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TRANSITION-METAL ALKYLS AND HYDRIDES
II. INVESTIGATION OF A COMPLEX COBALT HYDRIDE OBTAINED FROM COBALT STEARATE AND GRIGNARD REAGENTS[1]

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The dark-coloured, homogeneous solutions obtained from certain transition-metal compounds and metal alkyls show some important catalytic properties. In addition to their well-known activity as polymerisation catalysts, such systems have been effectively used as homogeneous catalysts for hydrogenation of olefinic[2-4] and aromatic[4,5] hydrocarbons, oligomerisation of monoolefins[6] and conjugated dienes[7,8], and the mixed oligomerisation of conjugated dienes with monoolefines[8,9]. In most cases, aluminium compounds are used as the metal alkyl component; only in one case[3] has an active catalyst been based on a Grignard reagent. The reason for this seems to be that alkylmagnesium halides often give insoluble products when in contact with transition-metal compounds[2,10].

Our work has been directed towards the development of organo-metallic homogeneous catalysts based on alkylmagnesium halides, since the easily accessible Grignard reagents would greatly facilitate the study and application of these novel catalysts. Also it was hoped, that the well-known chemical properties of Grignard reagents would help in the investigation of the reactions leading to the active catalyst, the elucidation of its structure and the clarification of the catalytic mechanism.

RESULTS

Iron, cobalt, and nickel stearate (dissolved in hydrocarbons) were found to react with different alkylmagnesium halides (dissolved in diethyl ether) to yield dark brown, homogeneous solutions, which effectively catalyse the hydrogenation of monoolefins at atmospheric pressure and room temperature, if the magnesium : transition metal ratio is 3–8 : 1. At Mg : metal ratios below 3, vivid coloured (blue, dark green, etc.) solutions are formed having no catalytic activity. On the other hand, above a ratio of 8, the colour of the solutions remains dark brown but the rate of hydrogenation is very much diminished.

This paper deals with reactions leading to the cobalt-containing active catalyst and the probable structure of the complex showing catalytic activity. To give some idea, however, of the catalytic activity of the systems investigated, Fig. 1 shows the hydrogenation of n-heptene-1 in the presence of a catalyst solution prepared from cobalt stearate and n-butylmagnesium bromide. The iron- and nickel-containing systems show similar activity.

The amount of hydrogen consumed in the catalytic experiments generally exceeded that theoretically required by the added olefin, as can be seen in Fig. 1. This was proved to be due principally to the consumption of hydrogen by the catalytic system itself. Table 1 lists the values of hydrogen absorption without added olefin.

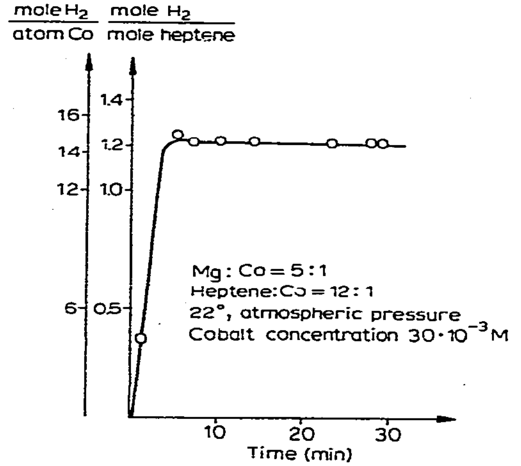


Fig. 1. Catalytic hydrogenation of n-heptene-1 with the Co(stear)$_2$+n-BuMgBr catalyst.

TABLE 1

ABSORPTION OF HYDROGEN BY SYSTEMS OBTAINED FROM COBALT STEARATE AND DIFFERENT ALKYL GRIGNARD REGENTS

Grignard reagent	*C_2H_5MgBr*					*n-C_4H_9MgBr*				*iso-C_4H_9MgCl*			*tert-C_4H_9MgCl*			
Mg:Co ratio	2	4	6	8	10	2	4	6	8	2	4	6	2	4	6	8
Moles of hydrogen	0	0.50	1.41	2.37	2.53	0.05	1.76	2.01	2.06	0	1.60	1.64	0.11	2.81	2.87	3.2
absorbed/atom Co[a]						0.01	1.68	1.90	1.90	0	1.54	1.56	0	2.14	1.87	1.90

[a] The data given in the first row are the observed values; in the second row these values are corrected for the olefin contained in the Grignard reagent (as the result of some dehydrohalogenation taking place during preparation[11]).

As can be seen from the data presented, significant absorption of hydrogen sets in at a Mg : Co ratio of 4 and is practically constant above Mg : Co ratios of 6–9 : 1. This quantity, within the limits of experimental error, is 2 moles H_2/atom cobalt and is in accordance with the excess hydrogen consumption observed in the catalytic experiments.

The absorption of hydrogen by such systems has been observed previously[12], and is generally thought to result from the hydrogenation of the transition-metal alkyls presumed to be formed as primary products in the reaction between transition-metal compounds and metal alkyls:

$$MR_2+2\,H_2 \rightarrow MH_2+2\,RH$$

(M = Fe, Co or Ni). Although this reaction scheme explains the reaction with hydrogen, it can be regarded only as one possible explanation, because, in spite of numerous efforts, no simple iron, cobalt or nickel alkyls have been isolated so far from such reaction products.

An alternative explanation—based on the catalytic properties of the system—could be the hydrogenation of some olefin formed in the reaction. When diethyl ether was distilled promptly from the reaction products obtained from cobalt stearate and n-butylmagnesium bromide, the quantity of olefin required was actually found in the distillate, giving support to this latter explanation. Table 2 gives the results showing the parallelism between H_2 absorption and olefin content.

TABLE 2

AMOUNT OF OLEFIN FORMED AND HYDROGEN ABSORBED BY THE COBALT STEARATE–n-BUTYLMAGNESIUM BROMIDE SYSTEM AT DIFFERENT Mg:Co RATIOS

Mg:Co ratio	*Olefin formation (mole/atom Co)*	*Hydrogen absorption (mole/atom Co)*
2	0.52	0.01
3	1.02	
4	1.55	1.68
5	1.95	1.98
6	1.96	1.90
7	2.04	
8	2.01	1.90

The olefin formed could be identified in the cases of ethylmagnesium bromide and tert-butylmagnesium chloride as ethylene and iso-butylene, respectively. In experiments with n-butylmagnesium bromide, the formation of all three n-butene isomers was proved by gas chromatography.

It can be assumed, therefore, that the complex alkylcobalt compounds formed primarily in the reaction between cobalt stearate and alkylmagnesium halides rapidly decompose yielding a complex cobalt hydride and two molecules of olefin (L = ligand):

$$\text{Co(stear)}_2 \xrightarrow{\text{RMgX}} [\text{L}_x\text{CoR}_2] \rightarrow \text{L}_x\text{CoH}_2 + 2\,\text{R}_{(-\text{H})}$$

The formation of the olefin is followed by olefin isomerisation, apparently a fast reaction in the presence of the complex cobalt hydride as catalyst.

The intermediate cobalt alkyls and the cobalt hydride are both regarded as complex compounds stabilised by coordinated molecules, since, to our knowledge, no simple alkyl or hydride derivatives of cobalt have been isolated, whereas numerous complex compounds of such types are known[13]. For the sake of simplicity, however, the complex cobalt compound containing hydridic hydrogen will be referred to only as cobalt hydride.

We are aware of only one clear example of the formation of a transition-metal hydride from a transition-metal alkyl by the splitting off of an olefin[14]. In another reaction, possibly of this type, the olefin was neither determined nor identified[15]. This type of reaction is, however, often supposed as one step in the isomerisation of olefins in the presence of transition-metal complexes[16].

The existence of this cobalt hydride could be proved by its ability to hydrogenate alkenes to alkanes in a slow stoichiometric reaction:

$$L_xCoH_2+R_{(-H)} \rightarrow L_xCo+RH$$

This stoichiometric hydrogenation explains why the amount of butene that can be distilled from the reaction mixture obtained from n-butylmagnesium bromide, gradually diminishes with time, as can be seen from Fig. 2.

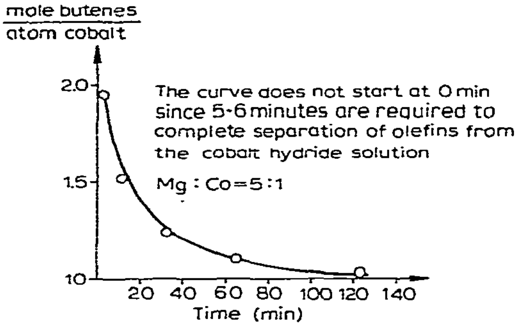


Fig. 2. Stoichiometric hydrogenation of butenes.

One mole of butene remains unchanged even on prolonged standing, which is in accordance with the stoichiometry of the olefin formation and hydrogenation.

The same stoichiometric hydrogenation could be observed after hydrogenating with hydrogen the butene formed during catalyst preparation, changing the hydrogen atmosphere to nitrogen and reacting the olefin-free, cobalt hydride-containing dark brown homogeneous solution thus obtained with different olefins. The results of these experiments are given in Table 3.

TABLE 3

STOICHIOMETRIC HYDROGENATION OF OLEFINS WITH THE COBALT HYDRIDE SOLUTION OBTAINED FROM COBALT STEARATE AND n-BUTYLMAGNESIUM BROMIDE

Mg:Co ratio = 5:1; reaction time 1 h.

Type of olefin	*Olefin added (mole/atom Co)*	*Olefin hydrogenated (mole/atom Co)*
ethylene	1.8	0.92
propylene	3.8	0.51
n-butenes[a]	2.0	1.09
pentene-1	1.0	0.63
	2.3	1.03
	3.0	0.94

[a] Mixture of isomers

It is apparent, on comparing Figs. 1 and 2, that the catalytic and the stoichiometric hydrogenation follow different mechanisms, since the appreciable velocity of the former cannot be explained by the stoichiometric reaction coupled with the regeneration of the hydride consumed. Furthermore, preliminary experiments indicate that the transformation of L_xCo to L_xCoH_2 is difficult, but this problem is still under investigation.

The formation of olefin and the stoichiometric hydrogenation give as end products 1–1 mole of alkene and alkane/cobalt atom, thus leading to the same overall picture as the familiar disproportionation reaction of unstable transition-metal alkyls:

$$MR_n \rightarrow M+\frac{n}{2}RH+\frac{n}{2}R_{(-H)}$$

The mechanism of this reaction is regarded as rather complex and no clear picture is available at present. Our results, which prove the formation of a hydride as intermediate, may eventually be useful as a basis for generalization. It should be noted, in this connection, that Müller and Fischer[17] also suspected hydride species in similar systems.

The *hydrides* obtained so far from transition-metal compounds, Grignard reagents and hydrogen[12] are all insoluble in the raction products. The solubility of the cobalt hydride investigated in this work must, presumably, be attributed to those molecules that are formed in the reaction between cobalt stearate and alkylmagnesium halide and which can function as ligands. Thus further experiments were carried out to investigate the transformation of the stearate group during the catalyst-forming reaction.

It could be shown that, besides olefins, saturated hydrocarbons corresponding to the alkyl group of the Grignard reagent are also formed in the reaction of cobalt stearate with alkylmagnesium halides. Approximately 2 moles of paraffin were observed/mole of olefin, practically independently of the Mg:Co ratio. Table 4 shows the amount of alkenes formed with different alkylmagnesium halides. A Mg:Co ratio of 8:1 was chosen in these experiments to ensure complete transformation of the reactants.

TABLE 4

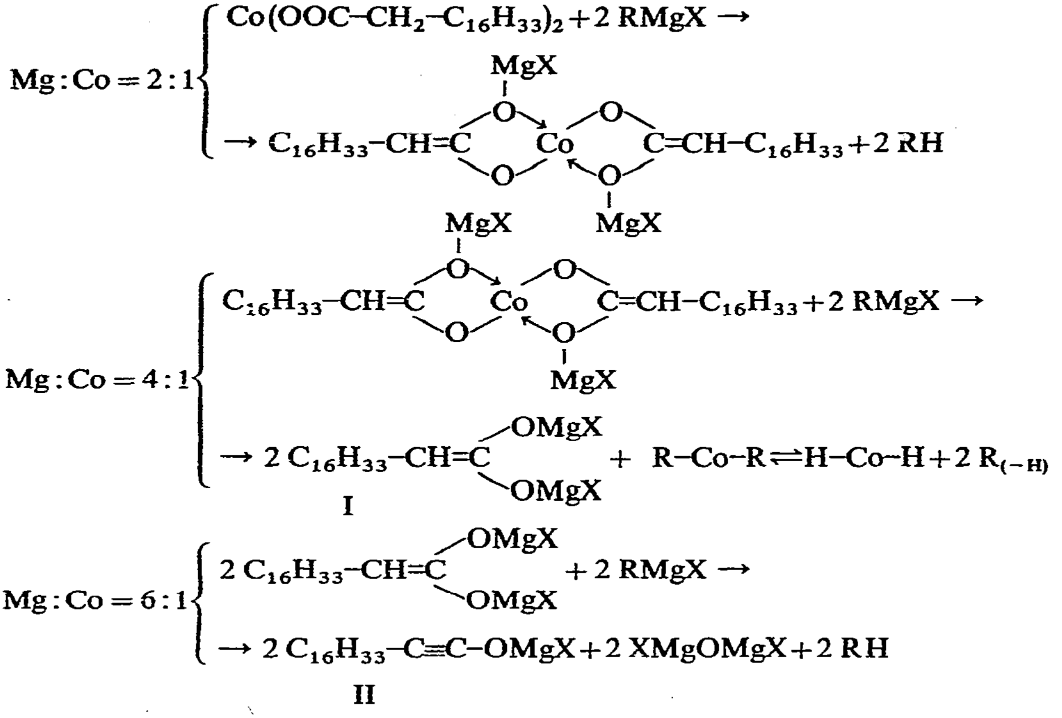
FORMATION OF ALKANES IN THE REACTION BETWEEN COBALT STEARATE AND ALKYLMAGNESIUM HALIDES

Grignard reagent	*Alkane formed*	*Mole alkane/ atom cobalt*
C_2H_5MgBr	C_2H_6	3.8
n-C_4H_9MgBr	n-C_4H_{10}	3.88
tert-C_4H_9MgCl	iso-C_4H_{10}	3.86

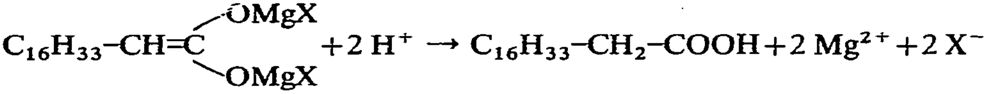
Mg:Co = 8:1

The reaction of magnesium stearate and alkylmagnesium halides yields ketones and tert-alcohols[18], in accordance with the generally observed fact that salts of carboxylic acids behave towards Grignard reagents like carboxylic acid esters. The cobalt-containing system under investigation, however, after hydrolysis with alcoholic sulphuric acid, separation of the cobalt sulphate solution and evaporation of solvents, yields the same stearic acid as used for the preparation of the cobalt stearate (identified by melting point and acid number). This result is obtained independently of the Mg:Co ratio.

These facts have suggested the following scheme for the reaction of cobalt stearate and alkylmagnesium halides:



This mechanism is in accordance with the quantities of olefin and paraffin formed and the regeneration of stearic acid after hydrolysis, since both the ene-diolate (I) formed at Mg : Co = 4 : 1, and the yne-olate (II) formed at Mg : Co = 6 : 1 yield stearic acid on hydrolysis:



$$C_{16}H_{33}{-}CH{=}C(OMgX)_2 + 2\,H^+ \rightarrow C_{16}H_{33}{-}CH_2{-}COOH + 2\,Mg^{2+} + 2\,X^-$$

$$C_{16}H_{33}{-}C{\equiv}C{-}OMgX + H^+ + H_2O \rightarrow C_{16}H_{33}{-}CH_2{-}COOH + Mg^{2+} + X^-$$

Compounds of type I and II have not yet been described. Experiments to obtain some other, eventually more conclusive derivatives, have so far failed.

Both I and II can function as ligands and can play a role in solubilizing the [CoH_2] entity. Further information is needed, however, on these unusual types of complex transition-metal hydrides.

EXPERIMENTAL

All experiments with systems containing cobalt stearate and Grignard reagent were performed in the absence of air and moisture.

1. *Preparation of cobalt stearate*

Cobalt stearate prepared from sodium stearate and a cobalt halide in alcoholic medium[19] is insoluble in hydrocarbons, and merely swells in n-heptane and toluene.

However, the solubility of cobalt alkanoates in hydrocarbons increases in the presence of carboxylic acids[20]. In our experience, a 0.3 *M* solution of cobalt stearate in n-heptane can be prepared in the presence of 10 mole % of stearic acid (based on cobalt stearate). The cobalt stearate used in our experiments was therefore prepared from cobalt carbonate and stearic acid (used in an excess of 5 mole %) by gradually raising the temperature. To facilitate the removal of water, xylene was used as azeotropic carrier during the early stages of the reaction. After separation of the theoretical amount of water, xylene was distilled under vacuum and the temperature gradually raised to 220° (Found: Co, 8.95. $C_{36}H_{70}O_4Co$ calcd.: Co, 9.40%. Free stearic acid content 0.11 mole/atom Co).

The stearic acid used in these preparations was of commercial purity (m.p. 51°, acid number 206 mg KOH/g; literature, m.p. 69.6°, acid number theor. 197 mg KOH/g) and contained some palmitic acid.

2. *Preparation of alkylmagnesium halides*

All Grignard reagents were prepared under nitrogen according to the general procedure of Kharasch[11]. The olefin content of the butyl Grignard reagents was estimated by distilling about 50% of the solvent ether into a receiver cooled to −70° and determining the butenes in the distillate by bromination.

3. *Measurement of hydrogen absorption and hydrogenation of olefins*

These experiments were carried out in a 250-ml flask equipped with thermometer and calibrated dropping funnels, and connected to a gas burette. The flask was agitated by means of a shaker and the temperature of the reaction mixture held constant at 22°. After the flask had been flushed with nitrogen, it was charged with 1.98 g (3 mg moles) of cobalt stearate dissolved in 20 ml of n-heptane and 50 ml of dry diethyl ether and then flushed several times with hydrogen. The required amount of Grignard reagent in diethyl ether was added and the volume of the reaction mixture made up to 100 ml with dry diethyl ether. Gas absorption usually took place within one minute.

To avoid errors caused by changes in vapour pressure of the reaction mixture, all experiments were repeated in nitrogen atmosphere and the amount of hydrogen absorbed was calculated from the difference of changes in gas volume observed under hydrogen and nitrogen.

If the system was used as catalyst for olefin hydrogenation, 3.53 g (36 mg moles) of n-heptene-1 was added together with the cobalt stearate solution.

4. *Formation of n-butenes and n-butane*

To 0.33 g (0.5 mg mole) of cobalt stearate dissolved in 8 ml n-heptane was added 7 ml dry diethyl ether and 1.33 ml ethereal n-butylmagnesium bromide containing 2.5 mg atom magnesium (Mg:Co ratio = 5:1). The n-butenes and n-butane formed were distilled together with diethyl ether into a receiver cooled to −70°. The distillate was investigated by gas chromatography on a column at 40° packed with 20% diethylsulpholane on celite, and was shown to contain (in the order of elution) n-butane, butene-1, *trans*-butene-2, and *cis*-butene-2. The total olefin content was determined on an aliquot sample of the distillate by bromination according the method of Kaufmann. The quantity of n-butane was calculated from the ratios of peak areas on the chromatogram and the quantity of olefin determined by bromination.

To avoid errors caused by butene and butane contained in the Grignard reagent, this reagent was freed from these contaminants by refluxing for about 30 min. The same procedure was applied in the case of tert-butylmagnesium chloride.

When ethylmagnesium bromide was used as Grignard reagent, the ratio ethane : ethylene was determined by gas chromatography on the gas evolved.

All results were corrected for the paraffin formed by the reaction of the Grignard reagent with the excess stearic acid in the cobalt stearate used.

5. *Stoichiometric hydrogenation of n-pentene-1 by "cobalt hydride"*

The homogeneous solution of complex cobalt hydride in ether and n-heptane prepared according to section 3 from 1.98 g (3 mg moles) of cobalt stearate dissolved in 20 ml n-heptane, 8.0 ml ethereal n-butylmagnesium bromide containing 15 mg atom of magnesium (Mg : Co ratio = 5 : 1) and 50 ml dry diethyl ether, absorbed 133 normal ml (5.94 g moles) of hydrogen. The flask was evacuated and flushed several times with nitrogen to remove hydrogen from the system; 0.635 g (9.0 mg moles) of n-pentene-1 were added and the mixture left to react at room temperature for 1 h. The C_4- and C_5-hydrocarbons, together with diethyl ether, were removed from the solution by distillation and collected at −70°. 6.18 mg moles of olefin were determined in the distillate by bromination, *i.e.*, the 3 mg moles of cobalt hydride hydrogenated 2.82 mg moles of n-pentene-1.

6. *Hydrolysis of the reaction products obtained from metal stearates and n-butylmagnesium bromide*

Cobalt stearate (or magnesium stearate) and n-butylmagnesium bromide were reacted as described in section 3. The reaction mixture was shaken for 15 min and hydrolyzed with 5 ml of ethanol and 50 ml of 10% sulphuric acid. The colourless organic layer was washed several times with water and dried over calcium chloride. Diethyl ether and heptane were removed by distillation and the residue maintained at 60° and 100 mm Hg until no further loss of weight could be observed. Table 5 shows the melting points and acid numbers of the solid products thus obtained.

TABLE 5

Metal stearate	*Mg : metal ratio*	*Atmosphere during reaction*	*Product obtained after hydrolysis*	
			melting point	*acid number (mg KOH/g)*
Co	4 : 1	N_2	50.5	202
Co	5 : 1	H_2	50.0	200
Co	8 : 1	N_2	48.5	198
Mg	8 : 1	N_2	30.0	81.5

SUMMARY

Cobalt stearate and alkylmagnesium halides react to form a dark brown homogeneous solution which catalyses the hydrogenation of olefins at Mg : Co

ratios of 3–8 : 1. Cobalt was shown to be present in the form of a complex dihydride L_xCoH_2, formed, presumably, by unstable cobalt alkyls splitting off the alkyl group in the form of an olefin. Besides having catalytic acitivity, this complex cobalt hydride stoichiometrically hydrogenates alkenes to alkanes. Unsaturated alkoxy-magnesium halides formed from the stearate group are proposed as ligands ensuring the solubility of the complex hydride in hydrocarbon–ether mixtures.

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