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

II *. ORGANOBIS(DIMETHYLGLYOXIMATO)COBALT(III) COMPLEXES

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Summary

The reaction between organocobaloximes and ICl in chloroform has been studied. In absence of an excess of added chloride ion the reaction is electrophilic in character; in presence of an excess of chloride ion both oxidative dealkylation and radical attack can occur.

Introduction

In a previous paper [1] the reactions of several organometallic cobalt(III) complexes (i.e. RCo(salen), RCo(acacen), RCo{(DO)(DOH)pn}H_2O) *** with halogens were discussed. It was shown that both electrophilic and radical attack on the carbon atom can occur, depending upon the nature of the axial organic group and the chelating agent. Of the organocobaloximes ☆, the most studied are the benzyl and ring-substituted benzyl derivatives [2,3]. The above reaction may occur by an oxidative dealkylation mechanism [3], consisting of an oxidation to RCo^{IV}, followed by a carbocation transfer to a nucleophilic acceptor. A similar mechanism, involving the formation of RCo^{IV}, was previously proposed by Halpern for the reaction between organocobaloximes and $IrCl_6^{2-}$ [4,5,6]. We describe below the extension of the study of such reactions to a large series of alkyl and aryl bis(dimethylglyoximates) of cobalt(III).

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

☆ Cobaloxime is the trivial name for a bis(dimethylglyoximato) complex of cobalt.

Results and discussion

All the reactions were performed in chloroform at room temperature in the dark with a slight excess of ICl present. Two series of experiments, in the absence and in the presence of a large amount of Cl^- (added as $(CH_3)_4NCl$), have been carried out. The organic halides obtained in the two cases (Table 1) have been identified by GLC, except the benzyl derivatives, identified by NMR spectra.

In the cases of methyl, ethyl, n-propyl and phenyl complexes, in the absence of Cl^- ion, organic iodides are formed exclusively; these reactions occur with the simple stoichiometry:

$$RCo(DH)_2H_2O + ICl \rightarrow RI + ClCo(DH)_2H_2O \quad (1)$$

Actually, the solid product isolated and identified by elemental analysis is not $ClCo(DH)_2H_2O$, but the $[ClCo(DH)_2Cl]^-H^+$ complex, which is formed in $CHCl_3$ in presence of ICl, as can be verified independently using an authentic sample of chloro—aquo complex. The absence of RCl (and ArCl) in the products suggests that with these compounds the reaction proceeds via an electrophilic substitution mechanism. In fact, both the oxidative dealkylation, which involves a preferential organic group transfer to the potentially negative chlorine atom of the ICl molecule [3], and the radical mechanism, which requires that both fragments of the ICl molecule must be equally active in attacking the leaving R group [1], would yield organic chloride.

When the reaction is carried out with Cl^- in excess, alkyl iodides and chlorides are both obtained, except with the phenyl derivative (see below). The presence of RCl can be regarded as evidence for oxidative dealkylation; on the other hand the presence of RCl and RI in the reaction products can be alternatively regarded as evidence for a radical mechanism. In effect, the normal oxidation potentials [7] of ICl and ICl_2^- (which is formed in the presence of excess Cl^-) [8] do not differ so as to suggest a change of mechanism from electrophilic substitution to oxidative dealkylation. On the contrary, as the linear molecule [9] of ICl_2^- would be a weaker electrophilic agent than ICl, owing to the negative charge density on the central atom, a competitive radical mechanism is possible.

The phenyl derivative, even in the case of the reaction with ICl_2^-, gives only

TABLE 1

ORGANIC PRODUCTS OF THE REACTION WITH ICl AND ICl_2^-

R	ICl	ICl_2^-
CH_3	CH_3I	CH_3I, CH_3Cl
C_2H_5	C_2H_5I	C_2H_5I, C_2H_5Cl
n-C_3H_7	n-C_3H_7I	
C_6H_5	C_6H_5I	C_6H_5I
$C_6H_5CH_2$ [a]	$C_6H_5CH_2Cl$, $C_6H_5CH_2I$	$C_6H_5CH_2Cl$, $C_6H_5CH_2I$
i-C_3H_7 [a]	i-C_3H_7Cl, i-C_3H_7I	

[a] See text.

TABLE 2

MOLAR RATIO OF RI/RCl IN THE REACTIONS WITH ICl_2^-

Complex	RCl(%)	RI (%)
$CH_3Co(salen)$	78	22
$CH_3Co\{(DO)(DOH)pn\}H_2O^+$	63	37
$C_6H_5Co\{(DO)(DOH)pn\}H_2O^+$	—	100
$CH_3Co(DH)_2H_2O$	25	75
$C_2H_5Co(DH)_2H_2O$	43	57
$C_6H_5Co(DH)_2H_2O$	—	100

C_6H_5I. In fact, owing to the strong electronegativity of the phenyl group, this compound reacts via electrophilic cleavage even with weak electrophilic agents, as it has been shown for some other cobalt(III) complexes [1] (Table 2).

The behaviour of the benzyl derivative appears to be more complicated. In the reaction of $C_7H_7Co(DH)_2H_2O$ with ICl in the absence of Cl^-, NMR evidence suggests that both benzyl chloride and benzyl iodide are formed; when an excess of Cl^- is added the reaction gives mainly benzyl chloride. On the other hand, the contemporaneous precipitation of iodine and the fact that addition of benzyl iodide increases the amount of benzyl chloride present, while the converse does not occur on addition of benzyl chloride, suggest that in these conditions the benzyl iodide undergoes a rapid exchange reaction with ICl (eq. 2).

$$C_6H_5CH_2I + ICl \rightarrow C_6H_5CH_2Cl + I_2 \qquad (2)$$

A detailed study of this reaction has been previously reported [10]. Thus the benzyl chloride present may be produced in the exchange reaction 2 rather than in the direct course of carbon—cobalt bond cleavage, and the benzyl iodide may be the only product of the transalkylation reaction. Consequently, the benzyl derivative reaction should be also regarded as an electrophilic substitution. This conclusion is in accord with the fact that the small difference in oxidation potential [6] realised on varying the R group seems insufficient to induce a change of mechanism along the series.

In the same way one can explain the formation of isopropyl chloride in the reaction of $i\text{-}C_3H_7Co(DH)_2H_2O$ with ICl.

The above results show that the aquocobaloximes are much more reluctant than the other cobalt(III) complexes to react via a radical mechanism. In fact, these are the only complexes among those previously studied which undergo electrophilic substitution when reacted with ICl. When the reagent is ICl_2^-, RCl is also formed but in a lower yield than that furnished by the complexes with different chelating rings (Table 2). Furthermore, no example of transalkylation reactions of organocobaloximes occuring via alkylic radical transfer has been reported; this is in contrast to the behaviour of other complexes of the type RCo(chel) [11,12,13]. Even in the case of reductive cleavage of the carbon—cobalt bond of $RCo(DH)_2H_2O$ complex by chromium(II) [14] the mechanism can be interpreted as an S_H2 displacement at the saturated carbon atom or as a cobalt(III)/cobalt(II) redox process, accompanied or followed by a transfer of a carbanion to the coordination sphere of chromium(III).

Experimental

Reaction of $ClCo(DH)_2H_2O$ with ICl.

$ClCo(DH)_2H_2O$ (100 mg) was suspended in chloroform, and treated with a slight excess of ICl. The mixture was stirred for a further 2 h and the green solid was filtered off, washed with diethylether and dried. (Found: C, 26.8; H, 4.22; N, 15.1. $C_8H_{15}N_4O_4CoCl_2$ calcd.: C, 26.6; H, 4.18; N, 15.5%.)

The organocobaloximes were prepared as pyridine derivatives. The preparations of the methyl and phenyl complexes are reported in ref. 15. The other alkyl derivatives were prepared following the procedure used for the methyl complex. The aquo complex has been obtained by hydrolysis of the pyridinate with dil. $HClO_4$ in methanol. The complexes with different chelating rings (Table 2) were prepared as reported in ref. 1. The alkyl and aryl halides (except benzyl halides) were identified by GLC. Chromatographic analyses were carried out with 2 m columns of Carbowax with a C. Erba Model G.T. gas cromatograph. NMR spectra were recorded by a JEOL C 60 HL spectrometer.

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