Table IV. Comparisons among Fe, Ru, and Os Nitrosyl Complexes

complex	$E_{1/2}(1)$, V[a]	$E_{1/2}(2)$, V[b]	pH[c]
$[Fe^{II}(NO^+)TPPS]^{3-}$	+0.35	−0.63[d]	>7
$[Ru^{II}(NO^+)(tpy)(bpy)]^{3+}$[g]	+0.23	−0.36[f]	2.3[e]
$[Os^{II}(NO^+)(tpy)(bpy)]^{3+}$[e]	−0.20	−0.51[f]	8.6[e]

[a] Potential for the first reduction at the nitrosyl ligand, $M-NO^+ + e^- \rightarrow M-MO^\bullet$. [b] Potential for the second nitrosyl-based reduction, $M-NO^\bullet + e^- \rightarrow M-NO^-$. [c] pH at which the nitro, $[M^{II}(NO_2)(tpy)(bpy)]^+$, and nitrosyl, $[M^{II}(NO^+)(tpy)(bpy)]^{3+}$, forms of the complex are present at equilibrium. For the Fe porphyrin the equilibrium is with free NO_2^- in solution, see text. [d] pH >2.6. [e] From ref 32. [f] Potentials are cited for pH ranges in which the wave is pH-independent.

version efficiency of about 31% with $Fe^{II}(phen)_3^{2+}$ (phen is 1,10-phenanthroline) as the catalyst.[4b] The current efficiencies quoted in this work are limited by competitive production of H_2 at the platinum electrodes used in the electrolyses.

The enzyme nitrite reductase reduces nitrite to NH_3 by a mechanism that at present is unknown. On the basis of the structural similarity between the iron isobacteriochlorin active site of the enzyme and our water-soluble iron porphyrin, it seems reasonable to suggest that the detailed redox events at the active site may be similar in detail to the events suggested in Scheme I. However, the demands on the biological system are far more complex, especially with regard to electron transfer into the heme site. Given the evidence presented here for sequential electron transfer, it is probable that the iron sulfur cluster that is associated with the iron isobacteriochlorin active site has an important role to play in providing reducing electron equivalents on demand. Related iron sulfur clusters are known to act as electron-transfer carriers in a number of biological redox systems.

Comparison of Properties Among the Fe, Ru, and Os Systems. The potentials for the first and second reductions at the nitrosyl ligand in the three complexes $[Fe^{II}(NO^+)TPPS]^{3-}$, $[Ru^{II}(NO^+)(tpy)(bpy)]^{3+}$, and $[Os^{II}(NO^+)(tpy)(bpy)]^{3+}$ and the ease with which they form nitrosyl from coordinated nitrite are compared in Table IV. Unfortunately, since we were unable to observe a complex with NO_2^- bound to the Fe(II) porphyrin, it is not possible to compare directly the acid–base equilibria that lead to nitrosyl formation. However, it is notable that $[Fe^{II}(NO^\bullet)(TPPS)]^{4-}$ persists in solution to nearly pH 7.

Considering the dissimilar coordination environments, the similarities are remarkable. It is notable that even in the relatively electron-rich porphyrin environment, the iron porphyrin nitrosyl is the strongest of the three as an oxidant and is thermodynamically the most easily reduced at the nitrosyl ligand. This is in marked contrast to the M(III)/(II) aqua couples. The Fe(III)/(II) aqua couple at $E^{\circ\prime} = -0.23$ V is a considerable weaker oxidant than either the Ru or Os cases, for $[M(H_2O)(tpy)(bpy)]^{3+/2+}$ $E^{\circ\prime} = +0.81$ V (M = Ru) and $E^{\circ\prime} = +0.37$ V (M = Os) (25 °C) at pH 0.

The relatively high oxidizing strength for $[Fe^{II}(NO^+)(TPPS)]^{3-}$ suggests that there is considerable NO^+ character in the bound nitrosyl group and that, as compared to the Ru and Os complexes, there is considerably less $d\pi \rightarrow p\pi^*(NO)$ back-bonding.

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Registry No. **1**, 73848-42-7; **2**, 53194-20-0; **3**, 64365-01-1; **4**, 103384-29-8; **5**, 103384-30-1; **7**, 103384-31-2; $[Fe^{II}(H_2O)_2TPPS]^{4-}$, 103384-32-3; $[Fe^{III}(H_2O)(TPPS^{\bullet+})]^{2-}$, 103384-33-4; $[Fe^{I}(TPPS)]^{5-}$, 103384-34-5; NO_2^-, 14797-65-0; NH_3, 7664-41-7; NH_2OH, 7803-49-8; N_2O, 10024-97-2; N_2, 7727-37-9; HONO, 7782-77-6.

Carbon–Carbon Bond Formation in the Reaction of Aliphatic Radicals with Alkylcobaloximes

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Abstract: Benzyl, methyl, ethyl, and isopropylaquocobaloximes, $R'Co(dmgH)_2OH_2$, react with aliphatic free radicals, $R^\bullet$, forming RR' and $Co^{II}(dmgH)_2OH_2$. This reaction is quite general for aliphatic radicals, except for R = benzyl. Rate constants with R = $C(CH_3)_2OH$ and $^\bullet CH(CH_3)OC_2H_5$ exhibit little sensitivity toward the steric bulk of substituents on the α-carbon atom of the organocobaloxime. This discounts homolytic displacement by attack at the organic group. It is proposed that the radical addition takes place at the nitrogen end of the N=C bond of the macrocycle cis to the Co–C bond, followed by the reductive elimination of RR'.

Although homolytic displacement reactions are observed for boron, tin, and lead, authenticated examples for saturated sp^3 hybridized carbon are still quite rare.[1] Organocobaloximes[2] are good candidates to employ in a search for these rarely encountered reactions, because the leaving group is the stable cobalt(II) cobaloxime. Some examples of homolytic substitution at the saturated α-carbon atom of organometallic complexes are (i) the reaction of Cr(II) with organocobaloximes,[3a,b] eq 1, organocobalamins,[3c] and organochromium ions[4] and (ii) the alkyl transfer reactions of bis(cyclohexanedionedioximato)(pyridine)cobalt(II), $Co(chgH)_2py$, with organocobaloximes,[5] eq 2.

$$Cr^{2+}(aq) + RCo(dmgH)_2OH_2 \rightarrow (H_2O)_5CrR^{2+} + Co(dmgH)_2OH_2 \quad (1)$$

$$RCo(dmgH)_2py + Co(chgH)_2py \rightleftarrows RCo(chgH)_2py + Co(dmgH)_2py \quad (2)$$

Catalytic reactions of selected organocobaloximes with tetrahalomethanes,[6] alkylsulfonyl chlorides,[6] and arenesulfonyl chlo-

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rides[7] are characterized by products and other features that suggest but do not prove homolytic displacement by $\cdot CX_3$, $RSO_2\cdot$, or $Co(dmgH)_2SO_2\cdot$.

The need for further study of these reactions was indicated by results[8] on the reactions of benzylaquocobaloxime with $\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$, in which highly specific carbon–carbon bond formation occurs between the α-carbon atom of the organocobaloxime and the attacking radical. We report here the results of quantitative kinetic studies of a family of organocobaloximes of varying degrees of steric crowding about the α-carbon atom toward these radicals. These data indicate that a direct bimolecular homolytic substitution at the saturated α-carbon atom is unlikely. The reactions (eq 3) appear to be best explained by an addition–elimination mechanism involving one of the oxime ligands or by attack at cobalt.

$$R\cdot + R'Co(dmgH)_2OH_2 \rightarrow RR' + Co(dmgH)_2OH_2 \quad (3)$$

Experimental Section

Organochromium(III) Reagents. The organochromium reagents were prepared by literature procedures;[9-11] $(H_2O)_5CrCH_2Ph^{2+}$ and $(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$ were purified by anaerobic ion-exchange chromatography on Sephadex C-25 ion-exchange resin. The organochromium complexes were eluted as yellow-brown bands with ice-cold 0.25 M $NaClO_4$ containing 0.01 M $HClO_4$. The ion-exchange column and eluants were maintained at 0 °C to retard decomposition. The organochromium complexes were characterized by their UV–vis absorption spectra.[9-14]

Organocobaloximes. The alkylaquocobaloximes, $R'Co(dmgH)_2OH_2$ where $R' = CH_3$, CH_2CH_3, and $CH(CH_3)_2$, were prepared by standard methods[15,16]. Benzylaquocobaloxime was prepared either from $Cl(H_2O)Co(dmgH)_2$[17] by reduction to Co^I with borohydride in the absence of pyridine or directly from benzyl(pyridine)cobaloxime. In the latter instance the compound, dissolved in the minimum amount of methylene chloride, was treated with twice the molar amount of aqueous $HClO_4$. The solution was shaken while protected from light throughout. Pyridinium perchlorate was removed by filtration, and the filtrate treated with ice-cold water to precipitate benzylaquocobaloxime in ca. 50% yield. The organocobaloximes were characterized by satisfactory elemental analyses, proton NMR, and UV–vis absorption spectra.

Reactions and Kinetics. The reactions were studied at 25 °C in aqueous solutions of 1.0 M ionic strength maintained with $HClO_4$–$LiClO_4$. The rate constants were evaluated by competition methods, the analytical method being generally a spectrophotometric measurement of the consumption of the organocobaloxime. Since the latter was usually used in a pseudo-first-order excess over the radical precursor, the error on the rate constants is estimated to be ±(40–50)%. Despite that the competition method used in this work has the advantage over the direct methods (say pulse radiolysis or flash photolysis) because low, steady-state concentrations of the radicals are maintained in all the experiments. This avoids the self-reactions of the radicals and allows the measurement of the rate constants for the processes which are too slow for the pulse or flash techniques.

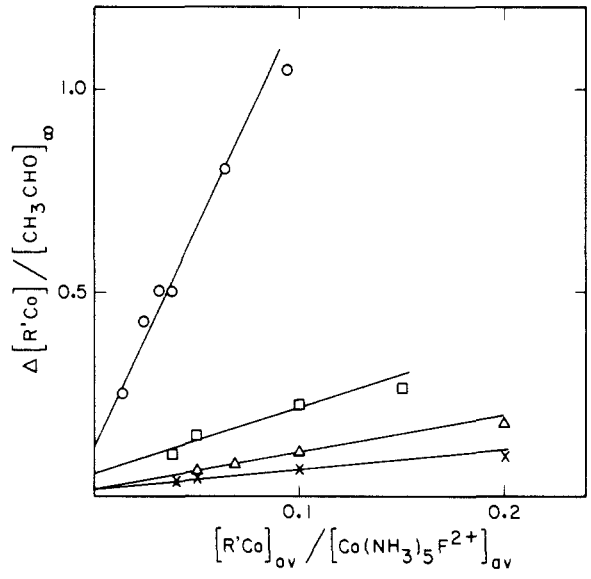

Figure 1. Analysis of competition kinetics for the reactions of $\cdot CH(CH_3)OC_2H_5$ with organocobaloximes at 1.0 M $[H^+]$ plotted according to eq 7: $PhCH_2$, circles; CH_3, squares; CH_2CH_3, triangles; $CH(CH_3)_2$, crosses.

Reactions were initiated by injection of a deaerated solution of the appropriate organochromium(III) reagent, which served (directly or indirectly) as the source of the aliphatic radicals.

Products. The organic products were identified by GC on 5% FFAP columns using a Varian model 3920B instrument with linear temperature programming and a FID. The products, depending on their identity, were extracted from the aqueous reaction solution into CH_2Cl_2, or 9:1 (v/v) ether/pentane mixture, or cyclopentane. The retention times were confirmed by using the authentic materials. Mass spectra were determined for selected products.

Results

Kinetics of the 1-Ethoxy-1-ethyl Radical. The radical was generated by the homolysis of $(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$, eq 4–5, in the presence of $Co(NH_3)_5F^{2+}$ and $R'Co(dmgH)_2OH_2$.

$$CrCH(CH_3)OC_2H_5^{2+} \rightarrow Cr^{2+}_{aq} + \cdot CH(CH_3)OC_2H_5 \quad (4)$$

$$Cr^{2+}_{aq} + Co(NH_3)_5F^{2+} \xrightarrow{(+5H^+)} CrF^{2+} + Co^{2+}_{aq} + 5NH_4^+ \quad (5)$$

The ion $Co(NH_3)_5F^{2+}$ was used to compete with the alkylcobaloximes for the α-ethoxyethyl radical because the rate constant for its reduction by $\cdot CH(CH_3)OC_2H_5$ in strongly acidic solution is known and is of an appropriate magnitude to compete successfully with the alkylcobaloximes;[14] it reacts very rapidly with Cr^{2+},[18] thereby promoting homolysis without the addition of yet another reagent; the products of this reaction are kinetically inert CrF^{2+} and Co^{2+}_{aq}; and $Co(NH_3)_5F^{2+}$ lacks intense absorptions in the visible region of the spectrum that would complicate the experimental analysis for the consumption of the organocobaloximes. The competition of the two substrates for the radical, eq 3 and 6, leads to eq 7. With $[Co(NH_3)_5F^{2+}]_0$ and $[R'Co(dmgH)_2OH_2]_0$

$$\cdot CH(CH_3)OC_2H_5 + Co(NH_3)_5F^{2+} \xrightarrow[(H_2O)]{(+4H^+)} CH_3CHO + C_2H_5OH + Co^{2+} + 5NH_4^+ + F^- \quad (6)$$

$$\frac{d[R'CH(CH_3)OC_2H_5]/dt}{d[CH_3CHO]/dt} = \frac{k_3[R'Co(dmgH)_2OH_2]}{k_6[Co(NH_3)_5F^{2+}]} \quad (7)$$

$\gg [CrCH(CH_3)OC_2H_5^{2+}]_0$, both substrate concentrations changed by a sufficiently small amount (≤15%) during the reaction so that they can be taken as constants in the solution

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Table I. Rate Constants[a] for Reaction of $PhCH_2Co(dmgH)_2OH_2$ with $\cdot CH(CH_3)OC_2H_5$ as a Function of $[H^+]$

$[H^+]$/M	$10^{-7}k_3/M^{-1}\ s^{-1}$ [b]	$[H^+]$/M	$10^{-7}k_3/M^{-1}\ s^{-1}$ [b]
1.00	1.2	0.25	1.1
0.75	1.4	0.25	1.2
0.75	1.4	0.15	0.9
0.50	1.2	0.15	0.9
0.50	1.3		

[a] At 25.0 °C, μ = 1.0 M. [b] Calculated by using $k_6 = 1.1 \times 10^6\ M^{-1}\ s^{-1}$ (ref 14).

Table II. Rate Constants ($10^{-6}k/M^{-1}\ s^{-1}$) for the Reaction of $\cdot CH(CH_3)OC_2H_5$ and $\cdot C(CH_3)_2OH$ Radicals with the Acid and Base Forms of $R'Co(dmgH)_2OH$

		$\cdot CH(CH_3)OC_2H_5$		$\cdot C(CH_3)_2OH$	
R′	K_H/M^{-1}	k_{3a}	k_{3b}	k_{3a}	k_{3b}
$PhCH_2$	2.6[a]	14	10	10	5
CH_3	3.2[b]	1.8	1.4	1	0.7
CH_2CH_3	3.4[b]	1	0.8	0.8	0.6
$CH(CH_3)_2$	4.2[b]	0.6	0.7	0.5	0.4

[a] Spectrophotometric determination; within experimental error of value from ref 19. [b] From ref 19.

of this equation. Integration of the rate ratio with this as a boundary condition yields

$$\frac{[R'CH(CH_3)OC_2H_5]_\infty}{[CH_3CHO]_\infty} = \frac{k_3[R'Co(dmgH)_2OH_2]_{av}}{k_6[Co(NH_3)_5F^{2+}]_{av}} \quad (8)$$

The directly measured quantities are $[CrCH(CH_3)OC_2H_5^{2+}]_0$, $[R'Co(dmgH)_2OH_2]_0$, and $[R'Co(dmgH)_2OH_2]_\infty$. With eq 8 recast in terms of these quantities, the expression is

$$\frac{\Delta[R'Co(dmgH)_2OH_2]}{[CrCH(CH_3)OC_2H_5^{2+}]_0 - \Delta[R'Co(dmgH)_2OH_2]} = \frac{k_3[R'Co(dmgH)_2OH_2]_{av}}{k_6[Co(NH_3)_5F^{2+}]_{av}} \quad (9)$$

The concentration of the various organocobaloximes was varied in the range (6.0–25.0) $\times 10^{-5}$ and that of the competing reagent, $Co(NH_3)_5F^{2+}$, 6.0×10^{-4}–4.00×10^{-3} M. The data obtained for benzylaquocobaloxime and alkylaquocobaloximes are given in Tables S-1 and S-2, respectively. Figure 1 illustrates a plot of the data obtained at 1.0 M H^+ according to eq 8. The small positive intercepts, not anticipated from eq 8, are believed to reflect a compilation of the random and systematic errors in the product determinations and data manipulation, rather than a chemically significant process. With $k_6 = 1.1 \times 10^6\ M^{-1}\ s^{-1}$ at 25 °C,[14] values of k_3 were obtained from the slopes of the individual lines at fixed acidity and are given in Table I.

The values of k_3 do not show a pronounced dependence on $[H^+]$, despite the fact that organocobaloximes participate in the rapidly established protonation equilibrium.[3,19,20] In that equilibrium one O–H···O unit of the $(dmgH)_2$ pseudomacrocycle is converted, by protonation, to two OH groups. The equilibrium can be written as

$$R'Co(dmgH)_2OH_2 + H^+ \overset{K_H}{\rightleftharpoons} R'Co(dmg_2H_3)OH_2^+ \quad (10)$$

where K_H symbolizes the equilibrium constant for the reaction as written. If it is assumed that both of the cobaloximes react with $\cdot CH(CH_3)OC_2H_5$, the expression for k_3 as a function of $[H^+]$ is

$$k_3 = \frac{k_{3b} + k_{3a}K_H[H^+]}{1 + K_H[H^+]} \quad (11)$$

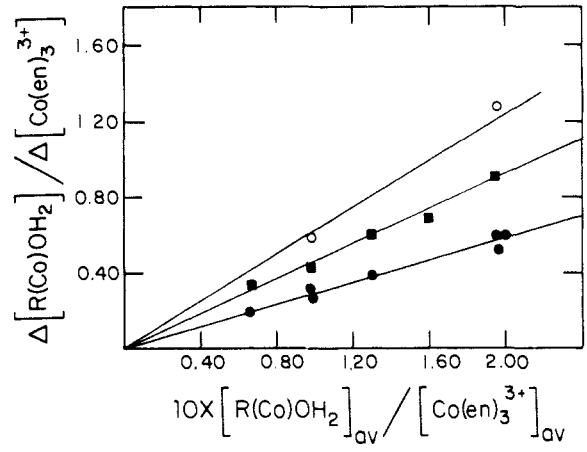

Figure 2. Plot of the data obtained for the competition between $RCo(dmgH)_2OH_2$ and $Co(en)_3^{3+}$ for the $\cdot C(CH_3)_2OH$ radical at 1.0 M H^+, eq 16: CH_3, open circles; CH_2CH_3, filled squares; $CH(CH_3)_2$, filled circles.

where k_{3a} and k_{3b} symbolize the rate constants for the acidic and basic species, respectively. Values of k_3 for $PhCH_2Co(dmgH)_2OH_2$ were fit to eq 11 with $K_H = 2.6\ M^{-1}$.[21] The rate constants obtained by a least-squares analysis are summarized in Table II.

Kinetics of the 1-Hydroxy-1-methylethyl Radical. Reactions utilizing $CrC(CH_3)_2OH^{2+}$ as a precursor of $\cdot C(CH_3)_2OH$ yielded significant amounts of pinacol, $HO(CH_3)_2CC(CH_3)_2OH$, possibly formed in the direct reaction of the radical with the organochromium complex. To avoid this complicating side reaction the radical was produced from $CrCH_2Ph^{2+}$, H_2O_2, and 2-propanol, eq 12–14. Hydrogen peroxide reacts rapidly with Cr^{2+}_{aq}, k_{14} =

$$CrCH_2Ph^{2+} \rightarrow Cr^{2+} + \cdot CH_2Ph \quad (12)$$

$$2\cdot CH_2Ph \rightarrow PhCH_2CH_2Ph \quad (13)$$

$$Cr(aq)^{2+} + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH \quad (14)$$

$7.06 \times 10^4\ M^{-1}\ s^{-1}$,[22] to yield hydroxyl radicals. They in turn react at nearly the diffusion controlled limit with 2-propanol[23] to afford α and β radicals.[24] Thus only 3–5-fold excess of H_2O_2 is necessary to ensure that radical formation is fast relative to homolysis of $CrCH_2Ph^{2+}$ ($k = 2.6 \times 10^{-3}\ s^{-1}$ at 25 °C).[12] Higher concentrations of H_2O_2 must be avoided, at least for the slower reacting cobaloximes, due to a competing chain reaction involving H_2O_2[25] and 2-propanol: $H_2O_2 + \cdot C(CH_3)_2OH \rightarrow \cdot OH + (CH_3)_2CO + H_2O$.

The benzyl radical, produced in reaction 12, is completely unreactive toward the organocobaloximes studied. It is also unreactive toward the competing $Co(en)_3^{3+}$.[12] The latter has the advantage over some other potential competitors because of its low reactivity toward the Cr^{2+}_{aq} ($k \sim 2 \times 10^{-5}\ M^{-1}\ s^{-1}$),[26] which permits quantitative conversion of Cr^{2+}_{aq} into the C-centered radical.

The kinetic expression for the competition of $R'Co(dmgH)_2OH_2$ (eq 3) and $Co(en)_3^{3+}$ (eq 15) for the radical is analogous to that shown in eq 7. With a pseudo-first-order excess of R′Co-

$$\cdot C(CH_3)_2OH + Co(en)_3^{3+} \xrightarrow{2H^+} (CH_3)_2CO + Co^{2+}_{aq} + 3enH^+ \quad (15)$$

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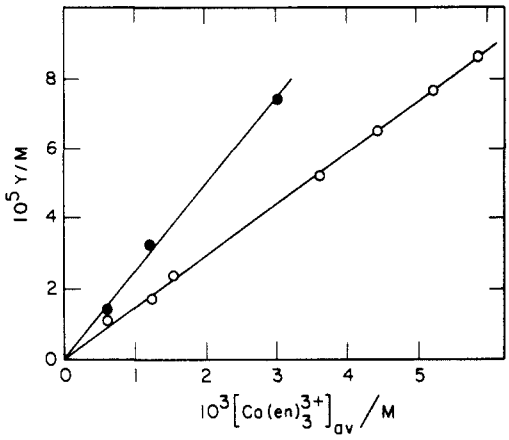


Figure 3. Plot of the data obtained for the competition for $^{\bullet}C(CH_3)_2OH$ between $PhCH_2Co(dmgH)_2OH_2$ and $Co(en)_3^{3+}$ at 1.0 M (open circles) and 0.10 M H^+ (filled circles). The quantity Y is defined as in eq 17.

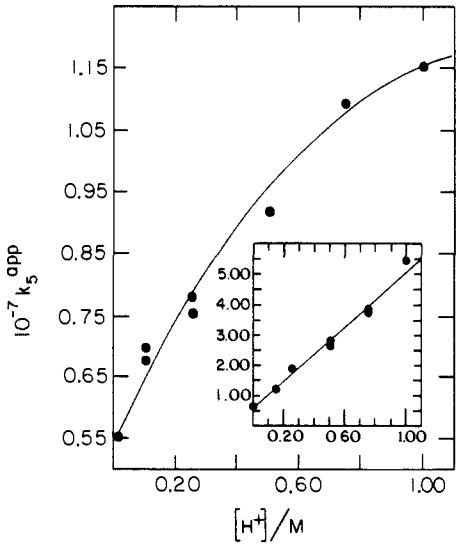


Figure 4. Variation of k_3 with $[H^+]$ for the reaction of $PhCH_2Co(dmgH)_2OH_2$ with $^{\bullet}C(CH_3)_2OH$. Inset: a plot of $k_3(1 + K_H[H^+])$ vs. $[H^+]$ according to eq 11 (K_H = 2.6 M^{-1}).

$(dmgH)_2OH_2$ and $Co(en)_3^{3+}$ over $CrCH_2Ph^{2+}$, the integrated expression of eq 16 is obtained. The plots according to eq 16

$$\frac{\Delta[R'Co(dmgH)_2OH_2]}{\Delta[Co(en)_3^{3+}]} = \frac{k_3}{k_{15}} \frac{[R'Co(dmgH)_2OH_2]_{av}}{[Co(en)_3^{3+}]_{av}} \quad (16)$$

for R′ = CH_3, C_2H_5, and 2-C_3H_7 are shown in Figure 2. Since k_{15} = 1.7 × 10^5 M^{-1} s^{-1},[14b] values of k_3 can be calculated, Table II. The high relative reactivity of $PhCH_2Co(dmgH)_2OH_2$ toward $^{\bullet}C(CH_3)_2OH$ necessitated the use of low concentrations of this cobaloxime, such that $[PhCH_2Co(dmgH)_2OH_2]_0 \sim (2\text{–}3)[CrCH_2Ph^{2+}]_0$. Under these conditions the integrated expression of eq 17 applies. The plot is shown in Figure 3. The pH

$$Y = \frac{\Delta[Co(en)_3^{3+}]}{[R'Co(dmgH)_2OH_2]_0} = \ln \frac{[R'Co(dmgH)_2OH_2]_0}{[R'Co(dmgH)_2OH_2]_0 - \Delta[R'Co(dmgH)_2OH_2]} = \frac{k_{15}}{k_3}[Co(en)_3^{3+}]_{av} \quad (17)$$

dependence was analyzed according to eq 11, permitting a resolution of the separate rate constants for the acidic and basic forms of the cobaloxime, Figure 4. The kinetic parameters are summarized in Table II.

Products. Homolysis of benzylchromium ion in the presence of H_2O_2 and a suitable organic substrate can be utilized to generate other radicals. The only constraints placed upon the substrate are modest water solubility, >0.01 M, and that it react with $^{\bullet}OH$ radical or Cr^{2+}_{aq}, to produce one or at most two carbon-centered radicals. Table III indicates that the coupling reactions are apparently quite general in nature. It is interesting to note that both $PhCH_2CH(CH_3)OH$ and $PhCH_2CH_2CH_2OH$ were obtained by using ethanol as the substrate. Hydroxyl radical reacts with ethanol to produce both α and β radicals in yields of 84.3 and 13.2%, respectively.[23,24] Analysis of the gas chromatographic peak areas of the two products gave the ratio α/β = 7, in agreement with the expected ratio of 6.4. 2-Propanol, on the other hand, yielded $PhCH_2C(CH_3)_2OH$ as the sole product owing to the more rapid reaction of the initially formed $^{\bullet}CH_2CH(CH_3)OH$ (~15%) with 2-propanol to yield the α-radical.[27]

Table III. Products Obtained from the Coupling Reactions of Selected Free Radicals with Benzylcobaloxime[a]

substrate	radical(s)	product(s)
CH_3OH	$^{\bullet}CH_2OH$	$PhCH_2CH_2OH$
CH_3CH_2OH[b]	$^{\bullet}CH(CH_3)OH$	$PhCH_2CH(CH_3)OH$
	$^{\bullet}CH_2CH_2OH$	$PhCH_2CH_2CH_2OH$
C_2H_4[b,c]	$^{\bullet}CH_2CH_2OH$	$PhCH_2CH_2CH_2OH$
$(CH_3)_2CHOH$[b]	$^{\bullet}C(CH_3)_2OH$	$PhCH_2C(CH_3)_2OH$[d]
$CH_3CH_2OC_2H_5$[b]	$^{\bullet}CH(CH_3)OC_2H_5$	$PhCH_2CH(CH_3)OC_2H_5$
$(CH_3)_3COOH$[e]	$^{\bullet}CH_3$	$PhCH_2CH_3$
$(CH_3)_2SO$[f]	$^{\bullet}CH_3$	$PhCH_2CH_3$
$(CH_3)_2CHC(CH_3)_2OOH$[e]	$^{\bullet}CH(CH_3)_2$	$PhCH_2CH(CH_3)_2$[g]
$(CH_3)_3CC(CH_3)_2OOH$[b,e]	$^{\bullet}C(CH_3)_3$	$PhCH_2C(CH_3)_3$
c-C_5H_{10}[b]	c-$C_5H_9^{\bullet}$	$PhCH_2$-c-C_5H_9
$CH_3C(O)OH$	$CH_2C(O)OH$	$PhCH_2CH_2C(O)OH$[h]
$CrCH_2Ph^{2+}$	$^{\bullet}CH_2Ph$	no reaction
m-ClPhC(O)OOH	*m*-chlorophenyl	no reaction

[a] All the products were identified gas chromatographically and the selected ones by mass spectrometry. [b] Identification by GC-MS. [c] Hydroxyl radical addition to the double bond of ethylene occurs exclusively. [d] Product identified from direct homolysis of $CrC(CH_3)_2OH^{2+}$ as well as from the kinetic competition solutions, $[PhCH_2Co(dmgH)_2OH_2] = 6 \times 10^{-5}$ M. [e] Hydrogen peroxide is unnecessary when substrates are hydroperoxides. The reactions with Cr(II) initially produce an alkoxy radical which undergoes rapid β-scission to yield the alkyl radical. [f] Hydroxyl radical addition to $(CH_3)_2SO$ followed by β-elimination of $^{\bullet}CH_3$ radical. [g] $PhCH_2CH(CH_3)_2$ was also produced by the reaction of $^{\bullet}CH(CH_3)_2$, obtained from direct homolysis of $CrCH(CH_3)_2^{2+}$ with benzylcobaloxime. [h] Chromatographed as the methyl ester, $PhCH_2CH_2C(O)OCH_3$.

Discussion

The reactions studied in this work involve highly specific carbon–carbon bond formation with concomitant one-electron reduction of the metal center. The organic product results from coupling of the α-carbon atom of the alkyl group with the free radical. Products derived from rearrangement of either the alkyl ligand or the free radical or those corresponding to solvolysis of either fragment were not observed. Quantitative analyses of the organic products have established a one-to-one correspondence with the yield calculated from the spectrophotometric change. Isolated yields of greater than 90%, based upon the amount of organocobalt complex reacted, were common. On the other hand, the reactions *cannot* be carried to substantial conversion without the interference of other reactions. The similar reactivity of the acidic and basic forms of the organocobaloximes resembles that observed for other reactions of organocobaloximes which involve reduction of the metal center.[3,28] This contrasts with electrophilic reactions (e.g., Hg^{2+} and Tl^{3+}),[19,20] where the protonated species is unreactive.

Mechanisms. Several mechanisms may be considered: (i) Rate-limiting homolysis of the cobalt–carbon bond, followed by rapid coupling of the two radical fragments

$$R'Co(dmgH)_2OH_2 \rightarrow {}^{\bullet}R' + Co(dmgH)_2OH_2$$

$$^{\bullet}R' + {}^{\bullet}R \rightarrow R'R$$

(27) Burchill, C. E.; Jones, P. W. *Can. J. Chem.* **1970**, *48*, 1232.
(28) Gjerde, H. B.; Espenson, J. H. *Organometallics* **1982**, *1*, 435.

(ii) A "redox" sequence involving rate-limiting electron transfer forming a transient "reduced cobaloxime", followed by loss of a carbanion and coupling of the two alkyl fragments.

$$R'Co(dmgH)_2 + {}^{\bullet}R \rightarrow [R'Co(dmgH)_2OH_2^-] + R^+$$

$$[R'Co(dmgH)_2OH_2^-] \rightarrow {}^-R' + Co(dmgH)_2OH_2$$

$${}^-R' + {}^+R \rightarrow R'R$$

As a variant, a rate-limiting electron transfer from the radical to one of the nitrogens of the oxime is followed by rapid collapse to an N-alkylated intermediate with reductive elimination of the coupled product. (iii) A bimolecular homolytic substitution, S_H2 mechanism, where the radical attacks at the α-carbon atom of the organocobaloxime. (iv) An addition–elimination sequence involving either a seven-coordinate bis(alkyl)cobalt(IV) species, a six-coordinate bis(alkyl)cobalt(IV) species having both the organic groups in a cis configuration, or a pathway involving addition of the incoming radical to one of the four nitrogen–carbon double bonds of the $(dmgH)_2$ pseudomacrocycle followed by reductive elimination to products.

Of the mechanistic pathways indicated, only the addition–elimination sequence appears to adequately conform to the experimental observations. The stability of the organocobaloximes when protected from light in the absence of the radical precursors and the lack of R_2 (and R'_2) products preclude a mechanism involving rate-limiting unimolecular homolysis of the organocobaloxime.

The second option, while consistent with the bimolecular reactions, is inconsistent with the formation of carbocations and carbanions, which would undergo solvolysis in aqueous solution. In addition, a mechanism leading to oxidized and reduced intermediates would be expected to exhibit marked sensitivity toward the reduction potential of the incoming radical as well as the respective organocobaloxime. Although only qualitative observations have been made concerning the reactivity of benzylcobaloxime toward a family of free radicals, the reaction seems largely independent of radical identity, whereas the potentials of the various radicals vary over a wide range. Finally, the methyl derivatives of other B_{12} model compounds[29] are better oxidants than the ethyl derivatives by approximately 0.2 V. If the reduction potentials of methyl and ethylcobaloximes are analogous, a rate constant ratio of $\sim 10^2$ might be expected.

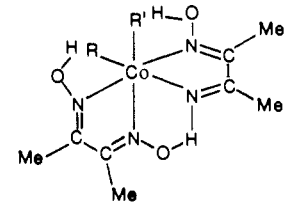
The rate constants for authentic S_H2 reactions[3,5] exhibit a marked sensitivity toward increasing steric bulk at both the α and β positions of the alkyl group, as expected. In both cases methylcobaloxime reacts some 10^5 times faster than isopropylcobaloxime. The nearly equal reactivity of methyl and isopropylcobaloximes toward these radicals makes an S_H2 mechanism unlikely. Either that or the stereochemical demand of an aliphatic radical in a displacement process is so much less than that of a metal complex that hardly any steric effect is observed. We tend to discount this possibility, since the absence of even a residual steric effect is quite striking.

Indeed, we must consider the validity of the claim[6] that $^{\bullet}CCl_3$ reacts with organocobaloximes by an S_H2 mechanism. That assignment was based entirely on the product observed. In light of the new results the mechanism may be different, despite the products obtained.

Addition–Elimination Mechanisms. Radical addition to a carbon–nitrogen double bond of the $(dmgH)_2$ pseudomacrocycle, followed by reductive elimination, appears to be most plausible in light of the lack of steric sensitivity. Reductive elimination to form RR must occur via an intermediate with cis disposed alkyl groups. Decomposition of the related complexes *trans*-$R_2Co^{IV}(dpnH)^+$ and *trans*-$R_2Co^{IV}(tim)^{2+}$ [30] has clearly shown the sole mode of decomposition of the trans species to be loss of *one* alkyl fragment to form a stable mono(alkyl)cobalt(III) complex[31]

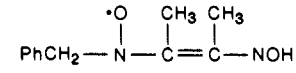
$$R_2Co^{IV}(chelate)^{n+} \rightarrow {}^{\bullet}R + RCo^{III}(chelate)^{n+} \quad (18)$$

A seven-coordinate bis(alkyl) intermediate seems unlikely in view of the lack of sensitivity toward steric bulk of the alkyl and radical fragment. Formation of a six-coordinate *cis*-bis(alkyl)-cobalt(IV) species by forcing a cis$(dmgH)_2$ structure of the form



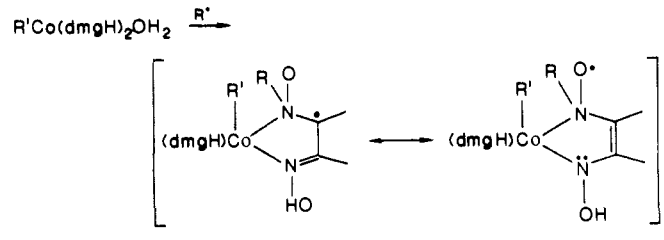
may be postulated to explain the steric insensitivity. It has been shown that *cis*-bis(alkyl)iron(IV) complexes, $R_2Fe(bipy)_2^+$, undergo reductive elimination to afford R_2 and $Fe^{II}(bipy)_2$.[32] Only one mononuclear *cis*-dimethyl–glyoxime complex of cobalt, ditrifluoroacetoxybis(butane-2,3-dionedioxime)cobalt(II), has been reported to date.[33] From the experimental observations and conditions used, it is clear that protonation of the O–H···O bridges of the trans complex is necessary to achieve the cis geometry. In view of this, the protonated form of the organocobaloxime would be expected to exhibit greatly enhanced reactivity toward aliphatic free radicals if such an intermediate were involved. We thus conclude that this pathway is likely to be unimportant.

The incoming aliphatic radical can add at either end of a carbon–nitrogen double bond. In anaerobic photolysis of $PhCH_2Co(dmgH)_2py$ in CH_2Cl_2[34] Giannotti and Merle have identified an apparent nitroxide radical formed from dimethylglyoxime



Preferential addition at the nitrogen atom may arise from a stabilizing interaction between the cobalt atom and the radical center. Free radical substitution reactions of vinylmercurials[35] and hydrogen atom abstraction by $^{\bullet}CCl_3$ from mercury alkyls[36] exhibit a similar stabilization of a radical center β to the metal atom.

To account for the quantitative yield of coupling product, radical addition to the double bond must be reversible on the time scale of reduction elimination, since trans addition would not result in reductive elimination. Alternatively, addition must preferentially occur cis to the alkyl fragment.



This mechanism not only allows for bimolecular formation of RR′ without additional side products but is much less subject to steric constraints. Although the two alkyl moieties are close enough to undergo reductive coupling, they are subject to much

(29) Costa, G.; Puxeddu, A.; Reisenhofer, E. *J. Chem. Soc., Chem. Commun.* **1971**, 993.
(30) The chelate dpnH and tim differ from $(dmgH)_2$ in the replacement of one and both of the O–H···O groups with $CH_2CH_2CH_2$ groups, respectively.
(31) Tamblyn, W. H.; Klinger, R. J.; Hwang, W. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3161.
(32) Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155.
(33) Alcock, N. W.; Atkins, M. P.; Curzon, E. H.; Golding, B. T. *J. Chem. Soc., Chem. Commun.* **1980**, 1238.
(34) Giannotti, C.; Merle, G. *J. Organomet. Chem.* **1975**, *99*, 145.
(35) Russell, G. A.; Hershberger, J. *J. Am. Chem. Soc.* **1980**, *102*, 7603.
(36) Kochi, J. K.; Nugent, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 5405.

less steric crowding than in the alternatives.

In summary, a direct S_H2 mechanism[37] appears highly unlikely for the radicals studied here. Radical addition to one of the double bonds followed by reductive elimination appears most likely, although a six-coordinate *cis*-bis(alkyl)cobalt(IV) intermediate remains a possibility. The failure of $PhCH_2^\bullet$ to react with the organocobaloximes is probably related to the stability of this radical.

(37) We would also consider that reaction occurs by displacement at cobalt, not carbon ($R^\bullet + R'Co(dmgH)_2 \rightarrow RCo(dmgH)_2 + R'^\bullet$). To retain the product specificity, however, this would require that displacement from CrR^{2+} occur more rapidly at carbon ($R^\bullet + R'Cr^{2+} \rightarrow RR' + Cr^{2+}$) than at chromium ($R^\bullet + R'Cr^{2+} \rightarrow R'^\bullet + CrR^{2+}$), else cross-coupled products would be seen. We tend to discount this, therefore, in light of the fortuitous combinations of rate constants needed.

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Supplementary Material Available: Tables of kinetic data from individual competition experiments (4 pages). Ordering information is given on any current masthead page.

Formation of Functionalized Dihydrobenzofurans by Radical Cyclization[1]

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Abstract: Treatment of the arenediazonium tetrafluoroborates **4a** and **4b** in Me_2SO solution with copper(II) bromide or chloride gave the cyclized halo compounds **5a**, **5b**, and **5c** in good yield. Copper(I) cyanide/pyridine effected ring closure of **4b** to afford the nitrile **5d**. Dihydrobenzofuran derivatives were also formed on treatment of **4a** or **4b** with benzenethiolate or butanethiolate ion in Me_2SO. Chain mechanisms involving cyclization of an intermediate aryl radical are suggested.

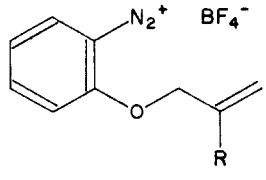
Aryl radicals with ortho substituents containing double bonds in the 5,6 or 6,7 positions relative to the radical center undergo rapid, regioselective cyclization (**1** → **2**) in the exo mode.[2-4]

Previously, such radicals had been generated for kinetic studies by treating the appropriate aryl iodide with tri-*n*-butyltin hydride.[3] This procedure, however, was unattractive for preparative work since reaction mixtures needed to be dilute to ensure the predominance of the cyclized product, complete removal of the tin compounds was difficult,[5-7] initiation was unreliable, and the considerable quantity of tributyltin hydride required was expensive.

We sought, therefore, alternative methods for effecting the ring closure of suitable aryl radicals. Procedures which were likely both to generate the radical and to introduce a new functional group (X) at the cyclized radical center (Scheme I) were of especial interest. Such reactions would afford functionalized products (e.g., **3**) suitable for further elaboration.

The radical precursors chosen for study were diazonium tetrafluoroborates. A large number of reactions involving diazonium salts are thought to involve free-radical intermediates,[8-10] and the tetrafluoroborate salts are easily prepared, are relatively stable, and are convenient to handle and purify.

This paper describes ring closures of *o*-(2-propenyloxy)-benzenediazonium tetrafluoroborate (**4a**) and *o*-((2-methyl-2-propenyl)oxy)benzenediazonium tetrafluoroborate (**4b**) induced by thiodediazoniation agents and copper-based "Sandmeyer" dediazoniation reagents.



a, R = H

b, R = Me

4

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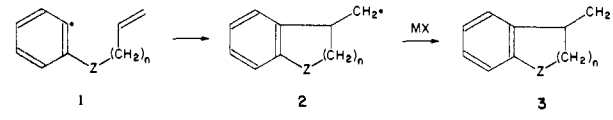
Scheme I



1 **2** **3**

Z = O, CH_2, NR

n = 1, 2

X = Br, Cl, CN, SR

Results and Discussion

Bromodediazoniation. Initial exploratory experiments employing copper(I) bromide were unsuccessful and gave cyclized material in only low yield accompanied by much intractable tarry material. Consequently, we turned to a method involving the use of copper(II) bromide in Me_2SO.[11] This procedure is an efficient modification of conventional Sandmeyer conditions and is espe-

(1) Part of this work has been reported in preliminary form: Beckwith, A. L. J.; Meijs, G. F. *J. Chem. Soc., Chem. Commun.* **1981**, 136-137.

(2) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 593-600.

(3) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 795-802.

(4) For a discussion of the regioselectivity of radical ring closures, see: Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482-483.

(5) For relatively nonpolar compounds partitioning with MeCN/pentane[6] to remove organotin residues is unsatisfactory; we find stirring with potassium fluoride solution[7] more satisfactory.

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