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Preliminary communication

The reactions of alkyl–cobalt Schiff base complexes with hydrogen sulfide ion

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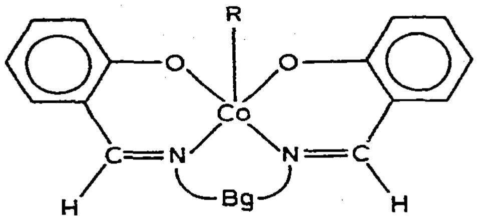
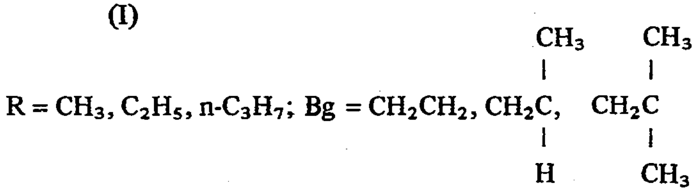
We have prepared a variety of alkyl–cobalt complexes [RCo(SalBg)] (I) containing tetradentate Schiff base ligands, using modifications of published syntheses[1,2]. All complexes gave satisfactory analyses.



(I)



$$\mathrm{R = CH_3, C_2H_5, n\text{-}C_3H_7;\ Bg = CH_2CH_2, CH_2\underset{H}{\overset{CH_3}{C}},\ CH_2\underset{CH_3}{\overset{CH_3}{C}}}$$

We attempted to break the cobalt–alkyl bond by treating [RCo(SalBg)] in methanol with a variety of potential nucleophiles under anaerobic conditions in the dark. Most of the nucleophiles did not cleave the cobalt–carbon bond, but excess sodium hydrogen sulfide (NaHS) breaks the cobalt–carbon bond at pH 10. The reaction is very slow at room temperature, but is readily observed at 48°C. The products obtained are shown in Eqn. 1. The alkane (RH) was identified by gas–liquid phase chromatography

$$\mathrm{[RCo(SalBg)] + 2HS^- \rightarrow RH + [(HS)_2Co^{III}(SalBg)]^-} \tag{1}$$

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(GLPC) and the isolated Na[$(HS)_2Co^{III}$ (SalBg)] gave a satisfactory analysis. The presence of the cobalt(III) product formed under anaerobic conditions suggest a carbanionic intermediate species. The absence of [Co^{II} (SalBg)] rules out both free radical and carbonium ion transfer mechanisms. Because no oxidizing agent is present, the [Co^{II} (SalBg)] formed during a free radical reaction would be a final product. The cobalt product of a carbonium ion transfer mechanism would be [Co^{I}(SalBg)]$^{-}$. The cobalt(I) complex is not stable at pH 10 in methanol, but is oxidized to [Co^{II} (SalBg)]. Despite a careful search using GLPC, not even a trace of a thiol (RSH) was found after acidification. A thiol would be a product of a carbonium ion transfer mechanism. The alkane product (Eqn. 1) is formed by proton abstraction by the carbanion from methanol. We found that homolytic pyrolysis of the cobalt–carbon bond resulting in an alkane and [Co^{II} (SalBg), is much slower under the reaction conditions in the absence of HS

The results of Schrauzer and Windgassen[3] and our present results suggest that the reactions of [RCo$(DMG)_2$Py] (R = CH_3, C_2H_5; DMG = dimethylglyoximato anion) with alkyl thiolates (CH_3S^- or $C_2H_5S^-$) go by a carbonium ion transfer in methanol at pH 13 under anaerobic conditions. After two days at room temperature we found traces of alkyl sulfides and unreacted [RCo$(DMG)_2$Py], but no alkane. The DMG complexes react by carbonium ion transfer to the alkyl thiolate ion to form an alkyl sulfide (Eqn. 2). Thus the [RCo(SalBg)] and the [RCo$(DMG)_2$Py] systems react by carbanion and carbonium ion transfer, respectively. This diverse behavior is rationalized by the results

$$[\mathrm{RCo(DMG)_2Py}] + \mathrm{R'S^-} \rightarrow \mathrm{R'SR}\ (\text{traces}) \tag{2}$$

of Costa and co-workers[4,5], who demonstrated that the DMG ligands are more electron-withdrawing than the SalBg ligands. The fact that is is much harder to reduce [Co^{II} (SalBg) than [Co^{II} $(DMG)_2$] to the Co^{I} complex before alkylation is in agreement with the higher stability of [Co^{I} $(DMG)_2$]$^{-}$.

The electrophilic cobalt–alkyl bond cleavage in the [RCo$(DMG)_2$Py] system by mercury(II) gave the following rate order: methyl $\gg$ ethyl $>$ n-propyl[6,7]. These results led to the conclusion that an S_E2 mechanism occurred with direct attack at the cobalt–carbon bond. The relative rate of alkane evolution in our experiments is. propane $\gtrsim$ ethane $\gg$ methane. This order indicates that HS$^-$ attacks *trans* to the alkyl group. This conclusion is in agreement with the instantaneous change in the spectrum of [RCo(SalBg)] upon adding HS$^-$. The *trans*-HS$^-$ group weakens the cobalt–carbon bond, the carbanion is ejected, and it abstracts a proton from the solvent to form the alkane. The probable mechanism of the reaction is given in Eqn. 3. We obtained analogous results when we anaerobically reacted thiolate

$$[\mathrm{RCo(SalBg)}] + \mathrm{HS^-} \xrightarrow[\mathrm{CH_3OH}]{\text{fast}} [\mathrm{RCo(SalBg)(SH)}]^- \tag{3a}$$

$$[\mathrm{RCo(SalBg)(SH)}]^- \xrightarrow{\text{slow}} \mathrm{R^-} + [\mathrm{Co^{III}(SalBg)(SH)}] \tag{3b}$$

$$[\mathrm{Co^{III}(SalBg)(SH)}] + \mathrm{HS^-} \xrightarrow{\text{fast}} [\mathrm{(HS)_2Co^{III}(SalBg)}]^- \tag{3c}$$

$$R^- + CH_3OH \xrightarrow{\text{fast}} RH \qquad (3d)$$

anions ($R'S^-$) with [RCo(SalBg)] at pH 10 and 48°C. Schrauzer *et al.* also postulate a *trans* attack when treating thiols with alkyl—cobalt complexes under neutral or slightly acidic conditions[8].

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