A New Organometallic Reagent, $KCo[P(OR)_3]_4$

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Summary Synthesis of $KCo[P(OR)_3]_4$ (R = Me and Et) from KH and $HCo[P(OR)_3]_4$ has provided entry to a variety of organometallic compounds containing $Co[P(OR)_3]_4$ and $Co[P(OR)_3]_3$ groups.

THE hydrogen atom in the *quasi* tetrahedral[1] hydrides $HM[P(OR)_3]_4$ (M = Co, Rh) is quite strongly bound in contrast to the hydrogen atom in the analogous carbonyl (cobalt) and phosphorus trifluoride-based hydrides. We have long sought the preparation of $M^+Co[P(OR)_3]_4^-$ as a reagent for the synthesis of stable cobalt alkyl derivatives and organometallic complexes with a $Co[P(OR)_3]_{3 \text{ or } 4}$ group. We have now successfully prepared $K^+Co[P(OR)_3]_4^-$ with R = Me and Et and find that the salt is, indeed, a versatile organometallic reagent.

Protonic media can not be employed for abstraction of H^+ from $HCo[P(OR)_3]_4$, and bulky reagents such as alkyllithium compounds are ineffective. KH as a slurry in tetrahydrofuran reacts slowly with $HCo[P(OMe)_3]_4$ to give analytically pure $KCo[P(OMe)_3]_4$. The analogous reaction with $HCo[P(OEt)_3]_4$ is about one-third as fast; $HCo[P(O\text{-}Pr^i)_3]_4$ does not react. Lack of reaction in the last of these *quasi* tetrahedral hydrides is ascribed to a protective envelopment of the hydrogen atom by the bulky isopropoxy groups. Ligand dissociation in the parent hydrides is not a primary step in "salt synthesis" because this ligand dissociation is many orders of magnitude slower than the *reaction with* KH as sensed by reaction (1) where k_1 is

$$\mathrm{HCo[P(OR^1)_3]_4} + \mathrm{P(OR^2)_3} \overset{k_1}{\rightleftharpoons} \mathrm{HCo[P(OR^1)_3]_3P(OR^2)_3} + \mathrm{P(OR^1)_3} \quad (1)$$

slightly larger for R^1 = Et and R^2 = Me than *vice versa*. Arylphosphitocobalt hydrides also react with KH but internal addition of an *ortho* carbon–hydrogen bond across the metal atom occurs and the products are complex. Rhodium hydrides with alkylphosphite ligands do not react with KH.

The salts, $\mathrm{KCo[P(OR)_3]_4}$, are essentially colourless solids that inflame on contact with air. Protonic solvents such as alcohols rapidly convert the salts into the hydrides. In the alcoholysis, there are indications that ligand dissociation in the anion, or more probably a tight ion pair $\{\mathrm{KCo[P(OR)_3]_4}\}$, is the first step. Methanolysis of $\mathrm{KCo[P(OEt)_3]_4}$ yields $\mathrm{HCo[P(OEt)_3]_4}$ and equivalent amounts of hydrides with ethoxy and methoxy groups. Fast *trans*-esterification cannot occur with bound phosphite[2] and this exchange demands ligand dissociation in the salt. (This process is too slow in the hydrides to account for the results.)

Methyl, allyl, and benzyl iodides are converted by the potassium salts, with increasing respective rates, to give stable $\mathrm{MeCo[P(OR)_3]_4}$ and h^3-$\mathrm{R^1Co[P(OR^2)_3]_3}$ (R^1 = allyl or benzyl) derivatives. The methyl derivative does not decompose below 100°, is unaffected by water, and will serve as a good model to explore the reactivity of the cobalt–carbon bond in this class of cobalt(I) complexes. Aryl iodides do not react with the potassium salts, but $\mathrm{C_6H_5N_2^+}$ is converted quantitatively into the phenylcobalt derivative and nitrogen. Introduction of bulky substituents such as $\mathrm{Me_3Si}$– and $\mathrm{Me_3Ge}$– was not successful; the salts and $\mathrm{Me_3GeCl}$ gave $\mathrm{[Me_3Ge]_2}$ and $\mathrm{Co_2[P(OR)_3]_8}$. The latter dimer which is a bitrigonal bipyramid ($\mathrm{AB_3}$ ^{31}P spectrum) has an effective hydrocarbon periphery and, accordingly, is very soluble in hydrocarbons. The dimer slowly decomposes above 100°. Mercuric chloride reacts instantly with $\mathrm{KCo[P(OMe)_3]_4}$ to give $\mathrm{Hg\{Co[P(OMe)_3]_4\}_2}$.

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