

REACTION OF ACID CHLORIDES WITH A HYDRIDO-NITROGEN-COBALT COMPLEX

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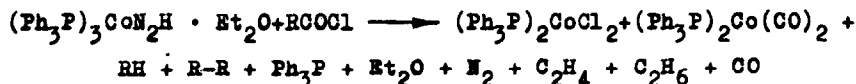
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Recently hydrido and nitrogen complexes of cobalt¹ have been described. The reactions of the cobalt complex $(\text{Ph}_3\text{P})_3\text{CoN}_2\text{H}\cdot\text{Et}_2\text{O}$ (I) with compounds with C=O bond were investigated.² We present here some new observations concerning the preparation of complex I and its reaction with acid chlorides. Complex I was prepared in diethyl ether by a modified Yamamoto method¹. The 0.62 mmoles of cobalt acetylacetonate and 1.90 mmoles of PPh_3 were flushed with nitrogen and 5 ml of diethyl ether was added. The mixture was cooled to -5°C . The 1.90 mmoles of AlEt_3 80% and $\text{AlEt}_2(\text{OEt})$ 20% was added dropwise, the use of both the organoaluminium compounds together was found to give the best results. The reaction mixture was kept at $+10^\circ$ to $+15^\circ$ during 1.5 to 2 hours. After that time it was completely homogeneous and orange crystals of I precipitated. After washing with diethyl ether the crystals were dried for 30 minutes in vacuo (0.8 mm Hg). Such a treatment does not eliminate the coordinated ether molecule, confirming the observations of Loberth et al.³ The yield was about 90%.

The dissolving of I in benzene gives a red solution of spectral characteristics the same as those previously reported.¹ We found that the gaseous atmosphere over the solution obtained in this manner contained C_2H_4 and C_2H_6 (approx. 2:3 respectively) plus minor quantities of C_3 and C_4 gases (parafins and olefins). It is suggested that the gases originate from small quantities of the organoaluminium compounds adsorbed on the surface of complex I which precipitated from diethyl ether reaction mixture (as described above). Complex I was precipitated from an 0.2 molar benzene solution by adding an equal volume of diethyl ether and cooling. The subsequent dissolving of I in benzene gives again a red solution but the atmosphere over it is free from the hydrocarbons.

The reaction of this complex with RCOCl in molar ratio 1:1 proceeds accor-

ding to the following equation:



The following acid chlorides were used in the reaction: R = CH₃; C₆H₅; C₆H₅-CH₂; C₆H₅OCH₂; (CH₃)₂CH. The complex (Ph₃P)₂CoCl₂, after the addition of heptane, precipitated almost quantitatively from the reaction mixture. In all cases the yield of (Ph₃P)₂CoCl₂ was .95 to 98% on RCOCl and approx. 50% on Co. The results of the elemental analysis of the complex (Ph₃P)₂CoCl₂ is in agreement with the proposed formula, its melting point being 230 to 232°C⁴ (with decomposition). The yield of hydrogenation products RH was 80% (on RCOCl) and yield of the coupling products R-R was 2 to 3%. The gases C₂H₄, C₂H₆ and CO were present in very small quantities.

We have not succeeded in isolating the phosphine carbonyl complex. We assume its presence in benzene solution on the following grounds: 1) The reaction solution exhibits two bands 1905-1910 cm⁻¹ (strong) and 1950-1960 cm⁻¹ (medium) characteristic of ν_{CO} in metal carbonyls. 2) The reaction solution reacts with Cl₂, CCl₄, Ph₃CCl and PhCH₂Cl giving correspondingly (Ph₃P)₂CoCl₂, CO and in the case of Ph₃CCl and PhCH₂Cl coupling products Ph₃CO₂CPh₃ (after air oxidation) and PhCH₂CH₂Ph. 3) NMR experiments exclude structures RCO-Co and R-Co. 4) There was no evidence of the presence of Co-H bond in the reaction mixture (CCl₄ does not give CHCl₃). Therefore we exclude the possibility of the formation of (Ph₃P)₃CoH(CO) and (Ph₃P)₂CoH(CO)₂. The structure of (Ph₃P)₂CoCl(CO)₂ has been eliminated because of the lack of chlorine in the reaction mixture (the (Ph₃P)₂CoCl₂ was filtered off).

The reaction of I with chelating acid chlorides is under investigation.

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