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REACTIONS OF ALKYLCOBALT COMPLEXES CONTAINING A TETRADENTATE NITROGEN-DONATING LIGAND

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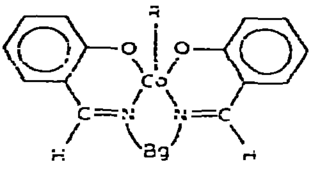
Summary

The reactions of $RCo(BDM1,3pn)(H_2O)^+$ with light, heat, acids, electrophiles and nucleophiles were studied. (HBDM1,3pn is a mononegative, tetradentate dioxime-diimine ligand formed by condensing 2,3-butanedionemonoxime with 1,3-propanediamine in a 2/1 molar ratio; R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, and $C_6H_5CH_2$.) Pyrolysis and photolysis of the alkyl complexes result in a cobalt(II) complex (anaerobic conditions) along with alkenes and alkanes. The major organic products from solid state pyrolysis at 200°C or photolysis in water are CH_4 (R = CH_3), C_2H_4 (R = C_2H_5), C_3H_6 (R = n-C_3H_7), C_4H_8 (R = n-C_4H_9) and $(C_6H_5CH_2)_2$ (R = $C_6H_5CH_2$). No alkyl—cobalt bond cleavage occurs with acids or bases in most cases. Two exceptions are the reactions with 3 *M* HNO_3 at 25°C and with 1 *M* NaOH at 52°C. Electrophiles like I_2 cleave the alkyl—cobalt bond forming RI and $Co^{III}(BDM1,3pn)I_2$. Nucleophilic reagents (N^-) displace the H_2O *trans* to the alkyl group to form RCo(BDM1,3pn)(N), but do not dealkylate the alkyl complex under the reaction conditions studied.

Introduction

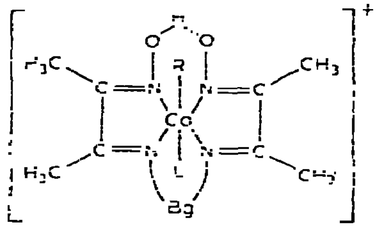
Two recent reviews [1,2] have summarized the vast amount of chemistry of alkylcobalt complexes. Some of the complexes covered in these reports are shown in Fig. 1. R is a substituted or unsubstituted alkyl or aryl group; L is a variety of monodentate ligands. Of particular interest to this paper are the complexes of $RCo(BDM1,3pn)(H_2O)^+$ among which only the methyl complex has been extensively studied. An X-ray study of $[CH_3Co(BDM1,3pn)(H_2O)]ClO_4$ [3] demonstrates that the complex consists of a planar array of nitrogen donors with *trans* CH_3 and H_2O ligands.

There have been several studies of the reactions of $RCo(BDM1,3pn)^+$ in which the alkyl—cobalt bond has been ruptured. Schrauzer, Sibert and Windgassen [4] studied the homolytic pyrolytic and photolytic reactions of



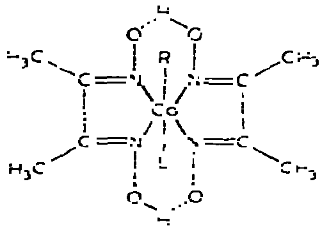
RCo(sal$_2$Bg)

Bg = $-(CH_2)_2-$(sal$_2$en), $-CH_2CH(CH_3)-$(sal$_2$1,2pn), $-CH_2C(CH_3)_2-$(sal$_2$1,2pn-2-me), o-C_6H_4(sal$_2$opn), and *trans*-1,2-cyclohexyl (sal$_2$cyclohex)



RCo(BDMBg)L$^+$

Bg = $-(CH_2)_2-$(en), $-(CH_2)_3-$(1,3pn)



RCo(DMG)$_2$L

Fig. 1. Examples of alkylcobalt complexes containing diimine and/or dioxime ligand. R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9 and $C_6H_5CH_2$.

$CH_3Co(BDM1,3pn)(H_2O)^+$ and the C_2H_5 analog. Magnuson and Weber [5] reported on the electrophilic dealkylation of the complexes by Hg^{2+}. The CH_3S^- anion was shown to break the methyl—cobalt bond in $CH_3Co(BDM1,3pn)(H_2O)^+$ with the formation of $(CH_3)_2S$ [6]. Costa and coworkers [7-9] have studied the carbanion donating ability of $CH_3Co^I(BDM1,3pn)^-$ and $(CH_3)_2Co(BDM1,3pn)$ toward other complexes. Schrauzer and coworkers [10,11] have demonstrated the reductive cleavage of the methyl—cobalt bond in $CH_3Co(BDM1,3pn)(H_2O)^+$ with diothioerythritol (pH 4.6) and alkaline solutions of CO, $Na_2S_2O_4$, and $K_2SnO_3 \cdot 3H_2O$. $(HOCH_2CH_2)Co(BDM1,3pn)(H_2O)^+$ reacts in a basic medium to form CH_3CHO [12]. Finally, $CH_3Co(BDM1,3pn)(H_2O)^+$ alkylates 1,4-naphthoquinone and 1,4-benzonquinone at 40-50°C [13].

We are presently engaged in a study of the alkyl—cobalt bond reactivity in a variety of complexes including the dealkylation of $RCo(BDMBg)(H_2O)^+$ by Hg^{2+} [5], of $(CH_3)_2Co(BDM1,3pn)$ by light and electrophiles [14,15], and of RCo(sal$_2$Bg) by light, heat, nucleophiles and electrophiles [16,17]. In this paper we will discuss the preparation and characterization of $RCo(BDM1,3pn)(H_2O)^+$ ($R = CH_3$, C_2H_5, n-C_4H_9, and $C_6H_5CH_2$) and their reactivity toward light, heat, H^+, OH^-, nucleophiles and electrophiles.

Experimental

Materials

The solvents and inorganic compounds were purchased from VWR, Aldrich, Eastman, or Fisher. A mixture of hydrocarbon standards C_1-C_4 was purchased from Scott Research Laboratories. All the chemicals were used as purchased.

Elemental analyses

The elemental analyses were performed by Mrs. Deanna Cardin on an F and M Model 185 CHN Analyzer.

Gas-liquid-phase-chromatography

A Varian Aerograph Series 1860-1 gas chromatograph, which has a flame ionization detector, was used to identify organic reaction products. Porapak Q (80-100 mesh) was used in 6′ × 1/8″ colums.

Ultraviolet-visible spectra

Most spectra were run on a Cary 14 spectrophotometer. Stock solutions (10^{-2} to 10^{-3} *M*) were prepared by dissolving samples in water. An 0.1 ml aliquot of the stock solutions was added to 2.9 ml of water in one of two matched 1 cm silica cells. When it was necessary to record spectra under anaerobic conditions, the cell was fitted with a septum. Then the solvent was flushed with nitrogen using inlet and outlet needles. An aliquot of air-free compound was added to the cell. When the reactions required several hours or days, a Spectronic 20 spectrophotometer was used.

Proton magnetic resonance spectra

The proton magnetic resonance (PMR) spectra were obtained using a JEOL JNM-MH 100 nuclear magnetic resonance spectrometer. All the alkylated complexes were studied in D_2O; sodium 2,2-dimethyl-2-silapentane-5-sulphonate was used as the internal standard. The chemical shifts are reported in ppm.

Preparation of $RCo(BDM1,3pn)(H_2O)^+$

The complexes, where $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, and $C_6H_5CH_2$, were prepared with a BF_4^- or ClO_4^- counterion as previously described [5]. The i-C_3H_7 and t-C_4H_9 complexes could not be prepared by these procedures.

Preparation of $CH_3Co(BDM1,3pn)(SC_6H_5)$

$[CH_3Co(BDM1,3pn)(H_2O)]ClO_4$ (0.073 mmol, 0.032 g) was dissolved in 5 ml of water. To this solution was added 2 to 3 ml of an aqueous (pH 14) benzenethiol solution. The resulting red crystals were filtered and vacuum dried. Found: C, 50.81; H, 6.47; N, 13.08. $C_{18}H_{27}CoN_4O_2S$ calcd.: C, 51.18; H, 6.40; N, 13.27%.

Preparation of RCo(BDM1,3pn)(CN)

[CH_3Co(BDM1,3pn)(H_2O)]ClO_4 (0.52 mmol, 0.222 g) was dissolved in 20 ml of 1 *M* NaCN—0.1 *M* NaOH. The solution was flushed with nitrogen. A yellow crystalline solid immediately formed. The solid was filtered and vacuum dried at 48°C; it analyzed as [CH_3Co(BDM1,3pn)(CN)]·0.5 H_2O. Found: C, 44.58; H, 6.43; N, 19.98. $C_{13}H_{23}CoN_5O_{2.5}$ calcd.: C, 44.82; H, 6.61; N, 20.11%.

Solid [C_2H_5Co(BDM1,3pn)]BF_4 (0.11 mmol, 0.048 g) or [$C_6H_5CH_2$Co(BDM1,3pn)(H_2O)]ClO_4 (0.103 mmol, 0.052 g) was dissolved in a minimum amount of water. A volume of 3 to 4 ml of 1.0 *M* NaCN—0.1 *M* NaOH was added to each, and the solutions were placed on ice. The yellow crystalline solids that formed were filtered and washed with slightly basic ice-water. These solids were vacuum dried in a heated (40°C) desiccator for 24 h. The C_2H_5 (a) and $C_6H_5CH_2$ (b) complexes analyzed as the di- and mono-hydrate, respectively. (a) Found: C, 42.91; H, 6.91; N, 17.95. $C_{14}H_{28}CoN_5O_4$ calcd.: C, 43.19; H, 7.20; N, 17.99%. (b) C, 53.14; H, 6.51; N, 16.37. $C_{19}H_{28}CoN_5O_3$ calcd.: C, 52.66; H, 6.46; N, 16.17%.

[n-C_4H_9Co(BDM1,3pn)(H_2O)]ClO_4 (0.43 mmol, 0.202 g) was treated as above except that the product was dried at 48°C for 24 h. Found: C, 51.01; H, 7.51; N, 18.54. $C_{16}H_{28}CoN_5O_2$ calcd.: C, 50.30; H, 7.62; N, 18.26%.

Stability of RCo(BDM1,3pn)(H_2O)$^+$ complexes to light

The various alkylcobalt complexes were subjected to light in order to study the photolytic stability of the alkyl—cobalt bond. Under anaerobic conditions 5-10 mg of solid were dissolved in 20 to 25 ml of water in a flask with a septum. The formation of alkanes and/or alkenes (GLPC) indicated that the cobalt—carbon bond is unstable to light. In the case of the benzyl derivative, the 1,2-diphenylethane product was identified after extracting the aqueous solution with hexane. The UV spectrum of the hexane solution was compared to an authentic spectrum [18]. No toluene was detected by GLPC. The cobalt product Co^{II}(BDM1,3pn)$(H_2O)_2^+$ was identified from its visible spectrum. Because of the photolytic reaction, all procedures involving alkylcobalt complexes were done in the dark.

Stability of RCo(BDM1,3pn)(H_2O)$^+$ complexes to heat

Aqueous anaerobic stock solutions of the various alkyl complexes were stable at 65°C over several weeks. Carefully ground solid samples in vials under N_2 were pyrolyzed by suspension in an oil bath maintained at 200-206°C. The reaction rates were monitored by GLPC and the products identified by GLPC and UV-visible spectra.

Stability of RCo(BDM1,3pn)(H_2O)$^+$ to acids and bases

Several different tests were conducted to test the stability of RCo(BDM1,3pn)(H_2O)$^+$ in acidic and basic solutions. Under anaerobic conditions in the dark the alkyl complexes were stable for several days to 1 *M* $HClO_4$ and 6 *M* HCl at 55°C and to HI at room temperature. However, the alkyl complexes were unstable to 6 *M* HNO_3 at 18°C.

Anaerobic solutions of RCo(BDM1,3pn)(H_2O)$^+$ (R = CH_3, C_2H_5, and n-C_3H_7) decompose in 0.1 *M* to 1.0 *M* NaOH solutions at 52°C over a period of several days. The organic products were detected by GLPC, and $Co^{III}(BDM1,3pn)(H_2O)_2^{2+}$ was identified after acidification of the solution.

Reaction of $RCo(BDM1,3pn)(H_2O)^+$ complexes with cyanide ion in basic solution

$[RCo(BDM1,3pn)(H_2O)]X$ ($R = CH_3, C_2H_5$; $X = BF_4^-, ClO_4^-$) complexes (0.10 mmol) were dissolved in separate 25 ml solutions of 1.0 *M* NaCN (pH 13) under N_2. There was no change in the UV-visible spectrum of the resulting RCo(BDM1,3pn)CN despite heating 2 days at 52°C, and no organic compounds were detected by GLPC.

Reaction of $RCo(BDM1,3pn)(H_2O)^+$ with iodine

Samples of $RCo(BDM1,3pn)(H_2O)^+$ ($R = CH_3, C_2H_5$, and n-C_3H_7) were added neat to solutions of iodine made by dissolving iodine (ca. 2 mmol) in 25 ml of methanol. The flasks were capped with septa and flushed with nitrogen, and the solutions were left in the dark for several weeks. They were checked periodically for the formation of crystals. Green crystals formed at varying lengths of time. Alkyl iodides, but no alkanes, were detected by GLPC. The visible spectrum of the cobalt product $Co(BDM1,3pn)I_2$ was compared to that of an authentic sample. In the case of the methyl reaction, the diiodo product was purified and recrystallized using acetone—water. Found: C, 24.22; H, 3.47; N, 9.92. $C_{11}H_{19}CoI_2N_4O_2$ calcd.: C, 23.90; H, 3.44; N, 10.14%.

Attempted dealkylation reactions of $RCo(BDM1,3pn)(H_2O)^+$ with I^-, Cl^- and HS^-

Aqueous solutions of 0.1 *M* NaI or 0.1 *M* NaCl did not dealkylate n-C_3H_7-$Co(BDM1,3pn)(H_2O)^+$ over a period of 8 days at 55°C.

$C_2H_5Co(BDM1,3pn)(H_2O)^+$ (0.12 mmol) was added neat to 25 ml of an aqueous 0.1 *M* NaSH solutions and the solution was kept at 52°C for several days. The spectral change due to the formation of $C_2H_5Co(BDM1,3pn)(SH)$ is reversed to the spectrum of the original aqueous complex by adding several drops of 1 *M* $HClO_4$.

Results and discussion

UV-visible spectra

The electronic spectra of the $RCo(BDM1,3pn)(H_2O)^+$ complexes contain four UV-visible bands between 250 and 483 nm. When $R = CH_3, C_2H_5$, n-C_3H_7, and n-C_4H_9, the wavelengths (molar absorptivities) are 467 ± 8 (ca. 2300), 404 ± 6 (ca. 1530), 325 (ca. 2700), and 270 ± 5 (ca. 4800) nm. The $C_6H_5CH_2Co(BDM1,3pn)(H_2O)^+$ values, which are somewhat different, are 483 (1520), 388 (4480), 283 (30200), and 260 (26900) nm. The band near 470 nm is diagnostically useful, because it disappears when the cobalt—alkyl bond is broken.

PMR spectra

The PMR spectra of $RCo(BDM1,3pn)(H_2O)^+$ in D_2O give useful structural information about the complexes (Table 1). The most obvious features of the spectra are the singlets due to CH_3 groups in $C{=}N{=}C{-}CH_3$ (ca. 2.4 ppm) and in $O{-}N{=}C{-}CH_3$ (ca. 2.3 ppm) observed in most of the alkylcobalt complexes. The

TABLE I

PROTON MAGNETIC RESONANCE DATA[a]

Compound	Chemical shift (ppm) (integrated area)	Multiplicity[b]	Assignment
$CH_3Co(BDM1,3pn)(H_2O)^+$	3.83 (4)	b	N—CH_2
	2.43 (6)	s	C—N=C—CH_3[c]
	2.32 (6)	s	O—N=C—CH_3[c]
	2.11 (2)	m	C—CH_2—C
	0.84 (3)	s	CH_3Co
$CH_3Co(BDM1,3pnBF_2)(H_2O)^+$	3.76 (4)	b	N—CH_2
	2.42 (6)	s	C—N=C—CH_3
	2.34 (6)	s	O—N=C—CH_3
	2.12 (2)	m	C—CH_2—C
	1.06 (3)	s	CH_3Co
$CH_3Co(BDM1,3pn)CN$	3.90 (4)	b	N—CH_2
	2.27 (6)	s	C—N=C—CH_3
	2.18 (6)	s	O—N=C—CH_3
	2.10-2.30 (2)	m	C—CH_2—C
	0.76 (3)	s	CH_3Co
$CH_3Co(BDMen)(H_2O)^+$	3 95 (4)	b	N—CH_2
	2.41 (6)	s	C—N=C—CH_3
	2.29 (6)	s	O—N=C—CH_3
	0.62 (3)	s	CH_3Co
$C_2H_5Co(BDM1,3pn)(H_2O)^+$	3.80 (4)	m	N—CH_2
	2.47 (6)	s	C—N=C—CH_3
	2.37 (6)	s	O—N=C—CH_3
	1.80-2.35 (4)	m	C—CH_2—C CH_2 of C_2H_5Co
	0.03 (3)	t	CH_3 of C_2H_5Co
n-$C_3H_7Co(BDM1,3pn)(H_2O)^+$	3.80 (4)	b	N—CH_2
	2 37 (6)	s	C—N=C—CH_3
	2.30 (6)	s	O—N=C—CH_3
	1.50-2.30 (4)	b	C—CH_2—C α-CH_2 of n-C_3H_7
	0.68 (5)	m	CH_3, β-CH_2 of n-C_3H_7
n-$C_4H_9Co(BDM1,3pn)(H_2O)^+$	3.54 (4)	b	N—CH_2
	2 18 (6)	s	C—N=C—CH_3
	2.00 (6)	d	O—N=C—CH_3
	1.90-2 42 (2)	b	—C—CH_2—C—
	1.10-1.52 (4)	b	—CH_2—CH_2—
	0.78 (5)	m	CH_3CH_2
$C_6H_5CH_2Co(BDM1,3pn)(H_2O)^+$	6 86 (5)	b	aromatic
	3.80 (4)	b	—N—CH_2
	2.24-2.40 (4)	b	C—CH_2—C CH_2Co
	2.24 (6)	s	C—N=C—CH_3
	2.12 (6)	s	O—N=C—CH_3

[a] Solvent, D_2O; internal standard, sodium 2,2-dimethyl-2-silapentane-5-sulphonate (DSS). [b] Multiplicity: b, broad; d, doublet; m, multiplet; s, singlet, t, triplet. [c] Based on assignments in ref. 19.

middle and end CH_2 groups in the $(CH_2)_3$ bridging group are observed near 2.1 and 3.9 ppm, respectively. These chemical shifts are consistent with those found for BDMenH [19]. Although the chemical shifts due to the in-plane ligand are of some interest, the major emphasis is on the assignment of the bands due to the alkyl groups bonded to the cobalt.

The PMR spectrum of $CH_3Co(BDM1,3pn)(H_2O)^+$ has been previously characterized [20-22] and our 0.84 ppm value for CH_3Co is in agreement with the previous studies. The singlet CH_3Co in the $CH_3Co(BDM1,3pnBF_2)(H_2O)^+$ [21], $CH_3Co(BDM1,3pn)(CN)$ and $CH_3Co(BDMen)(H_2O)^+$ complexes occurs as a singlet at 1.06, 0.76, and 0.62 ppm, respectively. The nature of the in-plane ligand or of the group coordinated *trans* to the CH_3 has a relatively small effect on the chemical shift of the CH_3Co.

Dodd and Johnson [1] reported that the chemical shifts of the cobalt-bonded alkyl group may be dependent on possible "ring currents" in the equatorial ligand as well as the cobalt metal. With organocobalt complexes containing aromatic rings [23] the chemical shifts, particularly of the protons on β- and γ-carbons, are more dramatic. This does not seem to be the case with the BDM-1,3pn complexes as the chemical shifts are more in line with DMG complexes which do not have a pseudoaromatic ring system [24].

The spectrum of the C_2H_5 complex, with respect to the CH_3CH_2Co group, is similar to the previously reported spectra of $C_2H_5Co(DMG)_2$ [24] and C_2H_5 Rh(sal$_2$en)py [25]. The CH_3 of the C_2H_5Co appears as a triplet at 0.03 ppm. The methylene protons next to the cobalt are partially obscured by the middle bridging methylene protons, but seem to occur as a quartet near 2.0 ppm.

The PMR spectra of the n-C_3H_7 and n-C_4H_9 complexes are more complicated and not as easily interpreted. In both cases there is no separation between the terminal CH_3 group and the methylene group next to it. The other alkyl protons are again mixed with the middle methylene protons of the $(CH_2)_3$ bridge in the ligand.

The $C_6H_5CH_2Co(BDM1,3pn)(H_2O)^+$ complex showed an aromatic multiplet near 6.9 ppm in agreement with the results found in the $(DMG)_2$ [26] and sal$_2$en [25] systems. The CH_2Co was again partially obliterated by the middle CH_2 in the $(CH_2)_3$ bridging group.

In conclusion the PMR spectra of the $RCo(BDM1,3pn)(H_2O)^+$ complexes are consistent with previously reported work on analogous organotransition metal complexes, and show that there is an alkyl—cobalt bond in the RCo-$(BDM1,3pn)(H_2O)^+$ complexes.

Reactions of the alkylcobalt complexes

The reactions of $RCo(BDM1,3pn)(H_2O)^+$ are summarized in Fig. 2. A variety of homolytic and heterolytic bond cleavage reactions are discussed below. In addition nucleophiles that substitute *trans* to the alkyl group will be considered. The reactions with Hg^{2+} have been previously reported [5].

Stability in acidic and basic aqueous solutions

$RCo(BDM1,3pn)(H_2O)^+$ is stable for several days to 6 *M* HCl or $HClO_4$ at 55°C, and to 6 *M* HI at 20°C, because there was no loss of the 470 nm band and no organic products were detected by GLPC. Only in HNO_3 at 3 *M* or greater concentration or in the presence of NO_3^- and a strong acid was the cobalt—carbon bond ruptured. This presumably occurs because an electrophilic species such as NO_2^+ is formed in low concentrations [27] (eqn. 1). The alkyl—carbon bonds of the complexes shown in Fig. 1 are very sensitive to electrophiles [1,5, 17].

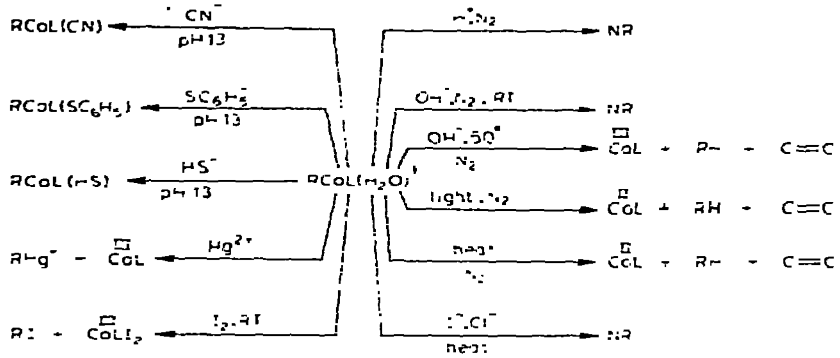


Fig. 2. Reactions of the cobalt—carbon bond and substitutions *trans* to the alkyl group of RCo(BDM1,3pn)-(H_2O)⁺.

$$2\ HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad (1)$$

These same organocobalt(III) complexes were stable in basic solutions containing 1 *M* or less NaOH at room temperature for several days. However, when the complexes were heated to 52°C for 7 to 14 days, they slowly decomposed (see below).

Pyrolytic and photolytic reaction of the alkyl—cobalt bond

The solid state anaerobic pyrolyses of several RCo(BDM1,3pn)(H_2O)⁺ complexes (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, $C_6H_5CH_2$) were studied (Table 2). At 200°C the reactions were rapid. During the experiments, the rates were monitored (GLPC) by measuring the relative amounts of hydrocarbons formed. Schrauzer, Sibert and Windgassen [4] identified the same organic products when R = CH_3 or C_2H_5 after solid state pyrolysis at 200-225°C. Co^{II}(BDM1,3pn)⁺ was identified by spectrophotometric comparison to an authentic sample, and $(C_6H_5CH_2)_2$ was identified from its UV spectrum (see Experimental).

The relative rates of pyrolysis as a function of R are: n-C_4H_9 > n-C_3H_7 > C_2H_5 > CH_3. The observed rate constants for R = CH_3 and C_2H_5 are 5.5×10^{-3} min^{-1} and 1.2×10^{-2} min^{-1}, respectively; the decomposition of the n-C_4H_9 and n-C_3H_7 complexes was too fast for quantitative results by the GLPC method.

TABLE 2

PRODUCTS FORMED BY PYROLYSIS OR PHOTOLYSIS OF RCo(BDM1,3pn)(H_2O)⁺ [a]

R	Pyrolysis products (%) [b]	Photolysis products (%) [c]
CH_3	CH_4 (70), C_2H_4 (3), C_2H_6 (27)	CH_4 (94), C_2H_6 (6)
C_2H_5	C_2H_4 (95), C_2H_6 (5)	C_2H_4 (99), C_2H_6 (1)
n-C_3H_7	C_3H_6 (100)	C_3H_6 (100)
n-C_4H_9	C_4H_8 (72), n-C_4H_{10} (28)	C_4H_8 (100)
$C_6H_5CH_2$	$(C_6H_5CH_2)_2$ (100)	$(C_6H_5CH_2)_2$ (100)

[a] All reactions were performed under N_2. The other product was Co^{II}(BDM1,3pn)⁺. [b] Reactions performed in the solid state at 200-206°C. [c] Water was the solvent.

The same relative rates were observed for $RCo(sal_2en)$ complexes [17]. This order is the same as the ease of formation of the free radicals [28].

The major products when R = CH_3 can be explained by the formation of a CH_3 radical followed by its abstraction of a hydrogen atom from the ligand or by its dimerization. The alkenes formed predominantly when a β-hydrogen is present could be formed by the transfer of a hydrogen atom from an alkyl radical to form $HCo^{III}(BDM1,3pn)^+$; or, as is known for $RCo(DMG)_2$ with secondary [29] or substituted [30] alkyl groups, the alkenes can be formed by elimination reactions also with the formation of the cobalt(III) hydride. In either case the cobalt(III) hydride complex would subsequently decompose to the observed $Co^{II}(BDM1,3pn)^+$.

Photolysis of aqueous solutions of organocobalt complexes under anaerobic conditions at room temperature results in the products shown in Table 2. The ratio of products when R = CH_3 or C_2H_5 are similar to those observed previously [4]. The resulting cobalt(II) complexes were identified by their red color and a visible band at 504 nm. The organic products are explained as discussed above for the pyrolytic reactions.

Cobalt—carbon bond cleavage by iodine

Iodine reacts with $RCo(BDM1,3pn)(H_2O)^+$ (R = CH_3, C_2H_5, and n-C_3H_7) under anaerobic conditions in the dark at room temperature (eqn. 2). GLPC experiments confirmed the presence of RI and the absence of alkanes. The green diiodo complex was identified by spectrophotometric comparison to an authentic example.

$$RCo(BDM1,3pn)(H_2O)^+ + I_2 \xrightarrow{CH_3OH} Co(BDM1,3pn)I_2 + RI \qquad (2)$$

The reaction products show that the electrophile I_2 cleaves the cobalt—carbon bond heterolytically with the formation of a carbanionic intermediate. If a carbonium ion intermediate was formed, one product would be the cobalt(I) complex, which would be oxidized to the red cobalt(II) species by I_2. The rates of the above electrophilic substitution reactions were much slower than that of I_2 with $CH_3Co(sal_2en)(H_2O)$ in CH_3OH [17]. The BDM1,3pn system forms carbanionic intermediates less readily than the sal_2Bg system because of the superior capability of BDM1,3pnH to withdraw electron density from the cobalt [8,9]. A similar result occurred in the reactions of $CH_3Co(BDM1,3pn)(H_2O)^+$ and $CH_3Co(BDM1,3pnBF_2)(H_2O)^+$ with Hg^{2+} [5]. The latter complex in which the electron-withdrawing BF_2 is substituted for the hydrogen-bonded H (Fig. 1) has a second order rate constant that is 10^{-5} the value of the hydrogen-bonded analog.

Reactions of $RCo(BDM1,3pn)(H_2O)^+$ with nucleophiles

Under certain experimental conditions nucleophiles will displace the H_2O *trans* to the alkyl in the alkylcobalt complexes of Fig. 1 [1]. In other cases nucleophiles will cause dealkylation through a *trans* attack with a carbanion [16, 17] or carbonium ion [6] intermediate.

The reactions of $RCo(BDM1,3pn)(H_2O)^+$ in water at pH 13 at room temperature with CN^-, $C_6H_5S^-$, or HS^- resulted only in a *trans* substitution reaction exemplified below (eqn. 3). This instantaneous substitution reaction is indicated by a spectral change and the isolation of several products (see Experimental). In all cases the spectrum of $RCo(BDM1,3pn)(H_2O)^+$ reoccurs upon acidification of the solution.

The carbanionic alkyl displacement reaction does not occur as was observed for the $RCo(sal_2Bg)$ system [16] because of the differing electron density on cobalt as discussed above. Schrauzer and Stadlbauer [6] did partially dealkylate $CH_3Co(BDM1,3pn)(H_2O)^+$ by CH_3S^- in CH_3OH, but alkyl corrin and DMG·BF_2 complexes dealkylate much more rapidly by a carbonium ion mechanism because of a lower cobalt electron density.

$$RCo(BDM1,3pn)(H_2O)^+ + CN^- \xrightarrow[\text{pH 13}]{H_2O} RCo(BDM1,3pn)(CN) + H_2O \qquad (3)$$

Reactions of $RCo(BDM1,3pn)(H_2O)^+$ with OH^- at 52°C

Several $RCo(BDM1,3pn)(H_2O)^+$ complexes ($R = CH_3$, C_2H_5, n-C_3H_7) were dealkylated in anaerobic 0.1 *M* to 1 *M* NaOH solutions at 52°C over a period of several weeks. In all cases the complex product is probably an equilibrium mixture of $Co^{III}(BDM1,3pn)(H_2O)(OH)^+$ and the dihydroxyo analog. Upon acidification the UV-visible spectrum of the diaquo complex reappears.

The CH_3 and n-C_3H_7 complexes form 100 percent alkanes suggesting the absence of CH_3 and n-C_3H_7 free radicals. As previously observed, the homolysis of the CH_3 complex in basic aqueous media results in a significant amount of C_2H_6 [4]. Photolysis of the n-C_3H_7 complex in aqueous 1 *M* NaOH resulted in 10% C_3H_6 and a green solution. The green color is due to the blue cobalt(I) and yellow cobalt(III) species formed from the initial cobalt(II) or cobalt(III) hydrido complex. Thus, the process for the CH_3 and n-C_3H_7 complexes is predominantly a nucleophilic substitution process in which the OH^- ejects a carbanionic intermediate that forms the alkane. β-elimination in the n-C_3H_7 complex would result in C_3H_6. These results are similar to those found in the reactions of RCo-(sal_2Bg) with HS^- [16].

The products of the reaction of $C_2H_5Co(BDM1,3pn)(H_2O)^+$ with OH^- are 34% C_2H_6 and 66% C_2H_4. These results indicate a carbanionic path to form C_2H_6 and the major free radical or β-elimination route to form the C_2H_4. Photolysis of the complex at pH 14 results in C_2H_4 and a green solution also in agreement with a predominant free radical or β-elimination mechanism.

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