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

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Recently hydrido and nitrogen complexes of cobalt[1] have been described. The reactions of the cobalt complex $(Ph_3P)_3CoN_2H\cdot Et_2O$ (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 method[1]. 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 $AlEt_2$ (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° to +15° 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 according to the following equation:

$$(Ph_3P)_3CoN_2H \cdot Et_2O + RCOCl \longrightarrow (Ph_3P)_2CoCl_2 + (Ph_3P)_2Co(CO)_2 + RH + R\text{-}R + Ph_3P + Et_2O + N_2 + C_2H_4 + C_2H_6 + CO$$

The following acid chlorides were used in the reaction: R = CH_3; C_6H_5; C_6H_5--CH_2; $C_6H_5OCH_2$; $(CH_3)_2CH$. The complex $(Ph_3P)_2CoCl_2$, after the addition of heptane, precipitated almost quantitatively from the reaction mixture. In all cases the yield of $(Ph_3P)_2CoCl_2$ was 95 to 98% on RCOCl and approx.50% on Co. The results of the elemental analysis of the complex $(Ph_3P)_2CoCl_2$ is in agreement with the proposed formula, its melting point being 230 to 232°C [4] (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 C_2H_4, C_2H_6 and CO were present in very small quantities.

We have not succeded 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 Cl_2, CCl_4, Ph_3CCl and $PhCH_2Cl$ giving correspondingly $(Ph_3P)_2CoCl_2$, CO and in the case of Ph_3CCl and $PhCH_2Cl$ coupling products $Ph_3CO_2CPh_3$ (after air oxidation) and $PhCH_2CH_2Ph$. 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 (CCl_4 does not give $CHCl_3$). Therefore we exclude the possibility of the formation of $(Ph_3P)_3CoH(CO)$ and $(Ph_3P)_2CoH(CO)_2$. The structure of $(Ph_3P)_2CoCl(CO)_2$ has been eliminated because of the lack of chlorine in the reaction mixture (the $(Ph_3P)_2CoCl_2$ was filtered off).

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

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