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Oxidative Homolysis of Pentaaquoorganochromium(III) Cations Induced by Macrocyclic Nickel(III) Complexes

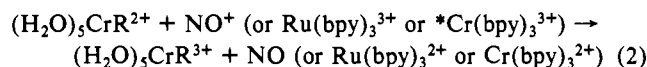Tetsuo Katsuyama,[1] Andreja Bakac,* and James H. Espenson*

The Ni(III) complexes Ni(cyclam)$^{3+}$ and Ni([9]aneN$_3$)$_2$$^{3+}$ oxidize the pentaaquoorganochromium(III) complexes (H$_2$O)$_5$CrR^{2+} to Cr^{3+} and olefins or alcohols. The rate constants for the oxidation by Ni(cyclam)$^{3+}$ have values <1 (R = CH$_3$), 13 (C$_2$H$_5$), 220 (2-C$_3$H$_7$), 2.45 × 10^3 (CH$_2$OCH$_3$), 3.44 × 10^3 (CH(CH$_3$)OC$_2$H$_5$), and 1.88 × 10^4 M^{-1} s^{-1} (PhCH$_2$). The oxidation by Ni([9]aneN$_3$)$_2$$^{3+}$ has similar rate constants: k = 95 (R = 2-C$_3$H$_7$) and 1.31 × 10^4 M^{-1} s^{-1} (PhCH$_2$). The one-electron oxidation of CrR^{2+} by the Ni(III) complexes yields a short-lived CrR^{3+} complex, which subsequently decomposes by homolysis (R = alkyl, benzyl) or by intramolecular electron transfer (R = alkoxyalkyl). The results are compared to the one-electron oxidation of organocobaloximes.

Introduction

One-electron oxidation of organometallic complexes often results in the homolytic cleavage of a metal–carbon bond.[2-5] Although numerous examples of this type of reactivity are found among both the main-group and transition-metal organometallic complexes, the kinetic data in the latter class are still quite rare. The studies of the oxidation of organocobaloximes[4] by IrCl$_6$$^{2-}$ and of the pentaaquoorganochromium complexes[5] by NO$^+$, Ru(bpy)$_3$$^{3+}$, and ^{2}E Cr(bpy)$_3$$^{3+}$ have provided the only kinetic data available to date on outer-sphere oxidation of organometallic complexes containing a single metal–carbon bond. These two series are especially instructive since a large number of relatively stable complexes have been prepared and characterized. The kinetic trends and patterns can thus be established for complexes containing alkyl, substituted alkyl, and aralkyl groups. The existence of a single metal–carbon bond in these molecules is quite advantageous in that the chemistry is not masked or complicated by the presence of additional sites of similar reactivity.

The rate constants for the oxidation of (H$_2$O)$_5$CrR^{2+} by the three oxidants studied[5] increase in the order CH$_2$Cl < CH$_2$Br < CH$_3$ < C$_2$H$_5$ < CH(CH$_3$)$_2$ < PhCH$_2$. The oxidation of the organocobaloximes by IrCl$_6$$^{2-}$ shows a similar pattern,[3] except for the positions of CH(CH$_3$)$_2$ and PhCH$_2$ relative to each other, CH$_3$ < C$_2$H$_5$ < PhCH$_2$ < CH(CH$_3$)$_2$. Despite all the obvious differences between the two series employed, one might expect a similar (same?) *qualitative* effect of the alkyl groups on the kinetics, provided both reactions take place by outer-sphere electron transfer (eq 1 and 2).[6] We consider several reasons for

$$RCo(dmgH)_2L + IrCl_6^{2-} \rightarrow RCo(dmgH)_2L^+ + IrCl_6^{3-} \quad (1)$$

$$(H_2O)_5CrR^{2+} + NO^+ \text{ (or Ru(bpy)}_3^{3+} \text{ or *Cr(bpy)}_3^{3+}) \rightarrow$$
$$(H_2O)_5CrR^{3+} + NO \text{ (or Ru(bpy)}_3^{2+} \text{ or Cr(bpy)}_3^{2+}) \quad (2)$$

the reversed reactivity of the 2-propyl and benzyl complexes in the two series. First, all the oxidants utilized in the organochromium series may be especially reactive toward (H$_2$O)$_5$CrCH$_2$Ph^{2+}. The bipyridine ligands in Ru(bpy)$_3$$^{3+}$ and *Cr(bpy)$_3$$^{3+}$ may favor the approach of the benzyl complex relative to the alkyls, and the reaction of NO$^+$ with (H$_2$O)$_5$CrCH$_2$Ph^{2+} may be facilitated by the attack of NO$^+$ at the benzene ring.[7] It is also possible that the reactions of the organocobaloximes with IrCl$_6$$^{2-}$ are not purely outer-sphere.[2f,8] It is not immediately obvious which alkylcobaloxime would react more rapidly in a reaction having elements of an inner-sphere mechanism. Finally, the reversed reactivity order for the benzyl and 2-propyl complexes in the two series might be a genuine result of the effect of the metal and the other ligands on the oxidizability of these organometallic complexes.

We have now studied the oxidation of (H$_2$O)$_5$CrR^{2+} with (H$_2$O)$_2$Ni(cyclam)$^{3+}$ and (briefly) with Ni([9]aneN$_3$)$_2$$^{3+}$.[8] In addition to having suitable reduction potentials,[9] these complexes were chosen because they contain only saturated ligands, which rules out any special interaction between the alkylchromium complexes and the oxidants. The reactivity order established with these oxidants should thus reflect clearly the electronic effects of the alkyl groups on the kinetics of outer-sphere oxidation in the alkylchromium series.

Experimental Section

The complexes Ni(cyclam)(ClO$_4$)$_2$,[10] Ni(cyclam)(CH$_3$CN)$_2$(ClO$_4$)$_3$,[11] and Ni([9]aneN$_3$)$_2$(ClO$_4$)$_3$[9b,12] were prepared by the literature methods. The ligands were purchased from Strem (cyclam) and Aldrich ([9]-aneN$_3$). The organochromium complexes were prepared in solution as described previously.[13] The concentration of CrR^{2+} in stock solutions was determined spectrophotometrically.[13]

The kinetic measurements were done at 23.4 °C under air-free conditions by use of the standard syringe-septa methods. All the kinetic experiments were conducted in the presence of a pseudo-first-order excess of the organochromium complexes. The disappearance of the Ni(III) complexes were monitored spectrophotometrically at λ 330–360 nm. The ionic strength was adjusted to 1.0 M with HClO$_4$ and LiClO$_4$.

Spectrophotometric measurements were done by use of a Cary 219 instrument. Standard spectrophotometric cells were used in the reactions

(1) On leave from the Faculty of Engineering, Yamagata University, Yonezewa, Yamagata 992, Japan.
(2) See for example: (a) Chen, J. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 1450. (b) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1855. (c) Chen, J. Y.; Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 6150. (d) Tamblyn, W. H.; Klingler, R. J.; Hwang, W. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3161. (e) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790. (f) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928. (g) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.
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(5) Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4104. Melton, J. D.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 3360. Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 3453.
(6) dmgH$^-$ is the monoanion of dimethylglyoxime (2,3-butanedione dioxime).
(7) Challis, B. C.; Ridd, J. H. *J. Chem. Soc.* **1962**, 5208. deFabrizo, E. C. R.; Kalatzis, E.; Ridd, J. H. *J. Chem. Soc. B* **1966**, 533.
(8) [14]aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane; [9]aneN$_3$ = 1,4,7-triazacyclononane.
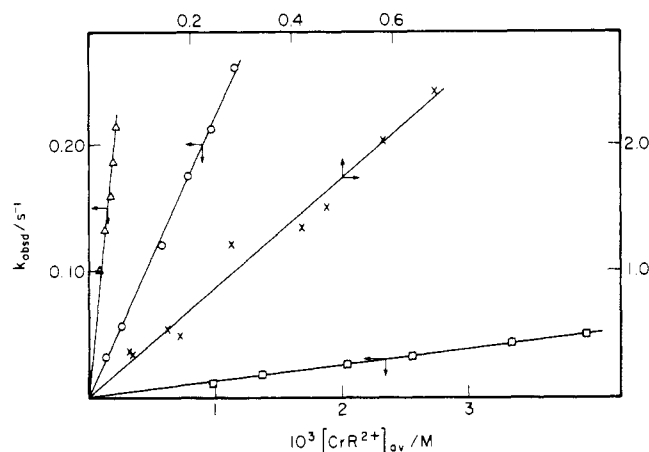(9) $E°$(Ni([14]aneN$_4$)$^{3+/2+}$) = 1.0 V; $E°$(Ni([9]aneN$_3$)$_2$$^{3+/2+}$) = 0.947 V: (a) Fairbank, M. G.; Norman, P. R.; McAuley, A. *Inorg. Chem.* **1985**, *24*, 2639. (b) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Küppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953.
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Figure 1. Plots of k_{obsd} vs $[CrR^{2+}]_{av}$ for R = CH_2OCH_3 ($\triangle$), $CH(CH_3)_2$ (O), $CH(CH_3)OC_2H_5$ ($\times$), and CH_2CH_3 ($\square$) for the reaction with Ni-(cyclam)$^{3+}$.
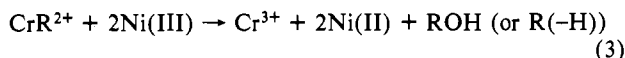
with $t_{1/2} \geq 10$ s. A SFA-11 rapid kinetic accessory (Hi-Tech Scientific) was used for faster reactions. The pseudo-first-order rate constants were evaluated by standard procedures.

Organic products of the reactions of $CrCH_2Ph^{2+}$, $CrCH(CH_3)_2^{2+}$, and $CrCH_2OCH_3^{2+}$ with Ni(cyclam)$^{3+}$ were determined by GC ($PhCH_2OH$ and CH_2=CHCH$_3$) and by the chromotropic acid method (CH_2O).[14]

Results

Stoichiometry and Products. Spectrophotometric titrations of Ni(cyclam)$^{3+}$ with CrR^{2+} were conducted for R = $CH(CH_3)_2$, CH_2Ph, CH_2OCH_3, and $CH(CH_3)OC_2H_5$. In each instance a 2:1 stoichiometric ratio of [Ni(III)]:[CrR^{2+}] was obtained.

The reaction of $CrCH_2Ph^{2+}$ with Ni(cyclam)$^{3+}$ produces $PhCH_2OH$ quantitatively. $CrCH(CH_3)_2^{2+}$ yields CH_2=CHCH$_3$, which could be determined only semiquantitatively in the gas phase. Formaldehyde and, by implication, methanol are produced quantitatively in the reaction of $CrCH_2OCH_3^{2+}$ with Ni(cyclam)$^{3+}$. The net reactions are in all cases well represented by eq 3.

$$CrR^{2+} + 2Ni(III) \rightarrow Cr^{3+} + 2Ni(II) + ROH \ (or \ R(-H)) \tag{3}$$

Kinetics. In the presence of a large excess of the organochromium cations, all the reactions obeyed pseudo-first-order kinetics. The pseudo-first-order rate constants vary linearly with the concentration of CrR^{2+} (Figure 1), yielding the rate law of eq 4. The second-order rate constants k_{obsd}, obtained from the

$$-\frac{d[Ni(III)]}{dt} = k_{obsd}[CrR^{2+}][Ni(III)] \tag{4}$$

slopes of the lines in Figure 1, are independent of [H$^+$] in the range 0.2–1.0 M. The addition of up to 0.014 M Ni(cyclam)$^{2+}$ had no effect on the kinetics of the reaction of $CrCH(CH_3)_2^{2+}$ with Ni(cyclam)$^{3+}$. All the data are summarized in Table I. The bromomethyl and the chloromethyl complexes reacted extremely slowly, and the decomposition of Ni(cyclam)$^{3+}$ interfered with the determination of the rate constant. No reaction was observed between 7×10^{-4} M $CrCH_3^{2+}$ and Ni(cyclam)$^{3+}$ in 30 min, but >50% $CrCH_3^{2+}$ underwent acidolysis during that time.[13]

The effect of oxygen was examined in the reaction of Ni(cyclam)$^{3+}$ with excess $CrCH_2OCH_3^{2+}$. In air-saturated solutions the reaction takes place with a rate constant $k_{obsd} = 950$ M^{-1} s^{-1}, i.e., by a factor of 2.6 more slowly than under air-free conditions. After the completion of the reaction, the absorbance at 360 nm decreases slowly. At this point all Ni(cyclam)$^{3+}$ had already been consumed, and this absorbance change indicates a further loss of $CrCH_2OCH_3^{2+}$ ($\epsilon_{360} = 330$ M^{-1} cm^{-1}). Since $CrCH_2OCH_3^{2+}$ does not react with O$_2$ or with Ni(cyclam)$^{2+}$ and since Ni(cyclam)$^{2+}$ is air-stable indefinitely, the reaction at 360 nm must

Table I. Summary of the Kinetic Data for the Oxidation of CrR^{2+} by Ni(cyclam)$^{3+}$ and Ni([9]aneN$_3$)$_2^{3+}$ at 23.4 °C and 1.0 M HClO$_4$

	k/M^{-1} s^{-1} [a]	
R	Ni(cyclam)$^{3+}$	Ni([9]aneN$_3$)$_2^{3+}$
CH_2Ph	1.88×10^4	1.31×10^4
$CH(CH_3)OC_2H_5$	3.44×10^3 [b]	
CH_2OCH_3	2.45×10^3 [c,d]	
$CH(CH_3)_2$	2.20×10^2 [e]	95.0
CH_2CH_3	1.30×10	
CH_3	<1	
CH_2Br	<0.1	
CH_2Cl	<0.1	

[a] $k_{obsd} = 2k_5$ (see text); the error limit is ±5%. [b] [H$^+$] = 0.23–1.0 M, μ = 1.0 M. [c] [H$^+$] = 0.40–1.0 M, μ = 1.0 M. [d] In air-saturated solutions $k = 9.5 \times 10^2$ M^{-1} s^{-1} (see text). [e] Unaffected by the presence of 0.014 M Ni(cyclam)$^{2+}$.

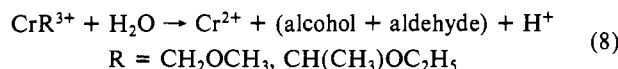involve $CrCH_2OCH_3^{2+}$ and the products of the reaction of $CrCH_2OCH_3^{2+}$ with Ni(cyclam)$^{3+}$.

A spectrophotometric titration of 2.5×10^{-5} M Ni(cyclam)$^{3+}$ with $CrCH_2OCH_3^{2+}$ at 360 nm in the presence of oxygen yielded an approximate 1:1 stoichiometric ratio. After the titration was completed, the spectrum of Ni(cyclam)$^{3+}$ reappeared over a period of ~10 min. This happens only when O$_2$ is present during the reaction.
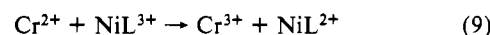
Discussion

The two nickel(III) complexes used in this study are strong[9] one-electron outer-sphere[9,12,15-17] oxidants that react with the organochromium complexes according to eq 3. The overall 2:1 stoichiometry, as well as the reaction products, can be accommodated by a rate-determining one-electron-transfer process (eq 5), followed by one of the two rapid decomposition modes of

$$CrR^{2+} + NiL^{3+} \rightarrow CrR^{3+} + NiL^{2+} \tag{5}$$

$$CrR^{3+} \rightarrow Cr^{3+} + R^{\bullet} \quad R = C_2H_5, CH(CH_3)_2, PhCH_2 \tag{6}$$

$$R^{\bullet} + NiL^{3+} \rightarrow ROH \ (or \ R(-H)) + NiL^{2+} \tag{7}$$

CrR^{3+}.[5] The complexes with oxidizing R groups (CH_2CH_3, $CH(CH_3)_2$, and $PhCH_2$) decompose homolytically (eq 6) to yield Cr^{3+} and a carbon-centered radical. The latter is rapidly oxidized by a second molecule of Ni(III) to the corresponding alcohol ($PhCH_2OH$) or olefin (CH_2=CHCH$_3$ and CH_2=CH$_2$) (eq 7). The oxidized organochromium complexes derived from ethers, R = CH_2OCH_3 and $CH(CH_3)OC_2H_5$, undergo intramolecular electron transfer (eq 8) to yield Cr^{2+} and a hemiacetal, which

$$CrR^{3+} + H_2O \rightarrow Cr^{2+} + (alcohol + aldehyde) + H^+$$
$$R = CH_2OCH_3, CH(CH_3)OC_2H_5 \tag{8}$$

rapidly hydrolyzes to a 1:1 mixture of the corresponding alcohol and aldehyde. Cr^{2+} is rapidly oxidized by a second molecule of Ni(III) as shown in eq 9. In both situations $k = 2k_5$, since the

$$Cr^{2+} + NiL^{3+} \rightarrow Cr^{3+} + NiL^{2+} \tag{9}$$

kinetic data were obtained in the presence of a pseudo-first-order excess of CrR^{2+}.

The two decomposition modes of CrR^{3+} have been demonstrated and discussed previously.[5] In the present work the formation of Cr^{2+} in the oxidation of $CrCH_2OCH_3^{2+}$ by Ni(cyclam)$^{3+}$ is strongly supported by the results obtained in air-saturated solutions. A change in stoichiometry from 2:1 under argon to 1:1 under oxygen, and a concomitant decrease in k_{obsd} by a factor of 2, is expected if O$_2$ competes effectively with NiL^{3+} for the Cr^{2+}
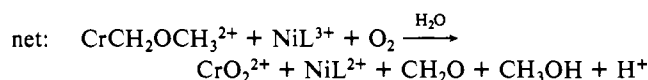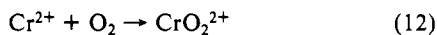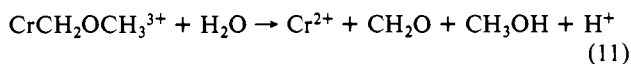
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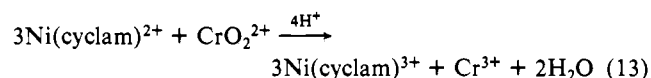(16) McAuley, A.; Macartney, D. H.; Oswald, T. *J. Chem. Soc., Chem. Commun.* **1982**, 274.
(17) Brodovitch, J. C.; McAuley, A. *Inorg. Chem.* **1981**, *20*, 1667.

produced (eq 10–12 and 9). The rate constants for the formation

$$CrCH_2OCH_3^{2+} + NiL^{3+} \rightarrow CrCH_2OCH_3^{3+} + NiL^{2+} \quad (10)$$

$$CrCH_2OCH_3^{3+} + H_2O \rightarrow Cr^{2+} + CH_2O + CH_3OH + H^+ \quad (11)$$

$$Cr^{2+} + O_2 \rightarrow CrO_2^{2+} \quad (12)$$

net: $CrCH_2OCH_3^{2+} + NiL^{3+} + O_2 \xrightarrow{\text{H}_2\text{O}}$
$$CrO_2^{2+} + NiL^{2+} + CH_2O + CH_3OH + H^+$$

of CrO_2^{2+} (eq 12) has a value of 1.6×10^8 M^{-1} s^{-1}.[18] The reaction of Ni(cyclam)$^{3+}$ with Cr^{2+} has not been studied, but it is expected also to be quite fast. In the presence of $(0.2–1) \times 10^{-3}$ M O$_2$, however, most or all of Cr^{2+} produced in reaction 11 reacts as shown in eq 12.

The same kinetic and stoichiometric effect of O$_2$ would be expected if the reaction proceeded according to eq 5 and 6, since the carbon-centered radicals also react rapidly with O$_2$[19] to yield alkylperoxy radicals. However, in this particular system the formation of carbon-centered radicals can be ruled out on the following grounds. After a spectrophotometric titration of Ni-(cyclam)$^{3+}$ with CrCH$_2$OCH$_3^{2+}$ in an oxygen-saturated solution was complete, the spectrum of Ni(cyclam)$^{3+}$ reappeared *slowly*. We attribute this to the oxidation of the product Ni(cyclam)$^{2+}$ by the long-lived[18,20] CrO$_2^{2+}$ that was formed in the sequence of reactions 11 and 12. The slowness of the reaction producing Ni(cyclam)$^{3+}$ is consistent[21] with reaction 13.   Had

$$3Ni(cyclam)^{2+} + CrO_2^{2+} \xrightarrow{4H^+}$$
$$3Ni(cyclam)^{3+} + Cr^{3+} + 2H_2O \quad (13)$$

CH$_3$OCH$_2$OO$^\bullet$ been formed, it would have to oxidize Ni(cyclam)$^{2+}$ much more rapidly (or not at all), owing to the competing self-reactions of the alkylperoxy radicals.[22]

The presence of O$_2$ introduces a kinetic factor of 2.6, rather than the expected factor of 2.0. This discrepancy is probably caused by the interference from reaction 13 that partly restores Ni(cyclam)$^{3+}$ in air- and oxygen-saturated solutions even under the kinetic conditions.

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(20) Brynildson, M. E.; Bakac, A.; Espenson, J. H. *J. Am Chem. Soc.* **1987**, *109*, 4579.
(21) The oxidation of Ni(cyclam)$^{2+}$ by independently prepared[20] CrO$_2^{2+}$ takes place on a comparable time scale: Brynildson, M. E.; Bakac, A.; Espenson, J. H. Unpublished observations.
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The lack of the effect of Ni(cyclam)$^{2+}$ on the kinetics of the oxidation of CrCH(CH$_3$)$_2^{2+}$ implies a very short lifetime of CrCH(CH$_3$)$_2^{3+}$, such that the reverse of reaction 5 cannot compete with the unimolecular reactions (6) and (11). The reduction potentials of the organochromium complexes are not known, which makes it impossible to estimate the equilibrium constant for reaction 5 and thus the lifetime of CrCH(CH$_3$)$_2^{3+}$ from the available kinetic data.

The rate constants for the oxidation of the organochromium complexes are nearly the same for the two Ni(III) complexes. This is expected for outer-sphere electron-transfer reactions with oxidants of very similar reduction potentials and self-exchange rate constants.[9,15,16] In both cases the benzylchromium complex reacts ~100 times faster than the 2-propyl. Qualitatively, the same reactivity order was observed earlier with all other oxidants.[5] Special interactions between the nickel(III) species and any of the organochromium complexes can be safely ruled out, a point that was less certain with other oxidants. There is thus little doubt that the greater oxidizability of CrCH$_2$Ph^{2+} relative to CrCH-(CH$_3$)$_2^{2+}$ reflects the genuine electronic effects of the two alkyl groups.

The different reactivity order observed[3] in the series of the organocobaloximes, CH(CH$_3$)$_2$ > PhCH$_2$, may be a result of a contribution from an inner-sphere path. On the other hand, the point may be more subtle than that. One-electron oxidation of the organocobaloximes yields the long-lived (time scale of seconds at room temperature) organocobalt(IV) complexes[3] (eq 1). Obviously, a reasonably strong Co–C bond exists in the transition state for this reaction.

The existence of the oxidized organochromium complexes, CrR^{3+}, has only been postulated. These species have never been observed directly (or even detected kinetically), presumably owing to their extremely short lifetimes. Actually, the transition state and the initial products of the reactions of eq 2 might be significantly dissociated (eq 14), in which case the kinetics would

$$CrR^{2+} \xrightarrow{\text{oxidant}} [Cr\cdots R^{3+}]^\ddagger \rightarrow Cr^{3+}, {}^\bullet R \quad (14)$$
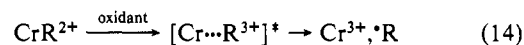
be strongly influenced by the stability of the radicals produced. In such a case one would expect CrCH$_2$Ph^{2+} to react more rapidly than the alkyl complexes.

A complete study of the oxidation of the organocobaloximes by such outer-sphere oxidants as used in this work could bring about a better understanding of the differences between the two series of complexes, CrR^{2+} and Co(dmgH)$_2$R, as well as of the other issues raised in this work.