Mono- and disubstitution of HCo(CO)₄ with tertiary phosphines and phosphites was studied by IR and ¹H-NMR spectroscopy. It was found that these substitutions proceed through phosphonium tetracarbonylcobaltate intermediates, leading to a mixture of isomers. The crystal and molecular structure of trans-HCo(CO)₃[P(O-p-C₆H₄Ph)₃] was determined by X-ray diffraction.

**Keywords**: Hydroformylation; cobalt carbonyl/tertiary phosphine system; ¹H-NMR; X-ray diffraction structure

1. **Introduction**

A major technical application of HCo(CO)₄ (1) is the hydroformylation of olefins in the presence of tertiary phosphorous ligands [1–4], PR₃ (R = alkyl, aryl, alkoxy, aryloxy) (2). It is generally assumed that PR₃ derivatives of 1 as HCo(CO)₃(PR₃) (4) and HCo(CO)₂(PR₃)₂ (6) were the actual catalysts in this process. Surprisingly, in spite of the technical importance of this process [3–5], not too much is known about the chemistry of the formation of complexes 4 and 6. It has been established that the reaction between 1 and 2 is very fast [6] and it is supposed to take a dissociative pathway [7,8]:

\[
\text{HCo(CO)₄} \xrightarrow{-\text{CO}} \text{HCo(CO)₃} \xrightarrow{+\text{PR₃}} \text{HCo(CO)₃(PR₃)} .
\]

It was our aim to learn more about this problem.

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2. Results and discussion

Now we report on preliminary results concerning the intermediates of the formation of mono- and disubstituted derivatives of 1 with ligands 2 and the isomerism of the products.

The preparative results are summarized in scheme 1. (The new compounds were characterized by analyses of some representatives and spectra, as shown in table 1).

Reaction of 1 with a Lewis base 2 at −78°C (reaction (i)) leads to the formation of the corresponding phosphonium tetracarbonylcobaltate (3). Slowly warming the reaction mixture results in the gradual formation of the monosubstitution product, HCo(CO)₃(PR₃), 4. Complexes 4 are formed in two isomeric forms 4A and 4B, as a mixture of 4A+4B (minimum of the observed A/B ratio was 4Ac : 4Bc ≈ 1 : 1 at −78°C in THF-d₈). Complex 4B generally isomerizes into 4A in a fast thermal reaction. These changes can be followed by in situ ¹H-NMR measurements (fig. 1). The structures of complexes 3 and 4 were established by

\[
\begin{align*}
\text{HCo(CO)}_4 + \text{PR}_3 & \rightarrow [\text{HPR}_3][\text{Co(CO)}_4] \quad (i) \\
\text{HCl} + \text{PR}_3 & \rightarrow [\text{HPR}_3]\text{Cl} \quad (ii) \\
\text{HCl} + \text{PR}_3 & \rightarrow [\text{HPR}_3]\text{Cl} \quad (iii) \\
\text{PR}_3 & \rightarrow [\text{HPR}_3][\text{Co(CO)}_3\text{PR}_3] \quad (iv) \\
\end{align*}
\]

Scheme 1. (i) 1 : 2 = 1 : 1, THF, −78 − −20°C, 1−30 min. (ii) Excess HCl (g), THF, +25°C, ~ 1 h. (iii) P : Co = 1 : 1, Et₂O, −78 − −20°C, 1−2 h. (iv) THF, −20 − +25°C, 1−120 min. (v) Excess PR₃, THF, +25°C, 1−24 h. (vi) 4 : PR₃ = 1 : 1, THF, +25°C, 1−10 min. (vii) PR₃ : Co = 1 : 1, Et₂O, +25°C, 1−2 h.