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The Reactivity of Cobalt(I) Complexes Containing Unsaturated Macrocyclic Ligands in Aqueous Solution[1]

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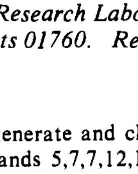
Abstract: The fast kinetics technique of pulse radiolysis has been used to generate and characterize, in aqueous solution, Co(I) complexes containing the tetradentate 14-membered macrocyclic ligands 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (4,11-dieneN_4), 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene (4,14-dieneN_4), and 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (1,3,8,10-tetraeneN_4). The reaction of the hydrated electron, e_{aq}^-, with the Co(II) complexes ($k \sim 5 \times 10^{10}\ M^{-1}\ sec^{-1}$) produces the corresponding Co(I) species. Co^I(1,3,8,10-tetraeneN_4) is also generated by the action of CO_2^- and $(CH_3)_2\dot{C}OH$ radicals on Co(II). The absorption spectra of these monovalent complexes have been determined and their decay kinetics studied as a function of pH and added scavengers. The Co(I) species behave as bases, reacting with proton donors such as H_3O^+, CH_3CO_2H, $H_2PO_4^-$, NH_4^+, HPO_4^{2-}, and H_2O. They also behave as powerful reducing agents, transferring an electron ($k \sim 10^9$ to $10^6\ M^{-1}\ sec^{-1}$) to a variety of organic acceptors and one-electron metal complex oxidants such as Fe(III), Co(III), Cr(III), and Ru(III) amine, bipyridyl, and macrocyclic complexes. The Co(I) species react rapidly with N_2O, CH_3I, and O_2.

The chemistry of cobalt complexes containing macrocyclic or tetradentate ligands with delocalized electronic structures may be taken as an approximate model for the reactions of vitamin B_{12} in biochemical processes.[3,4] Among the oxidation states of cobalt, the Co(I) state has been proposed as a reaction intermediate in the reduction of cobaloxime and aquocobalamin by CO[5,6] and in biological processes as vitamin B_{12S}.[4,7] Co(I) species display strong nucleophilic character, readily displacing halide ions from alkyl halides producing cobalt-alkyl complexes.[8-10] The catalytic role of some Co(I) complexes has recently been demonstrated in the reduction of several alkyl ammonium ions[10] and in the conversion of nitrogen and acetylene to ammonia and ethylene.[11]

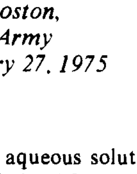
It has previously been reported[12,13] that Co(I) complexes containing the macrocyclic ligands 4,11-dieneN_4 and aneN_4[14] are exceptionally reactive and powerful reducing agents and cannot be handled in protic solvents when generated electrochemically from the corresponding Co(II) complexes. Because of their short lifetimes, these species, or any other Co(I) macrocyclic species, have not been characterized in aqueous solution.

The technique of pulse radiolysis is well suited to the study of such highly reactive low-valent species. The radiolysis of water provides a means of selectively generating one-electron reducing or oxidizing agents. The hydrated electron, e_{aq}^-, is produced directly by the ionizing radiation and is a powerful reducing agent (E_{ox}^0 = 2.8 V).[17] Other reductants, such as CO_2^- and $(CH_3)_2\dot{C}OH$ radicals, can be generated by the reaction of OH radicals, produced in the radiation pulse, with HCO_2^- and $(CH_3)_2CHOH$, respectively.[18,19] The reactions of the radicals with solutes, such as coordination complexes, can be monitored using fast kinetics absorption spectrophotometry with a time resolution of ~0.1 μsec enabling the spectra of short-lived transient intermediates to be observed and their kinetics characterized.

In this paper we describe the reactions of Co(II) complexes containing the 4,11-dieneN_4, 4,14-dieneN_4, and 1,3,8,10-tetraeneN_4 macrocyclic ligands with reducing radicals to generate the corresponding Co(I) species in aqueous solution. The spectra and reactivities of these low-valent complexes are examined in detail. It is important to note that the tetradentate equatorial ligand renders macrocyclic complexes of this type stable towards displacement of the ligand from the metal center so that at least the macrocyclic structure maintains its integrity upon change of the oxidation state of the metal.



Me_6 [14] 4,11-diene N_4



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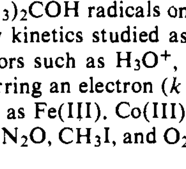
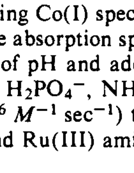


Me_4 [14] 1,3,8,10-tetraene N_4



Me_6[14]ane N_4

Experimental Section

Apparatus and Techniques. The pulse radiolysis apparatus has already been described in detail.[20-22] Single pulses of 2.3 MeV electrons of ~30 nsec duration were generated (Febetron 705) and absorbed by the solution contained in a quartz cell (optical path = 2 cm). A 450-W xenon lamp which could be pulsed, thereby increasing the light output by a factor of 20–25, was used as the monitoring light source. Glass filters and a synchronized shutter were used to minimize the photolytic effects of the monitoring light.

The pH of the solutions was adjusted by use of $HClO_4$, KOH, phosphate (1 m*M*) or tetraborate (1 m*M*) buffer, except as otherwise indicated. Solutions were prepared from the solid salt just prior to use and were deoxygenated (except where indicated) by an Ar purge or saturated with N_2O at 1 atm partial pressure (2.5×10^{-2} *M*). Extinction coefficients were evaluated by means of SCN^- dosimetry taking $\epsilon_{500} = 7.6 \times 10^3\ M^{-1}\ cm^{-1}$ for the $(SCN)_2^-$ radical.[23] Rate constants were determined by a least-squares computer fit of the kinetics data to the usual first- and second-order equations.

Preparation of Complexes. The 4,11-dieneN_4 ligand as the ClO_4^- salt was prepared[24] from acetone and ethylenediamine by the method of Curtis[25] and used in reaction with cobaltous acetate in methanol to prepare[26] $[Co(4,11\text{-diene}N_4)(ClO_4)]ClO_4$. $[Co(4,14\text{-diene}N_4)(ClO_4)]ClO_4$ was similarly prepared from 4,14-dieneN_4 in ethanol,[26] the free base having been obtained by the addition of cyanide[27] to the analogous Ni(II) complex.[28] Dissolution of these low-spin five-coordinate Co(II)-perchlorato complexes in water results in the displacement of the coordinated perchlorate group by H_2O giving complexes of the form $[Co(4,11\text{-diene}N_4)(H_2O)_2]^{2+}$ in aqueous solution.[26,29] A sample of $[Co(1,3,8,10\text{-tetraene}N_4)(H_2O)_2](ClO_4)_2$[32] was kindly supplied to us by Professor J. F. Endicott (Wayne State University).

The other complexes were available from our laboratory reserves. The sample of $Cr(bpy)_3^{3+}$ was also supplied to us by Professor Endicott and the Ru(III) complexes by Professor J. N. Armor (Boston University).

Results

Reactions of Co(II) with e_{aq}^- and Other Reducing Radicals. Kinetics. The reaction rate constants for the various Co(II) macrocyclic complexes (as their perchlorate salts) with e_{aq}^- were determined, in the presence of 1 *M tert*-butyl alcohol as an OH radical scavenger,[34] from the pseudo-first-order decay of e_{aq}^- monitored at 700 and 500 nm. From the dependence of these rate constants on the substrate concentration ($1.25\text{–}2.50 \times 10^{-5}$ *M*), the values of $k(Co(II) + e_{aq}^-)$ were calculated and are recorded in Table I. Decays were monitored over three-four half-lives.

No reaction was observed between the Co(II) complexes of 4,11-dieneN_4 and 4,14-dieneN_4 with the reducing radicals CO_2^- and $(CH_3)_2\dot{C}OH$ by monitoring the wavelengths at which the Co(I) species absorb (see following section) implying that $k \ll 10^7\ M^{-1}\ sec^{-1}$ for these processes. However, CO_2^- and $(CH_3)_2\dot{C}OH$ do reduce $Co^{II}(1,3,8,10\text{-tetraene}N_4)$ with rate constants of 4.7×10^9 and 5.5×10^8 $M^{-1}\ sec^{-1}$, respectively. These latter experiments were conducted with Ar-purged solutions containing 1×10^{-4} *M* Co(II) and 0.1 *M* HCO_2^- at pH 6.5 or 1×10^{-3} *M* Co(II) and 2 *M* 2-propanol at pH 1.25 and 6.5. Under these conditions, CO_2^- and $(CH_3)_2\dot{C}OH$ constitute approximately one-half of the total reducing equivalents in neutral solution with e_{aq}^- constituting the other half; in acidic solution $(CH_3)_2\dot{C}OH$ constitutes virtually all of the reducing equivalents. Low doses of radiation were employed in order to keep the radical concentrations $<2 \times 10^{-5}$ *M*. In this way, the complex radical reactions could compete effectively with the radical-radical combination reactions which have $2k$ values for CO_2^- and $(CH_3)_2\dot{C}OH$ of 1.4×10^9 and $2.0 \times 10^9\ M^{-1}\ sec^{-1}$, respectively.[20,35] It should be noted that these radicals also reduce the corresponding Co(III) complexes to Co(II).[36]

Table I. Rate Constants for the Reaction of Co(II) Macrocyclic Complexes with e_{aq}^-, CO_2^-, and $(CH_3)_2COH$ Radicals

Reductant, R	pH of experiment	$k(Co(II) + R)$, $M^{-1}\ sec^{-1}$		
		Co^{II}(4,11-dieneN_4)	Co^{II}(4,14-dieneN_4)	Co^{II}(1,3,8,10-tetraeneN_4)
$e_{aq}^{-\,a}$	6–10	4.4×10^{10}	3.4×10^{10}	4.9×10^{10}
$CO_2^{-\,b}$	6.5	—	—	4.7×10^9
$(CH_3)_2\dot{C}OH^c$	1.25, 6.5	—	—	5.5×10^9

[a] Determined in the presence of $(1.25\text{–}2.5) \times 10^{-5}$ *M* Co(II) substrate, 1 *M tert*-butyl alcohol, 1 m*M* phosphate or borate buffer in Ar-purged solutions. Value for Co^{II}(1,3,8,10-tetraeneN_4) was determined at pH 6.5 only. [b] Determined in the presence of 1×10^{-4} *M* Co(II) substrate, 0.1 *M* HCO_2^- in Ar-purged solutions. [c] Determined in the presence of 1×10^{-3} *M* Co(II) substrate, 2 *M* 2-propanol, perchloric acid, or 1 m*M* phosphate buffer in Ar-purged solutions.

Transient Spectra. The rapid reaction of e_{aq}^- with the macrocyclic complexes assured that transient species would be fully formed ≤0.5 μsec after the pulse and their absorption spectra determined before any appreciable decay had occurred. The transient species were observed in Ar-purged solutions containing 5×10^{-4} *M* Co(II), 1 *M tert*-butyl alcohol, and 1 m*M* buffer. All spectra were corrected for the depletion of the substrate and for the absorption of the radical derived from *tert*-butyl alcohol,[20] whenever necessary.

The transient optical absorption spectrum obtained from the reaction of e_{aq}^- with Co^{II}(4,11-dieneN_4) at pH 7 is shown in Figure 1. This spectrum, with bands at 630 (ϵ 9100 $M^{-1}\ cm^{-1}$), 450 (1060), 330 (3230), and 290 (3675) nm, is independent of pH from 3.5 to 10. Vasilevskis and Olson[13] have investigated the electrochemical reduction of this Co(II) complex in CH_3CN and report that the resultant Co(I) species has a spectrum with maxima at 679 (ϵ 15950 $M^{-1}\ cm^{-1}$), 450 (~1100), 350 (3300), 307 (3600), and 245 (2950) nm. Despite the small differences in λ_{max} and ϵ between the two solvents, there is little doubt that the action of e_{aq}^- on the Co(II) complex generates the Co(I) species. The transient spectrum obtained from the reaction of e_{aq}^- with Co^{II}(4,14-dieneN_4) at pH 7 (Figure 2) shows five bands of similar intensities (ϵ 2500–3500 $M^{-1}\ cm^{-1}$) in the uv-visible region. The spectrum of the Co^I(4,14-dieneN_4) species has not been previously reported.

The reaction of e_{aq}^- with Co^{II}(1,3,8,10-tetraeneN_4) at pH 6.5 produced a transient spectrum with a broad band centered at 700 nm (ϵ 8400 $M^{-1}\ cm^{-1}$) shown in Figure 3. A similar spectrum has been obtained by Endicott upon the electrochemical reduction of this Co(II) complex in aqueous solution.[37] The reduction of this complex by CO_2^- at pH 6.5 and by $(CH_3)_2\dot{C}OH$ at pH 1.25 and 6.5 produced the same transient spectra as from e_{aq}^-. Slightly higher ϵ values (9500–10200 $M^{-1}\ cm^{-1}$) were observed but these differences are deemed to be within the experimental errors.

Reactions of Co(I). With Acids. Both Co^I(4,11-dieneN_4) and Co^I(4,14-dieneN_4) were unstable in aqueous solution and their spectra decayed via pH-dependent first-order kinetics producing a residual absorption with bands at 280 and 320 nm (Figures 1 and 2). Plots of the first-order rate constants for the decay of Co^I(4,11-dieneN_4) and Co^I(4,14-dieneN_4), monitored at 630 and 590 nm, respectively, as a function of pH are shown in Figure 4 and in the insert to Figure 2. The Ar-purged *tert*-butyl alcohol (1 *M*) solutions contained 5×10^{-4} *M* Co(II) at pH >4.2 and 5×10^{-3} *M* Co(II) at pH ≤4.0 with 1 m*M* buffer or $HClO_4$. The ionic strengths of the solutions were not specifically controlled but were low and in a narrow range; $\mu = 0.002\text{–}0.004$ *M* at pH >4.2 and ~0.002 *M* at pH <4.0.

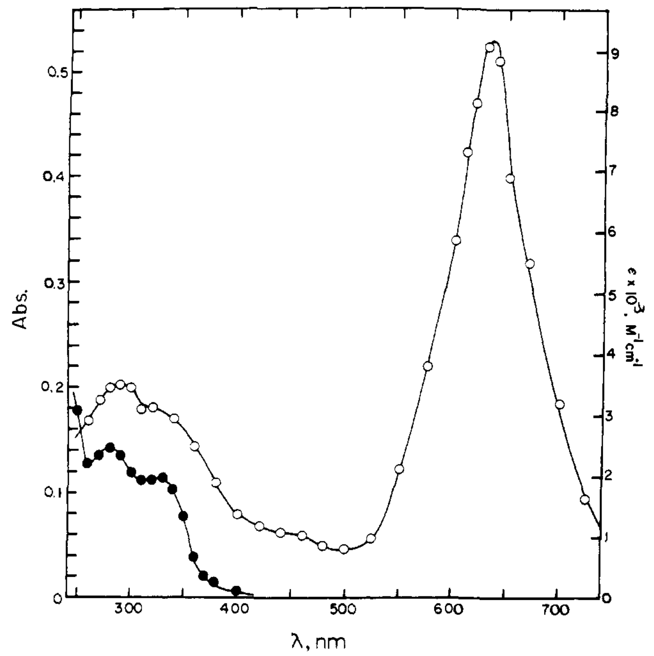


Figure 1. Absorption spectra of Co^I(4,11-dieneN$_4$) generated from the reaction of e_{aq}^- with Co(II) in 1 *M tert*-butyl alcohol and 1 m*M* phosphate buffer at pH 7, ○. Absorption spectrum resulting from the decay of Co^I(4,11-dieneN$_4$) at pH 7 (●) 20 sec after the pulse.

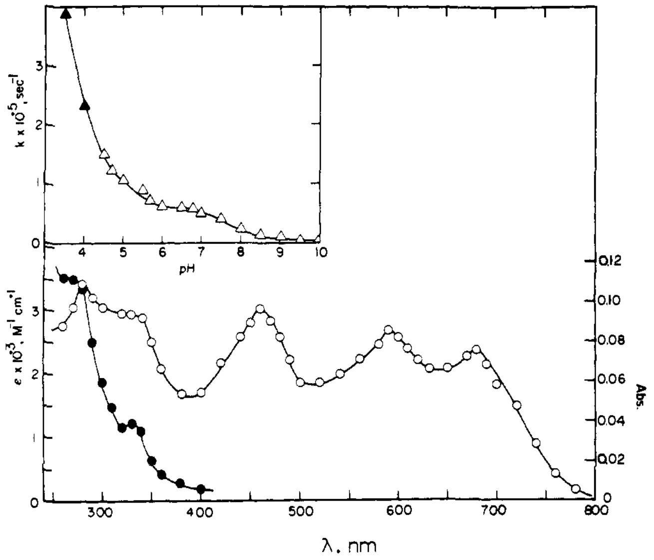


Figure 2. Absorption spectrum of Co^I(4,14-dieneN$_4$) generated from the reaction of e_{aq}^- with Co(II) in 1 *M tert*-butyl alcohol and 1 m*M* phosphate buffer at pH 7, ○. Absorption spectrum resulting from the decay of Co^I(4,14-dieneN$_4$) at pH 7 (●) 20 sec after the pulse. Insert: Dependence upon pH of the first-order rate constant for the decay of Co^I(4,14-dieneN$_4$) in deoxygenated solutions containing 1 *M tert*-butyl alcohol in the presence of 1 m*M* phosphate or tetraborate buffer, △; in the absence of buffer, ▲.

Several features of the decay rate constants should be noted: (1) there is nearly a 1000-fold variation of k over the pH range 3.5–10; (2) at pH <4.2 and constant ionic strength, the value of k increases rapidly upon addition of acid; (3) in solution buffered with phosphate, an inflection point at pH ~7.2 is observed. The results suggest that the Co^I(dieneN$_4$) species react with H^+ in acidic solution and with the conjugate forms of the phosphate buffer ($H_2PO_4^-$ and HPO_4^{2-}; pK_a = 7.2) in neutral solution. No effect of borate buffer was observed at pH 8.5–10.

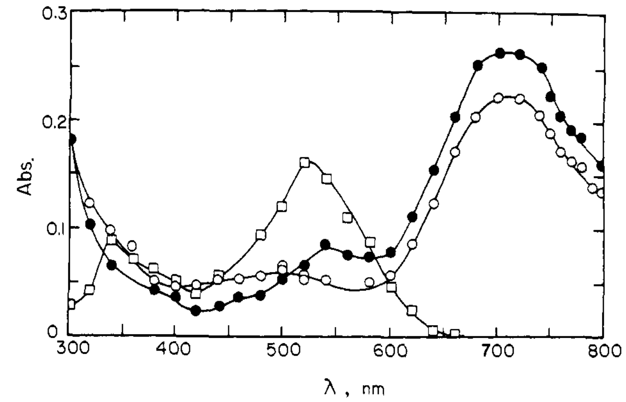


Figure 3. Absorption spectrum of Co^I(1,3,8,10-tetraeneN$_4$) generated from the reaction of e_{aq}^- with Co(II) in 1 *M tert*-butyl alcohol and 1 m*M* phosphate buffer at pH 6.5, ●. Absorption spectrum recorded 400 μsec after the pulse, ○. Absorption spectrum resulting from the decay of Co(I) (□) 20 sec after the pulse.

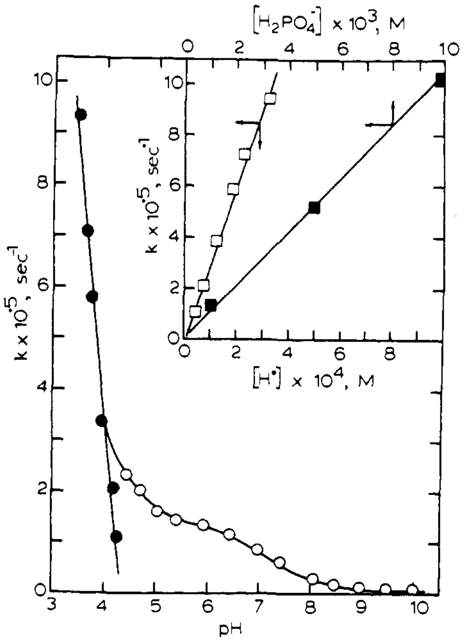


Figure 4. Dependence upon pH of the first-order rate constant for the decay of Co^I(4,11-dieneN$_4$): in the presence of 1 m*M* phosphate or tetraborate buffer, ○; in the absence of buffer with acidity controlled by $HClO_4$, ●. Insert: Dependence of first-order rate constant on [H_3O^+] (□) and [$H_2PO_4^-$] (■).

The first-order rate constants were found to be linearly dependent upon [H^+] and [phosphate] as well as the concentration of other proton donors such as CH_3CO_2H and NH_4^+. The data for Co^I(4,11-dieneN$_4$) are shown in Figures 4 and 5. From the slopes of these plots, the second-order rate constants for the reaction of Co(I) with various proton donors, HA, were evaluated (Table II). The values for H_2O were determined at pH 9–10 in the absence of buffer but at low radiation doses so as to maintain the pH constant. With one exception, the experiments were performed at pH values well below the pK_a of the acids in order to ensure the absence of the conjugate base. The pH of the acetic acid solution was 4.8 so that [CH_3CO_2H] = [$CH_3CO_2^-$]. For all these experiments, conditions were chosen such that all e_{aq}^- reacted with the Co(II) substrate and none with HA. Furthermore, the concentrations of HA and H^+ were established such that k(Co(I) + HA) ≥ 20k(Co(I) + H^+). In all cases, the decay of Co(I) was not affected by the presence of *tert*-butyl alcohol.

The Co^I(1,3,8,10-tetraeneN$_4$) species produced in *tert*-butyl alcohol solution at pH 6.5 decayed with $t_{1/2}$ ~ 50–

Table II. Rate Constants for the Reaction of Co(I) with Proton Donors

Proton donor, HA	pK_a of HA	pH of expt	k(Co(I) + HA, M^{-1}sec^{-1})[a] Co^I(4,11-dieneN$_4$)	 Co^I(4,14-dieneN$_4$)	 Co^I(1,3,8,10-tetraeneN$_4$)
H_3O^+	−1.75	Variable	3.1×10^9[b]	1.2×10^9[b]	1.6×10^5[c]
CH_3CO_2H	4.75	4.8	7.5×10^7[d]	—	6.2×10^4[e]
$H_2PO_4^-$[f]	7.2	5.5	9.8×10^7	3.0×10^7	—
NH_4^+[g]	9.25	7.0	6.8×10^5	—	—
HPO_4^{2-}[h]	12.25	10.0	1.0×10^5	—	—
H_2O[i]	15.74	9–10	4.8×10^1	2.0×10^1	—

[a] Determined in Ar-purged solutions at the λ_{max} for the Co(I) species. [b] $5 \times 10^{-3} M$ Co(II), 1 *M tert*-butyl alcohol, pH 3.5–4.2, ionic strength = 0.015 *M*. [c] $1 \times 10^{-3} M$ Co(II), 2 *M* 2-propanol, pH 0.25–1.25, ionic strength = 0.06–0.6 *M*. [d] $2 \times 10^{-3} M$ Co(II), $[CH_3CO_2H]$ = $[CH_3CO_2H]$ = $[CH_3CO_2^-]$ = $(2-10) \times 10^{-3} M$, 1 *M tert*-butyl alcohol, ionic strength = 0.01–0.05 *M*. [e] $2 \times 10^{-3} M$ Co(II), $[CH_3CO_2H]$ = $[CH_3CO_2^-]$ = $(2-10) \times 10^{-3} M$, 2 *M* 2-propanol, ionic strength = 0.01–0.05 *M* [f] $5 \times 10^{-4} M$ Co(II), $[H_2PO_4^-]$ = $(1-10) \times 10^{-3} M$, 1 *M tert*-butyl alcohol, ionic strength = 0.005–0.01 *M*. [g] $1.5 \times 10^{-3} M$ Co(II), $[NH_4^+]$ = $(1-10) \times 10^{-2} M$, 1 *M tert*-butyl alcohol, ionic strength = 0.015–0.1 *M*. [h] $5 \times 10^{-4} M$ Co(II), $[HPO_4^{2-}]$ = $(2-10) \times 10^{-2} M$, 1 *M tert*-butyl alcohol, ionic strength = 0.06–0.3 *M*. [i] $5 \times 10^{-4} M$ Co(II), 1 *M tert*-butyl alcohol, ionic strength = 0.001 *M*.

100 μsec to reveal a second transient absorption (Figure 3) virtually identical with the initial transient but about 16% less intense. This secondary absorption was not observed when the Co(I) species was generated by CO_2^- at pH 6.5 or $(CH_3)_2\dot{C}OH$ radicals at pH 1 and 6.5, indicating that the small loss of the original Co(I) absorption is dependent on the presence of *tert*-butyl alcohol. The rate of the decay of the Co(I) initially produced was independent of [Co(II)], [buffer], and pH (3.5-6.5) but dependent on the radiation dose and thus on [Co(I)], $[\cdot CH_2C(CH_3)_2OH]$, and/or the concentration of products formed from the disappearance of the alcohol radicals. It would appear that the secondary absorption is the Co(I) species remaining after reaction of some of it with scavengers associated with the *tert*-butyl alcohol. Indeed, the decay kinetics of the secondary absorption in the presence of *tert*-butyl alcohol at pH 5 (k = 3.7 × 10^1 sec^{-1}) are virtually identical with those of the initial Co(I) species generated from $(CH_3)_2\dot{C}OH$ in the presence of 2-propanol at pH 5 (k = 4.5 × 10^1 sec^{-1}). The decay of the secondary absorption revealed a residual absorption that was recorded ~20 sec after the pulse. The further stability of this final absorption (Figure 3) was not examined.

The second-order rate constants for the reaction of Co^I(1,3,8,10-tetraeneN$_4$) with proton donors were determined, therefore, in the presence of 2-propanol; k(Co(I) + H$^+$) = 1.6 × 10^5 M^{-1} sec^{-1} at pH 0.25-1.25 and k(Co(I) + CH_3CO_2H) = 6.2 × 10^4 M^{-1} sec^{-1} at pH 4.8. The normal decay of the Co(I) species was also affected by the presence of phosphate buffer and NH_4^+ but the values of k, which are <10^4 M^{-1} sec^{-1}, could not be determined, because of interference by reaction with H$^+$. Decay kinetics of Co^I(1,3,8,10-tetraeneN$_4$) in basic solution were not evaluated because of the instability of the Co(II) substrate at pH >7.

With Organic Electron Acceptors. The rate constants for electron transfer from Co^I(4,11-dieneN$_4$) and Co^I(1,3,8,10-tetraeneN$_4$) to various organic acceptors, A, were determined by monitoring the decay of the Co(I) band, the disappearance of A, or the formation of the corresponding reduced species, $\cdot A^-$ or $\cdot AH$, at a suitable wavelength.[38] Because of the high reactivity of the acceptors with e_{aq}^- to form $\cdot A^-$ or $\cdot AH$, the concentrations of Co(II) (1 × 10^{-3} M) and A (≤5 × 10^{-5} M) were chosen such that no more than 5% of e_{aq}^- would be lost through direct reaction with A. The experiments were carried out at pH 9.2 for Co^I(4,11-dieneN$_4$) and pH 6.5 for Co^I(1,3,8,10-tetraeneN$_4$) in order to minimize the reaction of Co(I) with H$^+$. Solutions contained 1 mM buffer and 1 *M tert*-butyl alcohol. The values of k for some organic acceptors are given in Table III with all but one acceptor (3-benzoylpyridine) showing 100% electron transfer. The spectrum of the $\cdot A^-$ species from the reaction of menaquinone with Co^I(4,11-dieneN$_4$) is shown in Figure 6a and it agrees well with the previously published spectrum.[39]

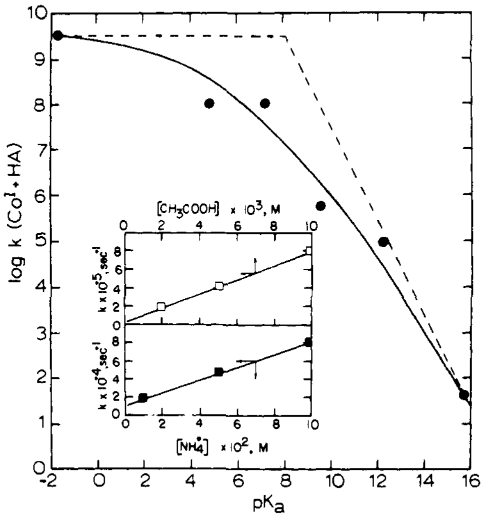


Figure 5. Dependence of log k (Co^I + HA) for Co^I(4,11-dieneN$_4$) on the pK_a values of HA; experimental points taken from Table II. The dashed lines represent slopes of 0 and −1. Insert: Dependence of first-order rate constant for the decay of Co^I(4,11-dieneN$_4$) on $[CH_3CO_2H]$ (□) and $[NH_4^+]$ (■).

The extent of electron transfer from Co(I) to A was determined by comparing the quantitative absorbance due to $\cdot A^-$ formed from the reaction of Co(I) with A with that obtained directly from the reaction of e_{aq}^- with A. Considering the very rapid latter reaction to be 100% efficient in generating $\cdot A^-$,[38] the efficiency of the electron transfer reactions of Co(I) with A could be determined. In Figure 6b a plot is made of the efficiency of electron transfer from Co^I(4,11-dieneN$_4$) as a function of the standard reduction potential of A at pH 9.2, E_m.[38] It can be seen that for acceptors with E_m values more negative than −0.88 V, no electron transfer was observed; for E_m more positive than −0.85 V, transfer was quantitative. The apparent oxidation potential for Co^I(4,11-dieneN$_4$) is evaluated from the midpoint of this "titration" curve to be +0.86 V.

In the same way, transfer from Co^I(1,3,8,10-tetraeneN$_4$) was quantitative to acceptors with E_m values at pH 6.5 more positive than −0.24 V; for acceptors with E_m values more negative than −0.35, no transfer was observed. From this we estimate the apparent oxidation potential of Co^I(1,3,8,10-tetraeneN$_4$) in aqueous solution to be ca. +0.28 V.

The reaction of Co(I) with A is not reversible under these experimental conditions. Indeed, the $\cdot A^-$ radicals themselves undergo irreversible bimolecular decay.[38a,b] Thus, the

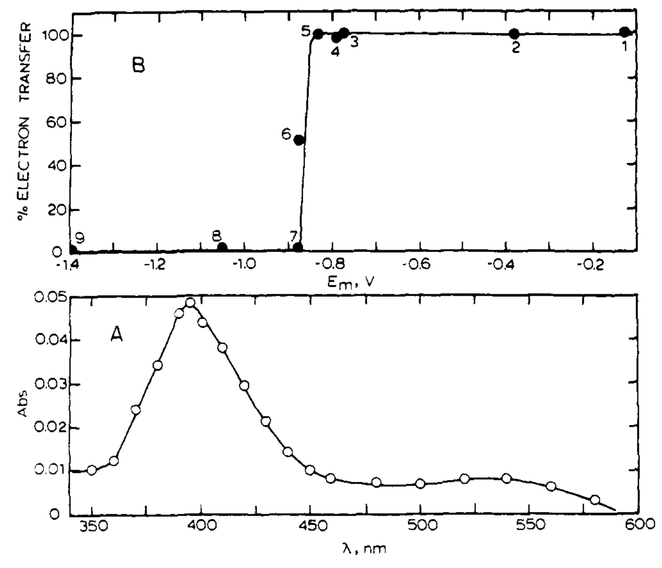


Figure 6. (A) Optical absorption spectrum of the semiquinone radical anion of menaquinone ($\cdot A^-$) produced from the reaction of $Co^I(4,11\text{-dieneN}_4)$ with menaquinone (5×10^{-5} *M*) in the presence of 1 *M tert*-butyl alcohol and 1 m*M* tetraborate at pH 9.2. (B) Dependence of the efficiency of electron transfer (expressed as percent) in the reaction of $Co^I(4,11\text{-dieneN}_4)$ with organic electron acceptors, as a function of the standard reduction potential of the acceptors at pH 9.2 in 1 *M tert*-butyl alcohol and 1 m*M* tetraborate. Acceptors used: 1, menaquinone; 2, 9,10-anthraquinone-2-sulfonate; 3, eosin Y; 4, fluorenone; 5, fluorescein; 6, 3-benzoylpyridine; 7, dimethyl maleate; 8, benzophenone; 9, acetophenone.

apparent oxidation potentials for the Co(I) species differ from the thermodynamic potential.[38f]

With Metal Complexes. $Co^I(4,11\text{-dieneN}_4)$ was generated by the e_{aq}^- reduction of the corresponding Co(II) complex (5×10^{-3} *M*) at pH 9.2 in the presence of $(0.1\text{–}2) \times 10^{-3}$ *M* metal complex oxidants, 1 *M tert*-butyl alcohol, and 1 m*M* tetraborate buffer in Ar-purged solutions. Experiments were performed as rapidly as possible in order to ensure that the M(III) complexes were in the mildly alkaline solution for <30 min. Under these conditions, <70% of e_{aq}^- reacted with Co(II) with the remainder reacting directly with the M(III) complexes. However, low doses of e_{aq}^- ($<2 \times 10^{-5}$ *M*) were used so that the loss of M(III) via reaction with e_{aq}^- was not significant. The conditions chosen also ensured that the Co(I) species reacted with the oxidant and not with H_2O or H^+. Co(I) decayed via first-order kinetics with the rate constant dependent on the concentration of the oxidant. From such pseudo-first-order data, using two–four different oxidant concentrations, the second-order rate constants given in Table III were calculated. Electron transfer from $Co^I(1,3,8,10\text{-tetraeneN}_4)$ to the M(III)-bipyridyl complexes were conducted in Ar-purged solutions at pH 6.5 in the presence of 5×10^{-4} *M* Co(II), 1 *M tert*-butyl alcohol, 1 m*M* buffer, and $(2.5\text{–}5.0) \times 10^{-5}$ *M* M(III).

With CH_3I, O_2, and N_2O. The second-order rate constants for the reaction of the Co(I) species with CH_3I, O_2, and N_2O are given in Table III. These values were determined from the pseudo-first-order decay of the Co(I) species as a function of the reactant concentration. The rate constants for the reaction with CH_3I were determined in Ar-purged solution containing $(2\text{–}5) \times 10^{-4}$ *M* CH_3I, 5×10^{-3} *M* Co(II), 1 *M tert*-butyl alcohol, and 1 m*M* buffer. Under these conditions, all e_{aq}^- reacted with Co(II).

In the presence of O_2, the Co(I) species decayed with *k* $\sim 1 \times 10^9$ M^{-1} sec^{-1}. As far as could be seen, the Co(I) + O_2 reaction did not regenerate the spectrum of the original Co(II) complex. Instead, the spectrum of a final product was observed with a tail absorption between 380 (the lower limit of observation) and 500 nm with ϵ_{380} 900 M^{-1} cm^{-1}.

Table III. Rate Constants for the Reaction of Co(I) with Oxidants

Compound, S	$k(Co(I) + S)$, M^{-1} sec^{-1} $Co^I(4,11\text{-dieneN}_4)^a$	$Co^I(1,3,8,10\text{-tetraeneN}_4)^b$
	Organic Acceptors^c	
Menaquinone	4.6×10^9	—
Indigosulfonate	—	4.9×10^9
9,10-Anthraquinone-2,6-disulfonate	—	3.8×10^9
Riboflavin	—	1.0×10^9
9,10-Anthraquinone-2-sulfonate	4.4×10^9	—
Fluorenone	4.3×10^9	—
3-Benzoylpyridine	4.6×10^8	—
	Metal Complex Acceptors^d	
$Cr(bpy)_3^{3+}$	1.2×10^9	1.6×10^8
$Co(bpy)_3^{3+}$	1.2×10^9	8.5×10^7
$Fe(bpy)_3^{3+}$	2.3×10^7	—
$Ru(NH_3)_6^{2+}$	4.0×10^8	—
$Ru(NH_3)_5NO^{3+}$	3.9×10^7	—
$Co(en)_3^{3+}$	7.9×10^6	—
$Co(NH_3)_6^{3+}$	7.5×10^6	—
$[Co(4,11\text{-dieneN}_4)(OH)_2]^+$	4.0×10^6	—
$[Co(1,3,8,10\text{-tetraeneN}_4)(OH)_2]^+$	6.7×10^6	—
	Other Acceptors	
O_2^e	1.7×10^9 $(9.0 \times 10^8)^f$	1.1×10^9
N_2O^g	3.9×10^7 $(9.0 \times 10^6)^f$	—
CH_3I^h	4.7×10^8	$<10^5$

[a] Determined at 630 nm in Ar-purged solutions containing 1 *M tert*-butyl alcohol at pH 9.2 unless otherwise indicated. [b] Determined at 700 nm in Ar-purged solutions containing 1 *M tert*-butyl alcohol at pH 6.5. [c] 1×10^{-3} *M* Co(II), [oxidant] = $(1.25\text{–}5.0) \times 10^{-5}$ *M*, ionic strength = 0.004 *M*. [d] 5×10^{-3} *M* $Co^{II}(4,11\text{-dieneN}_4)$, [oxidant] = $(2\text{–}10) \times 10^{-4}$ *M*, ionic strength = 0.016–0.028 *M*: 5×10^{-4} *M* $Co^{II}(1,3,8,10\text{-tetraeneN}_4)$, [oxidant] = $(2.5\text{–}5) \times 10^{-5}$ *M*, ionic strength = 0.002 *M*. [e] 7×10^{-3} *M* Co(II), $[O_2] = (7.5\text{–}25) \times 10^{-5}$ *M*, ionic strength = 0.02 *M*. [f] Value for $Co^I(4,14\text{-dieneN}_4)$. [g] 3×10^{-3} *M* Co(II), $[N_2O] = (7.5\text{–}25) \times 10^{-4}$ *M*, no alcohol present, ionic strength = 0.01 *M*. [h] 5×10^{-3} *M* Co(II), $[CH_3I] = (2\text{–}5) \times 10^{-4}$ *M*, ionic strength = 0.015 *M*.

Both of the $Co^I(\text{dieneN}_4)$ species reacted rapidly with N_2O at pH 9.2 ($k \sim 10^7$ M^{-1} sec^{-1}) in solutions containing 3×10^{-3} *M* Co(II), 1 m*M* tetraborate, and $(7.5\text{–}25) \times 10^{-4}$ *M* N_2O. The reaction of N_2O with $Co^I(4,11\text{-dieneN}_4)$ produced a dull tail absorption between 350 and 500 nm (ϵ_{350} ~2900 M^{-1} cm^{-1}) which was not due to the original Co(II) complex.

Discussion

The radiolysis of water and aqueous solutions generates e_{aq}^-, OH radicals, and H atoms as the radical species according to the overall reaction $H_2O \rightsquigarrow e_{aq}^-$ (2.8), OH (2.8), H (0.55) where the numbers in parentheses represent the G values of the species (number of radicals formed per 100 eV of energy absorbed by the solvent). By the use of selected scavengers, a particular reactive radical can be chosen to be the principal reactant in the solution. Thus, in the presence of *tert*-butyl alcohol, the OH radicals are effectively scavenged: $OH + (CH_3)_3COH \rightarrow \cdot CH_2C(CH_3)_2OH + H_2O$ ($k = 5.2 \times 10^8$ M^{-1} sec^{-1});[40] the resultant radical is relatively inert and its weak optical absorption[20] below 280 nm can easily be taken into account when transient absorption spectra are determined. In N_2O-saturated solution, e_{aq}^- is efficiently scavenged: $e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^-$ ($k = 8.7 \times 10^9$ M^{-1} sec^{-1});[41] in acidic solution e_{aq}^-

is converted to H atoms: $e_{aq}^- + H^+ \rightarrow H$ ($k = 2.2 \times 10^{10}$ M^{-1} sec^{-1}).[41] The reducing radicals CO_2^- and $(CH_3)_2\dot{C}OH$ can be generated conveniently from solutions containing formate or 2-propanol:

$$OH/H + HCO_2^- \rightarrow CO_2^- + H_2O/H_2$$
$$(k = 2.5 \times 10^9/2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1})^{40,42}$$

$$OH/H + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O/H_2$$
$$(k = 1.3 \times 10^9/5.0 \times 10^7\ M^{-1}\ \text{sec}^{-1})^{40,42}$$

Reaction of the Co(II) complexes with e_{aq}^- occurs at or near the diffusion-controlled limit. The values of k for the Co^{II}(dieneN$_4$) complexes are independent of pH (6–10) suggesting that the complexes do not undergo protonation–deprotonation reactions in that pH range; acid–base behavior can affect the value of k and is seen in the reactions of the corresponding Co(III) complexes with e_{aq}^-.[36] Because of the sensitivity of Co^{II}(1,3,8,10-tetraeneN$_4$) towards base, all experiments with that complex were performed at pH <7. The reaction of e_{aq}^- with Co(II) generates the spectrum of Co(I) directly with no evidence for the initial formation of a Co(II)-coordinated ligand radical species at a time resolution of ~0.1 μsec. However, neither of the Co^{II}(dieneN$_4$) complexes was reduced by CO_2^- or $(CH_3)_2\dot{C}OH$ suggesting either that the redox potentials of the systems are not favorable or that the reactions possess mechanistic barriers that render an otherwise spontaneous reaction too slow to compete with other bimolecular radical decay steps.

Proton Transfer Reactions. Unlike their known stability in dry CH_3CN solution,[13,30] these Co(I) species are unstable in aqueous solution. Their reactivity patterns indicate their involvement in proton transfer processes. Similar behavior has been observed for $Co^I(CN)_5^{4-}$ ($k = 2 \times 10^3$ M^{-1} sec^{-1} for reaction with H_2O)[43] and the reactivity of Co^I(4,11-dieneN$_4$)[13] and various Co(I) complexes containing tetradentate (nonmacrocyclic) ligands[10] with water has also been noted. Vitamin B_{12s}[4] reacts with H^+, the Co(III)-hydrido complex commonly being proposed as an intermediate species in the formation of H_2. Stable hydridocobaloximes have, however, been isolated as solids[44] as has the $Co^{III}(CN)_5H^{3-}$ complex.[45] Therefore, it is consistent with these previous studies to suggest that the proton transfer reactions reported here occur via direct addition of H^+ to the Co(I) center.

$$Co(I) + H^+ \rightarrow [Co(I)\text{-}H^+] \leftrightarrow [Co(II)\text{-}H] \leftrightarrow [Co(III)\text{-}H^-]$$

In support of this proposition, it should be noted that the complexes Ni^I(4,11-dieneN$_4$), Ni^I(aneN$_4$), and Cu^I(4,11-dieneN$_4$) also react with H^+.[46] The rates of proton transfer for these complexes are several orders of magnitude lower than those for the Co^I(dieneN$_4$) complexes and of the same order as Co^I(1,3,8,10-tetraeneN$_4$). The fact that proton transfer takes place to a complex containing a fully saturated macrocyclic ligand rules out proton attack on the imine functional groups as a requirement for this reaction. The spectra resulting from the reaction of Co^I(4,11-dieneN$_4$) with phosphate at pH 7.0 or water at pH 10.0 were identical and were stable for at least 20 sec following the pulse.

Eigen has shown[47] that a relationship exists between the rate constant for proton transfer and the difference in the pK of the donor acid and the acceptor base. When pK_a < pK_b such that ΔpK (pK_a − pK_b) < 0, "normally behaved" bases undergo diffusion-controlled reactions with k being independent of ΔpK. When ΔpK > 0, a plot of log k vs. ΔpK gives a slope of −1 with the rate constant decreasing with increasing values of ΔpK. In the vicinity of ΔpK ≈ 0, a sharp transition from a slope of zero to −1 is theoretically predicted. In practice, the limiting slopes are seldom achieved and the transition point usually shows decided curvature.

The data in Table II for Co^I(4,11-dieneN$_4$) are plotted in the form of log k vs. pK_a in Figure 5, inasmuch as pK_b for Co(I) is not known. The values of k were not derived at constant ionic strengths. However, inasmuch as the rate constant is a relatively weak function of ionic strength under these conditions,[48] we feel that the narrow range of ionic strengths of the solutions did not introduce any error of magnitude into the plot shown in Figure 5. The values of μ (and especially $\mu^{1/2}$) did not vary greatly for the individual donors used and did not significantly affect the linearity of the plots of k vs. [HA]. Thus, despite the limited number of points and the uncertainties involved, the trend depicted in Figure 5 supports our contention that the Co(I) species reacts with these acids via proton transfer reactions. Deviations from ideality, also seen in even simpler systems,[47] have been reconciled in terms of the asymmetry of charge, molecular structure and steric restriction, hydrogen bonding, and electron distribution in the donors and acceptors. From the general region of the transition shown in Figure 5, we estimate pK_b for Co^I(4,11-dieneN$_4$) to be in the range 6–10.

The limited data for the other Co(I) species shows Co^I(4,14-dieneN$_4$) to be only slightly less reactive than its isomer but Co^I(1,3,8,10-tetraeneN$_4$) is 3–4 orders of magnitude less reactive than the diene complexes. This implies that the value of k for the reaction of Co^I(1,3,8,10-tetraeneN$_4$) with H_2O may be of the order of 10^{-3} M^{-1} sec^{-1} (or less) and so the Co(I) species may show modest stability in alkaline solution[37] barring any hydrolysis of the ligand. At pH 6.5, however, the residual absorption 20 sec after the pulse resembles the original Co(II) substrate (Figure 3) which may be the end product of the reaction of Co^I(1,3,8,10-tetraeneN$_4$) with proton donors via some hydrido intermediate.

Electron Transfer Reactions. The Co(I) species are powerful reducing agents, reacting rapidly with a wide range of electron acceptors. The apparent oxidation potentials of these species in aqueous solution can be compared with existing data in the literature despite the nonthermodynamic character of the data presented in this paper and the nonaqueous solvent system employed by other workers. $E_{1/2}$ values for Co^I(4,11-dieneN$_4$) and Co^I(1,3,8,10-tetraeneN$_4$) in CH_3CN have been extrapolated to the aqueous system, and through an estimation of CH_3CH-H_2O junction potential, E_{ox}^0 values of +0.7 and +0.48 V, respectively, have been obtained.[49] Considering all the factors involved, the similarity of both sets of data is, perhaps, remarkable and the dieneN$_4$ complex is established as the stronger reducing agent. Even in their limited form, these data demonstrate the profound effect of the degree and position of unsaturation of the macrocyclic ligand on the redox potential of the complex.

The Co(I) species react rapidly with metal complex oxidants with rate constants that cover a range of three orders of magnitude (10^6–10^9 M^{-1} sec^{-1}). Values of $k < 10^6$ M^{-1} sec^{-1} cannot be determined by the pulse technique due to the high concentration of oxidant required to scavenge Co(I); the trivalent metal complexes used themselves react very rapidly with e_{aq}^- (k = 4–9 × 10^{10} M^{-1} sec^{-1}).[17,36] It can probably be safely assumed that these reactions occur via an outer-sphere mechanism inasmuch as the electron-transfer reactions of the oxidants employed are well established to be of that type.[50,51] Because of the lack of any information concerning the self-exchange rate constants for the Co(I) species and the lack of certainty about the exact values of their redox potentials in aqueous solution, we made no attempt to fit the data in Table III to the Marcus relationship in a quantitative manner.[52]

However, certain trends are apparent from the data. If one assumes that the electrostatic effects for $Co^I(4,11\text{-dieneN}_4)$ and $Co^I(1,3,8,10\text{-tetraeneN}_4)$ are similar, then the relative rate constants for their reactions will be dependent upon their relative reorganizational energies and redox potentials. In reaction with $Cr(bpy)_3^{3+}$ and $Co(bpy)_3^{3+}$, the rate constants for $Co^I(1,3,8,10\text{-tetraeneN}_4)$ are approximately an order of magnitude lower than are those for $Co^I(4,11\text{-dieneN}_4)$. It must be pointed out that the differences in the ionic strength of the solutions cannot account for the differences in k shown by the two Co(I) species. Because of the lower reducing ability of the $Co^I(\text{tetraeneN}_4)$ species, its reactivity would be expected to be lower than that of the $Co^I(\text{dieneN}_4)$ by approximately two orders of magnitude if the self-exchange rate constants of the two species were equal. From the very limited data it appears that the self-exchange rate constant for $Co^I(4,11\text{-dieneN}_4)$ would be an order of magnitude or so greater than that of $Co^I(1,3,8,10\text{-tetraeneN}_4)$ if the free energy correlation holds for these reactions. Indeed, Endicott has concluded[51] that this correlation does not hold true for electron transfer reactions of Co(III) complexes containing these macrocyclic ligands and that the self-exchange rate constant for the $[Co(4,11\text{-dieneN}_4)(OH_2)_2]^{3+,2+}$ couple is about seven orders of magnitude lower than that of $[Co(1,3,8,10\text{-tetraeneN}_4)(OH_2)_2]^{3+,2+}$. Finally, it should be mentioned that the $Cu^I(4,11\text{-dieneN}_4)$ complex, the redox potential of which is similar to that of $Co^I(1,3,8,10\text{-tetraeneN}_4)$, undergoes electron transfer to the metal complex oxidants with rates similar to those of the latter complex; $Ni^I(4,11\text{-dieneN}_4)$ and $Ni^I(\text{aneN}_4)$ tend to parallel $Co^I(4,11\text{-dieneN}_4)$ in both rates and redox properties.[46]

The values of k for $Co^I(4,11\text{-dieneN}_4)$ in Table III, measured at low and constant ionic strength at pH 9.2, provide some insight into the details of these electron transfer reactions. For $Co(en)_3^{3+}$ and $Co(NH_3)_6^{3+}$ (reduction potentials of -0.30[53] and $+0.10$ V,[54] respectively) the rate constants are virtually identical but, assuming the general validity of the Marcus relationship, can be attributed to the compensating effects of higher reducibility but lower exchange reactivity[50c] shown by $Co(NH_3)_6^{3+}$. The Co(III)-macrocyclic complexes, which have very similar redox potentials[55] and as +1 charged species will have a different electrostatic effect in their reaction with the +1 charged reductants compared to the other Co(III) complexes, show reactivity of the same magnitude as $Co(en)_3^{3+}$ and $Co(NH_3)_6^{3+}$. Perhaps the anomalous variations[51] in the Marcus reorganizational parameter are in effect here. $Ru(NH_3)_6^{3+}$,[56] which has a reduction potential (+0.05 V)[57] similar to that of $Co(NH_3)_6^{3+}$ and an electron exchange rate 10^{12} times faster,[50] reacts at a rate that is about two orders of magnitude faster; the Marcus correlation would predict a difference of about five-six orders of magnitude. The lower rate shown by the Ru(III)-NO[58] complex may be due to its lower reducibility[59] or may reflect electron delocalization in that complex allowing its behavior to be ascribed in part to its valence tautomeric $Ru(II)\text{-}NO^+$ form. $Cr(bpy)_3^{3+}$ ($E^0 = -0.40$ V)[56] and $Co(bpy)_3^{3+}$ ($E^0 = +0.37$ V)[60] show equal and very high rates while the more powerfully oxidizing $Fe(bpy)_3^{3+}$[61] ($E^0 = +1.1$ V)[60] reacts almost two orders of magnitude more slowly. The involvement of the ligand orbitals in the electron transfer process must be considered inasmuch as the π system of the aromatic ligand could provide a facile pathway as has been inferred from the rate constants for the reaction of CO_2^- radicals with complexes containing aromatic ligands.[62] The behavior of $Fe(bpy)_3^{3+}$, with its high reducibility and exchange reactivity, can only be viewed as anomolous at the present time.

Other Reactions. The reaction of O_2 with all three Co(I) species is very rapid. Cobalt complexes can behave as oxygen carriers[63] and the reaction of Co(I) with O_2 can be viewed as proceeding via electron transfer with the formation of O_2^- ($Co(I) + O_2 \rightarrow Co(II) + O_2^-$) or a coordination mechanism involving incorporation of O_2 into the coordination sphere of the Co(I) center:

$$Co(I) + O_2 \rightarrow [Co(I)\text{-}O_2] \leftrightarrow [Co(II)\text{-}O_2^-] \leftrightarrow [Co(III)\text{-}O_2^{2-}]$$

Inasmuch as the $Co(I) + O_2$ reaction did not regenerate the spectra of the original Co(II) species, it is possible that the reaction proceeds via the coordination route. We have also found that the reaction of $Cu^I(4,11\text{-dieneN}_4)$ with O_2 does not generate free O_2^- radicals but the Ni(I) macrocyclic species do.[46] In contrast, Sellers and Simic[64] have found that $Co_{aq}^+ + O_2$ generates O_2^-.

Pratt and co-workers[65] have shown that N_2O reacts rapidly with a number of Co(I) complexes of dimethylglyoxime, 2,2′-bipyridyl, 1,2-bis(diphenylphosphine)ethane, and with vitamin B_{12S} according to the overall stoichiometry: $2Co(I) + N_2O \rightarrow 2Co(II) + N_2$. All these reactions have been proposed to occur via the simple two-electron reduction of N_2O to N_2 with the concomitant formation of Co(III) which is then itself reduced by Co(I) to yield the Co(II) final product. No evidence has been obtained for the addition of N_2O into the coordination sphere of the metal. In our experiments, the rapid reaction of Co(I) with excess N_2O would deplete the supply of Co(I) prohibiting the further loss of Co(III). The residual spectrum after the decay of Co(I) did not resemble the Co(II) substrate but could be that of $Co^{III}(4,11\text{-dieneN}_4)$.[66]

The reaction of nucleophilic low-valent complexes with alkyl halides is one of the more general routes to the preparation of Co(III)-alkyl complexes.[8,9] The rate constant for the reaction of vitamin B_{12S} with CH_3I to form methylcobalamine is 3.4×10^4 M^{-1} sec^{-1}.[4] We find the rate constant for the reaction of $Co^I(4,11\text{-dieneN}_4)$ with CH_3I to be about four orders of magnitude higher suggesting, as Endicott has indicated,[12] that the $Co^I(4,11\text{-dieneN}_4)$ species does not follow the classical S_N2 mechanism found for other Co(I) nucleophiles, including vitamin B_{12S}, but rather reacts via an electron transfer mechanism generating Co(II), CH_3 radicals, and I^- in the first instance. Because of the high concentration of the Co(II) substrate we were required to use we were unable to make spectral observations at $\lambda < 370$ nm. It could not be established by this experiment whether the initial product of the $Co(I) + CH_3I$ reaction was Co(II) (λ_{max} 330 nm) or $Co(III)\text{-}CH_3$ (λ_{max} ~280 nm). However, we have determined that $Co^{II}(4,11\text{-dieneN}_4)$ reacts rapidly with CH_3 radicals at pH 9.2 with $k = (1\text{-}2) \times 10^8$ M^{-1} sec^{-1} producing the spectrum of the alkyl complex,[36] the rate constant being of the same magnitude as that determined[52] using CH_3 radicals generated in the charge transfer photochemistry of $Co(NH_3)_5O_2CCH_3^{2+}$[67] in highly acidic solution. Experimentally, alkyl complexes of $Co^{III}(4,11\text{-dieneN}_4)$ have not been isolated from the reaction of alkyl halides with the Co(I) species. This failure may be related to certain reaction conditions, such as acidity, allowing for competing reaction pathways (for example, direct electron transfer[68]) in the reaction of Co(II) with CH_3 radicals. The reaction of CH_3I with $Co^I(1,3,8,10\text{-tetraeneN}_4)$ was too slow to monitor by the pulse technique. This reaction and the reaction of the Co(II) species with CH_3 radicals have been shown to produce the $Co(III)\text{-}CH_3$ complex by other techniques.[9,68] Because of its slowness, the Co$^{\text{I}}$(1,3,8,10-tetraeneN$_4$) + CH$_3$I reaction presumably occurs via the S$_\text{N}$2 mechanism.[69]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors also wish to acknowledge their many conversations with Professor J. F. Endicott about this work.

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(1) Presented in part at the Symposium on Electron Transfer Mechanisms, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, INOR 131.

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