

ACYL- AND CARBOXYALKYL-COBALT(III) CHELATES

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We recently prepared^{1,2} the new series of stable organometallic derivatives of Co(III) chelates: $[R-Co(III)(BAE)L]$, (R = CH₃, C₂H₅, C₆H₅; BAE = bis(acetylaceton)ethylendiiminato; L=H₂O, pyridine) and $[R-Co(III)(salen)L]$, (R = CH₃, C₂H₅, C₃H₇, C₄H₉, C₆H₅; (salen) = bis(salicylaldehyde)ethylendiiminato; L = NH₃, H₂O, 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 different method for the preparation of the above and other organometallic complexes "via" reduction of the parent Co(III) complexes which point out strong analogies with the preparation of derivatives in the cobalamin series by reactions of the reduced species B₁₂S and suggests that the above complexes should be further investigated as model molecules for the vitamin B₁₂ group.

Co(III) or Co(II) chelates of (salen) (e.g. $[BrCo(III)(salen)PPh_3]$ or $[Co(II)(salen)]$) are reduced with 1% sodium amalgam in dry degassed THF giving a Co(I) deep green solution which by reaction with CH₃I and hydrolysis yields $[CH_3Co(III)(salen)H_2O]$. By the same way the reaction with RCOCl or (RCO)₂O yields the corresponding acyl derivatives $[R-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Co(III)(salen)H_2O]$ and with ClCOOR the carboxyalkyl-cobalt derivatives $[RO-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Co(III)(salen)H_2O]$. All products are well characterized, diamagnetic, crystalline, stable yellow to brown compounds.

In view of the magnetic susceptibility the new complexes are formulated as cobaltic compounds and the organic group is considered to be a carbanion.

The I.R. carbonyl absorptions (CH₂Cl₂ solution) were:

$[CH_3COCo(III)(salen)H_2O] \nu_{CO} = 1728 \text{ cm}^{-1}$; $[CH_3COCo(III)(salen)H_2O] \nu_{CO} = 1716 \text{ cm}^{-1}$.

The reduction of the cobalt chelates of (BAE) with 1% sodium amalgam gave similar results, but $[\text{ROCOCo(III)(BAE)H}_2\text{O}]$ complexes are unstable and $[\text{Co(II)(BAE)}]$ was obtained instead.

The reduction with sodium borohydride either of (salen) and (BAE) chelates of Co(III) gives only $[\text{Co(II)(salen)}]$ and $[\text{Co(II)(BAE)}]$ respectively. In the presence of CH_3I only $[\text{Co(III)(BAE)L}_2]^+$ or $[\text{Co(III)(BAE)LX}]$ give the methyl-cobalt derivative. The intermediate formation of the Co(I) species is assumed in this case.

The behaviour of Co(III) complexes of (salen) towards reduction parallels that of aetioporphyrin I, which gives with several reducing agents the Co(II) species but requires the reaction with 1% sodium amalgam to give the Co(I) species ³.

On the other hand either the cobalamins ⁴ and the Co(III)-dimethylglyoxime complexes ⁵ are reduced to Co(I) complexes even by sodium borohydride.

The preparations of above organocobalt derivatives by reactions of the reduction products of Co(III) complexes parallels the methods of obtaining the corresponding derivatives in the cobalamins series ⁴, of the organocobalt(III) derivatives of dimethylglyoxime ⁵ and of aetioporphyrin I ³.

References

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