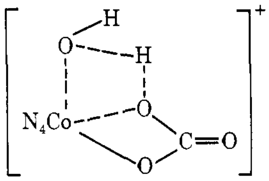
opening probably involves concerted protonation of the chelated carbonato group and insertion of a water molecule to form the highly unstable aquobicarbonato intermediate, according to the mechanism suggested by recent kinetic studies[28] of this type of reaction. While the hydroxobicarbonato tren congener is not entirely identical with the intermediate proposed as a result of acid-catalyzed ring opening, there is sufficient parallelism to visualize the ring-closure transition state for $Co(tren)(OH)(HCO_3)^+$ in the following form:



This requires that there be replacement of the departing OH_2 group by the entering free end of the chelating CO_3 group. This necessitates $Co\text{-}OH_2$ bond fission, a process which usually occurs at a considerably slower rate than what is observed here. For example, the highly accelerated solvent water exchange with the ion *cis*-$Co(en)_2(H_2O)(OH)^{2+}$ (as compared to its diaquo or dihydroxo congeners) has a rate constant[26] at 20° of not greater than 10^{-3} sec^{-1}, less than 0.03 as great as the tren carbonato ring-closure process under discussion. It seems likely that the considerable enhancement of the rate of water replacement by the potentially bidentate adjacent carbonato ligand is a result of a large decrease in enthalpy of activation, though the effect may be partially negated by a similarly large decrease in entropy of activation.[29] In the absence of definitive information on the temperature parameters for a more directly comparable water exchange process, further discussion of these factors is inappropriate at this time.

References and Notes

(1) A preliminary report of this study was presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973. See Abstract INOR No. 121.
(2) Part VII in this series: T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, **13**, 1275 (1974).
(3) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," Allyn and Bacon, Boston, Mass., 1974, Chapter 4.
(4) H. A. Scheidegger and G. Schwarzenbach, *Chimia*, **19**, 166 (1965).
(5) H. A. Scheidegger, Doctoral Thesis, Eidgenossichen Technischen Hochschule, Zurich, 1966.
(6) D. J. Francis and R. B. Jordan, *J. Am. Chem. Soc.*, **91**, 6626 (1969).
(7) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 57 (1968).
(8) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 1745 (1968).
(9) P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7**, 1872 (1968).
(10) S. C. Chan and G. M. Harris, *Inorg. Chem.*, **10**, 1317 (1971).
(11) E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Am. Chem. Soc.*, **95**, 4169 (1973).
(12) D. A. Palmer and G. M. Harris, *Inorg. Chem.*, **13**, 965 (1974).
(13) T. P. Dasgupta and G. M. Harris, to be submitted for publication (see Abstracts, INOR No. 113, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974).
(14) (a) J. MacB. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc.*, **96**, 2634 (1974); (b) B. T. Golding, J. MacB. Harrowfield, and A. M. Sargeson, *ibid.*, **96**, 3003 (1974).
(15) O. Nor and A. G. Sykes, *J. Chem. Soc., Dalton Trans*, 1232 (1973).
(16) G. Gustalla and T. W. Swaddle, *Can. J. Chem.*, **52**, 527 (1974).
(17) T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **93**, 91 (1971).
(18) Instranal Laboratory, Inc., Rensselaer, N.Y. 12144.
(19) (a) P. J. Ewing, J. M. Markwitz, and I. Rosenthal, *Anal. Chem.*, **28**, 1179 (1956). (b) A few runs were made in the same range using "tris" buffer, with no significant effect on the rates (see Table I).
(20) R. M. C. Dawson, W. H. Elliott, and K. M. Jones, Ed., "Data for Biochemical Research," Oxford University Press, London, 1959, p 205.
(21) The final absorbance value A_∞ at 503 nm is constant since the ring-closure reaction involves no absorbance change at this wavelength (see Figure 1).
(22) Only proton transfer is involved in the various acid-base equilibria, all of which are instantaneous as compared to the processes under investigation.
(23) This complex has also been symbolized[5] in the form Co(tren)$(OH_2)(CO_3)$. We prefer the hydroxobicarbonato formulation on the basis of arguments previously given (see, for example, K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, **70**, 171 (1970), footnote 268).
(24) At 20° and $I = 0.1$ *M*, pK_4 has been determined to be 8.7 (ref 5). On the basis of previous considerations concerning the effect of increasing the ionic strength from 0.1 to 0.5 *M* on the dissociation constants of carbonic acid (ref 11), we assign pK_4 a value of 8.4 at all three temperatures. Actually, our calculations show that variation of pK_4 within the range 8.3–9.0 has no significant effect on the magnitudes of the k_3's, but does shift the average k_2K_4 value somewhat farther from zero.
(25) D. A. Buckingham, J. MacB. Harrowfield, and A. M. Sargeson, *J. Am. Chem. Soc.*, **95**, 7281 (1973).
(26) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).
(27) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **75**, 4099 (1953).
(28) T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **91**, 3207 (1969); see also ref 17.
(29) The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for the various diaquo and dihydroxo water exchanges (see ref 26) fall within the limits 27–31 kcal/mol and 13–20 eu, respectively, but no such data are available concerning the aquohydroxo congeners.

Reactivity of Coordinated Nitrosyls. V. Generation and Characterization of a Ruthenium(II) Alkylnitroso Complex[1,2]

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Abstract: The radiolysis of $Ru(NH_3)_5NO^{3+}$ in aqueous *tert*-butyl alcohol solution generates the species $[Ru(NH_3)_5\{(N\text{-}O)CH_2C(CH_3)_2OH\}]^{2+}$ which can be formally viewed as a Ru(II) alkylnitroso complex with a C–N bond. The complex has been isolated as the tetraphenylborate salt and has been characterized by elemental microanalysis, ion exchange chromatography, and uv-visible, ir, and nmr spectroscopy. The product can be envisioned as resulting from the attack of the carbon-radical derived from the reaction of OH radicals with *tert*-butyl alcohol, $\cdot CH_2C(CH_3)_2OH$, with $Ru(NH_3)_5NO^{2+}$ generated by the reaction of H atoms and e_{aq}^- with the Ru(III) substrate. This stable, air-insensitive radical adduct can also be formulated as a Ru(III) nitroxide complex (valence tautomer).

The multielectron reduction of coordinated nitrosyls results in a variety of products including free or coordinated NH_2OH[3] and NH_4^+[4] and coordinated nitrides.[5] Fast kinetics stopped-flow studies of the reaction of $Ru(NH_3)_5NO^{3+}$ with Cr^{2+} in aqueous solution indicate the presence of at least four successive transient intermediates[6] in the course of the formation of $Ru(NH_3)_6^{3+}$ and these transient species have been observed using cyclic voltammetry at a hanging mercury drop electrode.[7] However, any study of the transients involved in this six-electron reduction is complicated by the reactive nature, and hence short lifetimes, of these intermediates. Recently, we applied the technique of pulse radiolysis to produce and characterize spectrally the one-electron reduction product[8] designated as $Ru(NH_3)_5NO^{2+}$. This species, generated in aqueous solution through the action of powerful one-electron reducing radicals (e_{aq}^-, H, CO_2^-, $(CH_3)_2\dot{C}OH$), exhibited an absorption maximum at 280 nm. The $Ru(NH_3)_5NO^{2+}$ species was found to be only moderately stable toward aquation and substitution ($\tau \sim$ seconds) but highly reactive toward O_2 ($k = 7.6 \times 10^6\ M^{-1}\ sec^{-1}$). This O_2 sensitivity is considerably greater than that displayed by other simple Ru(II)-ammines which led to the conclusion that $Ru(NH_3)_5NO^{2+}$ has reactivity characteristics presumably arising from the free radical nature of the coordinated nitrosyl.[8]

In the course of our continuous and pulse radiolysis study of the reduction of $Ru(NH_3)_5NO^{3+}$ by e_{aq}^-, *tert*-butyl alcohol was used as an efficient scavenger for OH radicals.[9] This process generated $\cdot CH_2C(CH_3)_2OH$, a radical that has a weak uv absorption and a relatively unreactive nature, its principal mode of disappearance being bimolecular decay ($2k = 1.4 \times 10^9\ M^{-1}\ sec^{-1}$).[10] Instead of this radical being inert to secondary reaction, we discovered the production of a new stable, air-insensitive product from the radiolysis of $Ru(NH_3)_5NO^{3+}$ in aqueous solutions containing *tert*-butyl alcohol (*t*-BuOH) which results from the reaction of $Ru(NH_3)_5NO^{2+}$ with $\cdot CH_2C(CH_3)_2OH$ radicals (*t*-B$\dot{u}$OH). In this paper we describe the generation and characterization of the combination product that results.

Experimental Section

Preparation of Compounds. $Ru(NH_3)_5NO^{3+}$ was prepared either by the direct addition of NO(aq) to $[Ru(NH_3)_6]Cl_3$ in acidic medium[11] or by the addition of $(NH_4)_2S_2O_8$ to $[Ru(NH_3)_5Cl]Cl_2$.[12] The nitrosyl complex was then recrystallized twice as the Cl^-, Br^-, ClO_4^-, or $TFMS^-$ (trifluoromethylsulfonate) salt.[3] Trifluoromethylsulfonic acid (3M Corporation) was distilled under vacuum at 10 Torr and 62°. The pure acid was diluted immediately to a concentration of 3 *M* and stored in a polyethylene bottle.

For the preparation of $[Ru(NH_3)_5{}^{15}NO]Br_3$, 0.5 g (1.6 mmol) of $[Ru(NH_3)_6]Cl_3$ was dissolved in 10 ml of 0.1 *M* HBr. The pale yellow solution was degassed under vacuum by repetitive freeze-pump-thaw. Approximately 1 atm of ^{15}NO was placed over the solution and the reaction mixture was stirred for 24 hr. The $Ru(NH_3)_5NO^{3+}$ in the resulting orange solution was isolated as the Br^- salt by the addition of solid NaBr.

The *t*-BuOH used was analytical reagent grade, and all other reagents were of the highest quality obtainable and were used without further purification. Solutions were prepared from triply distilled water.

Pulse Radiolysis. Solutions of $Ru(NH_3)_5NO^{3+}$ (as the Cl^- or $TFMS^-$ salt) were subjected to 30-nsec pulses of 2.3 MeV electrons using the Febetron 705 system at the U.S. Army Natick Laboratories. A rectangular flow-through Spectrosil quartz optical cell was used.[10] The monitoring light source was an Osram 450-W xenon lamp, and two high intensity Bausch and Lomb monochromators were used in series to reduce scattered light. A EMI 9558QB photomultiplier was coupled to an oscilloscope and a Polaroid picture of the resulting trace recorded the data permanently. The rate data were analyzed by computer using a least-squares analysis of the standard first- or second-order kinetics equations. The total dose absorbed per pulse was determined using SCN^- dosimetry from which could be evaluated the concentration of radicals and the extinction coefficients of transient and permanent species. Solutions were deoxygenated using an Ar-purge and buffered using phosphate.

Continuous Radiolysis. Radiolyses of solutions of $Ru(NH_3)_5NO^{3+}$ were carried out in serum-stoppered glass bottles that had been purged with Ar and filled using a Pt needle and a gas-tight syringe. Alternatively, a serum-stoppered round-bottom flask with provision for continuous Ar-purge was used. The solutions were irradiated for a measured length of time by γ-rays from a high or low dose (1.9×10^{18} or 6.0×10^{16} eV $ml^{-1}\ min^{-1}$, respectively) ^{60}Co source. The dose delivered to the solutions was determined by use of the Fricke dosimeter.[13] The solutions were sampled periodically during irradiation and their uv-visible spectra determined; their behavior on the cation ion-exchange resin was noted. The stable ruthenium product from the irradiation was isolated and characterized.

Ion Exchange. Our previous experience[14] with the behavior of metal ammine complexes adsorbed onto Dowex 50W-X8, 200-400 mesh, resin indicated that a complex of +1 charge is readily eluted with 0.3-0.5 *M* Na^+ or H^+, +2 charged species with 0.8-1.0 *M* Na^+ or H^+, and >+2 charged species with >2 *M* solutions of Na^+ or H^+ with Cl^- or Br^- as the counterion. The resin was cleaned by standard methods.[15]

Instrumentation. All uv-visible spectra were recorded on a Cary 14 or 118 recording spectrophotometer. Ir spectra of the complexes (in a KBr matrix) were recorded on a Perkin-Elmer 180 ir spectrometer previously calibrated with a polystyrene film. Nmr spectra of the BPh_4^- salt of the isolated stable product were recorded in DMSO-d_6, CD_3CN, or pyridine-d_5 with the use of TMS as an internal standard on a Jeolco HR-60 spectrometer at 28°.

Ruthenium Analyses. For the very stable ruthenium nitrosyls, it was necessary to use a modification[16] of the traditional method of Ru analysis.[17] The analysis involved decomposition of the ruthenium complex in alkaline solution for 1 hr on a steam bath followed by oxidation of the Ru with Br_2-water and further decomposition in basic solution on a steam bath for another hour. Additional Br_2-water was added until the characteristic green perruthenate color appeared. The spectrum of the product solution was recorded between 400 and 430 nm. Addition of a single crystal of NaI produced RuO_4^{2-} and its spectrum was also recorded in this region. The isosbestic point at 415 nm (ϵ $1.05 \times 10^3\ M^{-1}\ cm^{-1}$)[17] was used to determine the final Ru concentration.

Results and Discussion

Radiolysis of aqueous solutions generates e_{aq}^-, OH radicals, and H atoms with *G* values of 2.8, 2.8, and 0.6 radicals produced per 100 eV of energy absorbed, respectively.[18] In the presence of *t*-BuOH, OH radicals are efficiently scavenged ($k = 5.2 \times 10^8\ M^{-1}\ sec^{-1}$)[19] generating the weakly absorbing and generally unreactive *t*-B$\dot{u}$OH radical.[10] In acidic solution, e_{aq}^- is rapidly ($k = 2.2 \times 10^{10}\ M^{-1}\ sec^{-1}$)[20] scavenged by H^+ producing additional H atoms. Thus, in deoxygenated solutions containing *t*-BuOH, the only radical species are the strongly reducing and highly reactive hydrated electrons and H atoms and the relatively inert *t*-B$\dot{u}$OH. In the presence of O_2, e_{aq}^- and H are efficiently scavenged ($k = 2.0 \times 10^{10}$ and $2.0 \times 10^{10}\ M^{-1}\ sec^{-1}$, respectively)[9,20] to give HO_2-O_2^- radicals;[21] *t*-B$\dot{u}$OH forms the peroxy radical, $\cdot O_2CH_2C(CH_3)_2OH$, probably at a diffusion-controlled rate.[10]

Pulse Radiolysis. The reaction of e_{aq}^- + $Ru(NH_3)_5NO^{3+}$ ($k = 5.3 \times 10^{10}\ M^{-1}\ sec^{-1}$) and H + $Ru(NH_3)_5NO^{3+}$ ($k = 4.0 \times 10^8\ M^{-1}\ sec^{-1}$) generates $Ru(NH_3)_5NO^{2+}$ with λ_{max} 280 nm (ϵ $3.7 \times 10^3\ M^{-1}\ cm^{-1}$).[8] Figure 1 shows this transient spectrum (open circles) generated in a deoxygenated solution containing 5×10^{-4} *M* $Ru(NH_3)_5NO^{3+}$ and 1 *M* *t*-BuOH at pH 7.5. This spectrum decayed in a second-order manner which was exactly mirrored by the formation of a permanent product (closed circles) showing λ_{max} 340 (ϵ $3.7\ (\pm 0.6) \times 10^3\ M^{-1}\ cm^{-1}$). The rate constant for these coupled processes had a value of $3.7 \times 10^9\ M^{-1}\ sec^{-1}$ which was independent of [*t*-BuOH] (0.1-2.0 *M*) and $[Ru(NH_3)_5NO^{3+}]$ (5-50×10^{-4} *M*). Neither the rate of decay of the initial transient nor the absorption features illustrated in Figure 1 were significantly affected by pH (1.0-10.3). Variation of the dose of the pulse did not affect the value of *k* but did cause variation of $t_{1/2}$ of the reaction in a manner that established the second-

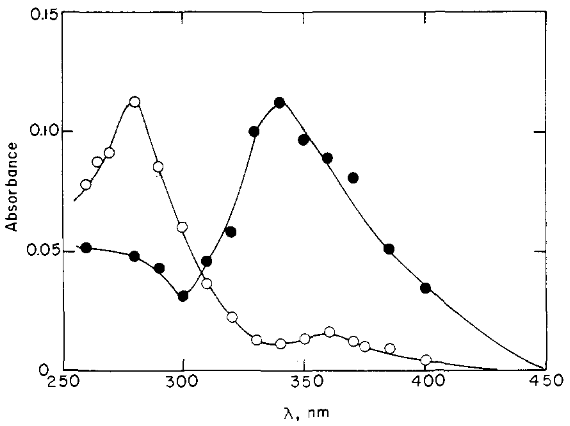


Figure 1. Absorption spectra from the pulse radiolysis of argon-purged solutions: ○, the transient spectrum generated from the reaction of e_{aq}^- with $Ru(NH_3)_5NO^{3+}$; ●, the spectrum of the permanent product produced from the decay of the 280-nm transient absorption. Dose/pulse = 8.0 krads; [t-BuOH] = 1 *M*, $[Ru(NH_3)_5NO^{3+}] = 5 \times 10^{-4}$ *M*, pH 7.5.

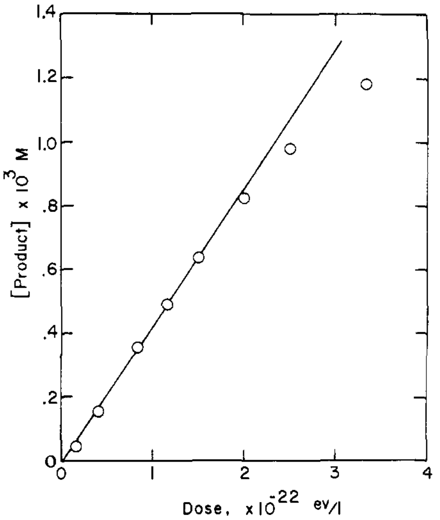


Figure 2. Formation of the green product upon the continuous radiolysis of argon-purged solutions of 4.0×10^{-3} *M* $Ru(NH_3)_5NO^{3+}$ in 1 *M* t-BuOH and 0.07 *M* acetate buffer. The dose rate of the source was 1.67×10^{18} eV l.$^{-1}$ min^{-1}.

order nature of the reaction.

Except for the original solutes, only $Ru(NH_3)_5NO^{2+}$ and t-Bu̇OH are the species present after the reaction of the primary radicals. The kinetics of the subsequent reaction rule out involvement of these species with the original solutes, and the conclusion must be reached that the permanent absorption at 340 nm arises from a direct interaction of $Ru(NH_3)_5NO^{2+}$ and t-Bu̇OH.

$$H_2O \longrightarrow e_{aq}^-,\ OH,\ H \qquad (1)$$

$$OH + t\text{-BuOH} \longrightarrow t\text{-B}\dot{u}\text{OH} + H_2O\ (k = 5.2 \times 10^8\ M^{-1}\ sec^{-1}) \qquad (2)$$

$$e_{aq}^- + Ru(NH_3)_5NO^{3+} \longrightarrow Ru(NH_3)_5NO^{2+}\ (k = 5.3 \times 10^{10}\ M^{-1}\ sec^{-1}) \qquad (3)$$

$$H + Ru(NH_3)_5NO^{3+} \longrightarrow Ru(NH_3)_5NO^{2+} + H^+\ (k = 4.0 \times 10^8\ M^{-1}\ sec^{-1}) \qquad (4)$$

$$e_{aq}^- + H^+ \longrightarrow H\ (k = 2.2 \times 10^{10}\ M^{-1}\ sec^{-1}) \qquad (5)$$

$$Ru(NH_3)_5NO^{2+} + t\text{-B}\dot{u}\text{OH} \longrightarrow \text{permanent product}\ (k = 3.7 \times 10^9\ M^{-1}\ sec^{-1}) \qquad (6)$$

Reaction 6 apparently competes successfully with the normal bimolecular decay of t-Bu̇OH.

The pulse radiolysis of an air-saturated ($[O_2] = 2.5 \times 10^{-4}$ *M*) solution containing 1×10^{-3} *M* $Ru(NH_3)_5NO^{3+}$ and 1 *M* t-BuOH at neutral pH generated $Ru(NH_3)_5NO^{2+}$ which decayed in a second-order manner ($k = 3 \times 10^9\ M^{-1}\ sec^{-1}$) *independent* of $[O_2]$ (up to 1.3×10^{-3} *M*). At the same time, *no* permanent product could be seen absorbing in the spectral region 250-400 nm. In the absence of t-BuOH (and hence t-Bu̇OH), $Ru(NH_3)_5NO^{2+}$ reacts with O_2 in a pseudo-first-order manner ($k = 7.6 \times 10^6\ M^{-1}\ sec^{-1}$).[8] The effect of O_2 in the experiments reported here must be the rapid scavenging of t-Bu̇OH to form a peroxy radical (reaction 7) which reacts with $Ru(NH_3)_5NO^{2+}$ (reaction 8). The product of reaction 8 is certainly not the same as that of reaction 6; it is entirely possible that the peroxy radical oxidizes $Ru(NH_3)_5NO^{2+}$ to $Ru(NH_3)_5NO^{3+}$

$$O_2 + t\text{-B}\dot{u}\text{OH} \longrightarrow \cdot O_2BuOH\ (k \sim 10^{10}\ M^{-1}\ sec^{-1}) \qquad (7)$$

$$Ru(NH_3)_5NO^{2+} + \cdot O_2BuOH \longrightarrow\ ?\ (k = 3 \times 10^9\ M^{-1}\ sec^{-1}) \qquad (8)$$

Continuous Radiolysis. The radiolysis of deoxygenated 1×10^{-3} *M* $Ru(NH_3)_5NO^{3+}$ solutions (in the presence or absence of 0.07 *M* acetate buffer) containing 0.1-1.0 *M* t-BuOH at pH 5 produced a green solution with λ_{max} 343 ± 2 nm. Ion exchange of the radiolyzed solution caused the green product to elute with 1 *M* NaCl and to be separated from the unreacted substrate. From a material balance and an evaluation of the concentration of the green product, the value ϵ_{343} 4.6 (±0.4) × 10^3 M^{-1} cm^{-1} was obtained. Considering the different bases for the determination of ϵ, the results obtained in the pulse and continuous radiolyses are in very good agreement. It can be immediately concluded that the green product arises from reaction 6. Figure 2 shows the yield of the green product as a function of dose from which can be calculated *G* (product) = 2.8. This *G* value would arise if reactions 1, 2, 3, and 6 were operative. Some H atoms would be scavenged by t-BuOH under the experimental conditions ($k = 1 \times 10^5\ M^{-1}\ sec^{-1}$)[9] in competition with reaction 4. Even prolonged irradiation (>20% conversion to green product) did not markedly alter the pH of the solution. The slight curvature of the points in Figure 2 which develops after >10% of reaction can be attributed to interaction of radicals with the products of the reaction. The *G* value of green product was not affected to any extent by the presence of millimolar quantities of Cl^-, ClO_4^-, or $TFMS^-$. The green product was not produced in the absence of t-BuOH.

Long term radiolysis of O_2-saturated solutions containing 7.8×10^{-3} *M* $Ru(NH_3)_5NO^{3+}$ and 1 *M* t-BuOH at pH 6.5 in 0.01 *M* $H_2PO_4^-$ yielded a weak absorbance in the 340-nm region of the spectrum amounting to <10% of the expected absorbance on the basis of Ar-purged solutions. Although the 340-nm band is somewhat masked by the absorbance of the substrate at the high concentration used, the lack of any appreciable green product in the continuous radiolysis can be attributed to reaction 7 and the scavenging of $Ru(NH_3)_5NO^{2+}$ by O_2.

Saturation of a solution containing 1×10^{-4} *M* $Ru(NH_3)_5NO^{3+}$ in 1 *M* t-BuOH with N_2O (2.5×10^{-2} *M*) caused only a weak absorption to be generated at 343 nm upon irradiation. Under these conditions, N_2O competes with $Ru(NH_3)_5NO^{3+}$ for e_{aq}^- thereby reducing the yield of $Ru(NH_3)_5NO^{2+}$ and the green product.

$$e_{aq}^- + N_2O \longrightarrow N_2 + OH + OH^-\ (k = 8.7 \times 10^8\ M^{-1}\ sec^{-1}) \qquad (9)$$

Radiolysis of a 1×10^{-2} M $Ru(NH_3)_5NO^{3+}$ solution in 1 M t-BuOH and 1.0 M HTFMS resulted in G (green product) = 1.8. The G value decreased as $[Ru(NH_3)_5NO^{3+}]$ was decreased and increased with increasing acidity. Under these experimental conditions, reactions 4 and 5 would be quantitative so that $G(Ru(NH_3)_5NO^{2+}) = 3.4$. However, reaction 2 would be in competition with the direct reaction of $Ru(NH_3)_5NO^{3+}$ + OH thus causing $G(t\text{-B\dot{u}OH}) < 2.8$. From the observed G value of green product and the knowledge of the concentration of the solutes, we estimate $k(Ru(NH_3)_5NO^{3+} + OH) \sim 10^{10}$ M^{-1} sec^{-1}. This is very similar to the rates of OH reaction with $Ru(NH_3)_5Cl^{2+}$, $Ru(NH_3)_6^{3+}$,[22] and NO(aq).[23]

$$OH + Ru(NH_3)_5NO^{3+} \longrightarrow ?\ (k \sim 10^{10}\ M^{-1}\ sec^{-1}) \quad (10)$$

It is important to note that the same permanent product is apparently obtained upon both continuous and pulse radiolysis of solutions of $Ru(NH_3)_5NO^{3+}$ in t-BuOH. Pulse radiolysis produces high concentrations of radicals and intermediate species which enhances the possibility of radical-radical reactions. In continuous radiolysis, second-order processes involving species present at very low concentrations would be very slow and would be in competition with reactions with the solvent or other solutes. Both t-BůOH and $Ru(NH_3)_5NO^{2+}$ are relatively stable toward solvent or solute interactions[8,10] and so they are able to react even at low concentrations in competition with the bimolecular combination of the radical or the aquation of the complex. The green product is produced because the rate of reaction 6 is faster than the rate of bimolecular radical decay.

The facile reaction between $Ru(NH_3)_5NO^{2+}$ and t-BůOH is analogous to that of NO(aq) with alcohol radicals. Both e_{aq}^- and H react rapidly with NO to produce NO^- ($k > 10^{10}$ M^{-1} sec^{-1}).[23-27] In the presence of alcohols,[28] the alcohol radical reacts with NO(aq) to yield N_2O, NO_2^-, and the aldehyde. In our case, reaction of t-BůOH at the coordinated NO of the reduced species is suggested; the inertness of the Ru center to substitution would allow the combination product to be stabilized. Writing the complex as $Ru^{II}\text{-}\dot{N}O$, reaction with t-BůOH can be viewed as a radical-radical combination.

The green product is not $Ru(NH_3)_5NO^{2+}$ nor $Ru(NH_3)_5NO_2^+$ which have been characterized in the past.[2,8,9] No green product is produced upon the radiolysis of $Ru(NH_3)_5OH^{2+}$ (pH 5) or $Ru(NH_3)_5OH_2^{2+}$ (pH 3) in 1 M t-BuOH. However, a green product of +2 charge absorbing intensity at 343 nm was detected from the radiolysis of 1×10^{-3} M *cis*- or *trans*-$Ru(NH_3)_4NO(OH_2)^{3+}$ in 1 M t-BuOH at pH 6.5.

Isolation of the Green Product. Attempts to isolate the green product produced from the continuous radiolysis of $Ru(NH_3)_5NO^{3+}$ in 1 M t-BuOH at pH 5 as the Br^-, ClO_4^-, BF_4^-, $TFMS^-$, or PF_6^- salts were frustrated by the extreme solubility of the green complex in a variety of solvents (water, acetone, methanol). Rotary evaporation to dryness of the green complex, obtained by ion exchange and elution with 2 M HBr of HCl, resulted in some decomposition. However, saturated filtered solutions of $NaBPh_4$ did precipitate the green product. This solid was invariably contaminated by trace impurities of Ru nitrosyls which could be removed by ion exchange of the product solution prior to precipitation of the BPh_4^- salt. In order to remove free t-BuOH, the product solution was washed repeatedly with ether. The aqueous layer was then adsorbed onto Dowex 50W-X8 resin and washed with several hundred milliliters of water. The green BPh_4^- salt was readily precipitated from the elution of the complex from the column with 1 M NaCl at pH 3. The solid was collected by filtration and allowed to dry in a vacuum desiccator. The BPh_4^- salt is readily soluble in anhydrous ether but is insoluble in water. The elution properties of the green complex were similar to those of other +2-charged metal ammine complexes.

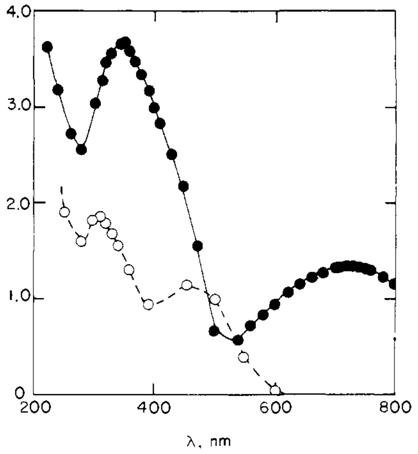


Figure 3. ○, absorption spectrum of $Ru(NH_3)_5NO^{3+}$ in 0.01 M HCl and 1.0 M NaCl; ●, absorption spectrum of the green product obtained upon ion exchange of the radiolyzed solution using 0.01 M HCl and 1.0 M NaCl to elute the product.

Uv-Visible Spectrum. Figure 3 shows the uv-visible spectrum of the green product in aqueous solution as the Cl^- salt compared to that of $Ru(NH_3)_5NO^{3+}$. Two absorption maxima are seen at 343 nm (ϵ 4.5 (± 0.4) $\times 10^3$ M^{-1} cm^{-1}) and 740 nm (ϵ 22 M^{-1} cm^{-1}). The values of ϵ are based upon the ruthenium analysis and material balance.

Elemental Microanalysis. The composite of several microanalytical results indicated that the precipitated green product contained 2 mol of BPh_4^- and 6 mol of N in two different oxidation states per mole of Ru. In addition, the total carbon was somewhat higher than that expected from BPh_4^- alone. Viewing the green product as an adduct between t-BůOH and the reduced nitrosyl, we obtain the following. *Anal.* Calcd for $[Ru(NH_3)_5\{(NO)CH_2C(CH_3)_2OH\}][B(C_6H_5)_4]_2 \cdot 2H_2O$: Ru, 10.5; N, 8.7; H, 7.1; C, 64.8; B, 2.2. Found:[30] Ru, 9.6 ± 0.1; N, 9.1 ± 0.1; H, 6.6 ± 0.1; C, 64.7 ± 0.3; B, 2.4 ± 0.1. The quality of the comparison of the calculated and found values is, of course, conditional to some extent on the number of moles of water of hydration one assumes to be present and the unknown number of moles actually present in the solid sample.

Nmr Spectrum. Figure 4 illustrates the nmr spectrum of the BPh_4^- salt of the green product in pyridine-d_5. In comparison with the spectrum of $NaBPh_4$ in the same solvent, new bands at τ 1.5 and 5.2 are similar to those obtained for free t-BuOH in this solvent. The broad band at τ 4.0 and the shoulder at τ 4.2 are consistent with those expected for pentaammine (as $Ru(NH_3)_5X$) protons. The additional weak peak at τ 4.8 may be attributed to the methylene hydrogens in the $-CH_2C(CH_3)_2OH$ moiety, possibly shifted downfield by interaction with the Ru-NO residue. The nmr spectrum suggests that the $-CH_2C(CH_3)_2OH$ is bound to the Ru-NO system through the methylene C atom and not the alcoholic O atom. The sharpness of the signal for the methyl protons at τ 1.5 suggests that the complex is diamagnetic in solution.

Ir Spectrum. An ir spectrum of the residue obtained from the roto-evaporation to dryness of the 1 M HBr ion-exchange eluent indicated a band at 3550 cm^{-1} due to free -OH in alcohols, bands due to C-H (in the 3000-cm^{-1} region), and an unidentified band at 1380 cm^{-1} in addition to those bands usually assigned to ammine vibration (3260

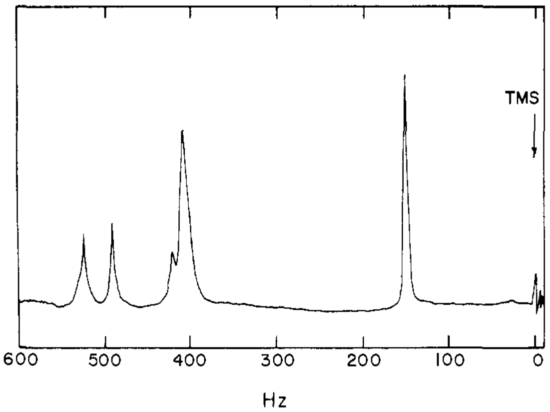
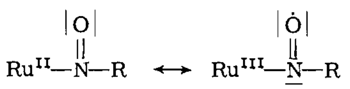


Figure 4. Proton nmr spectrum of the BPh_4^- salt of the green product in pyridine-d_5. All peaks are recorded relative to TMS.

(broad), 1620, 1300, and 790 cm^{-1}). The spectrum of the pure BPh_4^- salt is more difficult to interpret due to interference by the bands from the anion. However, several features are apparent from a comparison of the spectrum of the BPh_4^- salt with that of $NaBPh_4$ or $[Ru(NH_3)_5NO](BPh_4)_3$ (Figure 5): (1) there is no characteristic NO^+ absorption band in the 1900-cm^{-1} region, (2) a band of medium intensity appears at 3520 cm^{-1}, (3) new bands appear at 1370, 1365, 1340, 1305, and 1318 cm^{-1}. The 3520-cm^{-1} band, indicative of free OH, again is evidence for a carbon-bonded alcohol moiety. Using $Ru(NH_3)_5{}^{15}NO^{3+}$ as the source of the reduced nitrosyl and the green product, the BPh_4^- salt displayed a small but significant shift of ~10 cm^{-1} to lower energy of the 1370 and 1365-cm^{-1} bands.

It is more difficult to offer an explanation for the origin of the band system at 1365-1370 cm^{-1}. Reed and Roper[31] have generated alkylnitrites of the form $IrCl_3L_2(ONOR)$ from the reaction of $Ir(NO)Cl_3L_2^+$ with ROH. Their observed value of ν_{NO} = 1550 cm^{-1} indicates that our green product is not an alkylnitrite complex. Nitroso complexes of the form M(NO)R involving M-N and N-R bonds have been synthesized (for example, $PtCl_2(Ph\text{-}NO)_2)^{32}$ and they show ν_{NO} in the 1446-cm^{-1} region. Although the evidence previously presented favors a Ru(II) nitroso structure (I) for our green product, derived from the coupling of $Ru(NH_3)_5NO^{2+}$ and t-BuOH, the ir data do not support that structure. However, a Ru(III) nitroxide valence tautomeric form (II) can be written; at this stage we cannot determine whether II is in a singlet or triplet ground state. Indeed, Waters has isolated coordinated nitroxides and characterized them by esr methods.[33,34] A nitroxide of cobalt, $Co[ON(t\text{-}Bu)_2]_2X_2$, obtained by treating CoX_2 with $(t\text{-}Bu)_2NO$, exhibited ν_{NO} = 1326 cm^{-1}.[35] Although our formulation of the nitroxide (II) would contain reactive α-hydrogens,[36] coordination of the nitroxide could provide a stabilizing effect to some extent.[34]



$$\underset{\text{I}}{Ru^{II}\text{—}\overset{\overset{|O|}{\|}}{N}\text{—}R} \longleftrightarrow \underset{\text{II}}{Ru^{III}\text{—}\overset{\overset{|\dot{O}|}{\|}}{\underline{N}}\text{—}R}$$

The possibility also remains that the 1365-cm^{-1} band system arises from the nitroso formulation (I) in which hydrogen bonding exists between the nitroso oxygen and ammine hydrogens. However, one then would expect a shifting of ν_{NH} in the ammine ligand. The particular valence tautomerization I ↔ II that we suggest is unique in the sense that although individual nitroso or nitroxide complexes have been prepared in the past, the associated metal centers have primarily been those that do not exhibit variable valence.

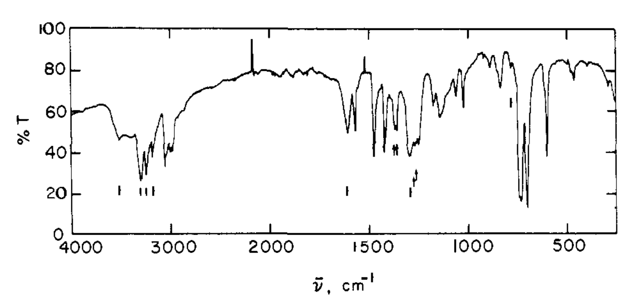


Figure 5. Ir spectrum of the BPh_4^- salt of the green product in KBr matrix. The arrows designate peaks which did not appear in a KBr matrix containing only $NaBPh_4$.

The resolution of the nitroxide form of the valence tautomer is analogous to the experimental evidence for pseudorotation. Although only one signal is observed for $Fe(CO)_5$ in the ^{13}C nmr,[37] the ir indicates two types of CO as expected for a trigonal bipyramid array.[38] If we interpret our ir data as representing structure II, the time scale of the proton-nmr experiment[39] is such that an averaging of the spins on Ru(III) and the nitroxide ligand would yield a net diamagnetism with no shifting or broadening of the proton resonance signals from the methyl protons alcoholic ligand fragment. In contrast, the shorter time resolution involved in ir measurements[40] permits the nitroxide form to be detected. Because of the numerous ir bands arising from the BPh_4^- anion, we cannot completely exclude the possibility of the presence of an equilibrium amount of the two valence tautomers. However, an impure sample of the green product as the Br^- salt (containing $[Ru(NH_3)_4(NO)Br]Br_2$) did not show any additional ir bands in the region 1300-1600 cm^{-1}. It should be noted that while individual M-NO^- or M^{n-2}-NO^+ complexes have been observed,[41-44] $Ru(NH_3)_5NO^{3+}$ displays only one ir band at 1908 cm^{-1} corresponding to ν_{NO}.[46] This complex also displays diamagnetic behavior and one assumes that the coupling of the electron spins between the nitrosyl ligand and the metal center produces a singlet ground state. Of course, the differences in the nmr and ir spectra for the green product may merely be due to different equilibrium concentrations of the tautomeric forms in solution (nmr) and in the KBr matrix (ir).

Conclusion

The one-electron reduction of $Ru(NH_3)_5NO^{3+}$ produces $Ru(NH_3)_5NO^{2+}$, a reactive radical-like species which reacts with the $\cdot CH_2C(CH_3)_2OH$ radical to form a N-C bonded adduct. This product has been isolated and fully characterized and can be written in two valence tautomeric forms: Ru(II) nitroso or Ru(III) nitroxide. This work represents a complete study of the radiolysis of a metal complex where the rate constants and transient and product spectra have been employed for the *radiolytic synthesis* of a new complex. The possibility now exists for similar radiolytic syntheses of metal-nitrosyl derived complexes by the judicious choice of metal center and radical.

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References and Notes

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(2) Presented in part at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, INOR 177.

(3) M. Buchbinder and J. Armor, *Inorg. Chem.*, **12**, 1086 (1973).
(4) J. N. Armor, *Inorg. Chem.*, **12**, 1959 (1973).
(5) R. Cheney and J. N. Armor, work in progress; M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, 1117 (1970).
(6) J. N. Armor, Symposium on the "Activation of Small Molecules by Transition Metals," Buffalo, N.Y., June 1972.
(7) J. N. Armor, G. Tom, S. Frank, M. Weaver, and F. Anson, submitted for publication.
(8) J. N. Armor and M. Z. Hoffman, *Inorg. Chem.*, **14**, 444 (1975).
(9) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).
(10) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73**, 3794 (1969).
(11) J. N. Armor, H. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 5928 (1968).
(12) K. Gleu and I. Buddecker, *Z. Anorg. Allg. Chem.*, **268**, 202 (1952).
(13) J. Spinks and R. Woods, "An Introduction to Radiation Chemistry," Wiley, New York, N.Y., 1964, p 106.
(14) J. N. Armor, Ph.D. Thesis, Stanford University, May 1970.
(15) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).
(16) Developed by R. Cheney in our laboratory.
(17) J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961).
(18) M. Anbar in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N.Y., 1968, p 65.
(19) L. M. Dorfman and G. E. Adams, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 46** (1973).
(20) M. Anbar, M. Bambenek, and A. B. Ross, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 43** (1972).
(21) B. H. J. Bielski and J. M. Gebicki, *Advan. Radiat. Chem.*, **2**, 177 (1970).
(22) J. H. Baxendale, M. A. J. Rogers, and M. D. Ward, *J. Chem. Soc. A*, 1246 (1970).
(23) W. A. Seddon and M. J. Young, *Can. J. Chem.*, **48**, 394 (1970).
(24) M. Grätzel, S. Taniguchi, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **74**, 1003 (1970).
(25) W. A. Seddon, J. Fletcher, and F. C. Sopchrphyn, *Can. J. Chem.*, **51**, 1123 (1973).
(26) W. A. Seddon and H. C. Sutton, *Trans. Faraday Soc.*, **59**, 2323 (1963).
(27) R. J. Knight and H. C. Sutton, *Trans. Faraday Soc.*, **63**, 2628 (1967).
(28) T. W. Woodward and H. C. Sutton, *Trans. Faraday Soc.*, **62**, 70 (1966).
(29) F. Bottomley and J. Crawford, *J. Chem. Soc., Dalton Trans.*, 2145 (1972).
(30) In the past, we have encountered some difficulty in elemental analysis of ruthenium nitrosyls. This particular analysis best represents at least four separate analyses of this complex by three independent microanalytical laboratories. The presence of boron complicates the Ru analysis. The results are presented with the upper and lower limits of the analysis.
(31) C. A. Reed and W. R. Roper, *J. Chem. Soc., Dalton Trans.*, 1243 (1972).
(32) A. L. Balch and D. Petridis, *Inorg. Chem.*, **8**, 2249 (1969).
(33) M. Swanwick and W. Waters, *Chem. Commun.*, 930 (1970).
(34) W. Waters, *J. Chem. Soc., Chem. Commun.*, 1087 (1972).
(35) W. Beck, K. Schmidtner, and H. J. Keller, *Chem. Ber.*, **100**, 503 (1967).
(36) A. R. Forrester, J. M. Hay, and R. H. Thompson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N.Y., 1968, pp 180–246.
(37) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).
(38) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N.Y., 1970, p 194.
(39) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).
(40) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).
(41) J. P. Collman, P. Farnham, and G. Docetti, *J. Amer. Chem. Soc.*, **93**, 1789 (1971).
(42) J. H. Enemark and R. D. Feltham, *Proc. Nat. Acad. Sci. U.S.*, **69**, 3534 (1972).
(43) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1479 (1971).
(44) C. G. Pierpont, D. G. van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 4760 (1970).
(45) A. F. Shreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm, and J. D. Gunter, *Inorg. Chem.*, **11**, 880 (1972).
(46) S. Pell and J. N. Armor, *Inorg. Chem.*, **12**, 873 (1973).

Catalytic Reactions Using Polymer-Bound vs. Homogeneous Complexes of Nickel, Rhodium, and Ruthenium

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Abstract: A series of styrene-divinylbenzene resins were diphenylphosphinated and then complexed with the homogeneous catalysts $(PPh_3)_2Ni(CO)_2$, $(PPh_3)_3RhCl$, $(PPh_3)_3RhH(CO)$, and $(PPh_3)_2RuCl_2(CO)_2$. Reactions catalyzed by the polymer-anchored catalysts were compared with the same reactions carried out with the corresponding homogeneous catalyst. Butadiene cyclooligomerization to 4-vinylcyclohexene, **6**, (*Z,Z*)-1,5-cyclooctadiene, **7**, and (*E,E,E*)-1,5,9-cyclododecatriene, **8**, was effected using $(PPh_3)_2Ni(CO)_2$ and its anchored analogs. Selective hydroformylation of the exocyclic double bond of **7** to a mixture of normal and branched aldehydes **14** and **15** was carried out over $(PPh_3)_3RhH(CO)$ and its anchored analogs as was the hydroformylation of 1-pentene. The rates of hydroformylation as a function of the polymer-bound $-PPh_2/Rh$ ratio, cross-link density, resin particle size, and diffusion effects are discussed. The hydrogenation of **6**, **7**, and **8** by $(PPh_3)_3RhCl$ and its anchored analogs gave ethylcyclohexane, cyclooctane, and cyclodecane. The effect of catalyst anchoring on rates was discussed. Selective hydrogenation of **6**, **7**, and **8** to ethylcyclohexene, (*Z*)-cyclooctene, and (*E*)-cyclododecene was effected using $(PPh_3)_2RuCl_2(CO)_2$ homogeneously and anchored, in the presence of excess PPh_3. Excess anchored phosphine units could not promote the selectivity of these hydrogenations. A comparison of homogeneous vs. anchored catalysts in terms of rates, diffusion, internal polymer mobility, and product selectivity is made where possible.

In recent years the discovery and utility of homogeneous hydrogenation,[1] isomerization,[2] hydrosilation,[3] oligomerization,[4,5] and carbonylation[6] reactions have expanded enormously. Commercial processes based on homogeneously catalyzed routes are becoming increasingly important as evidenced by the Wacker[7] process and others.[8] However, homogeneous catalysis can exhibit the problems of product contamination and catalyst loss, where the products are not readily separated from the catalyst. Anchoring homogeneous catalysts to polymers or other supports effectively "heterogenizes" them, allowing their use in fixed beds and simplifying catalyst recovery. Thus, the anchoring of homogeneous catalysts has recently been the object of several groups.[9]

When a homogeneous catalyst is heterogenized in such a way that it can react, mechanistically, in the same manner as its homogeneous counterpart, the greater selectivity and activity of the homogeneous catalyst is preserved. However, the distinction between homogeneous and heterogeneous catalysis can become difficult to distinguish,[10] especially when highly cross-linked resins or glass or metal surfaces are used to anchor the catalyst.[9c] Where reactants must diffuse into a swollen polymer matrix to reach a bound catalyst site, reaction rates may be lowered because diffusion becomes a rate limiting effect. This was noted by Grubbs[11] in hydrogenations over bound Wilkinson's catalyst, by Pittman, et al.[12] for hydroformylation reactions over polymers to which $Co_2(CO)_8$ was bound by phosphine replacement of