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Reactions of Cobalt(II) Macrocycles with Alkyl and Alkylperoxy Radicals

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The cobalt–carbon bond formation in the reactions of cobalt(II) macrocycles, LCo^{II} (L = *C-meso*-Me_6[14]aneN_4, Me_6[14]-4,11-dieneN_4, corrin, tim), with primary alkyl and substituted primary alkyl radicals takes place with rate constants in the range 10^7–10^9 M^{-1} s^{-1}. The kinetics are influenced by the nature of the macrocycle to a much greater extent than by the nature of the radicals, such that all the rate constants, k_{Co}, for a given cobalt complex fall within a factor of ~2. For example, the values of $10^{-8}k_{Co}/M^{-1}$ s^{-1} for B_{12r} are 4.2 (R = CH_3), 5.1 (C_2H_5), 5.1 (CH_3OCH_2), 5.8 ($ClCH_2$), 6.1 (C_3H_7), and 9.1 ($BrCH_2$). The alkylperoxy radicals $RO_2^{\bullet}$ (R = CH_3, C_2H_5, $BrCH_2$) react with $Co(tim)(H_2O)_2^{2+}$ with a rate constant $k = 1.4 \times 10^8$ M^{-1} s^{-1}.

Introduction

In our recent kinetic study of the reactions of some metal complexes with aliphatic radicals[1] we measured surprisingly small rate constants of $(1-2) \times 10^7$ M^{-1} s^{-1} for reaction 1.[2] These values

$$R^{\bullet} + Co([14]aneN_4)(H_2O)_2^{2+} \rightarrow RCo([14]aneN_4)H_2O^{2+} + H_2O \quad (1)$$

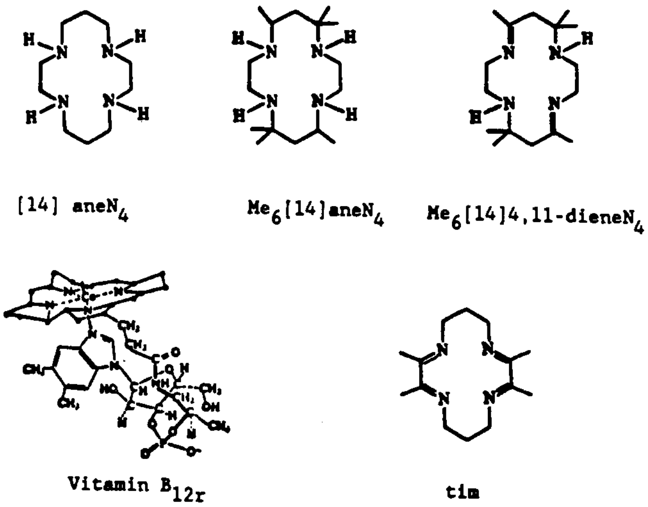
$$R = CH_3, C_2H_5$$

are 1–2 orders of magnitude smaller than the reported rate constants for the reactions of methyl radicals with several other macrocyclic complexes (Chart I) of cobalt(II).[2-5] The rates of all of these cobalt–carbon bond forming reactions are thought to be controlled by substitution of water at the metal center.[5] However, very little quantitative information is available on the substitution reactions of these cobalt(II) complexes. The rate constants for axial substitution in several $Co^{II}(macrocycleN_4)X_2^{n+}$ complexes have been reported as $\geq 10^6$ s^{-1} at 298 K.[6] The exchange of CH_3CN in $Co([14]aneN_4)(CH_3CN)_2^{2+}$ takes place with a rate constant of $\geq 8 \times 10^6$ s^{-1} at 266 K.[7]

Our results, combined with the available literature data,[3-5] seem to suggest that the axial positions in $Co([14]aneN_4)(H_2O)_2^{2+}$ are less labile than those in the other low-spin cobalt(II) macrocycles studied. However, the kinetic data[1,3-5,8-12] on the coupling of the alkyl radicals with tetraaza macrocyclic cobalt(II) complexes are so limited and nonsystematic that these conclusions have to be regarded as tentative.

Recently[1] we have used methyl viologen (1,1′-dimethyl-4,4′-bipyridinium) radical cation, $MV^{\bullet+}$, as a kinetic probe to determine the rate constants for the reactions of carbon-centered radicals with Cr^{2+} and $Co([14]aneN_4)(H_2O)_2^{2+}$. The radicals were generated photochemically from $RCo([14]aneN_4)(H_2O)^{2+}$. We have now applied this method to the reactions of several low-spin macrocyclic cobalt(II) complexes to examine the effects of the nature of the radicals and of the macrocyclic ligands on the kinetics of cobalt–carbon bond formation.

Chart I



Experimental Section

The complex $Co(C\text{-}meso\text{-}Me_6[14]aneN_4)(CoCl_4)$, also known as Co(tet a)($CoCl_4$), was prepared as described in the literature[13] and converted to the $CF_3SO_3^-$ salt by a procedure analogous to that reported for the preparation of the perchlorate salt. The purity was checked by the cobalt analysis and the UV–visible spectrum.[13] Neutral aqueous stock solutions showed no signs of isomerization even after several days at room temperature or several weeks in a refrigerator. Such aged solutions were spectrally and kinetically indistinguishable from the freshly prepared solutions, provided both had been handled under strictly air-free conditions. The complex *meso*-$Co(Me_6[14]4,11\text{-}dieneN_4)(ClO_4)_2$[2] was prepared according to the literature procedure.[13] The UV–visible spectrum [λ_{max} 444 nm (ϵ 117 M^{-1} cm^{-1}), 336 (2760), 204 (1.70×10^4)] matches well the reported one.[13,14] *rac*-$Co(Me_6[14]4,11\text{-}dieneN_4)^{2+}$ was prepared by letting a solution of the meso complex isomerize in 1 mM NaOH[14] and then acidifying it to $[H^+] = 0.01$ M. The shift of the 336 nm peak to 327 nm during this process was taken as evidence that the racemic isomer was formed.[14]

The $Co(tim)(H_2O)_2(ClO_4)_2$ was available from our laboratory reserves. It was purified by ion exchange, precipitated with $NaClO_4$, filtered out, and dried in a vacuum desiccator. The hydroxycobalamin hydrochloride and methylcobalamin were commercial products (Sigma). Solutions of B_{12r} were prepared by the zinc amalgam reduction of B_{12a} in neutral and acidic solutions.[15] The concentrations of B_{12r} in the stock

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(1) Bakac, A.; Espenson, J. H. *Inorg. Chem.*, in press.

(2) The stereochemistry of the coordinated macrocycles has been discussed in detail (Curtis, N. F. In *Coordination Chemistry of Macrocyclic Compounds*; Nelson, G. A., Ed.; Plenum: New York, 1979, Chapter 4). The abbreviations used are the following: [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane; Me_6[14]4,11-dieneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; *C-meso*-Me_6-[14]aneN_4 = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; B_{12r} = cob(II)alamin, the cobalt(II) derivative of vitamin B_{12}; B_{12a} = aquocob(III)alamin.

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(11) Ross, A. B.; Neta, P. *Rate Constants for Reactions of Aliphatic Carbon-Centered Radicals in Aqueous Solution*: *NSRDS-NBS 70*; National Bureau of Standards: Washington, DC, 1982.

(12) The reactions with $CO_2^{\bullet-}$ and $^{\bullet}C(CH_3)_2OH$ radicals yield the cobalt(I) complexes and do not necessarily involve the organocobalt intermediates: (a) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 86. (b) Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 4000.

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(15) (a) Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38. (b) Balasubramanian, P. N.; Pillai, G. C.; Carlson, R. R.; Linn, D. E., Jr.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 780.

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Table I. Summary of the Kinetic Data ($10^{-8}k_{Co}/M^{-1}\ s^{-1}$) for the Reactions of Cobalt(II) Macrocycles with Aliphatic Radicals[a]

	macrocycle					
R	corrin	[14]ane	*C-meso*-Me_6[14]ane	*meso*-Me_6[14]diene[b]	*rac*-Me_6[14]diene[b]	tim
CH_3	4.2[c] 4.2[f] 4.4 (MV)[f] 15–20[j]	0.16 (MV)[d,e]	0.42 (MV)[f]	2.3 (MV)[e,f] 7[g] 1–2[i]	0.73	~0.5 1[h]
C_2H_5	5.1[f]	0.11 (MV)[d,e]	0.29 (MV)[e,f]			
C_3H_7	6.1[f]			1.4 (MV)[e,f]		
CH_3OCH_2	5.1[f]		0.52[f]			
$ClCH_2$	5.8[f]					
$BrCH_2$	9.1[f]			1.5 (MV)[e,f]		

[a] Conditions: 23 ± 1 °C, $[R^\bullet]_0 = 2–4\ \mu M$. The values of the rate constants followed by (MV) were determined by the methyl viologen method. [b] The notation *meso* and *rac* pertains to the cobalt complexes of this ligand. [c] $[H^+] = 0.02–0.05$ M. [d] Reference 1. [e] $[H^+] = 2–20$ mM. [f] pH 7. [g] Acidic solutions; reference 3. [h] Reference 3; pH not specified. [i] pH 9.5; reference 4. [j] Reference 5. The reaction pH has not been specified, but from the spectral data given for B_{12r} and methylcobalamin, we infer pH ~7.

solutions were determined spectrophotometrically.[5,15a] The organocobalt complexes $RCo([14]aneN_4)(H_2O)^{2+}$ were available from our previous work.[1]

Methyl viologen was purchased as the dichloride salt (Aldrich) and recrystallized three times from methanol. Aqueous solutions of MV^{2+} were prepared under Ar and converted to MV^+ by reduction on Zn/Hg.

The kinetics of all the reactions were studied by use of a laser flash photolysis system described earlier.[16] The LD 490 dye (Exciton) was used throughout. The kinetics of the reactions of B_{12r} with carbon-centered radicals were monitored directly at 470 nm (loss of B_{12r}) and 520 nm (formation of alkylcobalamins). For R = CH_3 the kinetics were also determined by use of the MV^+ probe, in which case the monitoring wavelength was 600 nm (ϵ_{MV^+} 1.37 × $10^4\ M^{-1}\ cm^{-1}$).[17] The reaction of $CH_3^\bullet$ with $Co(tim)(H_2O)_2^{2+}$ was monitored directly at the 545-nm maximum of the cobalt(II) complex.

The absorbance changes accompanying the conversion of the three remaining LCo^{II} complexes ($Co(C\text{-}meso\text{-}Me_6[14]aneN_4)(H_2O)_2^{2+}$ and both isomers of $Co(Me_6[14]4,11\text{-diene})(H_2O)_2^{2+}$) to $LCo^{III}R$ are too small for the direct determination in the accessible wavelength range. The kinetics were thus determined by use of the MV^+ probe. The cobalt(II) complexes and MV^+ were used in a large excess over $[R^\bullet]$ in all the experiments to ensure pseudo-first-order conditions. The rate constants were evaluated by fitting the data to the standard first-order expression.

All the reactions involving carbon-centered radicals were studied under strictly anaerobic conditions, which were achieved by purging the solutions with a stream of argon.

The reactions of $Co(tim)(H_2O)_2^{2+}$ with the alkylperoxy radicals were monitored at 545 nm. The kinetics of the reaction of the methylperoxy radicals, $CH_3OO^\bullet$, with B_{12r} were monitored at 520 nm, where the molar absorptivity of B_{12r} is 4.2 × $10^3\ M^{-1}\ cm^{-1}$, and that of methylperoxycobalamin is expected to be close to 8 × $10^3\ M^{-1}\ cm^{-1}$, the value of B_{12a}. The radicals were produced by photolysis of an oxygen-saturated solution of methylcobalamin.

Results

The laser flash photolysis of the complexes $RCo([14]aneN_4)(H_2O)^{2+}$ yields alkyl radicals and the cobalt(II) macrocycle[1] (eq 2). In the presence of an externally added cobalt(II) complex

$$RCo([14]aneN_4)(H_2O)^{2+} \xrightarrow[H_2O]{h\nu} R^\bullet + Co([14]aneN_4)(H_2O)_2^{2+} \quad (2)$$

and MV^+, the radical disappears mainly in reactions 3–5.[18] The

$$2R^\bullet \rightarrow \text{nonradical products} \quad k_R \quad (3)$$

$$R^\bullet + MV^+ \rightarrow \text{nonradical products} \quad k_{MV} \quad (4)$$

$$R^\bullet + LCo^{II} \rightarrow RCo^{III}L \quad k_{Co} \quad (5)$$

$$-d[R^\bullet]/dt = k_{obs}[R^\bullet] = (k_R[R^\bullet] + k_{MV}[MV^+] + k_{Co}[LCo^{II}])[R^\bullet] \quad (6)$$

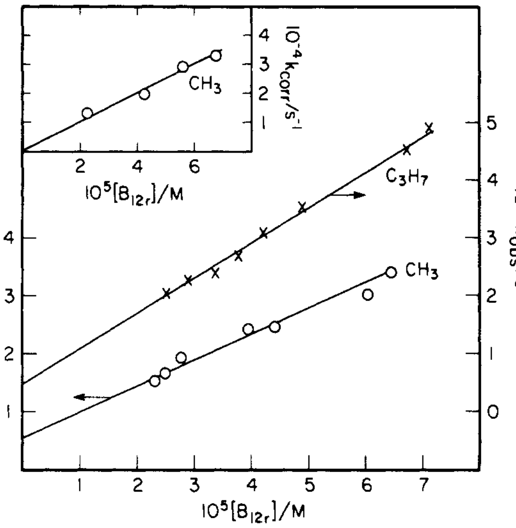

Figure 1. Plots of k_{obs} against the concentration of B_{12r} according to eq 7 for the reaction of B_{12r} with $CH_3^\bullet$ and $C_3H_7^\bullet$ monitored at 520 nm. Inset: plot of k_{corr} ($=k_{obs} - k_R[R^\bullet] - k_{MV}[MV^+]$) against $[B_{12r}]$ for the reaction of B_{12r} with $CH_3^\bullet$. The reaction was monitored at 600 nm in the presence of MV^+ as a kinetic probe. Conditions: T = 23 ± 1 °C, pH 7, $[R^\bullet]_0 = 2–3\ \mu M$.

kinetics of the loss of the radical are described by eq 6.[1] The importance of the term $k_R[R^\bullet]$ is minimized by keeping the concentrations of $R^\bullet$ low.[18] Of course, in the absence of MV^+ the term $k_{MV}[MV^+]$ disappears and eq 7 applies.

$$k_{obs} = k_R[R^\bullet] + k_{Co}[LCo^{II}] \quad (7)$$

The directly determined pseudo-first-order rate constants for the reactions of $CH_3^\bullet$ and $C_3H_7^\bullet$ with B_{12r} are plotted against the concentration of B_{12r} in Figure 1. The plots are linear as expected from eq 7 and yield the second-order rate constants k_{Co} in Table I.

The data obtained in the presence of MV^+ were first corrected[1] for the contribution of the radical self-reactions and the reactions of radicals with MV^+, such that $k_{corr} = k_{Co}[LCo^{II}]$. A plot of k_{corr} against $[B_{12r}]$ is shown in the inset in Figure 1. The slope of the line gives k_{Co} = 4.4 × $10^8\ M^{-1}\ s^{-1}$, in good agreement with the directly determined value of 4.2 × $10^8\ M^{-1}\ s^{-1}$. The kinetics are independent of pH in the range 1.3–7.0.

The kinetic results of the reactions of the carbon-centered radicals with $Co(C\text{-}meso\text{-}Me_6[14]aneN_4)(H_2O)_2^{2+}$ and both isomers of $Co(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2^{2+}$ are also summarized in Table I.

The complex $Co(tim)(H_2O)_2^{2+}$ reacts with the methyl radical (and presumably other radicals) relatively slowly. This necessitates

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[16] (a) Hoselton, M. A.; Lin, C.-T.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 2383. (b) Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4104. The energy of the laser pulse is 250 mJ, and the pulse width is 600 ns.

[17] Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

[18] The reverse of eq 2 is negligible owing to the low value of k_{Co} for this complex and its low concentration ($[(Co[14]aneN_4)(H_2O)_2^{2+}]_0 = [R^\bullet]_0$ = 2–4 μM).

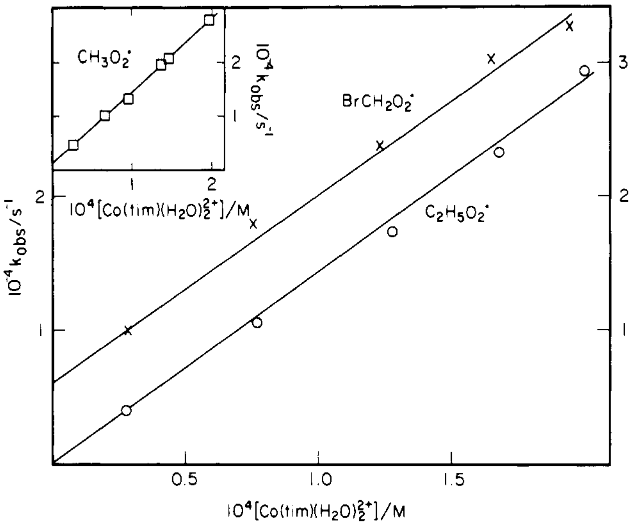

Figure 2. Plots of k_{obs} against the concentration of $Co(tim)(H_2O)_2^{2+}$ for the reaction of $Co(tim)(H_2O)_2^{2+}$ with $C_2H_5O_2^\bullet$, $BrCH_2O_2^\bullet$, and $CH_3O_2^\bullet$ (inset) at 23 ± 1 °C, pH 2–7, and $[RO_2^\bullet]_0 = 5$ μM.

the use of high concentrations of this complex in kinetic experiments to keep the contribution of the term $k_{Co}[LCo^{II}]$ in eq 7 large relative to the term $k_R[R^\bullet]$. Similar conditions were required for the weakly absorbing $Co(C\text{-}meso\text{-}Me_6[14]aneN_4)(H_2O)_2^{2+}$. However, unlike the latter complex, the $Co(tim)(H_2O)_2^{2+}$ absorbs strongly in the visible range and the use of high concentrations is precluded. Owing to these limitations, an accurate determination of the rate constant for the reaction with $CH_3^\bullet$ was not feasible and only an estimate of $(5 \pm 2) \times 10^7$ M^{-1} s^{-1} was obtained. It appeared that this rate constant increased with the age of the cobalt solutions. No attempt was made to study the reactions with other carbon-centered radicals.

The photolysis of $RCo([14]aneN_4)(H_2O)^{2+}$ in solutions containing oxygen yields the alkylperoxy radicals owing to the rapid scavenging of carbon-centered radicals with oxygen (eq 8).[11]

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \tag{8}$$

When the photolysis was carried out in the presence of $Co(tim)(H_2O)_2^{2+}$, the $RO_2^\bullet$ radicals (R = CH_3, C_2H_5, $BrCH_2$) disappeared mainly in the reactions with the cobalt complex[19] (eq 9) and in the self-reactions[20,21] (eq 10), suggesting the rate law

$$RO_2^\bullet + LCo^{II} \rightarrow LCo^{III}O_2R \tag{9}$$

$$2RO_2^\bullet \rightarrow \text{nonradical products} \tag{10}$$

$$-d[RO_2^\bullet]/dt = (k_9[LCo^{II}] + k_{10}[RO_2^\bullet])[RO_2^\bullet] \tag{11}$$

of eq 11. The decrease in absorbance at 545 nm obeyed first-order kinetics for at least 3 half-lives. The plots of the pseudo-first order rate constants against the concentration of $Co(tim)(H_2O)_2^{2+}$ are linear, as shown in Figure 2. The slopes of the lines yield an identical rate constant for all three radicals studied, $k_9 = (1.4 \pm 0.1) \times 10^8$ M^{-1} s^{-1}.

The intercepts in the reactions of $CH_3O_2^\bullet$ and $C_2H_5O_2^\bullet$ are quite small, consistent with reaction 9 being the dominant route for the loss of the $RO_2^\bullet$ radicals. The lack of a significant contribution from the radical self-reactions is expected under the concentration conditions used, given that the rate constants for reactions 9 and 10[20,21] are comparable.

The sizable intercept in the reaction of $BrCH_2O_2^\bullet$ with $Co(tim)(H_2O)_2^{2+}$ suggests that k_{10} is quite high for this radical. Both the size of the intercept and the effect of the concentration of the cobalt(II) complex on the absorbance changes in the kinetic runs yield $k_{10} \sim 10^9$ M^{-1} s^{-1} for $BrCH_2O_2^\bullet$. To our knowledge there has been no direct determination of this rate constant.

The rate constant for the reaction of $CH_3O_2^\bullet$ with B_{12r} is $(2 \pm 0.5) \times 10^9$ M^{-1} s^{-1}, in good agreement with the reported value.[5]

Discussion

The reactions of the cobalt(II) macrocycles with alkyl radicals to form organocobalt complexes take place with the rate constants of 10^7–10^9 M^{-1} s^{-1} (Table I). B_{12r} is the most reactive, with the rate constants varying between 4×10^8 M^{-1} s^{-1} ($CH_3^\bullet$) and 9×10^8 M^{-1} s^{-1} ($BrCH_2^\bullet$). We discard the literature[5] value of $\sim 2 \times 10^9$ M^{-1} s^{-1} for the reaction with $CH_3^\bullet$ as unreliable. This rate constant was determined by flash-photolyzing methylcobalamin and monitoring its partial recovery from B_{12r} and $CH_3^\bullet$. A significant portion of the radicals dimerized under the reaction conditions, yet it appears that the authors neglected to correct the observed rate constant for this contribution. A similar situation may have occurred in a study[3b] of the reaction of $meso\text{-}Co(Me_6[14]dieneN_4)(H_2O)_2^{2+}$ with $CH_3^\bullet$. The value reported,[3b] 7×10^8 M^{-1} s^{-1}, is somewhat higher than our value of 2.3×10^8 M^{-1} s^{-1}.[22] The rate constant obtained by pulse radiolysis,[4] $(1\text{–}2) \times 10^8$ M^{-1} s^{-1}, probably pertains to the racemic isomer, since under the experimental conditions (pH 9.5) the isomerization is quite rapid.[14] The lower limit of the range reported[4] is comparable to our result for this isomer, $k = 7.3 \times 10^7$ M^{-1} s^{-1}.

Under the experimental conditions of Table I (aqueous solution, pH 1.3–7) the B_{12r} is pentacoordinate.[23,24] The axial ligand varies with the pH such that the dominant species at the lower pH limit contains coordinated water and at the upper limit benzimidazole. Surprisingly, the rate constant for the reaction with the methyl radical is within the experimental error identical at the two pH extremes.

The complex $rac\text{-}Co(Me_6[14]4,11\text{-}dieneN_4)^{2+}$ is pentacoordinated in the solid state and probably in solution.[14] The reaction with the methyl radical yields the secondary racemic isomer of $(H_2O)Co(Me_6[14]4,11\text{-}dieneN_4)CH_3^{2+}$, such that the cobalt-bound methyl is located on the same side of the macrocyclic plane as the axial macrocycle-bound methyls.[14] This unusual geometry probably arises because the more accessible site in the cobalt(II) complex is already occupied by a molecule of water.[14] The coupling of the methyl radical with the cobalt at the sterically more crowded, but unoccupied, site is apparently more facile than the replacement of a coordinated water at the more accessible site. This does not seem unreasonable, since the latter process would have to be coupled with the coordination of an additional molecule of water at the congested site trans to the methyl in order for a six-coordinated organocobalt to be formed.

The complexes $Co([14]aneN_4)^{2+}$, $meso\text{-}Co(Me_6[14]4,11\text{-}dieneN_4)^{2+}$, and $Co(tim)^{2+}$ are hexacoordinated in the solid state.[6] The coordination number in solution is usually assumed to be 6, although there is no firm evidence to support this assumption.[6] No crystallographic data are available on $Co(C\text{-}meso\text{-}Me_6[14]aneN_4)^{2+}$. So far we have been unable to obtain crystals of sufficient quality for structural determinations. However, we expect this complex to be six-coordinated by analogy to the 4,11-diene analogue.

Our results are consistent with the cobalt–carbon bond formation taking place by a dissociative process, such that $k_{Co} = kK_{OS}$, as proposed earlier.[25] The equilibrium constant K_{OS}, for the formation of the outer-sphere complexes,[26] will vary somewhat with the macrocycle and the radical. However, for the five complexes with synthetic macrocycles, the values of K_{OS} should be fairly similar, ~(0.3–1), because the radicals are uncharged and the cobalt(II) complexes do not differ much in size.[6] The variation of k_{Co} thus reflects mainly the variation in k. The latter

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(20) Batt, L. *Int. Rev. Phys. Chem.* **1987**, *6*, 53.

(21) (a) Adachi, H.; Basco, N.; James, D. G. L. *Int. J. Chem. Kinet.* **1979**, *11*, 1211. (b) Adachi, H.; Basco, N.; James, D. G. L. *Int. J. Chem. Kinet.* **1980**, *12*, 949.

(22) A reviewer pointed out that different isomers may have been involved in the two studies. This appears unlikely, since the same method[13] was used in the preparation of the solid perchlorate complex and both studies utilized acidic solutions, where the isomerization is extremely slow.[14]

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(24) Lexa, D.; Saveant, J.-M. *Acc. Chem. Res.* **1983**, *16*, 235.

(25) Durham, B.; Endicott, J. F.; Wong, C.-L.; Rillema, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 847.

(26) See for example: Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

is probably best interpreted as the rate constant for interchange of H_2O and the radical at the hexacoordinated cobalt(II) center[25] within the outer-sphere complex or as the rate constant for the capture of the radical from the second coordination sphere by the pentacoordinated B_{12r} and *rac*-Co(Me_6[14]4,11-dieneN_4)$^{2+}$.

For a given cobalt complex the rate constants k_{Co} vary little with the nature of the radicals. Admittedly, only primary radicals were studied, but the near constancy of the values of k_{Co} is striking; for none of the complexes do these values vary by more than a factor of 2. One might be tempted to propose that the values of k ($=k_{obs}/K_{OS}$) represent the rate constant for water exchange by a D mechanism.[27] However, the picture has to be at least somewhat more complicated, since the coordination number, 5 or 6, has a minimal effect.[28] For example, the five-coordinated B_{12r} and six-coordinated *meso*-Co(Me_6[14]4,11-dieneN_4)$^{2+}$ react with $CH_3^\bullet$ with very similar rate constants. Also, the rate constants for the reactions of the two isomers of Co(Me_6[14]4,11-dieneN_4)$^{2+}$ differ only by a factor of ~3, despite the difference in the coordination number and the steric demands at the reaction site. The lack of a significant steric effect is also demonstrated by the similarity of the rate constants for reactions of the [14]aneN_4 and *C-meso*-Me_6[14]aneN_4 complexes. The latter is sterically much more crowded, and it might be expected that the axial Co–O bonds are longer and/or that the trans positions are more labile than those in the [14]aneN_4 complex. However, the two complexes differ in their reactivity toward the radicals by less than a factor of 3.

The apparent insensitivity of the cobalt–carbon bond forming reactions to the steric demands of the macrocycle is quite different from the recent observations on the substitution reactions of some macrocyclic methylcobalt(III) complexes.[29] In fact, the steric effects were so dramatic that different mechanisms had to be proposed for different isomers.[29] The high inherent lability of the 2+ oxidation state is undoubtedly the most crucial parameter responsible for such a different response to the steric effects by the two oxidation states.

With the steric effects playing at best a minor role in the kinetics of the cobalt–carbon bond forming reactions studied in this work, one might expect that the electronic effects will be more clearly recognizable. The most obvious correlation would be that between the kinetic data and the reduction potentials[15a,24] for the $Co^{III/II}$ couples, since the reactions with the radicals result in the oxidation of the metal center. The inspection of data in Table I shows that not even a qualitative correlation exists. B_{12r} has the same rate constant at pH 1 and pH 7, despite the change in the potential,[24] and the less reducing complexes (those containing unsaturated macrocycles)[15a] react more rapidly than the more strongly reducing saturated complexes. As a matter of fact, the latter observation seems to point to a pattern, although the values of the rate constants for the reaction of the methyl radical with the saturated Co(*C-meso*-Me_6[14]aneN_4)$^{2+}$, 4.2×10^7 M^{-1} s^{-1}, and the unsaturated *rac*-Co(Me_6[14]dieneN_4)$^{2+}$, 7.3×10^7 M^{-1} s^{-1}, are so close that this classification also seems doubtful.

It is now also obvious that the rate constants for the reactions of Co([14]aneN_4)$^{2+}$ with carbon-centered radicals, while still the lowest in Table I, are not so outstanding. This is due partly to the downward revision of the literature values[3b,5] for the reactions of $CH_3^\bullet$ with B_{12r} and *meso*-Co(Me_6[14]4,11-dieneN_4)$^{2+}$ and partly to the finding that three other complexes, Co(*C-meso*-Me_6[14]aneN_4)$^{2+}$, Co(tim)$^{2+}$, and *rac*-Co(Me_6[14]4,11-dieneN_4)$^{2+}$, also have rate constants below 10^8 M^{-1} s^{-1}. It thus appears that the reactivity of the cobalt macrocycles in Table I toward the radicals is determined primarily by the high lability of cobalt(II) modified by a subtle combination of steric and electronic effects.

The rate constant for the reactions of the $RO_2^\bullet$ radicals with Co(tim)$(H_2O)_2^{2+}$ obtained in this work, $k_9 = 1.4 \times 10^8$ M^{-1} s^{-1} ($RO_2 = CH_3O_2$, $C_2H_5O_2$, $BrCH_2O_2$) agrees well with the value reported earlier for the reaction of the same complex with $CH_3O_2^\bullet$ (1.2×10^8 M^{-1} s^{-1}).[19] The reaction of B_{12r} with $CH_3O_2^\bullet$ has $k_9 = 2.4 \times 10^9$ M^{-1} s^{-1}.[5] It is noteworthy that the reactions of the cobalt(II) complexes with alkylperoxy radicals are faster than with the alkyls. This might suggest a higher value for K_{OS} in the case of $RO_2^\bullet$. A stronger interaction between the more polar, oxygen-containing radicals and the cobalt complexes does seem reasonable. On the other hand, the minor differences in the rate constants for different incoming ligands are to be expected for an interchange process.

From the literature data on the reactions of Co(Me_6[14]dieneN_4)$(H_2O)_2^{2+}$ (isomer not specified) with $O_2^{\bullet-}$[30] and $X_2^{\bullet-}$[31] (X = Cl, Br, I), we obtain values of k_{obs}/K_{OS} in the range (3–20) $\times 10^8$ s^{-1}. These values are somewhat higher than those derived from the reactions of either isomer with alkyl radicals, but the difference again seems acceptable within the framework of an interchange process.

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Registry No. Vitamin B_{12r}, 14463-33-3; Co([14]aneN_4)$(H_2O)_2^{2+}$, 65554-13-4; Co(*C-meso*-Me_6[14]aneN_4)$(CF_3SO_3)_2$, 123264-74-4; *meso*-Co(Me_6[14]4,11-dieneN_4)$(ClO_4)_2$, 123264-75-5; *rac*-Co(Me_6[14]4,11-dieneN_4)$(ClO_4)_2$, 123355-22-6; Co(tim)$(H_2O)_2(ClO_4)_2$, 54343-72-5; CH_3, 2229-07-4; C_2H_5, 2025-56-1; C_3H_7, 2143-61-5; CH_3OCH_2, 16520-04-0; $ClCH_2$, 6806-86-6; $BrCH_2$, 16519-97-4; $CH_3O_2^\bullet$, 2143-58-0; $C_2H_5O_2^\bullet$, 3170-61-4; $BrCH_2O_2^\bullet$, 119437-62-6.

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(28) A reviewer also point out that the ~100-fold variation in k_{H_2O} for the complexes listed in Table I is unlikely.

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