Tricarbonylbis(triphenylphosphine)cobalt(I) salts

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Summary: The reaction between octacarbonyl-dicobalt and triphenylphosphine has been investigated. While other researches had obtained from this reaction a product formulated as $\{Co[(C_6H_5)_3P](CO)_3\}_2$, the present investigation showed that the actual product is an ionic compound, of formula $\{Co[(C_6H_5)_3P]_2(CO)_3\}^+[Co(CO)_4]^-$. By exchange from this, other salts, such as chloride, iodide, nitrate, perchlorate, periodide, trichlorocobaltate (II) and diiodocuprate(I) were obtained. Another synthesis for some salts of the above cation is also described; i. e. the reaction of carbon monoxide at high pressure with compounds of the type $Co[(C_6H_5)_3P]_2X_2$ which were unknown before this work.

It is well known that, when octacarbonyldicobalt is treated with bases, either strong or weak, such as e. g. ammonia, pyridine and o-phenanthroline, a disproportionation reaction takes place, in which derivatives of cobalt(II) and cobalt(-I), are formed:

$$3[Co(CO)_4]_2 + 12\,NH_3 = 2\,[Co(NH_3)_6]\,[Co(Co)_4]_2 + 8\,CO$$

The first step of the above reaction must be considered the following:

$$[Co(CO)_4]_2 + \mathfrak{B} \rightleftarrows [Co\,\mathfrak{B}\,(CO)_4]^+\,[Co\,(CO)_4]^-$$

but the cation $[Co\,\mathfrak{B}\,(CO)_4]^+$, where $\mathfrak{B}$ is ammonia, pyridine and o-phenanthroline, cannot be isolated as a further disproportionation occurs very soon:

$$3[Co\,\mathfrak{B}\,(CO)_4]^+ \rightarrow 3\,\mathfrak{B} + 2\,Co^{++} + [Co(CO)_4]^- + 8\,CO$$

It is well known that the reaction of octacarbonyldicobalt with isonitriles [1] gives a stable product corresponding to the first step of the scheme quoted above:

$$5\,RNC + Co_2(CO)_8 = [(RNC)_5Co]^+\,[Co(CO)_4]^- + 4\,CO$$

Therefore it appeared very interesting to investigate the behaviour of octacarbonyldicobalt with other ligands capable of double bonding, such as e. g. triphenylphosphine, which is known to substitute one or more molecules of carbon monoxide in metal carbonyls. In the case of nickel, the following products have been described: [2]

$$Ni(CO)_3PR_3;\ Ni(CO)_2(PR_3)_2;\ Ni(PCl_3)_4$$

In 1948 W. Reppe and co-workers [3] by reacting octacarbonyldicobalt and triphenylphosphine obtained a compound which was formulated as $[Co(Co)_3PR_3]_2$. However, as observed by W. Hieber, the solutions of this compound have a high electric conductivity; this fact ruled out the formula suggested by Reppe but left the problem unsolved. Therefore we decided to reinvestigate thoroughly this reaction.

The reaction between octacarbonyldicobalt and triphenylphosphine, in hexane solution and at room temperature, gives a product which on recrystallization from chloroform is obtained in the form of yellow-brown crystals, having a composition corresponding to $Co_2(PR_3)_2(CO)_7.CHCl_3$, which may be formulated as $[Co(PR_3)_2(CO)_3]^+\ [Co(CO)_4]^-.\ CHCl_3$.

The ionic character of this compound is confirmed by the high electric conductivity of its solutions ($\simeq 24$ ohm^{-1} cm^2 for a 10^{-3} M nitrobenzene solution) and by the fact that other salts, such as chloride, iodide, periodide, perchlorate, nitrate and trichlorcobaltate(II), can be obtained from it by exchange. These salts are quite stable in air, both in the solid state and in solution; they are diamagnetic, soluble in polar organic solvents such as chloroform, acetone, alcohol, nitrobenzene, insoluble in non-polar solvents such as benzene and petroleum ether. They are all pale-yellow in colour, with the exception of the periodide, brown, and of the trichlorocobaltate, green. The tetracarbonylcobaltate $[Co(PR_3)_2(CO)_3]$ $[Co(CO)_4]$, which is by far the less stable of the salts prepared, and decomposes in a few days if exposed to the air, on mild warming in benzene solution looses carbon monoxide giving an unsoluble, microcrystalline brown-red product which has a composition corresponding approximatively to the compound described by Reppe. This compound is also obtained directly on reacting carbonyldicobalt and triphenylphosphine in hot benzene solution.

The salts of tricarbonylbis(triphenylphosphine)cobalt(I) cation can also be prepared by a different method, using as starting material the addition product of triphenylphosphine with cobalt(II) iodide, that we have recently prepared for the first time, and will be described in a subseguent paper.

This compound, when heated with carbon monoxide at 200 atm. and 70° C, in presence of copper powder, give a product which, after crystallization from chloroform and hexane, has a formula correponding to $[Co(PR_3)_2(CO)_3]^+\ [CuI_2]^-.\ CHCl_3$.

Triethylphosphine reacts analogously to triphenylphosphine, while the reaction with aliphatic and aromatic phosphites gives substitution products of the type $\}Co[P(OR)_3](CO)_3\{_2$, already described by one of us [4].

It is interesting to remark that the salts of tricarbonyl(bistriphenylphosphine)cobalt(I) are the first exemple of compounds in which carbon monoxide is present in a positive complex ion. The carbon monoxide to metal bond is so strong, that the former is not evolved by treating these complexes with iodine in pyridine; while under the same conditions it is displaced quantitatively from the tetracarbonylcobaltate anion, the carbonyl itself and from its substitution compounds containing phosphites. However, carbon monoxide can be desplaced quantitatively by aromatic isonitriles.

It is therefore evident that trialkyl and triarylphosphines tend to stabilize the oxidation number + 1 for the cobalt, similarly to isonitriles: while trialkyl and triarylphosphites are, under this respect, more similar to carbon monoxide. This difference in behaviour between phosphines and phosphitès may be related to the fact that the phosphorus atom of phosphites has a stronger tendency to form double bonds, than the phosphorus atom of the phosphines; the same can be said of carbon monoxide with respect to isonitriles. The serie proposed by Hieber [5] can therefore be completed as follows:

$$[Co(NH_3)_6]^{+++};\ [Co(CNR)_5]^{+};\ [Co(PR_3)_2(CO)_3]^{+};$$

$$\}Co[P(OR)_3](CO)_3\{_2^0;\ [Co(CO)_4]_2^0;\ [Co(CO)_4]^{-}$$

In this series the double bond character acting between ligand and metal, which does not intervene in the ammine complex, should therefore increase from $[Co(CNR)_5]^{+}$ to $[Co(CO)_4]^{-}$.

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