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Preliminary communication

COBALT CHELATES WITH TETRADENTATE LIGANDS: REACTIONS WITH ACETYLENE

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Summary

The reactions between acetylene and Co^I, Co^{II} and Co^{III} chelates are described.

It is well known that the strong nucleophiles $[Co^I Chel]^-$ [Chel = *N,N'*-ethylenebis(acetylacetoneiminato); *N,N'*-ethylenebis(salicylideneiminato) (bae); *N,N'*-ethylenebis(7,7'-dimethylsalicylideneiminato) (salen)] react readily with acetylene to give vinylaquo-derivatives by addition of water to the triple bond [1, 2]. We have now found that cobalt(III) derivatives of the type $[Co^{III}Chel(OH)H_2O]$ also react with acetylene in anhydrous ethanol in the presence of NaOH, but to give ethynylaquo-derivatives of the type $[CH{\equiv}CCo(Chel)H_2O]$ by addition of water.

The products were isolated as pure compounds with satisfactory elemental analyses. The presence of the σ-bonded ethynyl group is confirmed by the infrared spectra, which show $\equiv$CH and C$\equiv$C stretching vibrations (Chel = salen : $\nu(\equiv CH)$ 3260, $\nu(C{\equiv}C)$ 1982 cm^{-1}). Analogous results were obtained with phenylacetylene. The complex $[PhC{\equiv}CCo(salen)Mid]$ (Mid = *N*-methylimidazole) shows the $\nu(C{\equiv}C)$ at 2110 cm^{-1}.

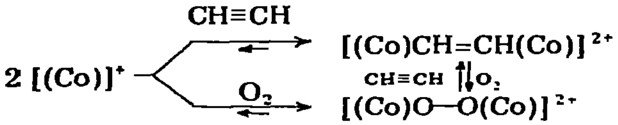
While the alkyl and aryl derivatives give five-coordinated forms readily in non-coordinating solvents [3] the ethynyl compounds do not form this kind of complex. On the other hand the water is displaced by nitrogen donor ligands and hexacoordinated derivatives can be obtained without difficulty. The higher stability of the hexacoordinated species can be explained by the *trans*-influence of the ethynyl group, which is lower than that of alkyl or aryl groups.

Reaction of Co^{II} with acetylene was observed with $[Co^{II}\{(DO)(DOH)pn\}H_2O]PF_6$ ({(DO)(DOH)pn} = diacetylmonoximeiminodiacetylmonoximatoiminopropane). With a stoichiometric ratio of 2/1, the reaction occurs rapidly in acetonitrile or methanol, to give a binuclear complex analogous to that obtained with pentacyanocobaltate [4]. The reaction is reversible and the starting chelate is reformed by bubbling nitrogen through the solution. The displaced acetylene was identified by GLC.

On reaction with $NaBH_4$ the binuclear complex gives the Co^{I} derivative and ethylene (100%). Pure crystalline complexes of the type $[(LCoChel)_2CH{=}CH]^{2+}$ can be isolated by coordination to the binuclear complexes of nitrogen donor ligands (L), which have stabilizing properties. Molecular oxygen also reacts reversibly in a 2/1 ratio.

The parallel behaviour of acetylene and dioxygen as bridge ligands in the binuclear complexes was shown by the facile displacement of acetylene by dioxygen and viceversa (Scheme 1).

SCHEME 1



This reaction was not observed with PhC≡CH probably owing to steric hindrance.

It is interesting to note that the {(DO)(DOH)pn} derivatives give binuclear complexes with both acetylene and oxygen, while the salen and bae derivatives only react with the latter [5, 6] . This is probably due to a more pronounced radical character in the DOH derivatives, associated with a less extended delocalization of the unpaired electrons. The study of the reactions of the binuclear adducts is in progress.

From the above results it can be assumed that the reaction between acetylene and Co in the different oxidation states involves initially π-coordination of the acetylene to the metal, followed for the Co^{I} derivatives by an electrophilic attack of the proton, and for the Co^{III} derivatives by a nucleophilic attack of the OH^- with proton abstraction. The adduct from the Co^{II} derivatives reacts as a radical species. It appears therefore that the nucleophilic, radical, and electrophilic character of the cobalt atom in the Co^{I}, Co^{II} and Co^{III} derivatives is transferred to the coordinated acetylene in the reaction intermediate. The clearly different mechanisms of the above reactions show the flexible behaviour of the cobalt atom when coordinated with a tetradentate system.

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