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TRANSMETHYLATION REACTIONS : ORGANOMETALLIC COBALT CHELATES AS GRIGNARD REAGENTS IN PROTOGENIC SOLVENTS

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It was recently shown (1,2) that the Co(I)-CH_3 derivative chemically or electrochemically generated by reduction of cobalt chelate of 1-diacetylmonoximato-imino-3-diacetylmonoxime imino propane monoanion {(DO)(DOH)pn} behaves as a methylating agent toward the Co(III) starting complex

$$[CH_3Co\{(DO)(DOH)pn\}H_2O]^+ + 2e \longrightarrow [CH_3Co\{(DO)(DOH)pn\}]^-$$

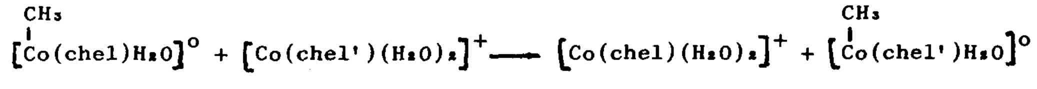
$$[CH_3Co\{(DO)(DOH)pn\}]^- + [CH_3Co\{(DO)(DOH)pn\}H_2O]^+ \longrightarrow [(CH_3)_2Co\{(DO)(DOH)pn\}]^0 + [Co\{(DO)(DOH)pn\}H_2O]^0$$

We also reported (3) that the dimethylderivative can in turn act as a methylating agent toward protons and electrophylic metal atoms including Co(III) in Vit.B_{12a} and model chelates (4)

$$[(CH_3)_2Co\{(DO)(DOH)pn\}]^0 + \underset{\text{I a-c}}{[Co(chel)(H_2O)_2]^+} \longrightarrow \underset{\text{II a-c}}{[CH_3Co(chel)H_2O]^0} + [CH_3Co\{(DO)(DOH)pn\}H_2O]^+$$

where chel is one of the following dianions : a) bae = N,N'-ethylene-bis-(acetylacetone iminato); b) salen = N,N'-ethylene-bis-(salicylidene iminato); c) saloph = N,N'-o-phenylene-bis-(salicylidene iminato).

We have now found that the transmethylation between two cobalt atoms of different chelates of the above type is a general reaction



$$\underset{\text{II a-c}}{[\overset{CH_3}{\overset{|}{Co}}(chel)H_2O]^0} + \underset{\text{I a-c}}{[Co(chel')(H_2O)_2]^+} \longrightarrow [Co(chel)(H_2O)_2]^+ + [\overset{CH_3}{\overset{|}{Co}}(chel')H_2O]^0 \qquad (A)$$

$$[\overset{CH_3}{\overset{|}{Co}}(chel)]^0 + \underset{\text{III}}{[Co\{(DO)(DOH)pn\}(H_2O)_2]^{2+}} \longrightarrow [Co(chel)(H_2O)_2]^+ + [\overset{CH_3}{\overset{|}{Co}}\{(DO)(DOH)pn\}H_2O]^+ \qquad (B)$$

Methyl donor and acceptor properties of metal atoms are determined by the nature of chelating agent.

Thus in water-methanol, at room temperature and in the dark, transmethylation occurs with high yield ($\sim$90%) from IIa to Ib or Ic and from IIa or b or c to III and to aquocobalamin (Vit.B_{12a}) but not in the reverse direction.

All the reaction products were isolated and characterized by visible and I.R. spectrum as compared with authentic samples.

Using III as the methyl acceptor we obtained preliminary data on the rate of reaction (B) which decreases in the order CH_3-Co(bae) $>$ CH_3Co-salen $>$ methylcobalamin.

The same order was observed in the reaction of methylderivatives with Ag^+ yielding metallic silver.

The above trend is fully consistent with the trend of other properties (4) related to the effective charge on cobalt atom decreasing from Co(III)bae to Co(III)$\{$(DO)(DOH)pn$\}$ chelates and strongly suggests a carbanion transfer mechanism.

The strong influence of the chelating agent in the donor complex rules out the dissociation of the acceptor aquocomplex as the rate determining step. A binuclear CH_3-bridged complex could be involved in the transition state.

All the above transmethylation reactions appear to go to completion but it could be anticipated that the reaction A between chelates showing only slightly different electronic structure should lead to an equilibrium.

Present transmethylation reaction can be studied as model of the Vit.B_{12} dependent methionine biosynthesis, methane formation and acetate biosynthesis. In the last two cases the methyl group is most likely transferred as a carbanion to the proton and to the CO_2 respectively (5).

The carbanionic reactivities of several organic groups in organometallic derivatives of above chelates are being studied to replace Grignard reagents in protogenic solvents.

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