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Preliminary communication

COBALT(I) AND COBALT(III) DERIVATIVES FROM THE REACTIONS OF PHOSPHINE LIGANDS WITH COBALT(II) SALTS CONTAINING LOW-COORDINATING ANIONS

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Summary

Complexes of the type $[Co(CO)_n(P)_{5-n}]ClO_4$, $[CoH_2(P)_4]ClO_4$, $[CoH(P)_5](ClO_4)_2$ and $[CoHX(P)_4]ClO_4$ (P = secondary or tertiary phosphine) have been prepared from $Co(ClO_4)_2 \cdot 6\,H_2O$ and phosphine in isopropyl alcohol.

Alcohol solutions of phosphines and cobalt(II) salts containing low-coordinating anions exhibit somewhat unexpected chemical behaviour. We previously reported that the reaction of phosphines with cobalt(II) nitrate gives nitrosyl derivatives $[Co(NO)(P)_3]$ (P = secondary and tertiary phosphines) [1]. We report below some reactions of the isopropyl alcohol solutions containing cobalt(II) perchlorate and phosphines, which react with π-acceptor ligands to give cobalt(I) derivatives; with molecules which undergo oxidative additions, cobalt(III) adducts are formed. The products are those expected if the reacting species were of the type $[Co(P)_4]^+$ or $[Co(P)_5]^+$ and this suggests the existence of a potentially general synthetic route to cobalt complexes in the oxidation states +1 and +3.

The synthetic procedures are illustrated in Scheme 1 and by the following examples.

When $Co(ClO_4)_2 \cdot 6\,H_2O$ is allowed to react in isopropyl alcohol at ambient conditions with phosphines in an atmosphere of carbon monoxide, cobalt(I) carbonyls of general formula $[Co(CO)_n(P)_{5-n}]ClO_4$ (n = 1, 2, 3) are formed. The rate of formation of the carbonyl complexes is very high with relatively small phosphines ($HPEt_2$, HPMePh), and decreases with increasing size of the ligands. With large tertiary phosphines, such as PPh_3 and PCy_3, no formation of carbonyls was observed. Carbon monoxide uptake measure-

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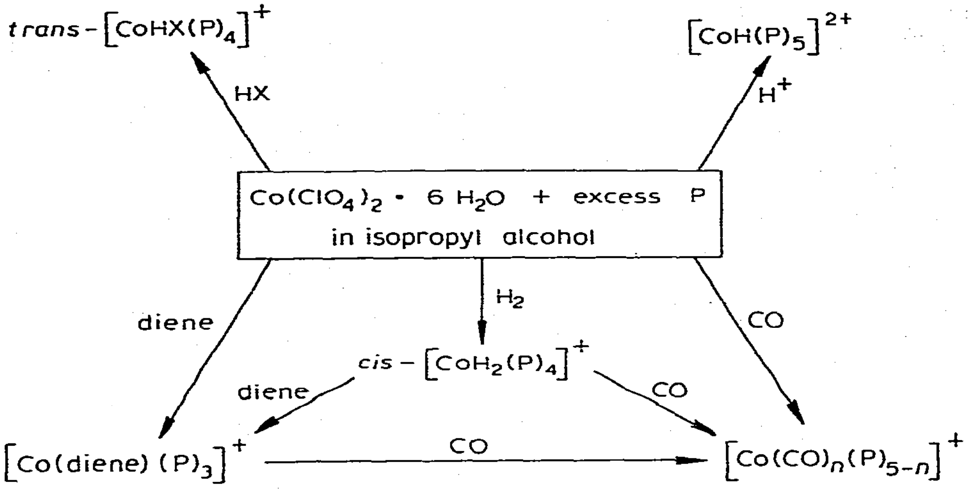
Scheme 1



P = secondary or tertiary phosphines

ments indicate that the cobalt(II) originally present in solution is quantitatively transformed into cobalt(I) complexes.

Other π-acceptors have been shown to promote the reduction of cobalt(II) to cobalt(I). For example, the reaction of cobalt(II) perchlorate with conjugated diolefins and phosphines in isopropyl alcohol yields $[Co(diene)(P)_3]^+$ complexes [2]. Preliminary data indicate that this method can also give cationic phosphino-isonitrilo complexes of cobalt(I). The stoichiometry and mechanism of all these reactions have not yet been established, but it is noteworthy that in many cases GLC analysis of the reaction mixtures revealed the presence of acetone, suggesting that isopropyl alcohol is involved in the reduction processes.

If the reaction between cobalt(II) perchlorate and phosphines is carried out in the presence of dihydrogen, slow formation of pale-yellow dihydrido complexes $[CoH_2(P)_4]^+$ occurs; again the rate of reaction is very sensitive to changes in the phosphine ligands. By this method we isolated as solids the complexes with the phosphines $HPPh_2$, PMe_2Ph and PMe_3, but with large tertiary phosphines the reaction failed. For the complexes $[CoH_2(P)_4]^+$ a *cis*-arrangement of the hydrido groups is indicated by the IR spectra, which show two bands in the 1900-2000 cm^{-1} region. The compounds are fairly unstable in the crystalline state and slowly decompose in solution, probably with elimination of H_2. If they are dissolved in the presence of π-acceptors, such as CO or conjugated dienes, reductive elimination of H_2 rapidly occurs to give the corresponding cobalt(I) derivatives $[Co(CO)_n(P)_{5-n}]^+$ or $[Co(diene)(P)_3]^+$ mentioned above. An alternative route to the dihydrido complexes, and therefore to carbonyl or diene derivatives, involves protonation of the $[CoH(P)_4]$ [3] species by $HClO_4$ to give $[CoH_2(P)_4]^+$.

Treatment of the isopropyl alcohol solutions of $Co(ClO_4)_2$ with the secondary phosphines HPMePh and HPEtPh slowly affords hydrido complexes of cobalt(III) of the type $[CoH(P)_5]^{2+}$ (ν(CoH) at about 1950 cm^{-1}), probably via protonation of a $[Co(P)_5]^+$ intermediate. The formation of these derivatives is much faster if powdered zinc is present.

Finally, in the case of diphenylphosphine, addition of HX (X = halogen or pseudohalogen) to the system $Co(ClO_4)_2$—phosphine in alcohols yields hydrido derivatives of cobalt(III) of the type *trans*-$[CoHX(P)_4]^+$ (ν(CoH) at about 2000 cm^{-1}). Detailed discussion of these processes will be presented later.

Acknowledgment

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Reference

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