velops. It can be generated either by controlled potential reduction of its parent neutral compound $Co(dmgBF_2)_2(H_2O)_2$ in acetonitrile in the presence of one equivalent of pyridine at −0.44 V (vs NHE) or by decomposition of alkyl–$Co(dmgBF_2)_2py^{2-}$ in acetonitrile. Formation of *n*-$C_3H_7Co(dmgBF_2)_2py^{2-}$ can be achieved by controlled potential electrolysis of *n*-$C_3H_7Co(dmgBF_2)_2py$ at −1.90 V (vs NHE) in 0.06 M $(CH_3)_4NBF_4$ acetonitrile solution. An air-free electrocell with a mercury pool working electrode, a platinum plate auxiliary electrode, and an Ag/AgCl reference electrode was used to conduct the electrolysis. Owing much to the higher solubility of *n*-$C_3H_7Co(dmgBF_2)_2py$ over $Co(dmgBF_2)_2(H_2O)_2$ in acetonitrile, the second method was adopted to obtain a crystal for this study. A three layer solution system in a test tube was employed for the crystal to grow. Diethyl ether was allowed to diffuse slowly from the top layer through a C_5H_{12} middle layer into the bottom layer of the dark blue acetonitrile solution containing the title compound, all at 0 °C. The middle layer, which is immiscible with the blue acetonitrile solution on the bottom, functions as a spacer to slow the diffusion of diethyl ether into the acetonitrile solution and ensure the quality of crystals for the diffraction study. Anaerobic conditions are required owing to the extreme sensitivity of $Co(dmgBF_2)_2py^-$ solution toward oxygen. The deep blue crystal of $[(CH_3)_4N][Co(dmgBF_2)_2py]\cdot CH_3CN$ is less air-sensitive.

X-ray Data Collection. A dark blue crystal of the title compound was taken from a nitrogen-filled test tube and attached to the tip of a glass fiber. The crystal was then moved into the cold stream of the low-temperature device on the diffractometer and slowly cooled to −75 °C. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information are given in Table I.

A total of 4741 reflections were collected in the $\pm h,+k,\pm l$ hemisphere. Lorentz and polarization corrections were applied. An absorption correction based on a series of ψ-scans was applied, and equivalent reflections were averaged.

Determination and Refinement of the Structure. The choice of the centric triclinic group was indicated initially by intensity statistics and later confirmed by the successful refinement of the structure. The positions of all of the non-hydrogen atoms of the complex and the associated counterion were found by an automatic Patterson interpretation method.[43] One molecule of acetonitrile was later located in a difference Fourier map. In the final stages of refinement, the non-hydrogen atoms were refined with anisotropic temperature factors, and hydrogen atoms were added in idealized positions. A common isotropic temperature factor was refined for each of these groups of hydrogen atoms: one for the methyl hydrogens of the complex, one for the pyridinyl hydrogens, and one for the methyl hydrogen atoms on the $[(CH_3)_4N]^+$ and CH_3CN moieties.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX-II computer using the SHELX-76 programs.[44]

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Supplementary Material Available: A full table of crystal data and a table of anisotropic temperature factors (4 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Reduction-Induced Cleavage of the Cobalt–Carbon Bond in Macrocyclic Organocobalt Complexes

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The one-electron reduction of $RCo(dmgBF_2)_2A$ ($dmgBF_2$ = (difluoroboryl)dimethylglyoximato, A = pyridine or H_2O, R = CH_3, C_2H_5, C_3H_7, $C_6H_5CH_2$, or 4-$XC_6H_4CH_2$) yields $RCo(dmgBF_2)_2A^-$ as transients. The ESR parameters (R = 4-$BrC_6H_4CH_2$, $g_\parallel = 2.23$, $A_\parallel = 111 \times 10^{-4}$ cm^{-1}, $g_\perp = 2.07$, $A_\perp = 54 \times 10^{-4}$ cm^{-1}) indicate that the unpaired electron resides in the $d_{x^2-y^2}$ orbital of the cobalt. The reduced complexes hydrolyze in H_2O to yield the alkanes RH and $Co(dmgBF_2)_2(H_2O)_2$. In acetonitrile the decomposition mode depends on the availability of β-hydrogens. For R = C_2H_5 and 1-C_3H_7, the final products are the corresponding alkenes and a cobalt(II) complex of a modified macrocycle. The benzyl and substituted benzyl complexes yield the hydrolysis products 4-$XC_6H_4CH_3$ and the unchanged cobalt(II) macrocycle. The kinetics of the reduction of $RCo(dmgBF_2)_2A$ by *R,S*,-*R,S*-Ni(tmc)$^+$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) in H_2O, pH 12, are biphasic for R = benzyl and substituted benzyl and monophasic for the primary alkyl complexes, consistent with the expected effect of the organic group on the lifetimes of the $RCo(dmgBF_2)_2A^-$ transients.

Introduction

Reduction-induced cleavage of cobalt–carbon bonds in organocobalt macrocyclic complexes presents challenging questions. Detailed mechanistic and kinetic information is still insufficient to understand fully the roles of vitamin B_{12} in catalysis of reactions such as skeletal 1,2-rearrangements,[1,2] reduction of ribonucleoside triphosphates,[3-5] and biosynthesis of methionine,[6,7] methane,[8-11] and acetate.[10,12-14] Studies of the "partial-strength" M–C σ-bonds[15] should provide additional insight into the mechanism of these reactions.

With some exceptions,[16] the electrochemcial reduction of alkylcobalt(III) complexes yields unstable alkylcobalt species that decompose by cleavage of the cobalt–carbon bond. Several decomposition pathways have been reported.[17-19] In the case of

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$RCo(salen)^-$, R = C_6H_5 and fluoroalkyl, the decomposition[17,18] yields R^- and Co(salen). For R = CH_3 and C_2H_5, $R^•$ and $Co(salen)^-$ are produced. Some other reduced organocobalt complexes have also been reported to decompose homolytically to $R^•$ and Co(I).[19,20] Yet another route involves disproportionation coupled with alkyl transfer, ultimately yielding cobalt(I) and a dialkylcobalt(III) complex.[19] Chemically reduced organocobalt complexes[21-25] decompose by analogous routes.

The equatorial ligand often plays an active role in stabilizing the one-electron-reduced organocobalt complexes. The recovery of the original organocobalt(III) complexes and the retention of configuration of the alkyl group upon one-electron reduction followed by reoxidation[26] have been explained by reversible trapping of the alkyl group by equatorial ligands. The electrochemical reductive cleavage of a steroidal cobalt porphyrin complex proceeds with retention of configuration.[27,28]

This paper reports our results on the chemical and electrochemical reductions of a series of organocobalt complexes, $RCo(dmgBF_2)_2A$ (R = CH_3, C_2H_5, 1-C_3H_7, $C_6H_5CH_2$, 4-$XC_6H_4CH_2$; A = H_2O, pyridine (py)). We have focused on the kinetics and mechanism of the reduction and decomposition of the organocobalt complexes, the participation of the equatorial ligand, and the electron configuration of the reduced organocobalt complexes $RCo(dmgBF_2)_2A^-$.

Experimental Section

Materials. The macrocyclic organocobalt(III) complexes, $RCo(dmgBF_2)_2A$ (A = pyridine, H_2O) were synthesized from $RCo(dmgH)_2A$ and BF_3·Et_2O according to the known methods[29] and recrystallized from acetone. All the complexes had satisfactory elemental analysis, UV–vis spectra,[30] and ^1H NMR spectra.[30] The cobalt(II) complex $Co(dmgBF_2)_2(H_2O)_2$[30] and *R,S,R,S*-$Ni(tmc)(ClO_4)_2$[31] (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were prepared by known procedures. Other reactants and solvents were obtained commercially and often used without purification.

Methods. Cyclic voltammetric experiments were conducted at room temperature in acetonitrile with 0.06 M Me_4NBF_4 (Aldrich) as the supporting electrolyte. The instrument used was a BAS-100 electrochemical analysis system with a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and an Ag/AgCl (3 M NaCl) reference electrode. Controlled-potential electrolysis of $RCo(dmgBF_2)_2A$ for product analysis was conducted in either dry acetonitrile or acetonitrile/water solution containing 0.06 M Me_4NBF_4. Experiments were performed by use of a BAS CV-27 voltammograph with a Hg-pool working electrode, a platinum-plate auxiliary electrode, and an Ag/AgCl (3 M NaCl) reference electrode. Electrochemical preparation of *R,S,R,S*-$Ni(tmc)^+$ (hereafter $Ni(tmc)^+$) was achieved by controlled-potential reduction of $Ni(tmc)^{2+}$ in aqueous solution containing 0.08 M $LiClO_4$ and 0.02 M NaOH.[32] Oxygen-free conditions were maintained by keeping solutions under an argon atmosphere.

Table I. Yields of Alkanes and Alkenes Produced by Electrochemical Reduction of $RCo(dmgBF_2)_2py$ in CH_3CN/H_2O

R	dry CH_3CN		$CH_3CN:H_2O$ = 2:1 (v/v)	
	RH	R(–H)	RH	R(–H)
CH_3	1.0	0	1.0	0
C_2H_5	0.38	0.62	0.55	0.45
1-C_3H_7	0.22	0.78	0.68	0.32
$C_6H_5CH_2$	1.0	0	1.0	0

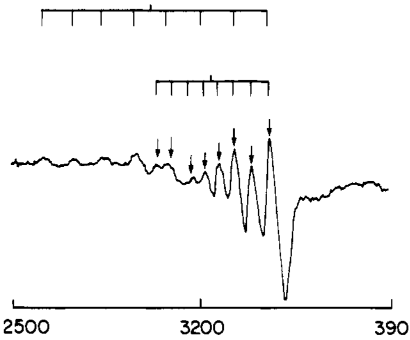

Figure 1. ESR spectrum of a frozen solution (100 K) of 4-$BrC_6H_4CH_2Co(dmgBF_2)_2py^-$ in acetonitrile after electrochemical reduction at –1 V vs Ag/AgCl.

The organic decomposition products were detected by GC and GC-MS techniques. The GC detection was performed on a Hewlett-Packard Model 5790 gas chromatograph with 6-ft columns packed with either VZ-10 or OV-101 as stationary phases. The instrument was calibrated by use of commercial organic compounds. The GC-MS spectra of the decomposition products of $C_3H_7Co(dmgBF_2)_2A^-$ were obtained on a Finnigan 4500 GC-MS spectrometer interfaced to an Incos data system. Samples were first cooled in liquid nitrogen, evacuated to remove the inert gas, and then rewarmed for analysis. A 30-m DB 624 capillary column was used for chromatographic separation before mass detection. In addition, the different relative abundance of mass 41 over mass 42 was utilized to detect cyclopropane in the presence of propene. For the latter the abundance of mass 41 is greater than that of mass 42.[33] Therefore, the three decomposition products, propane, propene, and cyclopropane, can be detected individually. The inorganic decomposition products were detected by their electronic spectra[30] and reduction potentials.

The ^1H NMR and ^{13}C NMR studies were conducted in dmso-d_6 solution at room temperature by use of a Nicolet 300-MHz and a Bruker WM 200-MHz nuclear magnetic resonance spectrometer. A Cary 219 and a Perkin-Elmer Lambda Array UV–vis spectrometer were used for spectrophotometric measurements, and an IBM/Bruker ER-200 spectrometer was used for the ESR spectra at 100 K.

The kinetics of the reactions between $RCo(dmgBF_2)_2py$ and $Ni(tmc)^+$ were studied at 25 ± 0.1 °C in aqueous solution. Owing to the low solubility of the organocobalt complexes in H_2O, it was necessary to use small amounts of a cosolvent, typically 1% acetone. The ionic strength of 0.1 M was controlled by $NaClO_4$, and pH 12 by NaOH. The reactions were monitored at 610 nm, an absorption maximum of $Co(dmgBF_2)_2^-$, by use of a Durrum-Dionex stopped-flow spectrometer. The same instrument was used for fast repetitive scans of the electronic spectra.

All the experiments were conducted under an argon atmosphere.

Results

Cyclic voltammograms of $RCo(dmgBF_2)_2A$ (A = H_2O, py; R = CH_3, C_2H_5, 1-C_3H_7) in the potential range 0 to –1.2 V vs Ag/AgCl at room temperature agree qualitatively with those obtained in dmf at 0 °C by Costa et al.[19] The cathodic peak corresponding to one-electron reduction of $RCo(dmgBF_2)_2A$ appears at $\sim$–1 V. The anodic peak is barely discernible with $i_{pa} \ll i_{pc}$. After the first cathodic scan, all the cyclic voltammograms develop a reversible wave at –0.50 V, corresponding to the $Co(dmgBF_2)_2(H_2O)_2^{0/-}$ couple. All the observations indicate

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that electrochemical reduction precedes a chemical reaction that cleaves the Co–C bond. The nature of the axial base, py or H_2O, had no apparent effect on the electrochemical behavior of any of the complexes studied.

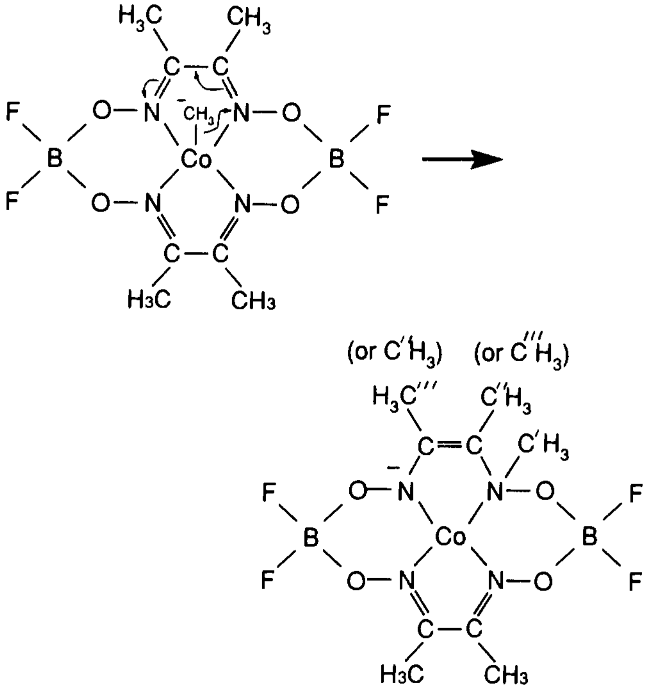
The values of $E_{1/2}$ obtained in this work are lower by some 0.15 V than those reported earlier.[19] The difference is probably too large to be attributed solely to different experimental conditions (temperature, solvent, and inert electrolyte) and the fact that no correction for junction potentials has been applied in either work. We ignored the difference, however, since the sole purpose of the voltammetric experiments was to determine the potential for one-electron reduction of the organocobalt complexes under our exact experimental conditions.

The controlled-potential electrolysis of $CH_3Co(dmgBF_2)_2(H_2O)$ at −1 V yields CH_4 as the only gaseous product. The ethyl complex yields ethane and ethylene, but no butane. In the case of 1-$C_3H_7Co(dmgBF_2)_2(H_2O)$ the products are propane, propylene, and traces of cyclopropane. The ratio alkane:alkene for R = C_2H_5 and 1-C_3H_7 increases with the water content of the solvent (Table I). The benzyl and substituted benzyl complexes yield the corresponding toluenes exclusively.

The one-electron reduction of $4\text{-}BrC_6H_4CH_2Co(dmgBF_2)_2py$ yielded a green transient exhibiting an ESR spectrum at 100 K. The data in Figure 1 yield $g_{\parallel} = 2.23$, $g_{\perp} = 2.07$, $A_{\parallel} = 111 \times 10^{-4}$ cm^{-1}, $A_{\perp} = 54 \times 10^{-4}$ cm^{-1}. After the spectrum was recorded, the frozen solution was warmed to room temperature and then cooled again to 100 K. The ESR spectrum obtained on such a sample was identical with that reported for $Co(dmgBF_2)_2(H_2O)_2$.[30b]

Reduction with $NaBH_4$. Upon addition of an excess of solid $NaBH_4$ to a solution of $RCo(dmgBF_2)_2py$ in dmso-d_6, the color of the solution changed from yellow to deep blue, indicating that cobalt(I) was formed. With R = 1-C_3H_7, propane and propylene were detected in a 1:4 ratio in the gas phase. Under identical conditions the methyl complex yielded only CH_4.

The blue solutions of the reduced organocobalt complexes so obtained (R = CH_3, C_3H_7, $C_6H_5CH_2$) are diamagnetic. The ^1H NMR spectrum for R = CH_3 (Figure 2) shows a set of five resonances at 1.75, 1.90, 2.01, 2.04, and 2.10 ppm. Those at 1.75 and 2.10 ppm are the only peaks that are also observed in a blank experiment starting with $Co(dmgBF_2)_2py$ and were thus assigned to $Co(dmgBF_2)_2A^-$, A = py and H_2O/dmso, respectively. The resonances at 1.90, 2.01, and 2.04 ppm were assigned to the methyl groups $C'H_3$, $C''H_3$, and $C'''H_3$ of a new product, a cobalt(I) complex of a modified macrocycle, shown as follows:



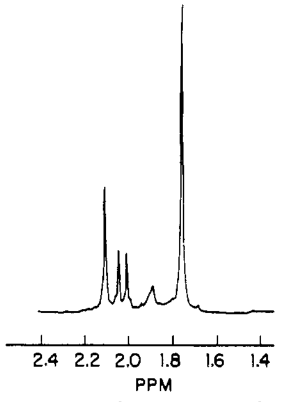


Figure 2. ^1H NMR spectrum of the product of reduction of 0.01 M $CH_3Co(dmgBF_2)_2py$ by excess $NaBH_4$ in dmso-d_6.

Table II. Kinetic Data for the Reduction of $RCo(dmgBF_2)_2py$ by $Ni(tmc)^+$ in Aqueous Solution[a]

R	$10^{-4}k_1/M^{-1}\ s^{-1}$	$10^{-4}k_2/M^{-1}\ s^{-1}$ [b]
CH_3	5.95	
C_2H_5	12.5	
1-C_3H_7	15.7	
1-C_3H_7[c]	11.4	
$4\text{-}CH_3C_6H_4CH_2$	77.8	3.06
$C_6H_5CH_2$	80.0	1.70
$4\text{-}BrC_6H_4CH_2$	114	2.90
$4\text{-}BrC_6H_4CH_2$[d]	175	2.70

[a] pH 12, 25.0 ± 0.1 °C, μ = 0.10 M (NaOH + $NaClO_4$). [b] Rate constant for reaction 9, observed only for benzyl derivatives; see text. [c] The compound is 1-$C_3H_7Co(dmgBF_2)_2H_2O$. [d] The compound is $4\text{-}BrC_6H_4CH_2Co(dmgBF_2)_2H_2O$.

A change of the magnetic field from 200 to 300 HMz had no effect on the chemical shifts, confirming that they are independent resonances, not components of a multiplet. Apparently, the resonances of the two methyl groups of the unchanged part of the complex appear together with those of $Co(dmgBF_2)_2^-$ at 1.75 and/or 2.10 ppm.

Reduction with $Ni(tmc)^+$. Upon addition of excess $Ni(tmc)^+$ to $RCo(dmgBF_2)_2py$ in aqueous solution, pH 12, the color changes from the pale yellow of an organocobalt complex to the intense blue, λ_{max} 610 nm, of cobalt(I). The reaction yields ethane and ethylene as the only gaseous products for R = C_2H_5. The formation of cobalt(I) follows mixed second-order kinetics for R = primary alkyl:

$$d[Co(I)]/dt = k_1[RCo(dmgBF_2)_2py][Ni(tmc)^+] \quad (1)$$

The rate constants k_1 were obtained under pseudo-first-order conditions by using $[Ni(tmc)^+]$ in a large excess over $[RCo(dmgBF_2)_2py]$. Table II summarizes the results, and Figure 3 illustrates the first-order dependence for both reactants. The rate constants are independent of the acetone concentration (0–3.8%), excess $[Ni(tmc)^{2+}]$ (0.5–3.0 mM), and pH (11–12).

For R = benzyl and substituted benzyl, the kinetic traces were biphasic. The two stages were well separated in time and were accompanied by comparable absorbance increases at 610 nm. The overall absorbance change corresponded to a quantitative conversion of the organocobalt complex to $Co(dmgBF_2)_2py^-$. In the presence of an excess of $Ni(tmc)^+$, both stages followed first-order kinetics, yielding the rate constants k_1 and k_2, both of which show first-order dependence on $[Ni(tmc)^+]$. All the kinetic data are summarized in Table II.

Discussion

The reduction of the alkylcobalt complexes (alkyl = C_2H_5 and 1-C_3H_7) by electrochemical means and by sodium borohydride under anhydrous conditions leads to the oxidation of the alkyl groups to olefins. Measurable amounts of the corresponding alkanes are also formed. These results, combined with the virtual

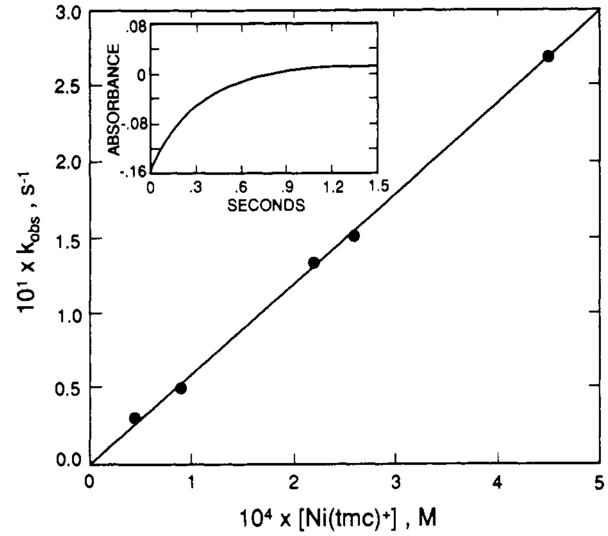


Figure 3. Plot of k_{obs} against the concentration of Ni(tmc)$^+$ for the reaction of $CH_3Co(dmgBF_2)_2py$ with Ni(tmc)$^+$ at 25.0 °C (pH 12, μ = 0.10 M (NaOH + $NaClO_4$)). The inset shows a stopped-flow trace at 610 nm and a first-order kinetic fit for a run having $[Ni(tmc)^+]_0$ = 0.27 mM and $[CH_3Co(dmgBF_2)_2py]_0$ = 0.037 mM.

irreversibility of the cyclic voltammograms, can be accommodated by eqs 2 and 3. The product of eq 2, $RCo(dmgBF_2)_2A^-$, formally

$$\mathrm{RCo(dmgBF_2)_2A + e^- \rightarrow RCo(dmgBF_2)_2A^-} \qquad (2)$$

$$\mathrm{RCo(dmgBF_2)_2A^-} \xrightarrow{H_2O} \mathrm{RH + Co(dmgBF_2)_2(H_2O)A + OH^-} \qquad (3a)$$

$$\mathrm{RCO(dmgBF_2)_2A^-} \xrightarrow{H_2O} \mathrm{R(-H) + Co(H{-}dmgBF_2)(dmgBF_2)(H_2O)A^-} \qquad (3b)$$

an alkylcobalt(II) complex, decomposes in two competing reactions, hydrolysis and β-hydrogen transfer. The former is a minor pathway in the absence of added water, and it increases in importance as the water content of the solvent increases, as shown in Table I.

The formation of disproportionately large amounts of alkenes relative to alkanes and the lack of the dimeric products R_2 rule out homolytic cleavage of the cobalt–carbon bond followed by radical coupling as a major decomposition route.

The β-hydrogen elimination of eq 3b is fully consistent with the experimental findings. The two-electron oxidation of the alkyl group and the two-electron reduction of the macrocyclic ligand result in the formation of the alkene and a cobalt(II) complex of the reduced macrocycle. The evidence for the latter comes from the ^{1}H NMR spectrum of the product of reduction of $CH_3Co(dmgBF_2)_2py$ by $NaBH_4$. The reductant was used in excess to convert the cobalt(II) product into a diamagnetic Co(I) complex which can be characterized by NMR. Although $CH_3Co(dmgBF_2)_2A^-$ does not have a β-hydrogen, it still does not decompose homolytically, but instead transfers a methyl group (formally as a carbanion) to a nitrogen of the macrocycle. This results in the appearance of a broad new resonance at 1.90 ppm. The two methyl groups in the vicinity of the methylated nitrogen, $C''H_3$ and $C'''H_3$, are now inequivalent and appear as two separate signals at 2.01 and 2.04 ppm. The appearance of three signals with identical peak areas in the H NMR spectrum and the significant broadening of the signal assigned to $C'H_3$ are consistent with the transfer of the methyl group to the nitrogen rather than the carbon end of the double bond. The latter mode of the benzyl group transfer was observed recently in a related organocobalt(III) complex.[34]

The products of the reduction of ethyl and 1-propyl complexes are presumed to have structures analogous to the methyl complex, except that a β-hydrogen is now transferred to nitrogen, the rest of the alkyl group appearing as alkene. Unfortunately, the resonance corresponding to the N–H group of the reduced macrocycle could not be identified in the NMR spectrum, presumably because the resonance of a single hydrogen bound directly to the nitrogen was too weak and too broad to detect.

It is important to note that excess $NaBH_4$ does not alter the products in any way, except that it reduces the cobalt center to a diamagnetic state. Thus the controlled-potential electroreduction and the chemical reduction by excess $NaBH_4$ gave identical distribution of gaseous products for R = C_2H_5 and 1-C_3H_7. Even the reaction with Ni(tmc)$^+$ in *aqueous solution*, where hydrolysis is favored, yields measurable amounts of alkene (in addition to alkane). This demonstrates that β-hydrogen transfer (alkyl transfer in the case of R = CH_3) is a genuine and often preferred decomposition mode of the reduced organocobalt complexes.

In the earlier work on similar complexes[17,19,20] it was found that the organocobalt(II) macrocycles decompose mainly by cobalt-carbon bond homolysis, eq 4, and by alkyl transfer/disproportionation, eq 5. The dialkylcobalt(III) product $LCo^{III}R_2$ was

$$\mathrm{LCo^{II}R \rightarrow LCo^{I} + R^{\bullet}} \qquad (4)$$

$$\mathrm{2LCo^{II}R \rightarrow LCo^{III}R_2 + LCo^{I}} \qquad (5)$$

identified unambiguously for L = (DO)(DOH)pn$^-$ and R = CH_3. Moreover, the reduced neopentylcobalt complex of the same macrocycle survives in solution for a long time.[16] Obviously, the intermolecular alkyl transfer for such a bulky alkyl group would be slow, but it is surprising that other decomposition pathways, homolysis and solvolysis, do not take over for such compounds.

The failure to observe homolysis of the cobalt–carbon bond in $RCo(dmgBF_2)_2^-$ seems to be related to its electronic structure. The ESR features of this species, $g_\parallel > g_\perp$ (R = 4-$BrC_6H_4CH_2$), are clearly different from those of typical low-spin macrocyclic cobalt(II) complexes, which normally have $g_\parallel < g_\perp$.[35-37] The ESR parameters in Figure 1 indicate that the unpaired electron resides in the $d_{x^2-y^2}$ orbital, not in the d_{z^2} orbital. Therefore, there is no obvious reason that the Co–C bond should homolyze in preference to other decomposition modes.

The reasons for the inverted energetics of the d_{z^2} and $d_{x^2-y^2}$ orbitals in $RCo(dmgBF_2)_2H_2O^-$ are not obvious, although the presence of the alkyl ligand seems to be crucial. The effect might be related to geometric distortions in the transition state, caused by the strong trans effect of the alkyl group. We note, however, that a simple elongation of the cobalt–axial ligand (H_2O or pyridine) bond does not represent a sufficient, or even a correct, type of distortion, since this would in effect decrease, and not increase, the energy of the d_{z^2} orbital relative to $d_{x^2-y^2}$.

The reduction of $RCo(dmgBF_2)_2py$, R = primary alkyl, by Ni(tmc)$^+$ is a single-stage reaction. The first-order dependence on each reactant and the lack of an effect of Ni(tmc)$^{2+}$ (0.7–3 mM) on the kinetics are consistent with rate-limiting electron transfer followed by fast decomposition and redox steps, eqs 6–8.

$$\mathrm{RCo(dmgBF_2)_2A + Ni(tmc)^+ \rightarrow RCo(dmgBF_2)_2A^- + Ni(tmc)^{2+}} \quad k_1 \qquad (6)$$

$$\mathrm{RCo(dmgBF_2)_2A^-} \xrightarrow[H_2O]{fast} \mathrm{Co(dmgBF_2)_2(H_2O)A\ (+other\ products)} \qquad (7)$$

$$\mathrm{Co(dmgBF_2)_2(H_2O)A + Ni(tmc)^+} \xrightarrow[py]{fast} \mathrm{Co(dmgBF_2)_2A^-} \quad k \geq 10^6\ \mathrm{M^{-1}\ s^{-1}}\ ^{32} \qquad (8)$$

The rate constants show little variation within the series, consistent with only a minor effect of R on the reduction potential of the alkylcobalt complexes.[16]

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The biphasic kinetics observed in the reaction of $Ni(tmc)^+$ with the benzyl and substituted benzyl complexes indicate that the one-electron reduction of eq 6 is followed by further reduction of the long-lived $RCo(dmgBF_2)_2A^-$ by $Ni(tmc)^+$, eq 9. Such a

$$RCo(dmgBF_2)_2A^- + Ni(tmc)^+ \rightarrow RCo(dmgBF_2)_2A^{2-} + Ni(tmc)^{2+} \quad k_2 \quad (9)$$

chemistry is reasonable on several grounds. Our results showed already that $4\text{-}BrC_6H_4CH_2Co(dmgBF_2)_2A^-$ has a relatively long lifetime; it was prepared electrolytically in solution prior to being cooled to 100 K for the ESR experiment. Also, the reduction potential of a number of $RCo(dmgBF_2)_2^{-/2-}$ couples (R = alkyl) in dmf have values around −1 V vs SCE.[16] We expect that the benzyl derivatives should be even easier to reduce, which makes reaction 9 thermodynamically favorable ($E_{1/2}(Ni(tmc)^{2+/+})$ = −1.10 V vs SCE).

The longer lifetime of $RCo(dmgBF_2)_2A^-$ for R = benzyl relative to R = alkyl can be easily rationalized. One decomposition mode, eq 3b, is eliminated by the lack of a β-hydrogen, and the hydrolysis, eq 3a, is severely inhibited by the ability of the benzyl group to delocalize electron density efficiently. The α-carbon in the reduced complex is thus less carbanionic, and solvolysis is slower than in the reduced alkyl complexes. The same reactivity pattern is observed in organometallic complexes in "normal" oxidation states. The hydrolysis of the parent organocobalt(III) complexes, $RCo(dmgBF_2)_2H_2O$, is too slow to be observed for any of the organic groups, but the more reactive organochromium(III)[38] and organonickel(II)[32b] complexes hydrolyze more readily when R is alkyl than when it is benzyl.

A different trend is observed in homolytic cleavages of metal–carbon bonds. As expected, the release of the benzyl radicals is faster than the release of primary alkyls and comparable to that of secondary alkyls.

Surprisingly, the nucleophilic attack by water on one-electron-oxidized organocobaloximes, $RCo(dmgH)_2H_2O^+$, is faster for R = benzyl than for the primary alkyls,[39-40] although one would expect the opposite on the basis of the above charge delocalization argument. In this case, it is possible that a homolytic path contributes to the decomposition of $RCo(dmgH)_2H_2O^+$, as was observed for a number of other oxidized organometallic complexes.

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Hydrogen Bonding between Guanosine 5′-Monophosphate and Coordinatively Saturated Cobalt(III) and Platinum(II) Ammine and Ethylenediamine Complex Cations

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The compounds $[Pt(NH_3)_4][5'\text{-}GMP]\cdot 5H_2O$, $[Pt(en)_2][5'\text{-}GMP]\cdot 4H_2O$, $[Co(NH_3)_6]_2[5'\text{-}GMP]_3\cdot 13H_2O$, and $[Co(en)_3]_2[5'\text{-}GMP]_3\cdot 14H_2O$, where en = 1,2-diaminoethane and 5′-GMP = guanosine 5′-monophosphate, have been synthesized and characterized. In addition to electrostatic interactions, hydrogen-bonding interactions between the N–H sites on the ligands and the 5′-GMP have been identified in all four solids by means of FT-IR spectroscopy. In $[Co(NH_3)_6]_2[5'\text{-}GMP]_3\cdot 13H_2O$ hydrogen bonding is occurring between the NH_3 donor and the N7 site of the guanine. In the other three compounds, both the N7 and O6 sites of the guanine act as hydrogen-bond-acceptor sites. Additional hydrogen bonding between the cation and the 5′-GMP phosphate is possible in all four compounds. This could be to the same cation as the guanine is binding or to a different cation. NMR studies show that cation–anion interactions, including hydrogen bonding, persist in solution for $[Pt(en)_2][5'\text{-}GMP]$ and $[Co(en)_3]_2[5'\text{-}GMP]_3$, even in very dilute solutions of the latter. Evidence comes from the concentration dependence of the $^3J_{Pt-H}$ coupling constant in $[Pt(en)_2][5'\text{-}GMP]$ and improved resolution of the CH_2 multiplet in $[Co(en)_3]_2[5'\text{-}GMP]_3$. 5′-GMP ($\beta$-D-) selectively precipitates $[\Lambda\text{-}(+)\text{-}Co(en)_3]^{3+}$ from racemic $[Co(en)_3]^{3+}$. Models show that the $[\Lambda\text{-}(+)\text{-}Co(en)_3]^{3+}$ enantiomer can hydrogen-bond much more effectively to the 5′-GMP than the $[\Delta\text{-}(-)\text{-}Co(en)_3]^{3+}$ enantiomer.

Introduction

Compound formation between transition-metal ions and nucleotides, including mononucleotides, oligonucleotides, and nucleic acids, has been known for many years.[1,2] When the nucleotide contains guanine as the base, the transition metal typically binds covalently to the N7 atom of the guanine.[1-3] In many compounds, hydrogen bonding between a ligand on the metal and the nucleotide provides an important secondary binding site. This hydrogen bonding can occur with a site on the nucleobase, with the phosphate, or with both.[1,2,4]

In the case of Pt(II)[5-9] and Co(III)[10] ammine complexes, hydrogen bonding of the ammine ligand to the nucleotide has been found to have an important influence on the biological structure and reactivity of the nucleotide or nucleic acid. For example, the antitumor drug *cis*-diamminedichloroplatinum(II) and its analogues exhibit higher drug activity when they are able to hydrogen-bond to the nucleic acid in addition to the primary Pt–nucleobase bond.[11] With nucleic acids, the principal hydrogen-

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