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PREPARATION AND REACTIONS OF ALKYL—COBALT COMPLEXES CONTAINING SCHIFF BASE LIGANDS

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Summary

A series of $Co^{II}(sal_2Bg)$ and $RCo(sal_2Bg)$ complexes have been prepared from the tetradentate $H_2(sal_2Bg)$ diimino ligands formed by the condensation of salicyclaldehyde and various diamines. The $RCo(sal_2Bg)$ complexes (R = methyl, ethyl, n-propyl, and i-propyl) are synthesized by the reactions of alkyl halides with $Co^{I}(sal_2Bg)^-$. The complexes are characterized by UV-visible, IR, and PMR spectra. The cleavage of the cobalt—carbon bond by light, I_2, CN^-, HS^-, $R'S^-$, and R'SH was studied. The organic products were identified by GLPC, and the cobalt complexes by isolation and analysis. A rich variety of mechanisms is discussed.

Introduction

Recent reviews have summarized the explosion in the chemistry of alkyl—cobalt complexes [1,2]. Some of the complexes covered in those 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 $RCo(sal_2Bg)$ complexes among which only $RCo(sal_2en)$ has been extensively studied. Papers by Costa et al. [3—7] and by others [8—12] give a variety of syntheses of $RCo(sal_2Bg)$ complexes. Several X-ray studies [13—15] of $RCo(sal_2Bg)$ demonstrate the presence of the cobalt—carbon bond.

There have been several studies of the reactions of $RCo(sal_2Bg)$ at the cobalt—carbon bond. Alkyl for alkyl substitution [16, 17], SO_2 insertion [18—20] CO insertion [21], photolytic [10, 21, 22], pyrolytic [9, 10], and reductive cleavage [9, 23, 24] reactions have been studied. In many cases the reaction mechanisms were not elucidated and often not all the products were identified.

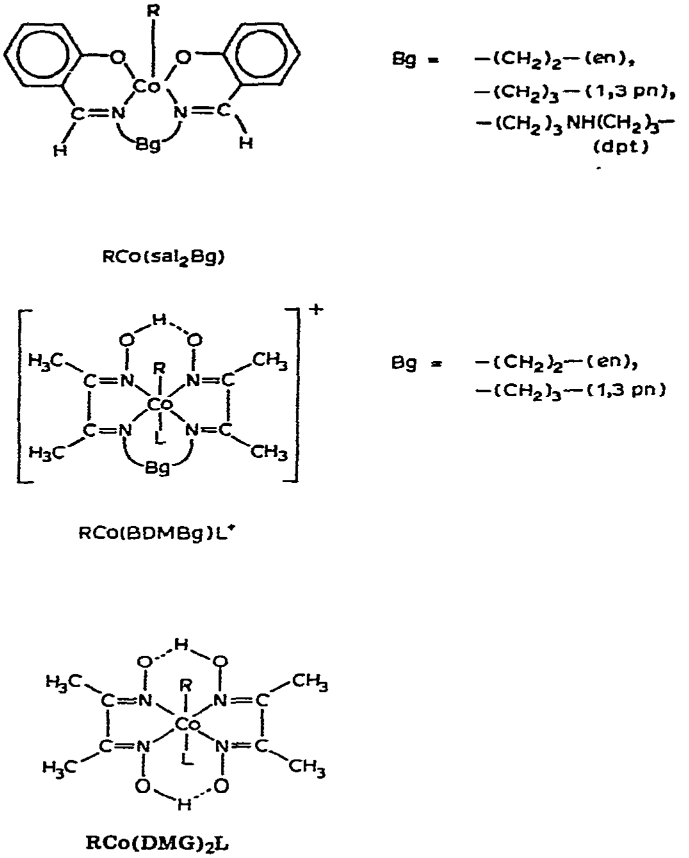
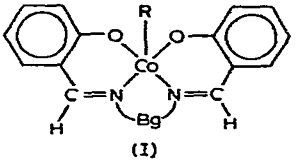


Fig. 1. Examples of alkyl—cobalt complexes containing diimine and/or dioxime ligands.

We are presently engaged in a general study of the reactivity of the cobalt—carbon bond in $RCo(BDMBg)^+$, $R_2Co(BDM\ 1,3pn)$ and $RCo(sal_2Bg)$. The reactions under study include bond cleavage by nucleophiles, electrophiles, light and heat. In a recent publication we showed that HS^- in basic methanol dealkylates $RCo(sal_2Bg)$ by an attack *trans* to the alkyl group [25]. Other current studies involve the dealkylation of $R_2Co(BDM\ 1,3pn)$ by a variety of metal ions [26] and of $RCo(BDMBg)^+$ by mercury(II) [27]. This paper includes the preparation of the $RCo(sal_2Bg)$ complexes (I) shown below, and several types of their dealkylation reactions.



(I)

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$oph), and *trans*-1,2-cyclohexyl (sal$_2$cyclohex); R = CH_3, C_2H_5, n-C_3H_7, and i-C_3H_7.

Experimental

Materials

The diamines, alkyl halides, most of the sulfur compounds, solvents, and inorganic compounds were purchased from Aldrich, Eastman, or Fisher. Methane thiol was purchased from Matheson. Most of the chemicals were used as purchased. Salicylaldehyde was purified by distillation; and tetrahydrofuran was dried by distillation from lithium aluminium hydride, and stored over Fisher 4A molecular sieves.

Elemental analyses

The analyses were performed by Mrs. Linda Heavner on an F. and M. Model 185 CHN Analyzer.

Gas-liquid-phase-chromatography (GLPC)

The gas chromatographs used were an Aerograph HY FI Model 600-C or a Varian Aerograph series 1860-1. Both have a flame ionization detector. The columns were 6′ × 1/8″. The packings used were Porapak Q (80-100 mesh) and Chromsorb W (80-100 mesh) with a 20% Carbowax 20 M liquid phase. Most compounds were identified on the Porapak Q column; methyl iodide was identified on Chromsorb W.

Pyrolysis

Pyrolysis was used as a diagnostic test for the formation of alkyl—cobalt bonds during syntheses. Under anaerobic conditions 5—10 mg of solid were pyrolyzed in a vial with a serum cap. The observation of alkanes and/or alkenes by GLPC (using Porapak Q) proved the presence of alkyl—cobalt complexes. Pyrolytic reactions were also done at 48° in methanol.

Ultraviolet-visible spectra

The spectra were run on a Cary 14 or Cary 15 spectrophotometer. In all cases, reagent grade methanol was used as the solvent. Stock solutions of the complexes were prepared within a concentration of 10^{-3} to 10^{-4} *M*. An aliquot of 50 μl or 100 μl was taken from the stock solution and transferred to one of two matched 1 cm silica cells, containing 3 ml of methanol. The anaerobic spectra were recorded after flushing a silica cell with nitrogen using a rubber serum cap with inlet and outlet needles. An aliquot of the air-free compound was then transferred to the anaerobic cell.

Proton magnetic resonance spectra

PMR spectra were obtained using a Varian Model A-60 or a JEOL JNM-MH 100 instrument. The ligand spectra were taken in deuterochloroform, and the spectra of $RCo(sal_2Bg)$ were taken in deuterated dimethyl sulfoxide. Tetramethylsilane or the $(CH_3)_2SO$ impurity in $(CD_3)_2SO$ was used as an internal standard. The chemical shifts are reported in ppm.

Electron spin resonance spectra

The ESR spectra were run in the solid state on a Varian E-4 EPR spectrometer.

TABLE 1

CHARACTERIZATION OF THE H_2(sal$_2$Bg) LIGAND AND COMPLEXES[a]

Compound	Color	M.p. (°C)[b]	Analyses found (calcd.) (%)		
			C	H	N
H_2(sal$_2$en)	Yellow	123—125	71.21 (71.61)	6.00 (6.01)	10.36 (10.44)
H_2(sal$_2$1,3pn)	Yellow	57—59	72.13 (72.31)	6.47 (6.43)	9.91 (9.93)
H_2(sal$_2$1,4bn)	Yellow	89—90	73.06 (72.95)	6.73 (6.81)	9.25 (9.46)
H_2(sal$_2$1,5pen)	Yellow	61—62	72.90 (73.54)	7.18 (7.15)	9.12 (9.03)
H_2(sal$_2$1,2pn-2-me)	Yellow	84—85	72 99 (72.95)	6.77 (6.81)	9.50 (9.46)
H_2(sal$_2$cyclohex)	Yellow	116—118	74.28 (74.50)	6.92 (6.88)	8.61 (8.69)
H_2(sal$_2$oph)	Orange	162—164	75.88 (75.92)	5.14 (5.10)	8.92 (8.86)
Co^{II}(sal$_2$en)	Dark red		59.45 (59.07)	4.38 (4.34)	8.67 (8.61)
Co^{II}(sal$_2$1,2pn)	Dark brown		59.62 (60.17)	4.69 (4.75)	8.19 (8.25)
Co^{II}(sal$_2$1,2pn-2-me)	Red-orange		61.35 (61.20)	5.16 (5.14)	7.95 (7.93)
Co^{II}(sal$_2$oph) · 0.5H_2O	Brown		62.79 (62.82)	4.50 (3.96)	7.15 (7.32)
Co^{II}(sal$_2$1,4bn) · 0.5H_2O	Green		59.59 (59.68)	5.69 (5.29)	7.46 (7.73)
Co^{II}(sal$_2$cyclohex)	Light brown		63.10 (63.32)	5.27 (5.32)	7.48 (7.38)
CH_3Co(sal$_2$en)H_2O	Red		56.73 (56.98)	5.24 (5.35)	7.74 (7.82)
C_2H_5Co(sal$_2$en)	Dark red		61.50 (61.01)	5.38 (5.41)	8.00 (7.91)
n-C_3H_7Co(sal$_2$en)·0.5H_2O	Black		60.58 (60.47)	5.71 (5.88)	7.46 (7.43)
i-C_3H_7Co(sal$_2$en)	Black		61.64 (61.95)	5.72 (5.75)	7.54 (7.60)
CH_3Co(sal$_2$1,2pn)	Red		60.76 (61.01)	5.52 (5.41)	7.82 (7.90)
C_2H_5Co(sal$_2$1,2pn)·H_2O	Brown		58.73 (59.06)	5.92 (6.00)	7.26 (7.25)
n-C_3H_7Co(sal$_2$1,2pn)·0.5H_2O	Brown		61 16 (61.40)	6.14 (6.18)	7.18 (7.16)
CH_3Co(sal$_2$1,2pn-2-me)·0.5H_2O	Dark red		59.95 (60.47)	5.79 (5.88)	7.36 (7.43)
C_2H_5Co(sal$_2$1,2pn-2-me)·H_2O	Black		60.23 (60.00)	5.72 (6.30)	7.08 (7.00)
n-C_3H_7Co(sal$_2$1,2pn-2-me)·H_2O	Black		60.74 (60.86)	6.00 (6.57)	7.07 (6.76)
CH_3Co(sal$_2$oph)·H_2O	Brown		62.23 (62 07)	4.46 (4.68)	7.08 (6.89)
C_2H_5Co(sal$_2$oph)·0.5H_2O	Black		64.28 (64.23)	4.86 (4.91)	6.90 (6.81)
n-C_3H_7Co(sal$_2$oph)·0.5H_2O	Black		64.94 (64.94)	4.82 (5.22)	6.96 (6.58)
C_2H_5Co(sal$_2$cyclohex)	Dark red		64 02 (64.61)	6.10 (6.16)	6.93 (6.86)
n-C_3H_7Co(sal$_2$cyclohex)	Dark red		64.86 (65 31)	6.37 (6.44)	6.64 (6.63)

[a] Most of the ligand abbrevations are listed in structure I; also Bg is —$(CH_2)_3$—(sal$_2$1,3pn), —$(CH_2)_4$—(sal$_2$1,4bn), and —$(CH_2)_5$— (sal$_2$1,5pen).

[b] Uncorrected. The complexes decompose.

Infrared spectra

The IR spectra were recorded in the 4000 to 400 cm^{-1} region with a Perkin—Elmer Model 337 Grating Spectrophotometer. The ligands, complexes, and alkyl complexes were recorded as solids in nujol and halocarbon mulls. The ligand H_2(sal$_2$1,2pn) was recorded neat.

Preparation of the H_2(sal$_2$Bg) ligands

Salicylaldehyde (600 mmol, 73.2 g) was dissolved in 300 ml of CH_3OH, and 300 mmol of the appropriate diamine were dissolved separately in 200 ml of CH_3OH. The diamine solution was added to the salicylaldehyde solution while using an overhead stirrer for complete mixing. Upon addition of the diamine, the solution turned yellow immediately and was allowed to react for 30 min. During this period, solid ligand was observed after 15 min of stirring in all cases except with 1,2-propanediamine. The solutions were cooled and filtered to obtain the crystalline ligands. Table 1 contains characterization data on the ligands.

Preparation of the Co^{II}(sal$_2$Bg) complexes

The Co^{II}(sal$_2$Bg) complexes were prepared by a modification of a procedure reported by Bailes and Calvin [28]. The ligands as prepared above were used in situ. Cobalt(II) acetate tetrahydrate (300 mmol, 75g) was dissolved in 1l of hot CH_3OH. Both the ligand solution and the cobalt salt solution were flushed vigorously with nitrogen for 15 min, and the hot cobalt salt solution was added to the ligand solution under nitrogen. The reaction mixture which turned dark red immediately was allowed to stir for 30 min. The complex solution containing microcrystalline solid was suction filtered under nitrogen. The solid was washed with CH_3OH and water, carefully ground, and dried in a vacuum desiccator for several days at room temperature. The yields ranged from 60% to 95% (Table 1).

Preparation of C_2H_5Co(sal$_2$en)

The procedure of Schrauzer et al [10] was followed until the solution turned green. After several minutes bromoethane (180 mmol, 19.6 g) was added. Immediately the solution returned to approximately its original color. The reaction mixture was allowed to stir for 15 min under nitrogen, and filtered into 15 ml of acetone. The residue was discarded, and the filtrate was diluted with distilled water until crystals were observed. The crystals were filtered, washed with CH_3OH and water, and then dried overnight in a vacuum desiccator at room temperature.

General preparation of RCo(sal$_2$Bg) from Co^{II}(sal$_2$Bg)

Based on the procedure published by Schrauzer et al. [10], 10 g of Co^{II}(sal$_2$Bg) were suspended in between 0.6 to 1l of CH_3OH which was deoxygenated with nitrogen. Sufficient 50% aqueous NaOH was added so that the CH_3OH was 0.4 *M* in NaOH. The suspension was cooled in an ice bath and sodium borohydride (26 mmol, 1.0 g) dissolved in 25 ml of water was added. Three ml of 2% $PdCl_2$ in 1 *M* aqueous KCl were added, and the solution usually turned green. The reactions involving Co^{II}(sal$_2$oph) did not change color, and those involving Co^{II}(sal$_2$cyclohex) turned dark brown. Upon addition of the appropriate alkyl halide the solutions [except those of Co^{II}(sal$_2$oph) and Co^{II}(sal$_2$-

cyclohex)] reverted to the color of the $Co^{II}(sal_2Bg)$. The flask was stoppered and stirred from 15 *min to several h*. Usually most, or all of, the solid dissolved. Any solid was filtered off, the filtrate going into a flask containing 25 ml of acetone, which decomposes excess $NaBH_4$. Approximately 400 ml of water were added to the filtrate. Crystals occured upon cooling or after evaporation on a rotary evaporator and cooling. The crystals were filtered off under vacuum, washed with CH_3OH and water, and dried overnight in a vacuum desiccator at room temperature. The colors and analytical data are tabulated in Table 1.

Attempted syntheses

Pure samples of $Co^{II}(sal_2 1,3pn)$, $Co^{II}(sal_2 1,5pen)$, and $i\text{-}C_3H_7Co(sal_2Bg)$ (sal_2Bg = sal_2oph, $sal_2 1,2pn$, and $sal_2 1,2pn\text{-}2me$) could not be prepared by the above procedures.

Stability of RCo(sal₂Bg) in methanol, basic methanol and acidic methanol

The $RCo(sal_2Bg)$ complex (0.24 mmol) (R = CH_3, C_2H_5, and $n\text{-}C_3H_7$; sal_2Bg = sal_2en, $sal_2 1,2pn$, and $sal_2 1,2pn\text{-}2\text{-}me$) was dissolved in 20.0 ml of CH_3OH, a methanolic solution of 0.1 *M* NaOH, or a methanolic solution of 0.1 *M* HCl. No appreciable amount of alkene or alkane was observed after stirring the solutions for a week at room temperature, but after several h at 48° traces of alkenes and/or alkanes were observed by GLPC.

Stability of RCo(sal₂Bg) to light

$RCo(sal_2Bg)$ (0.24 mmol) was dissolved in 20.0 ml of CH_3OH under nitrogen. A Beacon 150 watt spotlight was directed at an air-cooled flask from a distance of six inches. The reactions, run in duplicate, were finished in 3 days. GLPC was used to detect the increasing amounts of alkenes and alkanes. Because of the photolytic reaction all procedures involving alkyl—cobalt complexes were done in the dark unless stated otherwise.

Reactions of RCo(sal₂Bg) with alkane thiols in methanol

$RCo(sal_2Bg)$ (0.24 mmol) (R = CH_3, C_2H_5, and $n\text{-}C_3H_7$; sal_2Bg = sal_2en, $sal_2 1,2pn$, and $sal_2 1,2pn\text{-}2\text{-}me$) was dissolved in 20.0 ml of CH_3OH in a 25 ml Erlenmeyer flask. The flask was stoppered with a serum cap which was secured by wire. The solution was deoxygenated 15 min with nitrogen, and the alkane thiol (2.37 mmol) was added with a syringe. The reaction was stirred at room temperature or at 48° for several days, and was checked periodically by GLPC for volatile products. The inorganic products were isolated upon slow evaporation of the CH_3OH under nitrogen. The inorganic products were $Co^{II}(sal_2Bg)$, for example, $Co^{II}(sal_2en)$. (Found: C, 58.76; H, 4.46; N, 8.53. $C_{16}H_{14}CoN_2O_2$ calcd.: C, 59.07; H, 4.34; N, 8.61%.)

Reactions of C₂H₅Co(sal₂en) with ethane thiol in methanol under acidic and basic conditions

$C_2H_5Co(sal_2en)$ (0.20 mmol, 0.071 g) was dissolved in a methanolic solution which was 0.1 *M* in HCl or 0.1 *M* in NaOH. The solution was flushed with nitrogen and ethane thiol (0.24 mmol) was added using a 1 ml syringe. The reaction was stirred at room temperature or at 48° for a week. GLPC was used periodically to check for ethane, and other volatile products. $(CH_3CH_2S)Co(sal_2en)H_2O$ was isolated from the basic methanolic reaction by slow evaporation of the CH_3OH. (Found: C, 53.49; H, 4.72; N, 7.10. $C_{18}H_{21}CoN_2O_3S$ calcd.: C, 53.50; H, 5.24; N, 6.94%.)

Reaction of benzene thiol with $(HO)Co^{III}(sal_2en)H_2O$

$(HO)Co^{III}(sal_2en)H_2O$ [4] (0.57 mmol) was dissolved in 200 ml of hot CH_3OH. NaOH (0.54 mmol, 0.022 g) was dissolved separately in 10 ml of CH_3OH, and the solutions were mixed. The resulting solution was purged with nitrogen and capped with a serum cap before benzene thiol (0.57 mmol) was added. The solution immediately turned to a light red color. After the reaction stirred overnight at 48°, the volume of solution was reduced by bubbling nitrogen through it. Water was then added to the reaction mixture and a solid was observed. The solid was suction filtered and dried under vacuum. After it was recrystallized from methanol/water, its melting point was 60-62° in agreement with the 61-62° literature value for diphenyl disulfide.

Reaction of $RCo(sal_2Bg)$ with sodium cyanide under basic conditions

$RCo(sal_2Bg)$ (0.237 mmol) was dissolved in 20.0 ml of CH_3OH, which is 0.1 *M* in NaOH, and NaCN (2.37 mmol, 0.116 g) was added. The reactions were run under various conditions: with light and in the dark, at room temperature and at 48°, and with and without air. The reaction times varied from hours to days depending on the experimental conditions. The reactions are complete when the originally brown (or red) solution turns yellow or orange. The volatile products were identified by GLPC gas chromatography. The inorganic products were either identified spectrophotometrically or, wherever possible, isolated as the potassium salts. The procedure for isolation was the same in all experiments. The yellow or orange solution was evaporated to dryness. The resulting solid was dissolved in a minimum amount of hot water and filtered into a saturated solution of potassium cyanide in water. The orange crystals observed upon cooling were suction filtered, washed with water, and dried under vacuum at room temperature. For example, $K[Co(sal_2en)(CN)_2]$ was isolated and identified. (Found: C, 51.46; H, 3.36; N, 13.24. $C_{18}H_{14}CoKN_4O_2$ calcd.: C, 51.97; H, 3.39; N, 13.47%.)

Reaction of $Co^{II}(sal_2en)$ with iodine

The $Co^{II}(sal_2en)$ complex (3.08 mmol) was suspended with stirring in 50 ml of CH_3OH or anhydrous tetrahydrofuran. Iodine (3.1 mmol, 0.79 g) was added and the reactions were run overnight under anaerobic or aerobic conditions. The resulting suspension was filtered and a brown powder was obtained after vacuum drying. The reaction of $Co^{II}(sal_2en)$ with iodine gives a more pure $ICo(sal_2en)$ product when anhydrous tetrahydrofuran is the solvent. The products isolated from CH_3OH had an iodine impurity that was removed by continuous extraction with CCl_4 in a soxhlet extractor. The reaction did not occur for sal_2Bg = $sal_21,2pn$ and $sal_21,2pn$-2-me. (Found: C, 42.31; H, 3.24; N, 5.99. $C_{16}H_{14}CoIN_2O_2$ calcd.: C, 42.51; H, 3.12; N, 6.20%.)

Reaction of $CH_3Co(sal_2en)H_2O$ with iodine [9]

Iodine (3.0 mmol, 0.76 g) was dissolved in 20 ml of CH_3OH and

$CH_3Co(sal_2en)H_2O$ (3.00 mmol, 1.07 g) was added. The solution was flushed with nitrogen and then capped. After one hour a positive test for methyl iodide was obtained using GLPC. Crude ICo(sal$_2$en), isolated by slow evaporation of the solvent, was purified by extraction with CCl_4 as described above. ICo(sal$_2$en) was identified by spectrophotometric comparison to the sample prepared above.

Synthesis and characterization

We have prepared 15 complexes of the form RCo(sal$_2$Bg) (structure I) where R = CH_3, C_2H_5, n-C_3H_7, and i-C_3H_7 (see Table 1). All the complexes except C_2H_5Co(sal$_2$en) were prepared starting with Co^{II}(sal$_2$Bg). Pure RCo(sal$_2$Bg), where Bg = $-(CH_2)_3-$, $-(CH_2)_4-$, and $-(CH_2)_5-$, could not be prepared from their pure or crude Co^{II}(sal$_2$Bg) precursors. This failure can be traced to the geometry of the Co^{II}(sal$_2$Bg) which has been studied in the solid state and in solution [29, 30]. In non-coordinating solvents their geometry is pseudo tetrahedral, in contrast to Co^{II}(sal$_2$en) which is square planar due to the short length of the $-(CH_2)_2-$ bridging group. As the number of methylene bridging groups increases, the ligand becomes more flexible making a pseudo tetrahedral geometry possible. Steric effects due to this geometry apparently prevent the reduction of Co^{II}(sal$_2$B to Co^{I}(sal$_2$Bg)$^-$ and/or the bonding of an alkyl group to the cobalt.

The stability of the cobalt—carbon bond drastically decreases in the order: primary > secondary > tertiary. Secondary alkyl groups are rare for the RCo(chel of Fig. 1, and tertiary alkyl groups are unknown. The most stable secondary alkyl derivatives occur with RCo(DMG)$_2$L. However, i-C_3H_7Co(sal$_2$en) was isolated in 15% yield. The UV-visible spectrum (see below) of i-C_3H_7Co(sal$_2$en) is consistent with that of the other RCo(sal$_2$Bg) complexes, but i-C_3H_7Co(sal$_2$en) decomposes in methanol in less than 30 min. This rapid decomposition demonstrates the lability of the secondary cobalt—carbon bond, and explains the low synthetic yield. All attempts to make i-C_3H_7 complexes when sal$_2$Bg is sal$_2$1,2pn or sal$_2$1,2pn-2-me ended in failure. Models of these complexes clearly show the steric hindrance introduced by substituting methyl groups for hydrogens in the bridging group.

In preparing the large number of different alkyl—cobalt complexes, we were able to acquire a broad picture of the physical and chemical properties of both the Co^{II}(sal$_2$Bg) and the RCo(sal$_2$Bg) complexes. Their physical and chemical properties can be associated with a change in the alkyl group, the equatorial chelate, or both.

Infrared and electronic spectra

The infrared spectra of H_2(sal$_2$Bg), Co^{II}(sal$_2$Bg) and RCo(sal$_2$Bg) were measured in 4000 to 400 cm^{-1} region. The observed ca. 1635 cm^{-1} stretching frequency in H_2(sal$_2$Bg) decreases to ca. 1625 cm^{-1} in the Co^{II}(sal$_2$Bg) and RCo(sal$_2$Bg) complexes in agreement with the results of Coleman and Taylor [8] for Bg = $-(CH_2)_3NH(CH_2)_3-$.

The electronic spectra in CH_3OH clearly distinguish the RCo(sal$_2$Bg) complexes from the Co^{II}(sal$_2$Bg) species, but do not distinguish among RCo(sal$_2$Bg) or among Co^{II}(sal$_2$Bg) complexes, except for RCo(sal$_2$oph) and Co^{II}(sal$_2$oph), probably because of the aromatic bridging group. For RCo(sal$_2$Bg) typical wavelengths (molar extinction coefficients) are: 330 (9×10^3), 390 (5.7×10^3, sh), 440 (2.5×10^3 sh), and 510 nm (1×10^3, sh). The spectra of Co^{II}(sal$_2$Bg) contain the following maxima (extinction coefficient): 330 (6.1×10^3, sh), 390 (6×10^3), and 460 nm (1.4×10^3, sh). The bands near 330 and 390 nm distinguish RCo(sal$_2$Bg) from the analogous Co^{II}(sal$_2$Bg).

TABLE 2

PROTON MAGNETIC RESONANCE DATA OF THE H_2(sal$_2$Bg) LIGANDS AND RCo(sal$_2$Bg) COMPLEXES[a]

Compound	Chemical shift, ppm[b] (integrated area)	Multiplicity	Assignment
H_2(sal$_2$en)	12 (2)	Broad	OH
	8.07 (2)	Singlet	N=CH
	7.20 to 6.47 (8)	Complex pattern	C_6H_4
	3.73 (4)	Singlet	CH_2
H_2(sal$_2$1,2pn-2-me)	13.5	Broad	OH
	8.42, 8.36 (2)	Doublet	N=CH
	7.42 to 6.80 (8)	Complex pattern	C_6H_4
	3.68 (2)	Singlet	CH_2
	1.35 (6)	Singlet	CH_3
H_2(sal$_2$oph)	12.5 (2)	Broad	OH
	8.3 (2)	Singlet	N=CH
	7.22 to 6.47 (12)	Complex pattern	C_6H_4
H_2(sal$_2$cyclohex)	12.5 (2)	Broad	OH
	7.97 (2)	Singlet	N=CH
	7.11 to 6.58 (8)	Complex pattern	C_6H_4
	3.30 (2)	Broad	CH
	1.66 (8)	Broad singlet	CH_2
CH_3Co(sal$_2$en)H_2O	8.02 (2)	Singlet	N=CH
	7.22 to 6.34 (8)	Complex pattern	C_6H_4
	3.78 to 3.34 (6)	Complex pattern	CH_2, H_2O
	2.14 (3)	Singlet	CH_3
C_2H_5Co(sal$_2$en)	7.98 (2)	Singlet	N=CH
	7.22 to 6.30 (8)	Complex pattern	C_6H_4
	3.78 to 3.30 (8)	Complex pattern	CH_2
	−0.20 (3)	Triplet	CH_3
CH_3Co(sal$_2$1,2pn-2-me)	8.08 (2)	Doublet	C=NH
	7.50 to 6.42 (8)	Complex pattern	C_6H_4
	3.42 (2)	Singlet	CH_2
	2.26 (3)	Singlet	CH_3—Co
	1.42 (6)	Singlet	CH_3 (ligand)
CH_3Co(sal$_2$oph)H_2O	8.96 to 6.60 (14)	Complex pattern	C=NH, C_6H_4
	3.4 to 3.12 (2)	Broad doublet	H_2O
	0.64 (3)	Broad singlet	CH_3
C_2H_5Co(sal$_2$oph) · 0.5H_2O	8.94 to 6.58 (14)	Complex pattern	C=NH, C_6H_4
	3.46 to 3.18 (4)	Complex pattern	H_2O, CH_2
	−0.32 (3)	Triplet	CH_3

[a] The ligands and complexes were studied in $CDCl_3$ and $(CD_3)_2SO$, respectively. [b] Chemical shifts are relative to tetramethylsilane.

Proton magnetic resonance spectra

The ligand PMR data (Table 2) gives useful structural information about the ligands, and aids in the assignment of the PMR spectra of $RCo(sal_2Bg)$. The acidic phenol OH protons, distinguished by their rapid exchange with deuterium oxide, were observed between 12 and 13.5 ppm. This unusually large phenol OH chemical shift is due to intramolecular hydrogen bonding between the *ortho* imine nitrogen and the OH. Aromatic protons from the salicylaldimine part of the ligand and from the *o*-phenylene bridging group occur in the 6.5 to 7.2 ppm range. The methine protons of the ligands occur in the 8.1 to 8.4 ppm range as a singlet or doublet. A doublet occurs for $H_2(sal_21,2pn\text{-}2\text{-}me)$ because of the branched bridging groups. The CH_2 and CH protons of aliphatic bridging groups occur in the 3.2 to 3.9 ppm range. The complexity of the splitting depends upon the number of CH_3 branches on the bridging group. The CH_3 branches in $H_2(sal_21,2pn\text{-}2\text{-}me)$ occur at 1.35 ppm.

The PMR spectra of the sufficiently soluble $RCo(sal_2Bg)$ complexes were run in $(CD_3)_2SO$ (Table 2). However, some spectra were not of the desired quality because of low solubility. In addition, the presence of water in many complexes, and the non-deuterated $(CH_3)_2SO$ further complicated the spectra. All spectra obtained for $RCo(sal_2Bg)$ were consistent with the proposed stucture. The CH_3—Co group occured between 2.14 and 2.26 ppm for aliphatic bridging groups, but moved up-field to 0.64 ppm in $CH_3Co(sal_2oph)H_2O$. The methylene protons in CH_3CH_2—Co are found in the same 3.3 to 3.8 ppm range as are the CH_2 protons of the bridging groups and the H_2O (when present). The CH_3 in CH_3CH_2—Co occur at —0.20 and —0.32 ppm. These results prove beyond doubt the presence of the alkyl—cobalt bond. Previously reported PMR spectra [9, 31] of $CH_3Co(sal_2en)H_2O$ and $CH_3CH_2Co(sal_2en)$ in $(CD_3)_2SO$ agree with our data and intrepretation.

Reactions of the cobalt—carbon bond

Cobalt—carbon bond cleavage can be initially divided into heterolytic and homolytic processes. In heterolytic bond cleavage the alkyl group can leave without the shared electrons forming a carbonium ion intermediate and $Co^I(chel)^-$ (eqn. 1), or take them forming a carbanion intermediate and $Co^{III}(chel)^+$ (eqn. 2).

$$RCo(chel) \rightarrow R^+ + Co^I(chel)^- \qquad (1)$$

$$RCo(chel) \rightarrow R^- + Co^{III}(chel)^+ \qquad (2)$$

In the homolytic process an alkyl radical and $Co^{II}(chel)$ are formed (eqn. 3). The alkyl radical can form an alkane (RH), which can dimerize to an alkane (RR) and/or can lose a hydrogen atom to form an alkene.

$$RCo(chel) \rightarrow R^\cdot + Co^{II}(chel) \qquad (3)$$

In the RCo(BDMBg) system an electrophilic attack by, e.g., Hg^{2+} causes the alkyl group to leave with both bonding electrons (eqn. 4) [27]. A nucleo-

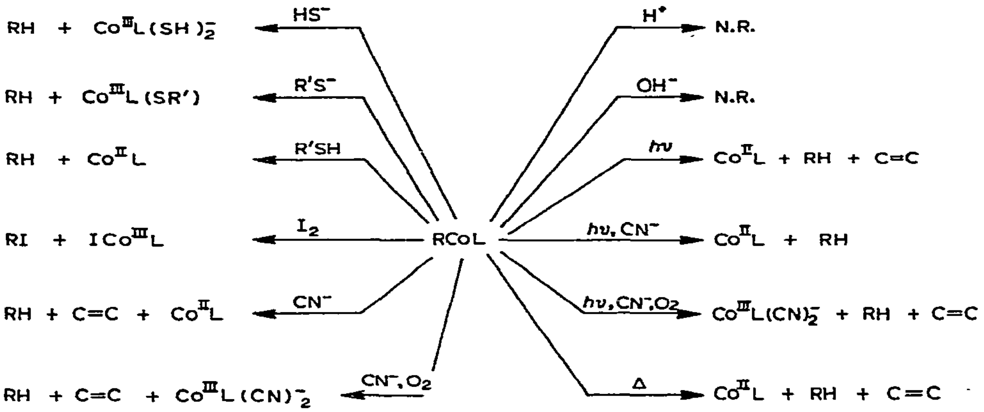


Fig. 2. Some reactions of the cobalt—carbon bond reported in this paper. L = sal_2Bg^{2-}, RH = alkane, and C=C = alkene.

$$RCo(BDMBg)^+ + Hg^{2+} \rightarrow RHg^+ + Co^{III}(BDMBg)^{2+} \quad (4)$$

$$RCo(sal_2Bg) + 2HS^- \rightarrow Co^{III}(sal_2Bg)(SH)_2^- + R^- \quad (5a)$$

$$R^- + HSolv \rightarrow RH + Solv^- \quad (5b)$$

philic attack on $RCo(sal_2Bg)$ by, e.g., HS^- occurs by a mechanism in which a carbanion intermediate is protonated by the solvent (eqn. 5) [25]. In the $RCo(DMG)_2H_2O$ system in contrast, CH_3S^- acts by a carbonium ion mechanism (eqn. 6) [32]. We studied the homolytic and heterolytic cobalt—carbon bond cleavage reactions shown in Fig. 2. The reactions were done in the absence of light and oxygen unless stated otherwise.

$$RCo(DMG)_2H_2O + CH_3S^- \rightarrow R^+ + Co^I(DMG)_2^- \quad (6a)$$

$$R^+ + CH_3S^- \rightarrow CH_3SR \quad (6b)$$

Stability in acidic and basic methanol

The stability of $RCo(sal_2Bg)$ complexes as a function of acidity was measured by placing the complexes in CH_3OH containing 0.1 *M* NaOH or 0.1 *M* HCl. The $RCo(sal_2Bg)$ complexes were stable at room temperature under the above conditions for several days with one exception; $i\text{-}C_3H_7Co(sal_2en)$ was very unstable even in pure methanolic solution. The instability or lower stability of secondary alkyl groups is also well known for similar alkyl—cobalt complexes like $RCo(DMG)_2H_2O$ and $RCo(sal_2dpt)$ [8]. As discussed above, the observed stability for R, primary > secondary > tertiary, can be attributable to steric effects. Electronic effects are also a factor in the instability of secondary alkyl groups. The poor electron accepting ability of $(sal_2Bg)^{2-}$ in $RCo(sal_2Bg)$ [33, 34] in conjunction with the excellent donating ability of the $i\text{-}C_3H_7$ group [35] also result in a weak cobalt—carbon bond.

Pyrolysis and photolysis: homolytic cobalt—carbon bond cleavage

We studied the anaerobic pyrolysis of $RCo(sal_2Bg)$ (R = CH_3, C_2H_5, and n-C_3H_7; sal_2Bg = sal_2en, $sal_21,2pn$, and $sal_21,2pn$-2-me) in CH_3OH at 48°. In all cases the resulting complex was $Co^{II}(sal_2Bg)$. The hydrocarbon products for R = CH_3 (99% CH_4 and a C_2H_6 trace), R = C_2H_5 (99% C_2H_4 and a C_2H_6 trace), and R = n-C_3H_7 (99% C_3H_6 and a C_3H_8 trace) were identified by GLPC. Schrauzer et al. [10] in the solid phase pyrolysis of $CH_3Co(sal_2en)(H_2O)$ and $C_2H_5Co(sal_2en)(H_2O)$ identified the same hydrocarbon products, but in different ratios. The relative rates of pyrolysis in CH_3OH as a function of R for the same ligand are: n-$C_3H_7 > C_2H_5 > CH_3$. This order is the same as the ease of formation of the free radicals [35].

The CH_4 and C_2H_6 products for R = CH_3 are formed by free radical hydrogen abstraction and dimerization processes, respectively. The alkane and alkene products when R = C_2H_5 or n-C_3H_7 can also be explained by two radical pathways. The alkane occurs by hydrogen abstraction and the alkene results from the oxidative process shown for CH_3CH_2 in eqn. 7 [10, 22]. Unstable $HCo(sal_2Bg)$ decomposes to H_2 and $Co^{II}(sal_2Bg)$.

$$CH_3CH_2 + Co^{II}(sal_2Bg) \rightarrow C_2H_4 + HCo(sal_2Bg) \qquad (7)$$

The anaerobic photolysis of $RCo(sal_2Bg)$ in CH_3OH at room temperature gave the same products and product ratio as the analogous pyrolysis reactions, and presumably occurs by the same mechanism.

The photolysis of $CH_3Co(sal_2en)(H_2O)$ under aerobic conditions in CH_3OH containing excess NaCN gave the products shown in eqn. 8.

$$CH_3Co(sal_2en)CN^- \xrightarrow[O_2]{CN^- h\nu} CH_4 + Co^{III}(sal_2en)(CN)_2^- \qquad (8)$$

$Co^{III}(sal_2en)(CN)_2^-$ was identified by spectrophotometric comparison to an authentic sample. Under anaerobic conditions CH_4 and a CN^- complex of $Co^{II}(sal_2en)$ were observed. Since a cobalt(II) complex is formed in the absence of any reducing agent the anaerobic reaction goes by a free radical, not an ionic, process. The mechanism presumably is like the one in the absence of CN^-; the CH_3 radical abstracts a hydrogen atom from the CH_3OH or ligand.

Reaction with the iodine electrophile

Iodine reacts with $CH_3Co(sal_2en)H_2O$ in CH_3OH in the absence of light and oxygen according to eqn. 9. The reaction takes about 2 h at room temperature, and the complex product slowly decomposes in CH_3OH. The CH_3I and

$$CH_3Co(sal_2en)H_2O + I_2 \xrightarrow{CH_3OH} ICo^{III}(sal_2en) + CH_3I \qquad (9)$$

$ICo^{III}(sal_2en)$ were identified, respectively, by GLPC and spectrophotometric comparison to an authentic sample. Floriani et al. [9] identified the complex, but not the CH_3I of this reaction.

Iodine also oxidizes $Co^{II}(sal_2en)$ in CH_3OH (eqn. 10).

$$Co^{II}(sal_2en) + 1/2\ I_2 \rightarrow ICo^{III}(sal_2en) \qquad (10)$$

The analogous reaction with $Co^{II}(sal_21,2pn)$ or $Co^{II}(sal_21,2pn\text{-}2\text{-}me)$ did not occur under the same conditions. Because the oxidation potentials of the $Co^{II}(sal_2Bg)$ complexes are undoubtedly similar, the difference in reactivity is due to steric effects.

Reactions with cyanide ion

We studied the reactions of $RCo(sal_2Bg)$ ($R = CH_3$, C_2H_5, and $n\text{-}C_3H_7$; $sal_2Bg = sal_2en$ and $sal_21,2pn\text{-}2\text{-}me$) with NaCN in CH_3OH containing 0.1 *M* NaOH. When excess CN^- is added to the $RCo(sal_2Bg)$ solution in the dark, CN^- coordinates *trans* to the alkyl group within 10 min (eqn. 11). This reaction is indicated by a shift in the $RCo(sal_2Bg)$ band near 330 to 335 nm in the presence

$$RCo(sal_2Bg) + CN^- \xrightarrow{\text{fast}} RCo(sal_2Bg)\,(CN)^- \tag{11}$$

of CN^-. After about 5 days at room temperature under aerobic conditions, the dealkylation has occurred. The products shown in eqn. 12 for $C_2H_5Co(sal_2en)$ exemplify the reaction. The dicyano product, which has a strong absorption at

$$C_2H_5Co(sal_2en)(CN)^- + CN^- \rightarrow Co^{III}(sal_2en)(CN)_2^- + C_2H_4 \tag{12}$$

388 nm, was identified by spectrophotometric comparison to an isolated, analyzed sample.

A faster reaction under anaerobic conditions gave as products 67% C_2H_6, 33% C_2H_4, and a $Co^{II}(sal_2en)$ complex, which was identified by ESR and visible spectra. Because of the absence of $Co^{III}(sal_2en)(CN)_2^-$ and the presence of C_2H_4, the anaerobic CN^- reaction is not entirely a nucleophilic substitution reaction with the ejection of a carbanionic species. As shown in the RS^- (see below) and the HS^- [25] reactions, ethyl—cobalt compounds form C_2H_6 and $Co^{III}(sal_2Bg)$ complexes exclusively in nucleophilic substitution reactions. The absence of a reducing agent to reduce a cobalt(III) product to the observed $Co^{II}(sal_2en)$ complex is further evidence against a nucleophilic substitution reaction. Instead CN^- induces homolytic bond cleavage with the formation of a C_2H_5 radical, which reacts in the manner discussed for anaerobic pyrolytic and photolytic reactions. A base-induced β-elimination reaction can be discounted because of the stability of $C_2H_5Co(sal_2Bg)$ in basic CH_3OH, and because an activating group is generally necessary [36].

Reactions with thiol anions

The anaerobic reaction of $C_2H_5S^-$ with $C_2H_5Co(sal_2en)$, run in basic CH_3OH (0.1 *M* in NaOH) at 48° in the dark, gave the products shown in eqn. 13. The C_2H_6 was determined by GLPC and the thiolate complex by isolation and analysis. No $(C_2H_5)_2S$ was found, and a carbonium ion mechanism is inoperative.

$$C_2H_5Co(sal_2en) + C_2H_5S^- \xrightarrow[OH^-]{CH_3OH} Co^{III}(sal_2en)(SC_2H_5)H_2O + C_2H_6 \tag{13}$$

The mechanism difference between the $RCo(DMG)_2H_2O$ (eqn. 6) [32] and $RCo(sal_2Bg)$ systems can be explained by half-wave potentials [33, 34]. The more electronegative DMG ligand decreases the electron density on the cobalt favoring a carbonium ion mechanism.

In agreement with the results of the reactions of HS^- with RCo(sal_2Bg) [25], the evidence disagrees with an S_N2 attack at the cobalt—carbon bond. As shown by a spectral change, a rapid *trans* coordination of RS^- occurs, and a slower dealkylation step follows within 3 or 4 days (eqn. 14). The fact that a cobalt (III) product is formed proves that a carbanion mechanism rather than a free

$$RCo(sal_2Bg) + R'S^- \xrightarrow{fast} RCo(sal_2Bg)(SR')^- \qquad (14a)$$

$$RCo(sal_2Bg)(SR')^- \xrightarrow[H_2O]{slow} Co^{III}(sal_2Bg)(SR')H_2O + RH \qquad (14b)$$

radical mechanism occurs. There is no oxidizing agent present to oxidize the $Co^{II}(sal_2Bg)$ resulting from a free radical to the cobalt(III) analog.

Reactions with alkane thiols

Alkane thiols (R'SH) were reacted in CH_3OH with RCo(sal_2Bg) (R = CH_3, C_2H_5 and n-C_3H_7; sal_2Bg = sal_2en, $sal_21,2pn$, and $sal_21,2pn$-2-me). The reactions, which were run in the dark under anaerobic conditions at 48°, often took several days. The products agree with reaction 15. The $Co^{II}(sal_2Bg)$ were identified by isolation and elemental analysis. GLPC experiments identified the alkanes and demonstrated the absence of dialkyl sulfides (RSR').

$$RCo(sal_2Bg) + R'SH \rightarrow Co^{II}(sal_2Bg) + RH \qquad (15)$$

After correcting for alkane formation due to pyrolysis the relative rates of the reaction between RCo(sal_2Bg) and C_2H_5SH are: for R, n-$C_3H_7 \simeq C_2H_5 > CH_3$; for sal_2Bg: $sal_21,2pn$-2-me > $sal_21,2pn$ > sal_2 en. These relative rates demonstrate that the rate determining step is not a direct attack on the cobalt—carbon bond. An S_N2 attack by R'SH at the cobalt—carbon bond would have the following rate order for R in RCo(sal_2Bg): $CH_3 \gg C_2H_5 >$ n-C_3H_7. The similar rates observed for the reactions of i-C_3H_7SH and C_2H_5SH with identical RCo(sal_2Bg) complexes are additional evidence against a bimolecular attack at the cobalt—carbon bond.

Comparison of the spectra of, e.g., $C_2H_5Co(sal_2en)$ before and immediately after adding C_2H_5SH proves that the alkane thiol coordinates before the dealkylation step. $C_2H_5Co(sal_2en)$ has a maximum at 334 nm which shifts to 325 nm upon the addition of C_2H_5SH. After the C_2H_5SH coordinates, dealkylation slowly occurs to form the RH and $Co^{II}(sal_2Bg)$ products (eqn. 15).

The isolation of the $Co^{II}(sal_2Bg)$ product suggests the free radical mechanism observed for photolysis and pyrolysis. However, the fact that alkanes instead of alkenes were found when R = C_2H_5 and n-C_3H_7 suggests that C_2H_5 and n-C_3H_7 radicals are not intermediates. Photolysis of $C_2H_5Co(sal_2en)$ even in the presence of a large excess of 1-mercaptoethanol yields 40% C_2H_4 [10]. Thus, the alkane products suggest a major non-radical reaction pathway; a carbonium mechanism is not important because no R'SR is observed by GLPC. The presence of the cobalt(II) product in a nucleophilic displacement reaction can be rationalized by the reduction of the cobalt(III) intermediate by R'SH. This behavior was observed in the DMG system [23, 32, 37] and by us in the sal_2Bg system using benzene thiol (eqn. 16) and ethane thiol.

$$(HO)Co^{III}(sal_2en)H_2O + C_6H_5SH \xrightarrow{CH_3OH} Co^{II}(sal_2en) + 1/2\ C_6H_5SSC_6H_5 \qquad (16)$$

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