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Heterolytic Cleavage of Cobalt–Carbon Bond by Thiocyanogen in Benzyl Cobaloximes. Part IV*

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Abstract

Benzyl and *para*-substituted benzylcobaloximes react readily with thiocyanogen in the dark under anaerobic conditions to give a variety of products: thiocyanates, isothiocyanates, bibenzyl and benzyl ether of dimethylglyoxime. The products are believed to result from an oxidative dealkylation process on the intermediate five-coordinate organocobaloxime species.

Introduction

Several σ bonded organotransition metal complexes are known to be susceptible to metal carbon bond cleavage by electrophiles [1]. Organopenta-aquochromium(III) ions, by far, offer the most clean reactions [2]. The most interesting, yet less understood substrates include the organocobalt(III) and organoiron(II) complexes [3]. This is because of the seemingly endless variety of reactions they undergo, the former being particularly important in view of their relation to coenzyme B_{12}. Though studies with Hg^{2+} have led to a more rationalised picture about the mode of metal carbon bond cleavage [4], considerable complexities arise with halogens because of the attack of the latter at various sites of the complex and many mechanisms have been proposed for such a cleavage [5]. Thiocyanogen as a pseudohalogen, offers analogy with halogens except for its mild reactivity and low oxidising ability**. Furthermore, this being a heteronuclear species having two reactive sites (S and N), it offers a better probe to study the mechanistic features from the point of view of the products themselves. Since the mechanism through which the cobalt–carbon bond is cleaved and the factors that promote (or inhibit) such cleavage are of considerable importance, the study with thiocyanogen should prove useful. We, therefore, report the first study of the reaction of thiocyanogen with benzyl cobaloximes.

TABLE I.

$RCo^{III}(dmgH)_2Py + (SCN)_2 \longrightarrow$ R =	Organic products (product number)	Ratio[a] (%)
$C_6H_5CH_2$ (1)	$C_6H_5CH_2SCN$ (7)	100
4-$MeC_6H_4CH_2$ (2)	4-$MeC_6H_4CH_2SCN$ (8)	100
4-$MeOC_6H_4CH_2$ (3)	4-$MeOC_6H_4CH_2SCN$ (9)	85
	4-$MeOC_6H_4CH_2ON$=CMe–CMe=NOH (10)	15
4-$ClC_6H_4CH_2$ (4)	4-$ClC_6H_4CH_2SCN$ (11)	65
	4-$ClCl_6H_4CH_2NCS$ (12)	15
	4-$ClC_6H_4CH_2ON$=CMe–CMe=NOH (13)	20
4-$CNC_6H_4CH_2$ (5)	4-$CNC_6H_4CH_2SCN$ (14)	72
	4-$CNC_6H_4CH_2NCS$ (15)	8
	4-$CNC_6H_4CH_2$–CH_2–C_6H_4CN-4 (16)	15
	4-$CNC_6H_4CH_2ON$=CMe–CMe=NOH (17)	5
4-$NO_2C_6H_4CH_2$ (6)	4-$NO_2C_6H_4CH_2SCN$ (18)	32
	4-$NO_2C_6H_4CH_2NCS$ (19)	27
	4-$NO_2C_6H_4CH_2$–CH_2–$C_6H_4NO_2$-4 (20)	30
	4-$NO_2C_6H_4CH_2$–ON=CMe–CMe=NOH (21)	11

[a] Based on ^1H NMR and HPLC.

Results

Benzyl- and 4-methylbenzyl cobaloximes (**1** and **2**) react with thiocyanogen at ambient temperature under dark and anaerobic conditions to give benzyl (**7**) and 4-methylbenzyl (**8**) thiocyanates as the exclusive organic products. However, similar reactions with 4-methoxy, 4-chloro, 4-cyano and 4-nitrobenzyl cobaloximes (**3**–**6**) under identical conditions form a mixture of products including thiocyanates, isothiocyanates, bibenzyls and benzyl ethers of dimethylglyoxime (**9**–**21**) (Table I). The course of reaction which usually takes 0.7–1.5 h is monitored by TLC on silica gel G. When the same reaction is carried out in the presence of 1 mole excess of pyridine, benzylthiocyanates are the exclusive organic prod-

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*For part III see ref. 5i.

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**The reactivity of thiocyanogen falls between Br_2 and I_2 and $(SCN)_2 \rightarrow (SCN)_2^{\dot{-}}$ (E° = 0.783 V) [6a].

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TABLE II. Characteristics of Organic Products (7–21) Obtained from the Reaction of Thiocyanogen with Organocobaloximes (1–6) in Chloroform under Nitrogen

Organic compound[a]	Melting/boiling point (°C)	^1H NMR, $CDCl_3$ (TMS): (200 MHz)			Mass (m/e) (%)[b]
		Aromatic	CH_2	Other	
7	42	7.34(m)	4.15(s)		149(14); 91(100)
8	24	7.41(s)	4.19(s)	2.50(Me)	163(7); 105(100)
9	82/0.6 mm	6.85(m)[c]	3.97(s)	3.68(OMe)	178(2); 121(100)
10	72	6.85–7.3(m)	5.1(s)	3.75(OMe) 2.0, 2.06(dmgH)	236(19); 121(100)
11	17	7.33(s)	4.10(s)		183, 185(10); 125, 127(100)
12	145/1 mm	7.40(s)[c]	4.75(s)		183, 185(18); 125, 127(100)
13	98	7.20(s)	5.16(s)	1.90, 2.30(dmgH)	239(1.5); 124(100)
14	76	7.59, 7.84[c] (8 Hz)	4.22(s)		174(16); 116(100)
15	73	7.53, 7.78[c] (8 Hz)	4.68(s)		174(22); 116(100)
16	198	7.16–7.94(m)	3.36(s)		232(42); 116(100)
17	95	7.40, 7.52	5.16(s)	1.95, 2.04(dmgH)	231(10); 116(100)
18	85	7.69, 8.37[c] (10 Hz)	4.25(s)		194(15); 136(100)
19	36	7.56, 8.34[c] (10 Hz)	4.91(s)		194(21); 136(100)
20	180	7.23, 8.1[c] (9 Hz)	3.08(s)		272(50); 136(100)
21[d]	99	A 7.50, 8.20 B 7.50, 8.20	5.35(s) 5.10(s)	2.05, 2.35(dmgH) 2.18, 2.22(dmgH)	250(60); 135(100)

[a] ν(SCN): 2150–2165 cm^{-1} and ν(NCS): 2070–2075 cm^{-1}. [b] First value corresponds to $M^{+\cdot}$ peak and the second value corresponds to $4\text{-}RC_6H_4CH_2^{+}$, however, for 13 and 21 the values refer to $(M - H)^+$ and $(M - H - dmgH)^+$. [c] A_2B_2 pattern is clearly observed and the coupling constants are given in parentheses. [d] Both isomers (*syn* and *anti*) are observed in the ^1H NMR.

ucts formed. The inorganic product in all these cases is the sulphur bonded $NCSCo^{III}(dmgH)_2Py$.

Furthermore, the following information is obtained from independent experiments:

(i) The reaction of 4-chlorobenzyl cobaloxime (4) with thiocyanogen at −20 °C forms exclusive 4-chlorobenzyl thiocyanate (11). However, when the same reaction is carried out in a sealed tube at 90 °C, both 4-chlorobenzyl thiocyanate (11) and 4-chlorobenzyl isothiocyanate (12) in a 85:15 ratio are formed.

(ii) The reaction of 4-chlorobenzyl cobaloxime (4) with thiocyanogen under photolytic conditions (irradiation by 400 W tungsten lamps) forms 4-chlorobenzyl thiocyanate, 4-chlorobenzyl isothiocyanate and 4-chlorobenzyl dimer in a ratio of 55:25:20, respectively.

The only inorganic product isolated in all the above reactions is sulphur bonded thiocyanatobis(dimethylgloximato)pyridinitocobalt(III) as confirmed by IR spectroscopy.

(iii) Benzyl thiocyanates do not isomerise to isothiocyanates under these reaction conditions, for example, 4-chlorobenzyl thiocyanate stays stable in solution for several hours without any isomerisation*.

Characteristics of the organic products 7–21 are given in Table II.

Discussion

The reactions of benzyl cobaloximes with thiocyanogen are clean and provide moderate to good yields of the corresponding benzyl thiocyanates, for example, the formation of benzyl and 4-methylbenzyl thiocyanate as exclusive organic products from the reaction of thiocyanogen with 1 and 2 may suggest that thiocyanogen is particularly electrophilic towards the saturated Co–benzyl bond. In contrast, the formation of a variety of products in 3–6 indicates that we are dealing with a mixture of mechanisms which include free radical processes;

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*However, benzyl thiocyanates are known to isomerise to isothiocyanates at high temperature in nucleophilic solvents [7].

for example, the formation of bibenzyls points to the participation of benzyl radicals, the formation of benzyl ethers of dimethylglyoxime points to the intermediate formation of organocobalt(IV) species in solution and the formation of both benzyl thiocyanates and benzyl isothiocyanates points to the free radical participation of thiocyanogen. Since the negative charge resides more on sulphur in the thiocyanate ion, the formation of benzyl thiocyanates may also be rationalised in terms of a conventional nucleophilic attack (either S_N2 or S_N2') by thiocyanate ion on the intermediate organocobalt(IV) complex. Because of the side reactions such as the formation of polymeric thiocyanogen, detailed mechanistic studies on these reactions are not possible. The formation of the products can be rationalised as follows.

As homolytic cleavage of the S–S bond in thiocyanogen* and unimolecular homolysis of the Co–C bond in benzyl cobaloximes are highly unlikely processes under the reaction conditions, a direct free radical process seems to be out of question. Therefore, bibenzyls and isothiocyanates must be formed by an induced free radical process originating from the oxidised species in solution. But it is to be noted that thiocyanogen is a weak oxidising agent and is not capable of oxidising six coordinate benzyl cobaloximes in view of their large differences in oxidation potentials**. However, the formation of benzyl ether of dimethylglyoxime definitely points to the intermediate formation of the oxidised species since such a product is a characteristic decomposition product of organocobalt(IV) species in solution [9]. Since dissociation of pyridine is a very facile process in such benzyl cobaloximes as observed by Okamoto *et al.* [10] and the resulting base free five-coordinate species are very reactive and easily oxidisable even by weaker oxidising agents like I_2† ($I_2 \rightarrow I_2^{\dot{-}}$, $E° = 0.54$ V), it is quite likely that the oxidation is occurring on a five-coordinate species in the present case. This is supported by the experimental observation that in the reactions in the presence of excess pyridine, when six-coordinate benzyl cobaloxime is the predominant species in solution, no oxidation takes place and benzyl thiocyanates are the exclusive organic product formed. Though penta-coordinate base free cobalt(III) complex is less frequently found as a stable form, it is postulated as an intermediate in many ligand exchange reactions [11]. The importance of the five-coordinate complex is also noted for iron complexes where molecular oxygen reacts easily with a five-coordinate iron(II) porphyrin complex to give μ-oxo iron(III) dimers [12]. The six-coordinate base-on form is unreactive, however. Thus, base free five-coordinate complexes are expected to contribute as reactive intermediates in reactions of cobalt complexes other than ligand exchange reactions such as oxidation–reduction. However, little is known so far. The contribution of the five-coordinate base free form in the reaction of molecular oxygen with alkylcobaloximes is reported [13] but the results are criticised later [14].

$$\mathrm{RCo^{III}(dmgH)_2Py} \underset{+\mathrm{Py}}{\overset{-\mathrm{Py}}{\rightleftharpoons}} \mathrm{RCo^{III}(dmgH)_2} \tag{1}$$

$$\mathrm{RCo^{III}(dmgH)_2} + \mathrm{(SCN)_2} \longrightarrow [\mathrm{RCo^{IV}(dmgH)_2}]^+ + \mathrm{(SCN)_2}^{\dot{-}} \tag{2}$$

$$\mathrm{(SCN)_2}^{\dot{-}} \longrightarrow \mathrm{(SCN)^-} + \mathrm{(NCS)^{\bullet}} \tag{3}$$

$$[\mathrm{RCo^{IV}(dmgH)_2}]^+ \begin{cases} \xrightarrow[\mathrm{a}]{\mathrm{(SCN)^-}} \mathrm{RSCN\ (or\ RNCS)} + \mathrm{Co^{II}(dmgH)_2} \\ \xrightarrow[\mathrm{b}]{} \mathrm{R{-}ON{=}CMe{-}CMe{=}NOH} \end{cases} \tag{4}$$

$$\mathrm{RCo^{III}(dmgH)_2} \xrightarrow{\mathrm{(NCS)^{\bullet}}} [\mathrm{RCo^{IV}(dmgH)_2SCN}] \tag{5}$$

$$[\mathrm{RCo^{IV}(dmgH)_2SCN}] \longrightarrow \dot{\mathrm{R}} + \mathrm{Co^{III}(dmgH)_2SCN} \tag{6}$$

$$\dot{\mathrm{R}} \begin{cases} \xrightarrow[\mathrm{a}]{\dot{\mathrm{R}}} \mathrm{R{-}R} \\ \xrightarrow[\mathrm{b}]{\mathrm{(NCS)_2}} \mathrm{RSCN\ or\ RNCS} \end{cases} \tag{7}$$

$$\mathrm{RCo^{III}(dmgH)_2Py} \xrightarrow{\mathrm{(NCS)^{\bullet}}} \mathrm{RSCN\ or\ RNCS} + \mathrm{Co^{II}(dmgH)_2Py} \tag{8}$$

$$\mathrm{Co^{II}(dmgH)_2Py} + \mathrm{(SCN)_2} \longrightarrow \mathrm{NCSCo^{III}(dmgH)_2Py} + \mathrm{(SCN)^{\bullet}} \tag{9}$$

$$\begin{array}{l} \mathrm{Co^{II}(dmgH)_2} + \mathrm{(SCN)_2} \longrightarrow \mathrm{NCSCo^{III}(dmgH)_2} + \mathrm{(SCN)^{\bullet}} \\ \qquad\qquad\qquad\qquad\qquad\quad \Big\downarrow \mathrm{Py} \\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{NCSCo^{III}(dmgH)_2Py} \end{array} \tag{10}$$

Scheme 1.

The results can be explained by the reaction Scheme 1.

After one electron oxidation of five-coordinate species (eqn. (2)), $\mathrm{(SCN)_2}^{\dot{-}}$ must break to $\mathrm{(SCN)^-}$

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*It is reported that if the reactions are carried out in the dark at room temperature and under an inert atmosphere, the homolytic cleavage of the S–S bond by thiocyanogen is largely prohibited [6a].

**$\mathrm{(SCN)_2} \rightarrow \mathrm{(SCN)_2}^{\dot{-}}$ ($E° = 0.783$ V), $4\text{-}\mathrm{RC_6H_4CH_2Co^{III}(dmgH)_2Py} \rightarrow 4\text{-}\mathrm{RC_6H_4CH_2Co^{IV}(dmgH)_2Py}$ (R = H, Me, Cl, CN, NO_2) ($E° > 0.80$ V) [8].

†The rate of dissociation of pyridine from $4\text{-}\mathrm{RC_6H_4CH_2Co^{III}(dmgH)_2Py}$ (R = H, Me, Cl, CO, OMe) is very high [(>0.4–61) × 10^4 s^{-1}] [10].

and (NCS)$^{\cdot}$ (eqn. (3)). The fate of $(SCN)^-$ whose nucleophilic reactivity is better than Cl^-, will be to undergo bimolecular nucleophilic attack at the organocobalt(IV) species to form benzyl thiocyanate [8] (eqn. (4a)). The fate of (NCS)$^{\cdot}$, however, is difficult to assess since it can undergo many reactions including a homolytic displacement at carbon in $RCo^{III}(dmgH)_2Py$ (eqn. (8)) to form both thiocyanate and isothiocyanate*. It may oxidise more of $RCo^{III}(dmgH)_2$ to form $RCo^{IV}(dmgH)_2NCS$ (eqn. (5)) which will undergo unimolecular homolysis to form R$^{\cdot}$ and $Co^{III}(dmgH)_2NCS$ (eqn. (6)). R$^{\cdot}$ so formed may dimerise to form R–R (eqn. (7a))** or it may react with $(NCS)_2$ to form RSCN or RNCS (eqn. (7b)).

Though it is very difficult to assess the relative contribution of each factor towards the formation of total benzyl thiocyanates, it is beyond doubt that oxidative dealkylation occurs on the five-coordinate organocobaloxime species and it definitely induces free radical reactions in solution. Interestingly, it seems that the reactivity and mechanism of thiocyanogen resembles iodine reactions in these systems. For example, 4-methoxybenzyl cobaloxime (3) on reaction with Cl_2 and Br_2 forms exclusively the ring substituted toluene, 2-halo-4-methoxy toluene, by a concerted electrophilic mechanism [51] whereas 3 on reaction with I_2 it forms exclusively 4-methoxybenzyl iodide via an oxidative dealkylation mechanism on the intermediate five-coordinate species [10].

It is surprising to find that the only inorganic product obtained is the sulphur bonded $NCSCo^{III}(dmgH)_2Py$, though one may expect the formation of both N- and S-bonded cobaloxime.

Experimental

Benzyl and substituted benzyl cobaloximes were prepared by the literature procedure from cobaloxime(I) and the corresponding benzyl halide [5h]. The cobaloxime(I) was generated *in situ* by the anaerobic disproportionation of cobaloxime(II) in methanol by Schrauzer's method [15]. Thiocyanogen was prepared fresh for each experiment as described below. (A small percentage (10%) is known to polymerise within the reaction time and conditions.)

A solution of Br_2 (10% solution, 4.3 mmol in 10 ml chloroform) was added dropwise to a stirred suspension of lead thiocyanate* (4-fold excess, 5.6 g, 17.3 mmol in 20 ml chloroform). The suspension was stirred for a further 20 min after the bromine colour was discharged. The solution was used immediately after filtration.

Reaction with Thiocyanogen

A freshly prepared solution of thiocyanogen (4.3 mmol in 30 ml chloroform) was added dropwise to a dilute solution of organocobaloxime (2.1 mmol in 20 ml chloroform) in the dark under a nitrogen atmosphere. The course of the reaction was monitored by TLC on silica gel G (Merck). After the reaction was over (0.7–1.5 h) the reaction mixture was filtered into a large excess of pentane. The solvent was removed in vacuum and the products were further separated on silica gel G or alumina (neutral) and/or by GLC. The inorganic product was separated and characterised as $NCSCo^{III}(dmgH)_2Py$.

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*This statement is supported by an independent experiment; for example, 4-chlorobenzyl cobaloxime (4) with thiocyanogen under free radical conditions (irradiation by 2 × 200 W tungsten lamps) at room temperature forms both 4-chlorobenzyl thiocyanate and 4-chlorobenzyl isothiocyanate.

**This is the only route by which R–R can be formed.

*A pure sample was prepared from potassium thiocyanate (19.4 g, in 85 ml water) and lead(II) nitrate (33.1 g in 150 ml water) by the procedure of Gardener and Weinberger [16].

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