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NOTE

TRANSITION-METAL ALKYLS AND HYDRIDES
IV*. DIRECT SYNTHESIS OF COBALT CARBONYL HYDRIDE AT LOW TEMPERATURE AND ATMOSPHERIC PRESSURE

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The reaction between cobalt stearate (dissolved in hydrocarbons) and different alkylmagnesium halides (dissolved in diethyl ether) yields a homogeneous dark brown solution possessing catalytic activity for hydrogenation of alkenes[1]. The presence of a complex cobalt hydride in the reaction product was suggested. We now report on the reaction of this cobalt-containing catalytic system with carbon monoxide.

If the cobalt stearate and alkylmagnesium halide solutions are mixed at −78° and the reaction mixture is allowed to warm to room temperature in a stream of carbon monoxide, cobalt carbonyl complexes are formed. This is shown by the strong absorption bands between 2200 and 1800 cm^{-1} in the IR spectrum of the dark, homogeneous liquid reaction product obtained. In the case of higher alkylmagnesium halides (n-butyl, n-octyl, cyclohexyl) the IR spectra prove the formation of a rather complex mixture of cobalt carbonyls: besides unknown complexes, dicobalt octacarbonyl and acylcobalt carbonyls [$RCOCo(CO)_4$] can be identified by their characteristic C–O stretching frequencies[2,3]. Use of ethylmagnesium bromide however, gives a product which contains only $HCo(CO)_4$ as cobalt carbonyl complex.

The formation of cobalt tetracarbonyl hydride was proved as follows. First, the IR spectrum of the reaction product showed at 2116, 2052 and 2030 cm^{-1} the absorption bands characteristic of $HCo(CO)_4$[2], even the relative intensities of these bands being in approximate agreement with literature data (full agreement can not be expected because of the difference in the solvents used). Second, $HCo(CO)_4$ was converted into $HCo(CO)_3(PPh_3)$ by adding triphenylphosphine to the reaction product[4] and the monosubstituted carbonyl hydride present in the solution was identified by its IR spectrum (bands at 2053 and 1978 cm^{-1})[5]. Third, the substituted hydride complex was transformed to bis(triphenylphosphine)dicobalt hexacarbonyl[6] by storing its solution at room temperature for 24 h. The precipitate thus formed was identified by elementary composition and IR spectrum (broad band at 1960–50 cm^{-1} in KBr pellet)[7] as $Co_2(CO)_6(PPh_3)_2$ of about 90% purity.

This latter method enabled the estimation of the approximate quantity of

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* For Part III see ref. 11.

$HCo(CO)_4$ formed, since both reactions leading from $HCo(CO)_4$ to $Co_2(CO)_6(PPh_3)_2$ can be regarded as practically quantitative. It was found, that highest yields of cobalt carbonyl hydride are obtained with Mg/Co ratios of 6, and amount to about 70%, based on cobalt stearate used.

To our knowledge this is the first reported example of the formation of a metal carbonyl hydride at low temperature and atmospheric pressure which does not start from preformed metal carbonyl. The formation of cobalt carbonyl hydride provides new independent evidence for the presence of some complex cobalt hydride in the cobalt stearate/alkylmagnesium halide catalytic system.

Earlier experiments have shown[8], that the catalytic system obtained from cobalt stearate and triethylaluminium under somewhat different conditions yields propionylcobalt tetracarbonyl as the main cobalt carbonyl complex. This was found now to be the case also under the experimental conditions used in this work. These results show that the metal alkyls used in the formation of these homogeneous catalysts play a significant rôle in determining the structure and composition of the cobalt complexes present (probably by being incorporated in these complexes in some form). Thus triethylaluminium stabilizes the ethylcobalt group, whereas in the case of alkylmagnesium halides the alkyl group is split off as alkene[1] and a cobalt hydride group is formed. This does not, however, lead to an appreciable difference in the catalytic hydrogenating activity of the two systems[1,9].

The observed formation of dicobalt octacarbonyl and acylcobalt carbonyls in the case of higher alkyl Grignard reagents may be explained by the reactions[10] between cobalt carbonyl hydride first formed and the olefin of higher molecular weight split off from the alkylcobalt intermediate. These secondary reactions probably do not occur when ethylmagnesium halide is used because the ethylene formed is carried off by the stream of carbon monoxide.

Use of iron and nickel stearates and ethylmagnesium bromide under carbon monoxide led to the formation of iron pentacarbonyl and nickel tetracarbonyl, respectively, as evidenced by IR spectroscopy. With these metals the formation of simple carbonyl hydrides is not favoured. Formation of metal carbonyls was not observed with manganese and copper stearates under these conditions.

EXPERIMENTAL

In a 250 ml reaction vessel 24 mmoles of an ethereal EtMgBr solution (about 100 ml) were chilled under stirring to −78° and a stream of CO was started through a gas inlet tube reaching under the surface of the liquid reaction mixture. After thorough purging by CO, 4 mmoles of cobalt stearate (dissolved in 50 ml hexane) were added. After 30 min at −78° the system was allowed to come to room temperature (about 30 min), stirring and the stream of CO being continued the whole time. The colour of the reaction mixture gradually changed during warming from dirty grey to deep brown.

After taking a sample for IR spectroscopy, 4 mmoles of triphenylphosphine were added (IR spectrum). After 24 h the reddish-brown precipitate formed was filtered, washed with hexane and methanol and dried. The yield was 1.32 g. (Found: Co, 12.7; P, 7.0. $C_{42}H_{30}Co_2O_6P_2$ calcd.: Co, 14.55; P, 7.65%.)

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