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A NEW PHOTOCHEMICAL REACTION OF ORGANO-COBALT(III) COMPLEXES WITH CARBON MONOXIDE IN ALCOHOL

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We recently prepared[1,2] the new series of stable organometallic derivatives of Co(III) chelates :$[R\text{-}Co(III)(BAE)L]$, ($R = CH_3$, C_2H_5, C_6H_5; BAE = bis(acetylacetone)ethylendiiminato; L = H_2O, pyridine) and $[R\text{-}Co(III)(salen)L]$, ($R = CH_3$, C_2H_5, C_3H_7, C_4H_9, C_6H_5; (salen) = bis(salicylaldehyde)ethylendiiminato; L = NH_3, H_2O, pyridine) by reaction of Co(III) chelates $[Co(III)(BAE)L_2]^+$, $[Co(III)BAE)LX]$, $[Co(III)(salen)L_2]^+$ or $[Co(III)(salen)LX]$, with the appropriate Grignard reagent.

We now report a new photochemical reaction of the alkyl-cobalt chelates of (salen) with carbon monoxide and the thermal and photochemical cleavage of the cobalt-carbon bond.

When $[R\text{-}Co(III)(salen)H_2O]$ ($R = CH_3$, C_2H_5, nC_4H_9) is irradiated with visible light in alcohol solution in the presence of carbon monoxide at atmospheric pressure, the complexes $[R'O\text{-}\underset{\displaystyle O}{C}\text{-}Co(III)(salen)H_2O]$ ($R' = CH_3$ in methanol, C_2H_5 in ethanol and isoC_3H_7 in isopropyl alcohol solution) are obtained in almost quantitative yield. No reaction was observed in the dark. The products are well characterized, crystalline, stable, orange-yellow compounds. They are identical to those obtained from $[Co(II)(salen)]$ by reduction with 1% sodium amalgam, followed by reaction with ClCOOR' ($R' = CH_3$, C_2H_5).

The complexes $[RCOCo(III)(salen)H_2O]$ which can be obtained from $[Co(II)(salen)]$ by reduction and reaction with RCOCl, are not formed by the photochemical reaction with CO.

Cleavage of the cobalt-carbon bond in the organocobalt complexes of (salen) takes place either by thermal and photochemical reaction. Heating $[RCo(III)(salen)H_2O]$ (R = alkyl) in the solid state to 200°C under vacuum gives $[Co(II)(salen)]$ in quantitative yield. Solutions of $[RCo(III)(salen)H_2O]$ are light sensitive and formation of $[Co(II)(salen)]$ was observed in anaerobic condition (photoreduction). The Co(II) complex readily undergoes reoxidation to a dicyano-Co(III) derivative in the presence of the CN^- ions and air. In the presence of cyanide ions (methanol-water solution, aerobic condition) $[RCo(III)(salen)H_2O]$ undergoes both photolysis of Co-C bond and substitution of the trans ligand yielding $[Co(III)(salen)(CN)_2]^-$. An analogous reaction was reported for the alkyl-cobalt aetioporphyrin I [3].

The thermal and photochemical reduction of cobaltic derivatives to cobaltous complex of (salen) takes place by the homolytic cleavage of the Co-C bond as was proposed in the chemistry of vitamin B_{12} [4,5].

In view of the photochemical reaction of $[RCo(III)(salen)H_2O]$ under anaerobic conditions to give $[Co(II)(salen)]$, the initial cleavage of the Co-C bond in the carbon monoxide reaction is suggested. The subsequent step is likely to be hydrogen abstraction by the methyl group from R'OH followed by carbonyl insertion.

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