Halogenation of organocobaloximes: a direct competition between ring halogenation and Co–C bond cleavage. Part VI*

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(Received May 14, 1990; revised October 4, 1990)

Abstract

Organocobaloximes, $PhYCH_2Co^{III}(dmgH)_2Py$ (Y = S, O, NH) react with 1:1 and 1:2 molar equivalents of halogens (Cl_2, Br_2, I_2, ICl) in chloroform in the dark at room temperature. A variety of products including the ring halogenated organometallic product and the organic product from the direct Co–C cleavage of the parent cobaloxime are formed indicating that the present set of cobaloximes represents a unique class of cobaloximes where both the aromatic ring as well as the Co–C bond are simultaneously activated towards attack by halogen.

Introduction

Sigma bonded transition metal organometallic complexes are known to show diverse reactivity towards electrophiles due to the presence of a variety of functional groups having widely different reactivities on the organic ligands and/or other ligands attached to the metal [1, 2]. These complexes are thus akin to more complex organic molecules and a true understanding of their reactivities requires an understanding of the reactivities of several component parts. Benzyl metal complexes provide classic examples of such cases where the attack of the electrophile may take place at the aromatic ring, at the metal–carbon bond and/or at the other ligands [3].

We have been interested in the halogenation studies [4–7] in organo bis(dimethyl glyoximato)pyridine cobalt(III) complexes, trivially known as organocobaloximes [8–20], mainly because of the yet incomplete understanding of the structure versus Co–C bond relationship in such complexes which are widely accepted as coenzyme B_{12} model systems [21, 22]. From earlier works of Johnson and co-workers [23a], Tauzher and co-workers [23b] and our group [5] with benzyl and substituted benzyl cobaloximes, it has been observed that (i) Co–C bond cleavage is the predominant process in all these cases, (ii) no electrophilic substitution into the aromatic ring occurs, (iii) the mechanism of Co–C bond cleavage changes significantly with the change in the axial organic ligand and (iv) the $-CH_2Co(dmgH)_2Py$ group is activating in nature and its magnitude is more than the methoxy group.

We have recently, for the first time, suggested [7] that in the process of activating or deactivating the aromatic ring, the competitive cleavage of the Co–C bond is also affected by such substituents, for example, the substitution of groups like $-NMe_2$, $-OMe$, $-NHCOMe$ etc. into the *para* position of the benzene ring activates the ring as well as Co–C bond reactivity [7]. The results were rationalized in terms of a σ–π delocalization model.

To provide further evidence for such a viewpoint, we have specifically chosen organocobaloximes of the type $PhYCH_2Co^{III}(dmgH)_2Py$ (Y = S(**1**), O(**2**), NH(**3**)) for the present halogenation studies.

Results

Cobaloximes **1–3** react with 1:1 or 1:2 molar equivalents of halogen (Cl_2, Br_2, I_2 and ICl) in chloroform in the dark at room temperature and under nitrogen atmosphere. All the reactions are carried out under conditions where the concentration of the halogen is kept as low as possible so that the reactions of higher order in halogen are negligible. A smooth reaction occurs and is complete within 1 h (Cl_2 and Br_2) and 4 h (I_2 and ICl). Within the reaction time scale, none of the cobaloximes show any sign of decomposition in the absence of halogen.

*For Part V see ref. 7a.
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0020-1693/91/$3.50

TABLE 1. Products of the reaction of halogens with organocobaloximes (**1–3**)

$PhYCH_2Co^{III}(dmgH)_2Py$ + (1 mol)	$X_2 \longrightarrow$ (1 or 2 mol)	Product (product number)	Isolated yield (%)
Y=S (**1**)	Cl_2	4-$ClC_6H_4SCH_2Co^{III}$ (**4**)	69
		$C_6H_5SCH_2Cl$ (**13**)	30
Y=S (**1**)	Br_2	4-$BrC_6H_4SCH_2Co^{III}$ (**5**)	57
		$C_6H_5SCH_2Br$ (**14**)	43
Y=S (**1**)	Br_2[a]	4-$BrC_6H_4SCH_2Br$ (**25**)	53
		$C_6H_5SCH_2Br$ (**14**)	43
Y=S (**1**)	I_2	4-$IC_6H_4SCH_2Co^{III}$ (**6**)	85
		$C_6H_5SCH_2I$ (**15**)	10
		$C_6H_5SCH_2-ON=C(Me)-C(Me)=NOH$ (**22**)	5
Y=S (**1**)	ICl	4-$IC_6H_4SCH_2Co^{III}$ (**6**)	55
		$C_6H_5SCH_2I$ (**15**) + $C_6H_5SCH_2I$ (**13**)	37
		$C_6H_5SCH_2-ON=C(Me)-C(Me)=NOH$ (**22**)	8
Y=O (**2**)	Cl_2	4-$ClC_6H_4OCH_2Co^{III}$ (**7**)	88
		$C_6H_5OCH_2Cl$ (**16**)	12
Y=O (**2**)	Br_2	4-$BrC_6H_4OCH_2Co^{III}$ (**8**)	54
		$C_6H_5OCH_2Br$ (**17**)	42
Y=O (**2**)	Br_2[a]	4-$BrC_6H_4OCH_2Br$ (**26**)	56
		$C_6H_5OCH_2Br$ (**17**)	42
Y=O (**2**)	I_2	4-$IC_6H_4OCH_2Co^{III}$ (**9**)	72
		$C_6H_5OCH_2I$ (**18**)	17
		$C_6H_5OCH_2-ON=C(Me)-C(Me)=NOH$ (**23**)	8
Y=O (**2**)	ICl	4-$IC_6H_4OCH_2Co^{III}$ (**9**)	57
		$C_6H_5OCH_2Cl$ (**16**) + $C_6H_5OCH_2I$ (**18**)	32
		$C_6H_5OCH_2-ON=C(Me)-C(Me)=NOH$ (**23**)	10
Y=NH (**3**)	Cl_2	4-$ClC_6H_4NHCH_2Co^{III}$ (**10**)	56
		$C_6H_5NHCH_2Cl$ (**19**)	40
Y=NH (**3**)	Br_2	4-$BrC_6H_4NHCH_2Co^{III}$ (**11**)	81
		$C_6H_5NHCH_2Br$ (**20**)	16
Y=NH (**3**)	Br_2[a]	4-$BrC_6H_4NHCH_2Br$ (**27**)	80
		$C_6H_5NHCH_2Br$ (**20**)	16
Y=NH (**3**)	I_2	4-$IC_6H_4NHCH_2Co^{III}$ (**12**)	85
		$C_6H_5NHCH_2I$ (**21**)	5
		$C_6H_5NHCH_2-ON=C(Me)-C(Me)=NOH$ (**24**)	10
Y=NH (**3**)	ICl	4-$IC_6H_4NHCH_2Co^{III}$ (**12**)	80
		$C_6H_5NHCH_2Cl$ (**19**) + $C_6H_5NHCH_2I$ (**21**)	5
		$C_6H_5NHCH_2-ON=C(Me)-C(Me)=NOH$ (**24**)	10

[a]The reaction is continued for a longer time (12–15 h) with 2 mol of bromine.

Though the ring substituted organometallic product (**4–12**) is the main product isolated in each case, some organic product (**13–21**) is also formed and characterized by ^1H NMR spectra and by comparison with the authentic samples, in many cases. The inorganic product is the corresponding halocobaloxime. In all the reactions with I_2 and ICl, an additional product, *o*-organodimethylglyoxime mono ether (**22–24**) is also isolated and characterized. When the reaction of **2** with bromine (1:2 molar ratio) is monitored by taking aliquots at regular interval of 10 min, it indicates that **8** and **17** are formed simultaneously. When the reaction of **1–3** with 2 mol of bromine is left for a longer time (12–15 h) at room temperature, the products **25–27** are formed instead of **5**, **8** and **11** (Table 1). A similar product **25** is formed when **5** is brominated under similar conditions. However, the reaction is slow. All efforts to put the second halogen into the ring fail. The reaction of **2** with bromine (1:1) in the presence of an equimolar amount of anisole forms **8** and **17** and anisole is recovered. The spectral characteristics of the organic and organometallic products are given in Tables 2–4.

Preliminary ESR and cyclic voltametric studies of these reactions have been carried out. When a so-

TABLE 2. Spectral characteristics of X– ⟨◯⟩ –Y–CH_2–$Cl^{III}(dmgH)_2Py$ (**4–12**)[a]

Compound no.	Y	X	^{1}H NMR chemical shift ($CDCl_3$): δ (ppm)						UV–Vis (CH_3OH): λ_{max} (nm)
			dmgH	Aromatic	$-CH_2$				
1	S	H	2.00	6.98–7.63	3.10	7.74	8.10	8.52	435, 385, 287, 232
2	O	H	1.90	6.60–7.42	4.80	7.54	7.98	8.53	427, 327, 250, 230
3	NH	H	1.85	6.30–7.35	5.15	7.82	8.06	8.60	450, 308, 272, 240
4	S	Cl	2.05	6.91–7.26	2.40	7.60	8.30	8.56	430, 381, 286, 232
5	S	Br	1.94	7.02–7.40	2.37	7.66	8.25	8.52	432, 283, 286, 232
6	S	I	1.98	6.82–7.32	2.22	7.56	8.26	8.50	231, 284, 280, 233
7	O	Cl	1.94	6.68–7.34	4.46	7.50	7.85	8.28	420, 320, 250, 230
8	O	Br	1.90	6.76–7.38	4.30	7.64	8.14	8.36	430, 322, 242, 230
9	O	I	1.84	6.80–7.32	4.20	7.70	7.85	8.41	436, 328, 254, 231
10	NH	Cl	1.96	6.69–7.40	4.66	7.40	7.62	8.16	457, 318, 282, 242
11	NH	Br	1.91	6.52–7.31	4.46	7.54	7.52	8.20	459, 321, 288, 240
12	NH	I	1.90	6.51–7.30	4.30	7.20	7.64	8.10	457, 326, 276, 238

[a]All compounds give satisfactory C, H, N and halogen analyses.

TABLE 3. Characteristics of the organic products **13–21** and **25–27** from the reaction of halogens with PhY–CH_2–$Co^{III}(dmgH)_2Y$ (Y = S (**1**) O (**2**) NH (**3**))

Compound no.	Boiling point (°C)	^{1}H NMR chemical shift ($CDCl_3$: δ (ppm)		UV (CH_3OH): λ_{max} (nm)
		Aromatic	CH_2	
13	66/0.2 mm	7.42(m)	4.91(s)	247
14	82/0.2 mm	7.31(m)	4.82(s)	249, 239
15	[b]	7.26(m)	4.56(s)	251, 226
16	92/20 mm	6.82–7.30(m)	5.82(s)	259
17	110/20 mm	6.9–7.4(m)	5.92(s)	254
18	173/14 mm	6.98–7.40(m)	6.01(s)	253
19	203 sub	6.68–7.30(m)	3.38(s)	240, 247
20	[a]	6.70–7.20(m)	3.46(s)	240, 249
21	[a]	6.76–7.30(m)	3.90(s)	240, 252
25	[a]	7.06–7.51(m)	4.76(s)	249, 238
26	[a]	7.06–7.54(m)	5.85(s)	254
27	[a]	6.86–7.26(m)	3.40(s)	241, 247

[a]Compounds unstable. [b]Low melting solid.

lution of organocobaloxime (e.g. $PhSCH_2$-$Co^{III}(dmgH)_2Py$, 10^{-4} molar solution in CH_2Cl_2) and Br_2 (1:1 molar ratio in CH_2Cl_2) under N_2 is quenched to liquid N_2 temperature, a well defined EPR spectrum consisting of eight relatively broad (20 G) but well resolved lines (Fig. 1) is exhibited corresponding to one unpaired electron on cobalt(IV) with nuclear spin ^{59}Co ($I = 7/2$) ($g_{iso} = 2.024$). Although a slight anisotropy is evident, the resolution is insufficient to permit evaluation of both parallel and perpendicular components and only a single G value (relative to DPPH) of $M = 7/2$ and $M = -7/2$ hyperfine com-

TABLE 4. Characteristics of $PhY-CH_2-ON=C(Me)-C(Me)=NOH$ (22–24)

Compound no.	Melting point (°C)	^1H NMR ($CDCl_3$) (TMS): δ (ppm)			UV: (CH_3OH) λ_{max} (nm)
		Aromatic	$-CH_2$	dmgH	
22	101	7.26, 7.40	5.54	2.24, 2.28	312
23	99	7.35	5.95	2.22, 2.30	222
24	74	7.30, 7.46	5.20	2.24, 2.27	228

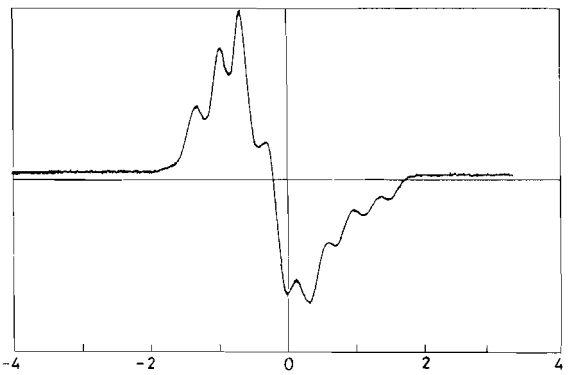

Fig. 1. First derivative EPR spectrum of [$PhSCH_2Co(dmgH)_2Py$] in frozen CH_2Cl_2 at liquid N_2 temperature. Microwave frequency is 9.34 GHz. Field set 3300 G, with a scan range of 500 G. Microwave power used 2 mW.

ponent lines and a single A value are determined. When the frozen solution is brought to room temperature the eight-line Co^{IV} signal disappears instantaneously.

However, the same organocobaloxime under similar conditions with I_2 or ICl (1:1 and 1:4 molar) in CH_2Cl_2 does not give any signal of Co^{IV}. When an independent experiment of **2** with I_2 is set up at room temperature and the aliquots of the reaction mixture every half hour are subjected to ESR investigations at liquid N_2 temperature, no ESR signal is observed. Cyclic voltammograms of the organocobaloximes **1–3** were recorded in acetonitrile having tetrabutylammonium perchlorate as supporting electrolyte. All voltammograms show a irreversible one electron oxidation process (Fig. 2).

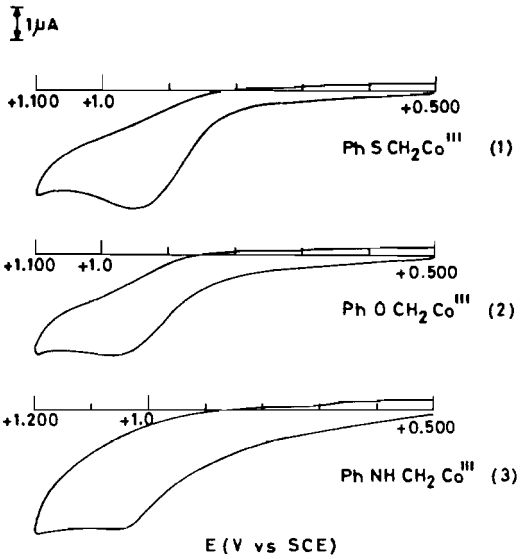

Fig. 2. Cyclic voltammogram of acetonitrile solution of organocobaloximes **1–3** (*c.* 10^{-4} mol/l) containing tetraethylammonium perchlorate as supporting electrolyte.

Discussion

The substantial formation of ring halogenated organocobaloximes along with a low to moderate yield of the Co–C cleavage product of the parent cobaloxime suggests that the present system represents a unique class of organocobaloximes where both the aromatic ring as well as the Co–C bond are simultaneously activated towards attack by halogen. To rationalize the results one needs to understand factors which promote such activation, for example, (i) the substituent effect of the $-CH_2Co(dmgH)_2Py$ group on the aromatic ring and (ii) the substituent effect of appended ligands like $-YCH_2Ph$ towards the reactivity and cleavage of the Co–C bond. ^{19}F NMR studies [24–26] and chemical studies [27, 7] have confirmed the strong electron donating and hyperconjugative nature of the metallomethyl group. The present results also support the σ–π mechanism and further indicate that the hyperconjugative influence of the metallomethyl group is transmitted to the aromatic ring via the lone pair on the heteroatom.

Since it is possible that the heteroatom alone may be responsible for such ring activation in these cobaloximes, a comparison of charge densities at different centres in $PhCH_2Cl$ and $PhOCH_2Cl$ was made. This revealed that the charge densities are increased 200-fold in $PhOCH_2Cl$ compared to $PhCH_2Cl$ and are more pronounced in σ_R than σ_I [28–30]. We observe from an independent experiment that, when an equimolar mixture of anisole and **2**

is halogenated with one mole of Br_2, anisole remains unreactive and is recovered, and the nature and yield of the products are identical to the reaction done in the absence of anisole. This suggests that the metallomethyl group has a considerable effect on the activation of the aromatic ring.

Furthermore, a geometrical consideration must be made since it may reveal more about the σ–π process. For example, the spatial position of the O–CH_2 group attached to the benzene ring is defined by the angles α (Ar–O–CH_2) and β (the angle by which the $-CH_2$ group is twisted out of the benzene plane) [29]. The value of α remains fairly constant (118–120°) and is characteristic of an sp^2 oxygen whereas the β value changes significantly from compound to compound. Only a very low value of β (close to zero) places the oxygen p_z orbital in perfect location for resonance interaction with the ring. This is likely to be the case in the present cobaloximes.

It seems from the above discussion that the effect of the metallomethyl group is transmitted to the aromatic ring via the heteroatom resulting in enhanced ring substitution.

When considering the substituent effect of $-$YPh (Y = NH, O, S) on the $-CH_2Co^{III}$ group, a $-$I effect of YPh decreases the electron density at the Co–C bond whereas a +M effect increases it. In view of the present experimental results and with support from the literature it seems that both the aromatic ring as well as the Co–C bond are simultaneously sufficiently activated towards attack by the molecular halogens. It is very difficult to quantity the relative extent of activation at the aromatic ring and at the α-carbon by the σ–π process. However, we have recently shown that the Co–C cleavage is the primary process in the halogenation of furfuryl and 2-thienylmethyl cobaloximes whereas exclusive ring substitution is observed in the corresponding three-substituted derivatives. The results were best explained in terms of π delocalization process involving whel and intermediates [7]. The electrochemical data has been correlated with the activation of the Co–C bond in organocobaloximes [7a, b] and other systems [7c, d].

Mechanism of Co–C cleavage

In the absence of detailed kinetic studies in these systems, it is at present very difficult to pin down the exact mechanism of this reaction. However, the following observations are noteworthy.

1. The EPR spectrum of a solution of $PhSCH_2Co^{III}$ (10^{-4} M solution in CH_2Cl_2) and Br_2 (1:1 molar ratio) in CH_2Cl_2 under N_2 at liquid N_2 temperature gives a well resolved spectrum consisting of eight well-resolved lines corresponding to one unpaired electron on cobalt with a ^{59}Co nuclear spin ($I = 7/2$ $g_{iso} = 2.024$) (Fig. 1). An electron transfer process seems important in these studies.

2. In the case of the reaction of ICl with $PhSCH_2Co^{III}$ both $PhSCH_2Cl$ and $PhSCH_2I$ are formed. The former is formed by the following exchange reaction.

$$PhSCH_2I + ICl \longrightarrow PhSCH_2Cl + I_2$$

3. The contribution of five coordinate complexes may be important in certain reactions [31–36].

Experimental

Chloromethylphenyl sulfide was prepared by the chlorination of thioanisole with sulfuryl chloride in dichloromethane [37]. Chloromethylphenyl sulfide was reacted with NaI to give the unstable iodo analogue [38]. Chloromethylphenyl ether was prepared from chloromethyl sodium sulfonate in three steps as outlined by Schollkopf [39].

Phenoxymethyl and thiophenoxy methyl cobaloximes (**1** and **2**) were synthesized by the method of Schrauzer [40] from cobaloxime(I) and the corresponding organic halide. Cobaloxime(I) was generated *in situ* by the disproportionation of cobaloxime(II) under anaerobic and alkaline conditions. *N*-Methylene aniline cobaloxime was prepared from hydrido cobaloxime and aniline in the presence of formaldehyde as described by Blackmer *et al.* [41].

Iodine monochloride was prepared by the treatment of iodine with dry chlorine at ambient temperature and was distilled before use.

Reaction of organocobaloximes with halogen

In a typical experiment, a bromine solution (2.1 mmol in 10 ml $CHCl_3$) was added dropwise over a period of 20 min to a solution of phenoxymethyl cobaloxime (1.05 mmol in 15 ml $CHCl_3$) in the dark under nitrogen at room temperature. The progress of the reaction which took less than 45 min was monitored by TLC on silica gel G using ethyl acetate as the eluent. On completion, the reaction mixture was concentrated and poured into ether solvent* (50 ml). The precipitated solid was filtered off and washed with ether. The combined ether extracts were concentrated to give an organic product which was characterized either directly by comparison with authentic samples or by ^1H NMR. The precipitated inorganic product was further purified on preparative thin layer silica gel plate using a mixture of di-

*In reactions with I_2 and ICl, the solution was washed initially with aqueous 5% sodium thiosulfate and water before further workup.

chloromethane:methanol:pyridine (90:9:1, vol./vol. as eluent.

Reaction of phenoxymethyl cobaloxime with bromine in presence of anisole

Bromine (1 mmol in 10 ml dry chloroform) was added dropwise over a period of 20 min to a solution of phenoxymethyl cobaloxime (1 mmol, 15 ml chloroform) in the presence of anisole (1 mmol) under conditions as described above. The reaction was concentrated *in vacuo* and poured on a neutral alumina column for flash chromatography. The elution with ether solvent gave back the total amount of unreacted anisole.

Reaction of $PhSCH_2I$ with ICl

An ethereal solution of iodomethylphenyl sulfide, prepared from chloromethylphenyl sulfide and sodium iodide, was mixed with ICl and the mixture was stirred for 2 h. Iodine gas was liberated and the solution turned violet in colour. The reaction mixture after usual workup showed the formation of chloromethyl phenyl sulfide by ^1H NMR.

Physical measurements and instruments

Electronic spectra were recorded on Cary 17D instrument. ^1H NMR spectra were taken on 80 MHz (Brucker WP80), 90 and 100 MHz (Varian EM390 and HA 100) spectrophotometers. Shimadzu chromatograph (GC-9A) and Iatroscan (TH 10) were used for finding the percentage ratios of organic product mixtures. Elemental analysis was done at RSIC, Lucknow and at I.I.T. Kanpur.

Cyclic voltammetry measurements on organocobaloximes (0.5 mmol l^{-1}) in dry degassed acetonitrile using tetrabutyl ammonium perchlorate as a supporting electrolyte were done on a Bioanalytical assembly (BAS-100) using a conventional three electrode assembly. The reference electrode was Ag wire and the working electrode was a platinum wire.

EPR measurements were recorded on a Varian E-109 (X band) instrument. Organocobaloxime in dichloromethane (*c.* 10^{-4} mol l^{-1}) and bromine in dichloromethane (*c.* 10^{-4} mol l^{-1}) were mixed together in a 1:1 molar ratio under nitrogen and the solution was immediately cooled to liquid N_2 temperature and the spectrum was recorded.

Similar measurements were made on reactions of organocobaloximes with iodine and ICl.

Acknowledgement

We thank the Department of Science and Technology for financial assistance to this project.

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