± 0.06 for II.

Identification of $(NH_3)_5CoNCC_6H_4CH_2Cr(OH_2)_5^{5+}$ (III). The major product of the reaction of I and Cr(II) is believed to be III. The details of the product distribution are described in a following section. The high charge of III is consistent with the fact that it is eluted from Sephadex SP-C25 only with >1.0 M

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(2) Anet, F. A. L.; Blanc, E. *J. Am. Chem. Soc.* **1957**, *79*, 2649.
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(4) Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.
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(8) Srinivasan, V. S.; Hu, Y.-R.; Gould, E. S. *Inorg. Chem.* **1980**, *19*, 3740.
(9) Lewis, N. A.; Balahura, R. J. *Inorg. Chim. Acta* **1987**, *130*, 151.
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Scheme I

Scheme II

$$(NH_3)_5CoYC_6H_4CH_2Cr^{5+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \{(NH_3)_5CoYC_6H_4CH_2^{\cdot3+}\} +$$

$$Cr^{2+} \xrightarrow{\text{oxidizing agent}} \text{product} + Cr^{3+}$$

Table I. Kinetics of Decomposition of $(NH_3)_5CoNCC_6H_4CH_2Cr^{5+}$ in the Presence of Oxidizing Agents[a]

oxidant	oxidant concn range, M	no. of runs	10^4k, s^{-1}
O_2	saturated, ~1×10^{-3}	2	1.72
$(NH_3)_5CoBr^{2+}$	$(0.55–1.65) \times 10^{-3}$	5	1.72 ± 0.05
$Fe(OH_2)_6^{3+}$	$(0.74–2.23) \times 10^{-3}$	5	1.9 ± 0.1
Cu(II)	$(0.55–1.64) \times 10^{-3}$	3	1.91 ± 0.07

[a] Reactions at 25 °C in 1.0 M $NaClO_4$, 0.11 M $HClO_4$, monitored at 400 nm, with initial cobalt(III) in the range $(4–5) \times 10^{-5}$ M.

$NaClO_4/HClO_4$. The electronic spectrum has maxima at 320, 420, and 470 nm, but the species is too unstable to permit determination of absorption coefficients. The instability is expected since $CrCH_2C_6H_5^{2+}$ is known[4] to decompose by homolytic dissociation with a half-time of a few minutes in air. The absorbance maxima at 320 and 420 nm are consistent with a $CrCH_2C_6H_4–$ chromophore, while that at 470 nm is assigned to $(NH_3)_5CoY-C_6H_4CH_2–$.

The reaction of III with aqueous $Hg(ClO_4)_2$ causes the peaks at 320 and 420 nm to disappear while that at 470 nm remains. This is expected due to electrophilic attack of Hg(II) on the Cr–C bond[8] as shown in eq 1. Species IV is quite stable, and this property was exploited in the product analysis studies.

$$(NH_3)_5CoYC_6H_4CH_2Cr^{5+} + Hg^{2+} \rightarrow$$
$$\text{III}$$
$$(NH_3)_5CoYC_6H_4CH_2Hg^{4+} + Cr(OH_2)_6^{3+} \quad (1)$$
$$\text{IV}$$
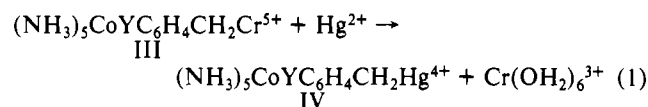
Homolysis of $(NH_3)_5CoNCC_6H_4CH_2Cr(OH_2)_5^{5+}$. The rate of decomposition of III in air and under argon in the presence of $(NH_3)_5CoBr^{2+}$, $Fe(OH_2)_6^{3+}$, and $Cu(OH_2)_4^{2+}$ has been studied. The solutions of III are product mixtures from the reaction of 2 $\times 10^{-3}$ M Cr(II) and 5×10^{-4} M I in 0.10 M $HClO_4$. The reaction was quenched in air after 50 min and the products stored at 5 °C under argon for further use. The kinetic results are summarized in Table I. The rate is independent of the concentration and nature of the oxidizing agent with $k = (1.8 \pm 0.1) \times 10^{-4}$ s^{-1}. These observations are consistent with homolytic cleavage as shown in Scheme II.

The rate constant for homolysis of the cobalt complex is somewhat smaller than that of 5.6×10^{-4} s^{-1} for $(H_2O)_5CrCH_2C_6H_4(4\text{-}CN)^{2+}$.[4] If the correlation with the Hammett σ_p noted by Nohr and Espenson is extended to III, then σ_p = 1.2 for $(NH_3)_5CoNC–$ and the latter is a better electron-withdrawing group than –CN (σ_p = 0.68).

Separation and Identification of Products of Cr(II) Reduction of I and II. Preliminary experiments showed that a major reaction product was too unstable to be separated by ion exchange chro-

Table II. Products of the Reaction[a] of $(NH_3)_5CoNCC_6H_4CH_2Br^{3+}$ with Cr(II) after Quenching with O_2 and Treatment with Hg(II).

eluent ionic strength,[b] M	product color	$10^4 \times$ mol of cobalt (% Co)	$10^4 \times$ mol of chromium (% Cr)	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
0.1–0.2	colorless	0.164 (9.7)	0	
0.40	blue	0	2.85 (3.7)	570 (14.4), 408 (16.3)
0.50	yellow	0.298 (17.5)	0.318 (4.1)	467 (74.5), 326 (82.3)
0.80	blue-green	0	4.70 (61.2)	580 (17.8), 418 (23.0)
1.2[c]	orange	0.882 (51.9)	0	470 (146)
resin	red-orange	0.274 (16.1)	0	

[a] The initial solution contains 1.70×10^{-4} mol of $(NH_3)_5CoNCC_6H_4CH_2Br^{3+}$, 7.68×10^{-4} mol of Cr(II) in 100 mL of 0.10 M HClO$_4$. The quoted yields are for a single experiment which is the result of a several trials to optimize separation conditions. Comparison to earlier trials indicates that the yields are reproducible to ±2%. [b] The eluent is 0.10 M HClO$_4$ plus varying concentrations of NaClO$_4$ unless otherwise indicated. [c] The eluent is 0.2 M HCl in 1.0 M NaClO$_4$.

Table III. Products of the Reaction[a] of $(NH_3)_5CoNHC(OH)C_6H_4CH_2Br^{3+}$ with Cr(II) after Quenching with O_2 and Treatment with Hg(II)

eluent ionic strength,[b] M	product color	$10^4 \times$ mol of cobalt (% Co)	$10^4 \times$ mol of chromium (% Cr)	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
0.1–0.4	blue	0.121 (7.0)	2.62 (34.1)	570 (13.3), 408 (15.2)
0.50	yellow-pink	0.373 (21.6)	0.322 (4.2)	476 (77.8), 340 (102)
0.80	blue-green	0	5.33 (69.4)	582 (17.6), 418 (23.2)
1.2[c]	pink-orange	0.790 (45.9)	0	476 (131)
resin	orange	0.396 (23.0)	0	

[a] The initial solution contains 1.72×10^{-4} mol of $(NH_3)_5CoNHC(OH)C_6H_4CH_2Br^{3+}$, 7.68×10^{-4} mol of Cr(II) in 100 mL of 0.10 M HClO$_4$. The quoted yields are for a single experiment, which is the result of a several trials to optimize separation conditions. Comparison to earlier trials indicates that the yields are reproducible to ±2%. [b] The eluent is 0.10 M HClO$_4$ plus varying concentrations of NaClO$_4$ unless otherwise indicated. [c] The eluent is 0.2 M HCl in 1.0 M NaClO$_4$.

matography even at 5 °C under an argon atmosphere. This unstable product is III as described in the preceding paragraph. In order to obtain a quantitative analysis of the products, III was converted to IV (eq 1) by quenching the reaction mixture with dioxygen after 15 min and immediately adding Hg(ClO$_4$)$_2$ before ion-exchange separation. The product analysis results are summarized in Tables II and III for I and II respectively.

The species in the 0.1–0.4 M eluant are $Co(OH_2)_6^{2+}$ and $Cr(OH_2)_6^{3+}$. The former was identified by the characteristic blue color of the cobalt(II)–thiocyanate complex in aqueous acetone,[12] and the latter by its electronic spectrum and ion-exchange properties. The probable source of the cobalt(II) is discussed in the following section.

The yellow (from I) and yellow-pink (from II) species collected in 0.5 M eluant have electronic spectra quite similar to those of their pentaamminecobalt(III) parents. However, the known reaction rates indicate that there should be <0.1% of the reactant left after 15 min. These fractions gave a negative test for bromide (as AgBr) after heating in 0.1 M NaOH and reacidifying, although I and II both give AgBr. Therefore, the yellow and yellow-pink fractions are tentatively identified as the respective $(NH_3)_5CoYC_6H_4CH_3^{3+}$ complexes derived from I and II. The chromium(III) in the 0.5 M eluant is believed to be the leading edge of the following 0.8 M band. The latter is assigned to $Cr(OH)_2Cr^{4+}$, which is the main product of the oxidation of Cr(II) by dioxygen.

The orange (from I) and orange-pink (from II) products could not be removed from Sephadex SP-C25 even with 2 M NaClO$_4$/HClO$_4$. However they are easily removed with 0.2 M HCl in 1.0 M NaClO$_4$. This behavior is consistent with the formulation $(NH_3)_5CoYC_6H_4CH_2Hg^{4+}$, which will complex with chloride to give $(NH_3)_5CoYC_6H_4CH_2HgCl^{3+}$ and possibly higher chloro complexes. These organomercury species are derived from III as described in eq 1.

Finally there is a red to orange product that could not be removed from the ion-exchange resin. This product was analyzed by physically separating the resin and warming it in 0.1 M NaOH to decompose the products before analysis. These fractions are assigned to $((NH_3)_5CoYC_6H_4CH_2)_2^{6+}$, consistent with the high charge, color, and absence of chromium.

The amounts of monomeric chromium(III) product (eluant ≤0.5 M; Tables I and II) are consistent with the amounts of the

other products. There should be one chromium(III) per cobalt(III) from the halogen abstraction, plus one per $(NH_3)_5CoYC_6H_4CH_2Hg^{4+}$ (liberated by eq 1), plus one per $(NH_3)_5CoYC_6H_4CH_3^{3+}$,[13] plus about 5% from O_2 oxidation of excess chromium(II), which is calculated to remain before quenching. For Y ≡ CN, these values respectively are $(1.70 + 0.882 + 0.298 + 0.24) \times 10^{-4}$ mol to give a total of 3.12×10^{-4} mol compared to the observed 3.17×10^{-4} mol. For Y ≡ NHC(OH), the calculated and observed amounts at 3.12×10^{-4} and 2.94×10^{-4} mol respectively.

Decomposition Products of $(NH_3)_5CoYC_6H_4CH_2Cr^{5+}$ (III). The instability of III made it impossible to prepare pure solutions of III, which would be necessary to fully assess its decomposition products. However, it is possible to determine the amount of cobalt(II) produced from III.

Solutions of I or II (1.7×10^{-3} M) and Cr(II) (7.7×10^{-3} M) were allowed to react for 50 min, quenched with dioxygen, and then split into three equal portions (A, B, and C). Fractions A and B were treated immediately with Hg(ClO$_4$)$_2$ to convert III to IV (eq 1), and A was analyzed immediately for cobalt(II).[12] Fractions B and C were allowed to stand in air for 24 h before analysis. Fraction B serves as a blank test for any cobalt(II) produced by decomposition of IV, and since IV is expected to be stable, B also serves as a replicate analysis for the amount of cobalt(II) present after the halogen abstraction reaction.

For Y ≡ NC, the amounts of cobalt(II) are as follows: A, 16.0%; B, 16.4%; C, 41.4%.[14] For Y ≡ NHC(OH), the amounts are 13.6%, 13.4%, and 26.5% respectively. The larger amounts of cobalt(II) in fraction C for both reactants shows that III decomposes in air at least partly to produce cobalt(II).
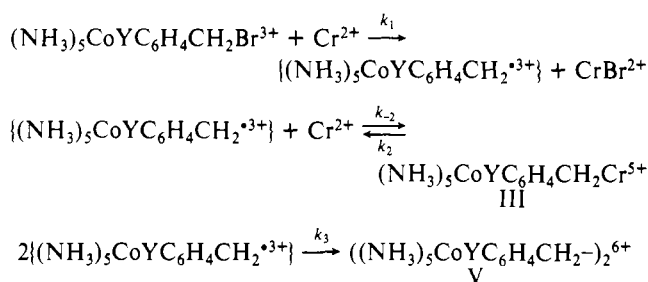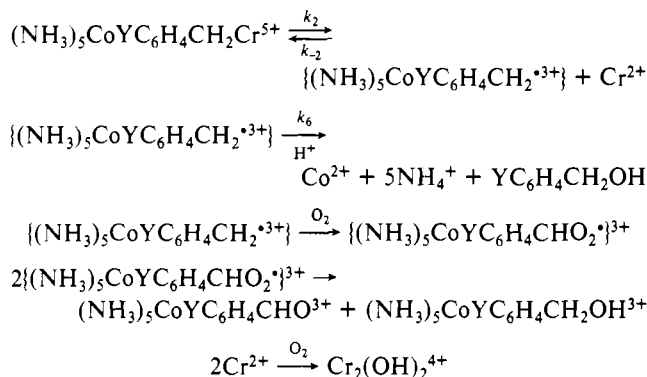
The amounts of cobalt(II) after 15 min (9.7%, Table II) and after 50 min (16.2%) differ and might appear to be due to spontaneous decomposition of III over the longer time period. But the rate of decomposition of III in the presence of Cr(II) is much too slow ($k = 3.3 \times 10^{-5}$ s^{-1} in 0.01 M Cr(II)) to account for this. It appears more reasonable that there is a parallel outer-sphere reduction of the cobalt(III) complexes by Cr(II). The rate constant for reduction of $(NH_3)_5CoNCC_6H_5^{3+}$ by Cr(II)[15] is 4.2 $\times 10^{-2}$ M^{-1} s^{-1} in 1.0 M HClO$_4$ and $\sim$2.3 $\times 10^{-2}$ in 0.5 M HClO$_4$.

(12) Kitsen, R. E. *Anal. Chem.* **1950**, *22*, 664.

(13) The source of this product is uncertain, but it is assumed to require a reducing equivalent that may involve Cr(II) either directly or indirectly.
(14) The percentages are based on the total cobalt in the original reaction solution.
(15) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 3469.

Scheme III

$$(NH_3)_5CoYC_6H_4CH_2Br^{3+} + Cr^{2+} \xrightarrow{k_1}$$
$$\{(NH_3)_5CoYC_6H_4CH_2{}^{\bullet 3+}\} + CrBr^{2+}$$

$$\{(NH_3)_5CoYC_6H_4CH_2{}^{\bullet 3+}\} + Cr^{2+} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}}$$
$$(NH_3)_5CoYC_6H_4CH_2Cr^{5+}$$
$$\text{III}$$

$$2\{(NH_3)_5CoYC_6H_4CH_2{}^{\bullet 3+}\} \xrightarrow{k_3} ((NH_3)_5CoYC_6H_4CH_2-)_2{}^{6+}$$
$$\text{V}$$

Scheme IV

$$(NH_3)_5CoYC_6H_4CH_2Cr^{5+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$
$$\{(NH_3)_5CoYC_6H_4CH_2{}^{\bullet 3+}\} + Cr^{2+}$$

$$\{(NH_3)_5CoYC_6H_4CH_2{}^{\bullet 3+}\} \xrightarrow[H^+]{k_6}$$
$$Co^{2+} + 5NH_4^+ + YC_6H_4CH_2OH$$

$$\{(NH_3)_5CoYC_6H_4CH_2{}^{\bullet 3+}\} \xrightarrow{O_2} \{(NH_3)_5CoYC_6H_4CHO_2{}^{\bullet}\}^{3+}$$

$$2\{(NH_3)_5CoYC_6H_4CHO_2{}^{\bullet}\}^{3+} \rightarrow$$
$$(NH_3)_5CoYC_6H_4CHO^{3+} + (NH_3)_5CoYC_6H_4CH_2OH^{3+}$$

$$2Cr^{2+} \xrightarrow{O_2} Cr_2(OH)_2{}^{4+}$$

Therefore, a value of about 1.5×10^{-2} might be expected in 0.1 M $HClO_4$. If $k = 1.3 \times 10^{-2}$, then there would be 5.6% cobalt(II) after 15 min and 16% after 50 min, assuming that all the cobalt(III) species are reduced at a similar rate. These calculations show that outer-sphere reduction gives a reasonable account of the cobalt(II) produced in the presence of Cr(II) although the system is too complex to model exactly. A similar explanation can be applied to the carbamoyl complex.

In order to determine the percentage of III that decomposes to cobalt(II), it is necessary to estimate the amount of III present after 50 min when the reaction was quenched. If all three cobalt(III) products are reduced at similar rates, as seems most probable,[15] each will change between 15 and 50 min by (16% − 9.7%)/3 for Y ≡ NC, and the amount of III after 50 min would be (51.9% − 2.2%) = 49.7%. For the carboxamido system, the amount would be (45.9% − 2.2%) = 43.7%.

The above analysis indicates that, after 50 min, there will be 50% of III present for the nitrile complex. This decomposes in air to give another (41.4% − 16.2%) = 25.2% of cobalt(II). Therefore, 50% of the $(NH_3)_5CoNCC_6H_4CH_2Cr^{5+}$ decomposes to give cobalt(II). A similar analysis shows that $(NH_3)_5CoNHC(OH)C_6H_4CH_2Cr^{5+}$ decomposes 30% of the time to cobalt(II).
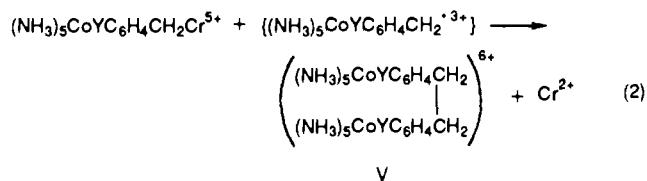
Conclusions

In a general way, the product distributions in Tables II and III indicate that $(NH_3)_5CoYC_6H_4CH_2Br^{3+}$ reacts with Cr(II) to give ~50% $(NH_3)_5CoYC_6H_4CH_2Cr^{5+}$ (III), ~20% $((NH_3)_5CoYC_6H_4CH_2)_2{}^{6+}$, ~20% $(NH_3)_5CoYC_6H_4CH_3{}^{3+}$, and ~10% cobalt(II) from outer-sphere reduction of the reactant and products. The first two products can be explained by the reactions in Scheme III.

However there is at least one significant problem with Scheme III. It requires that the bimolecular combination of the radical intermediate to form V is competitive with the pseudo-first-order reaction of the intermediate with Cr(II). It is known[16] that aqueous Cr(II) reacts with the benzyl radical with $k_{-2} = 8.5 \times 10^7$ M^{-1} s^{-1}. If the same value is used for the formation of III, then competitive formation of V in ~5×10^{-3} M Cr(II) requires[17]

that the radical dimerization must have $k \sim 7 \times 10^{15}$ M^{-1} s^{-1}. The latter value is about 10^6 times larger than allowed by diffusion control and is similarly larger than the rate constant of ~2×10^9 M^{-1} s^{-1} found[18] for dimerization of the benzyl radical. Conversely, if $k_3 = 2 \times 10^9$, then the observed product distribution gives $k_{-2} = 3 \times 10^4$ M^{-1} s^{-1}. It could be argued that the latter value is much smaller than that for the benzyl radical because of charge and electron distribution differences in the coordinated radical. However these same factors would be expected to reduce the dimerization rate constant (k_3).

The above analysis indicates that V cannot be produced by simple dimerization as shown in Scheme III and is more likely to result from a secondary reaction of the radical with primary products as they accumulate. Recent work of Cohen and Meyerstein[19-21] suggests the following possibility.

$$(NH_3)_5CoYC_6H_4CH_2Cr^{5+} + \{(NH_3)_5CoYC_6H_4CH_2{}^{\bullet 3+}\} \longrightarrow$$
$$\begin{pmatrix} (NH_3)_5CoYC_6H_4CH_2 \\ | \\ (NH_3)_5CoYC_6H_4CH_2 \end{pmatrix}^{6+} + Cr^{2+} \qquad (2)$$
$$\text{V}$$

Available results indicate that the rate constants for such reactions may be $> 10^8$ M^{-1} s^{-1}, so that this path may compete effectively with Cr(II) as the concentration of III increases during the primary reaction.

The decomposition of III in air produces significant quantities of cobalt(II) (~50% for Y ≡ NC and ~30% for Y ≡ NHC(OH)). This is attributed to intramolecular electron transfer in the radical intermediate formed by homolysis of the $Cr-CH_2$ bond as shown in Scheme IV.

The intramolecular decomposition is not observed significantly when the radical intermediate is produced in the halogen abstraction reaction because the Cr(II) present reacts to form III in effective competition with the intramolecular electron transfer.

It is possible to estimate the rate constant for intramolecular transfer (k_6) if one assumes that the coordinated radical reacts with O_2 at a diffusion-controlled rate (~2×10^9) like the benzyl radical. Then, if $[O_2] \approx 1 \times 10^{-3}$ M and 50% of the reaction gives Co(II), then $k_6 \approx 10^6$ s^{-1}. The (p-nitrophenyl)cyano radical anion complex[5] has the same group attached to cobalt(III) and a rate constant of 1×10^3 s^{-1}. However, the processes are different in that oxidation of the nitro anion produces the parent species while oxidation of the benzyl radical yields the carbonium ion in principle, but this process is probably coupled with H_2COH bond formation in water.

Experimental Section

Materials. 1-Cyano-4-(bromomethyl)benzene (VI) was prepared by adding 16 g of bromine dropwise to 12 g of 1-cyano-4-methylbenzene at 200 °C in a round bottomed flask equipped with a dropping funnel and water-cooled condenser. About 20 min after the addition of bromine was complete, the reaction mixture was cooled and the contents slurried with ethanol and filtered. The solid product was recrystallized from ethanol to yield VI as a white solid.

The $[(NH_3)_5CoNCC_6H_4CH_2Br](ClO_4)_3$ (I) was prepared by mixing solutions of 5 g of VI in 20 mL of sulfolane and 5 g of $[(NH_3)_5CoO_3S-CF_3](O_3SCF_3)_2$[23] plus 5–6 drops of HO_3SCF_3 in 20 mL of sulfolane and allowing the reaction to proceed at ambient temperature for 20 h and then at 40 °C for 12 h. The reaction mixture changed from reddish purple to reddish brown and yielded a brown oil on treatment with 400 mL of ether. The oil was dissolved in 100 mL of 0.02 M HCl at 40 °C, filtered and treated with 60% $HClO_4$ to yield a solid product, which was recrystallized from dilute perchloric acid. The proton NMR spectrum in DMSO-d_6 has the expected features: 6.55 τ (trans NH_3), 6.10 τ (cis NH_3), 5.18 τ (-CH_2Br), 1.93, 2.01, 2.13, 2.23 τ (-C_6H_4 multiplet). The electronic spectrum has the following absorbance maxima in nm (molar

(16) Blau, R. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 3530.
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(21) Sauer, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988**, *27*, 4578.
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(23) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1982**, *21*, 2089.

extinction coefficients, M^{-1} cm^{-1}): 470 (72.1), 330 (94.1).

The conjugate base of the carboxamido complex (II) was prepared by alkaline hydrolysis[24] of I. A solution containing 0.64 g of I in 25 mL of water was treated with 2.2 mL of 0.68 M NaOH. The solution immediately changed from yellow to pink, and after 20 s, solid NaClO₄ was added to precipitate the product, which was collected by filtration after cooling for 1 h at 5 °C. The product was recrystallized from warm water at pH 9.5 by addition of NaClO₄ as before. The proton NMR spectrum in DMSO-d_6 has the expected features: 6.72 τ (trans NH₃), 6.55 τ (cis NH₃), 5.40 τ (HNC=O), 5.25 τ (-CH₂Br), 2.45, 2.40, 2.20, 2.13 τ (-C₆H₄ multiplet). The electronic spectrum shows maxima at 485 (99.5) and 340 nm (146).

For the homolysis study, the oxidizing agents were Fe(NH₄)(SO₄)₂·12H₂O and CuSO₄·5H₂O from commercial sources, and [Co(NH₃)₅Br](ClO₄)₂ was prepared by standard methods.[25]

Other reagents and procedures have been described previously.[26]

Product Analysis. The ion exchange separations were done on Sephadex SP-C25 resin at 5 °C in a cold room. The amount of cobalt was determined spectrophotometrically[12] after alkaline decomposition of the cobalt(III) complexes when appropriate. Chromium was determined as chromate after oxidation with alkaline hydrogen peroxide.

Instrumentation. The electronic spectra for species characterization were done on a Cary 219 spectrophotometer while the kinetic measurements were on a Hewlett-Packard diode-array system as described previously.[26] The NMR spectra were recorded on a Bruker AM-300 spectrometer.

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Convenient Synthesis of [(n-Bu)₄N]₃[RuᴵᴵᴵCN)₆]: First Access to a Pure Salt of the Hexacyanoruthenate(III) Anion and to a Coordination Polymer Thereof

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The preparation of pure salts of the hexacyano*ruthenate(III)* anion, [A]₃[RuᴵᴵᴵCN)₆], is, in contrast to corresponding Fe and Os homologues, still poorly documented. Actually, as late as 1984, i.e. more than three decades after first systematic attempts by DeFord and Davidson to oxidize alkali-metal salts of the [RuᴵᴵCN)₆]⁴⁻ anion,[1] Crean and Schug have repeated the longstanding statement that the [RuᴵᴵᴵCN)₆]³⁻ anion is intrinsically unstable in water.[2] In 1979 Vogler et al. demonstrated that, in CHCl₃ solution, in situ prepared [Et₄N]₄[RuᴵᴵCN)₆][3a] may be successfully photooxidized to [RuᴵᴵᴵCN)₆]³⁻ ions; however, a solid product described as "analytically pure" [Et₄N]₃[RuᴵᴵᴵCN)₆] has never been characterized in any detail.[3b]

In view of the evidently greater chances to oxidize [R₄N]₄[RuᴵᴵCN)₆] systems (with R = alkyl) in *nonaqueous* solvents, we have reexamined some early findings by Gray et al. according to which [(n-Bu)₄N]₃[OsᴵᴵᴵCN)₆] results spontaneously from [(n-Bu)₄N]₄[OsᴵᴵCN)₆] in EtOH/Et₂O.[4] Apparently, even the attempted preparation of [(n-Bu)₄N]₄[FeᴵᴵCN)₆] (**1b**) from

H₄FeᴵᴵCN)₆ and [(n-Bu)₄N]OH in MeOH had led exclusively to [(n-Bu)₄N]₃[FeᴵᴵᴵCN)₆] (**2b**).[4,5] We have reproduced this facile (i.e. in the presence of air!) access to **2b** and prepared, moreover, both pure [Et₄N]₄[FeᴵᴵCN)₆] (**1d**), from H₄FeᴵᴵCN)₆ and [Et₄N]OH under a strict N₂ atmosphere, and [Et₄N]₃[FeᴵᴵᴵCN)₆] (**2d**),[6c] from **1d**/EtOH in the presence of air. However, all attempts to also oxidize the salts [R₄N]₄[RuᴵᴵCN)₆] (R = n-Bu (**1a**); R = Et (**1c**)) in a corresponding manner simply by air were unsuccessful in EtOH and MeOH as well as in numerous other solvents. Yet, as we wish to emphasize here, the above route becomes also viable for [RuᴵᴵCN)₆]⁴⁻ when (a) the solvent is dimethylformamide (DMF) and (b) the countercation is [(n-Bu)₄N]⁺.

$$[n\text{-}Bu_4N]_4[Ru^{II}(CN_6)] \xrightarrow[\text{(b) Et}_2\text{O}]{\text{(a) DMF, air}}$$
1a

$$[n\text{-}Bu_4N]_3[Ru^{III}(CN)_6] + \text{other products} \quad (1)$$
2a
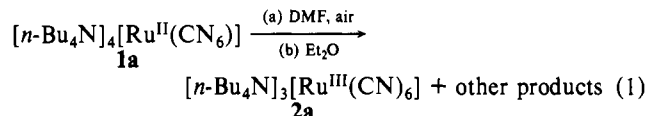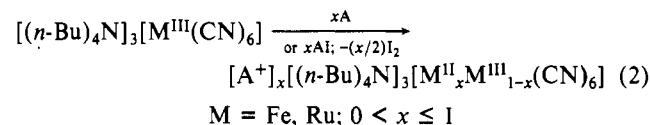
Again, complete and quick oxidation by air takes place in DMF, while in H₂O oxidants stronger than O₂ are required.[1] Attempts to also prepare pure [Et₄N]₃[RuᴵᴵᴵCN)₆] (**2c**) from [Et₄N]₄[RuᴵᴵCN)₆] (**1c**) remained unsatisfactory even in DMF due to incomplete reaction. A sensitive synergism, reminiscent of the well-known influence of the nature of both the solvent and the countercation [R₄N]⁺ (R = Et or n-Bu) on the half-wave potential $E_{1/2}$ of the reduction of the [FeᴵᴵᴵCN)₆]³⁻ ion,[6d] seems to govern the oxidation of [RuᴵᴵCN)₆]⁴⁻, too, and might be best described by Gutmann's concept of the "acceptor number" (AN).[6] Actually, the AN values of H₂O (54.8), MeOH (41.3), and EtOH (37.1) exceed appreciably the AN value of DMF (16.0),[6a] suggesting, in view of the notable change of $E_{1/2}$ of the couple [FeᴵᴵᴵCN)₆]³⁻/[FeᴵᴵCN)₆]⁴⁻ from +0.24 V (solvent EtOH) to −0.61 V (solvent DMF),[6d] a correspondingly large reduction of the redox potential of the couple [RuᴵᴵᴵCN)₆]³⁻/[RuᴵᴵCN)₆]⁴⁻ when EtOH is replaced by DMF.[7] The availability of **2a** and the facile tunability of its rather high reduction potential (ca. +0.86 V in H₂O[1]) might make this compound an interesting oxidant in organic, organometallic, and inorganic chemistry.

The brilliant yellow salt **2a** is thermally stable up to 220 °C and soluble in e.g. MeCN, CH₂Cl₂, and CHCl₃ but not in hexane, toluene, and CCl₄. Solutions even in N₂-conditioned H₂O display spontaneous decomposition accompanied by a color change toward green. The reappearance of the ν(CN) absorption bands of the [RuᴵᴵCN)₆]⁴⁻ ion in the IR spectra of KBr pellets, but not of Nujol mulls, of initially pure **2a** suggests partial oxidation of Br⁻ ions in the pellet.

Like its Feᴵᴵᴵ homologue, **2a** is a paramagnetic low-spin system (μ_{eff}^{cor}(25 °C) = 2.00 μ_B). The electronic absorption maxima and extinction coefficients between 20 000 and 40 000 cm^{-1} compare well with corresponding literature data for both [RuᴵᴵᴵCN)₆]³⁻ and [OsᴵᴵᴵCN)₆]³⁻.[3,4,8] In Table I, the ν(CN) vibrational bands of **2a** are compared with e.g. those of **1a**, **1d**, **2a**, and **2b**.

Not quite unexpectedly (vide supra), **2a** may be applied as an effective solid-state oxidant by simple grinding at room temperature with various solid reductants (eq 2).

$$[(n\text{-}Bu)_4N]_3[M^{III}(CN)_6] \xrightarrow[\text{or } xAI; -(x/2)I_2]{xA}$$
$$[A^+]_x[(n\text{-}Bu)_4N]_3[M^{II}{}_xM^{III}{}_{1-x}(CN)_6] \quad (2)$$
$$M = Fe, Ru; \ 0 < x \leq 1$$

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(2) Crean, F. M.; Schug, K. *Inorg. Chem.* **1984**, *23*, 853.
(3) (a) By reacting Ag₄[Ru(CN)₆] with [Et₃NH]Cl (!) in CHCl₃. (b) Vogler, A.; Losse, W.; Kunkely, H. *J. Chem. Soc., Chem. Commun.* **1979**, 187.
(4) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260.

(5) Das, B.; Carlin, R.; Osteryoung, R. A. *Inorg. Chem.* **1989**, *28*, 421. These authors have apparently overlooked ref 4 and describe another, but not the first, route to compound **2b**.
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(7) Electrochemical studies of the variation of $E_{1/2}$ of the redox reaction [RuᴵᴵCN)₆]⁴⁻ − e⁻ ⇌ [RuᴵᴵᴵCN)₆]³⁻ as a function of the AN of the solvent are presently underway.
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