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CLEAVAGE BY HALOGENS OF CARBON—COBALT BONDS IN ORGANOMETALLIC COMPLEXES OF COBALT(III)

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Summary

Axial alkyl or aryl groups, σ-bonded to the metal atom in some tetradentate Co^{III} complexes, are readily removed by iodine or iodine monochloride; electrophilic and radical attack on the carbon atom both can occur, depending upon the nature of the axial organic group and the chelating agent.

Introduction

It has been shown that the halogens are effective reagents for the displacement of an organic group σ-bonded to a cobalt atom. The study of these reactions, first observed in methylpentacyanocobalt(III) complexes [1] and in alkylcobalamin coenzymes [2], has been extended to some alkylcobaloximes*. For the latter complexes several routes to carbon—cobalt bond cleavage have been described, including direct electrophilic substitution [3] and oxidative dealkylation [4], the latter consisting in an oxidation of the complex by the halogen to a transient alkylcobalt(IV) compound followed by a rapid subsequent nucleophilic attack at the α-carbon by the halide ion. However, the interplay of a radical process could not be ruled out [5].

In the present work we examine the reaction between halogens and some other Co^{III} complexes of the general formula $RCo^{III}(chel)L$ [6], where R is a σ-coordinated organic (aliphatic or aromatic) group, L, the sixth ligand, is water or absent and chel is a planar tetradentate chelating ring, i.e.: salen, acacen, (DO)(DOH)pn**. Furthermore, the complexes $R^1R^2Co^{III}[(DO)(DOH)pn]$ [7], where R^1 and R^2 ($R^1 \neq R^2$ or $R^1 = R^2$) are two organic groups bonded to the cobalt atom in mutually *trans* relationship to one other, will be considered (Fig. 1).

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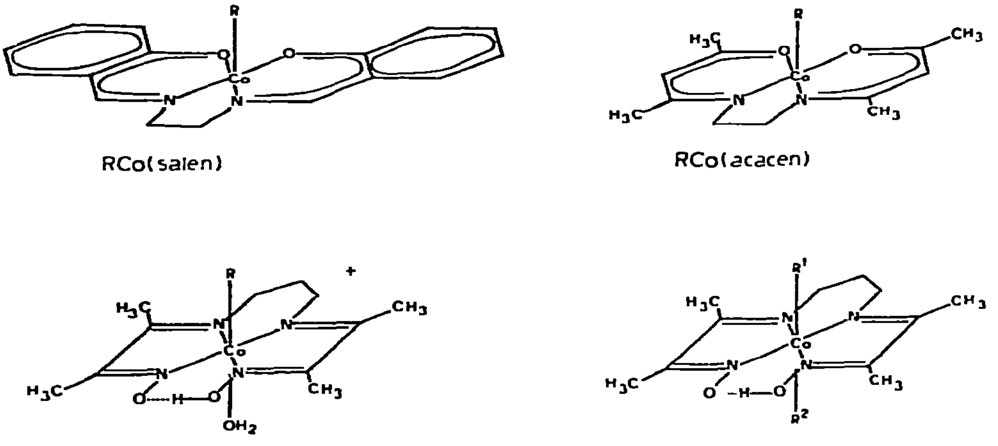
* The name cobaloxime is used to denote bis(dimethylglyoximato) complexes of cobalt.

** salen = *N,N'*-ethylenebis(salicylideneiminato); acacen = *N,N'*-ethylenebis(acetylacetoneiminato). (DO)(DOH)pn = 1-diacetylmonoximeimino-3-diacetylmonoximatoiminopropane.



RCo(salen) RCo(acacen)

$RCo[(DO)(DOH)pn]H_2O^+$ $R^1R^2Co[(DO)(DOH)pn]$

Fig. 1. Some Co^{III} complexes of general formula $RCo^{III}(chel)L$ and $R^1R^2Co^{III}[(DO)(DOH)pn]$.

Results

All the reactions were studied in chloroform at room temperature in the dark. The halogens used were I_2 and ICl.

As far as the stoichiometry of the reaction is concerned, the use of I_2 instead of ICl simplifies the problem of the identification of the products, since it limits the number of the species formed. On the other hand, the product obtained by the polarized molecule of ICl gives additional information about the reaction.

The stoichiometry of the reaction

The reactions of the monoalkyl and monoaryl derivatives occur with the simple stoichiometry (eqn. 1):

$$RCo^{III}(chel) + I_2 \rightarrow ICo^{III}(chel) + RI \qquad (1)$$

The dealkylation (or dearylation) of the $R^1R^2Co[(DO)(DOH)pn]$ complexes, as exemplified by the dimethyl derivative, can be obtained with two different stoichiometries, using a molar ratio I_2/complex equal to 1 or 2, respectively (eqns. 2 and 3).

$$(CH_3)_2Co^{III}[(DO)(DOH)pn] + I_2 \rightarrow CH_3Co^{III}[(DO)(DOH)pn]I + CH_3I \qquad (2)$$

$$(CH_3)_2Co^{III}[(DO)(DOH)pn] + 2\ I_2 \rightarrow Co^{III}[(DO)(DOH)pn]I_2 + 2\ CH_3I \qquad (3)$$

Several examples of these reactions are reported in Table 1, where it is shown also that in one case traces of ethane and ethylene are detected as byproducts.

TABLE 1

DEALKYLATION OF COBALT(III) COMPLEXES

Cobalt(III) complex	Molar ratio I_2/complex	Products
MeCo(salen)	1	ICo(salen)[a], MeI[b]
MeCo(acacen)	1	Unidentified cobalt complex, MeI[b]
$(Me)_2Co[(DO)(DOH)pn]$	1	MeCo[(DO)(DOH)pn]I[c], MeI[b]
$(Me)_2Co[(DO)(DOH)pn]$	2	$Co[(DO)(DOH)pn]I_2$[c], MeI[b]
EtCo(salen)	1	ICo(salen)[a], EtI[b], traces of C_3H_6, C_2H_4[b]

[a] Identified by elemental analysis. [b] Identified by GLC. [c] Products identified by electronic spectra.

The mechanism of the reaction

When CH_3Co^{III}(salen), $C_2H_5Co^{III}$(salen) and CH_3Co^{III}(acacen) are treated with ICl in the molar ratio Co/ICl $\geqslant$ 2, the following stoichiometry is observed (eqn. 4).

$$RCo^{III}(chel) + \tfrac{1}{2}\,ICl \rightarrow Co^{II}(chel) + \tfrac{1}{2}\,RCl + \tfrac{1}{2}\,RI \qquad (4)$$

Since in these reactions the molar ratio RI/RCl is ca. 1 (Table 2) it is inferred that both fragments of the ICl molecule must be equally active in attacking the leaving group R. This can occur only when the R group behaves as a radical.

The presence of Co^{II}(chel) (identified by electronic spectra) in the products of the reaction affords further evidence for a radical mechanism, suggesting that the halogen preferentially attacks the carbon atom rather than the cobalt atom. When the ratio Co/ICl is lower than 2, the Co^{II} complex is oxidized to a Co^{III} complex by excess halogen. This can be verified independently starting from Co^{II}(chel) and halogen (eqn. 5) and has previously been reported for the Co^{II}(salen) complexes [8].

$$Co^{II}(chel) + \tfrac{1}{2}\,X_2 \rightarrow XCo^{III}(chel) \qquad (5)$$

The $C_6H_5Co[(DO)(DOH)pn]H_2O^+$ complex reacts with ICl following the stoichiometry:

$$C_6H_5Co^{III}[(DO)(DOH)pn]H_2O^+ + ICl \rightarrow ClCo^{III}[(DO)(DOH)pn]H_2O^+ + C_6H_5I \qquad (6)$$

The absence of C_6H_5Cl in the products suggests that only the potentially positive iodine attacks the carbon atom. This may occur only when the R group behaves as a carbanion. Therefore the reaction can be classified as an electrophilic substitution.

TABLE 2

MOLAR RATIO OF RI/RCl IN REACTIONS 4 AND 6

Cobalt(III) complex	RI (%)	RCl (%)
$MeCo[(DO)(DOH)pn]H_2O^+$	73.2	26.8
$EtCo[(DO)(DOH)pn]H_2O^+$	82.4	17.6
$PhCo[(DO)(DOH)pn]H_2O^+$	100	
MeCo(salen)	50	50
EtCo(salen)	50	50
MeCo(acacen)	59.8	40.2

TABLE 3

DEALKYLATION AND DEARYLATION OF BIS-ORGANOCOBALT COMPLEXES WITH ICl

Cobalt(III) complex	Products	
	ICl/complex = 1	ICl/complex = 2
$(Me)_2Co[(DO)(DOH)pn]$	MeI	MeI, MeCl
MePhCo[(DO)(DOH)pn]	MeI, PhI (traces)	MeI, PhI, MeCl (traces)
EtPhCo[(DO)(DOH)pn]	EtI, PhI (traces)	EtI, PhI
$(Ph)_2Co[(DO)(DOH)pn]$	PhI	PhI

When CH_3 and C_2H_5 groups are bonded to the Co[(DO)(DOH)pn] moiety, both RI and RCl are formed and the ratio RI/RCl exceeds unity (Table 2). The excess of RI over RCl indicates that in these types of complexes a competition between radical and electrophilic attack occurs.

The reciprocal effect of the axial organic group

In Table 3 the results of dealkylation and dearylation reactions (with ICl) of the bis-organocobalt complexes are reported.

Carrying out the reaction with a molar ratio ICl/complex = 1 the equation is as follows:

$$R^1R^2Co^{III}[(DO)(DOH)pn] + ICl \rightarrow R^1Co^{III}[(DO)(DOH)pn]Cl + R^2I \qquad (7)$$

These reactions show the following features: *(i)* The second carbon—cobalt bond is broken less readily than the first, as demonstrated by the absence of R^1I, $R^2Co^{III}[(DO)(DOH)pn]Cl$ and $Co^{III}[(DO)(DOH)pn](H_2O)_2^{2+}$ in the products. *(ii)* In the unsymmetrical complexes the reaction occurs more readily at the aliphatic carbon than at the arylic carbon. *(iii)* One of the organic groups promotes the cleavage of the other group by an electrophilic mechanism even when the latter is an alkyl group.

By using a molar ratio ICl/complex = 2 both carbon—cobalt bonds are broken. The reaction products indicate that the process occurs in two stages. The first is described by reaction 7, the second consists in the dealkylation or dearylation of the intermediate $R^1Co^{III}[(DO)(DOH)pn]Cl$ complex.

Discussion

As far as the dealkylation reactions with ICl are concerned, the complexes examined fall into three categories: (1) complexes which undergo homolytic cleavage, i.e. RCo^{III}(salen) and RCo^{III}(acacen); (2) complexes which show both homolytic and heterolytic types of cleavage, i.e. CH_3- and C_2H_5-$Co^{III}[(DO)(DOH)pn]H_2O^+$; (3) complexes which react only via electrophilic cleavage, i.e. the $R^1R^2Co^{III}[(DO)(DOH)pn]$ complexes, in the first dealkylation stage.

The tendency to conform to one of the above types of reaction could be a relative measure of the state of polarization of the carbon—cobalt bond. Thus, the three categories are representative of complexes with virtually unpolarized, partially polarized and strongly polarized carbon—cobalt bonds, respectively. However, it would be of some interest to examine the reaction when some other reagents than ICl are considered. It has been found that $CH_3Co(salen)$ methylates mercury(II) by a fast reaction in water [9]:

$$CH_3Co(salen)H_2O + Hg^{2+} \rightarrow Co^{III}(salen)(H_2O)_2^{+} + CH_3Hg^{+} \quad (8)$$

and that the same complex is an efficient methylating agent toward some other Co^{III}(chel) and Co^{II}(chel) complexes [10]:

$$CH_3Co^{III}(salen) + Co^{III}(chel) \rightarrow CH_3Co^{III}(chel) + Co^{III}(salen \quad (9)$$

$$CH_3Co^{III}(salen) + Co^{II}(chel) \rightarrow CH_3Co^{III}(chel) + Co^{II}(salen) \quad (10)$$

Therefore, while reactions 8 and 9 suggest that the complex is a carbanion donor, reaction 10 and that with ICl (reaction 4) suggest that it is a radical donor. The aptitude of this complex to give two types of reaction can be attributed to the existence of an electron pool in the planar chelating ring. This is a highly conjugate system, which would help to decrease, at least in the ground state, the electron density at the cobalt atom when an alkyl group is present in the axial position. The opposite sense of charge displacement may occur when strong electrophiles approach the axial ligand. Thus, when an electrophilic agent as weak as ICl approaches the carbon—cobalt bond, it does not promote a strong charge redistribution and consequently the bonded CH_3 group maintains its radical nature. Conversely, when a strong electrophile (Hg^{2+} or Co^{III}(chel) complex) attacks the carbon atom, the planar ring may act as a charge donor group by virtue of its large electron availability, increasing the charge concentration at the group attacked, which is eliminated as a carbanion.

A quite different reaction pattern is followed by the bis-organocobalt complexes, where the carbon—cobalt bond is so polarized that the R group leaves as a carbanion in all cases, irrespective of the electrophilic power of the reagent. In fact, the experimental data indicate that these complexes are able to methylate a substrate only via electrophilic cleavage. Thus they easily transfer the organic group to another Co^{III}(chel) complex, but not to a Co^{II}(chel) complex, which requires a homolytic type of carbon—cobalt cleavage [10]. Comparison of the reactivities of the mono- and bis-organocobalt complexes suggests that the polarization of the carbon—cobalt bond is determined by the strong σ-donor power of the *trans* organic group, rather than by the effect of the chelating (DO)(DOH)pn ring.

In contrast to the dealkylation reactions examined above, which can follow more than one mechanism, the dearylation reactions seem to be exclusively electrophilic in character. This can be easily explained in terms of electronegativity, the phenyl group being more electronegative than the alkyl group.

Finally, we wish to draw attention to the behaviour of the phenylmethyl derivative of the Co[(DO)(DOH)pn] complex. In this unsymmetrical complex reaction occurs more readily at the alkyl than at the aryl carbon, while the inverse sequence is generally found in the alkyl—aryl mercurials in electrophilic substitution reactions [11]. This behaviour appears to be also in contrast to the kinetic data for the reaction of the $RCo[(DO)(DOH)pn]H_2O^{+}$ complexes with Hg^{2+} in water, where the phenyl derivative reacts with a higher rate constant than the methyl derivative [9]:

$$RCo^{III}[(DO)(DOH)pn]H_2O^{+} + Hg^{2+} \rightarrow Co^{III}[(DO)(DOH)pn](H_2O)_2^{2+} + CH_3Hg^{+} \quad (11)$$

Since the direction of the cleavage seems anomalous, some further experiments, including kinetic measurements, are in progress.

Experimental

The complexes were prepared as reported in refs. 6 and 7.

The reactions were performed in chloroform analytical grade Riedel—De Haën.

In some cases the Co complexes resulting from reaction were identified by comparison with the electronic spectra of authentic samples. A spectrophotometer Unicam SP 700 was used.

The alkyl and aryl halides were identified by GLC. Chromatographic analyses were carried out with 2 m columns of Carbowax 20M with a C. Erba Model G.T. gaschromatograph.

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