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THE NATURE OF COBALT SPECIES FORMED DURING THE REACTION OF COBALT(III) ACETYLACETONATE WITH TRIISOBUTYLALUMINIUM IN AROMATIC HYDROCARBONS UNDER HYDROGEN

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Summary

The reaction of $CoAA_3$ with i-Bu_3Al in aromatic hydrocarbons under hydrogen leads to the formation of a mixture which catalyses the hydrogenation of olefines. Reactions of this mixture with benzyl bromide, diphenylmercury and styrene were carried out. On the basis of the results of these reactions the following formulae of cobalt compounds present in the mixture have been proposed: $[Co_2H]_x$ for molar ratios $CoAA_3$/i-Bu_3Al = 1/1 to 1/5 and $[Co—H]_y$ for molar ratios 1/5 to 1/10. These compounds exist in solution when x and y are small and in the form of a precipitate when x and y are large.

Introduction

In 1963 Sloan [1] found that the product of reaction of cobalt(III) acetylacetonate ($CoAA_3$) with organoaluminium compounds catalyses the hydrogenation of olefines. This observation was followed by several publications and patents regarding this subject. They have been reviewed by James [2]. It is believed that the best catalytic system is that described in one of the patents by Lassau et al. [3]. It is prepared by reaction of the cobalt salt with $M[AlH_mX_{4-m}]_p$ where: m = 1, 2, 3, M = mono- or di-valent metal of Group IA or IIA, p = valence of metal M, X = R, OR, NR_2 or another group of this type. Another very effective reductor is AlH_nX_{3-n}, where n = 1 or 2.

The structure of the compounds formed in this type of reaction has been considered by many authors. Ziegler [4] found that these reactions lead to the formation of metals in a state of high dispersion. Prince and Weiss [5] investigated the reaction of cobalt halides with R_3Al and observed the formation of

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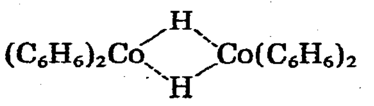
precipitates having ferromagnetic properties. The precipitate formed from $CoCl_2$ contained at least 97% of cobalt. The formation of metallic cobalt has been also postulated by Tamai et al. [6] who were investigating the reaction of $CoAA_3$ with Et_3Al.

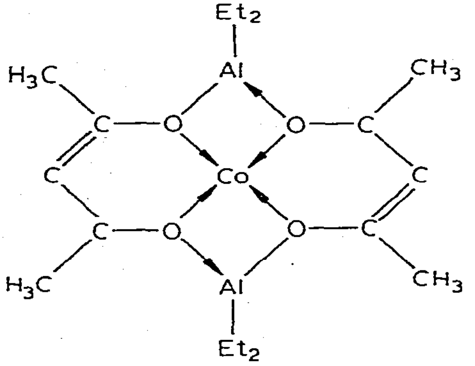
On the basis of EPR studies Saraev et al. [7] proposed a structure for the product of reaction of $CoAA_2$ with Et_3Al (1/5) which is probably a catalyst for the hydrogenation of olefines. According to these authors the structure of this compound is:



$$(C_6H_6)_2Co\overset{H}{\underset{H}{\rightleftarrows}}Co(C_6H_6)_2$$

It is prepared in an argon atmosphere. At higher Co/Al molar ratios an ionic compound having the structure $[(C_6H_6)_2Co]^+[(Et_3AlH]^-$ is postulated.

In a later publication Szmidt [8] announced that the paramagnetic compound formed by reaction of $CoAA_2$ with Et_3Al in toluene in an argon atmosphere has the following structure:



It is a compound of $[Co]^0$ having the configuration d^9. Addition of hydrogen to a solution of this compound causes disappearance of one EPR signal.

Reduction of cobalt stearate with triethylaluminium carried out by Szabó and Markó [9] gave C_2H_5CoX. In this work the authors observed the "ageing" of solutions of cobalt compounds having the structure postulated above. They noticed the phenomenon of "ageing" on the basis of an observation that after 24 h the reaction mixture $[Co(stear)_2 + Et_3Al]$ does not react with CO whereas the freshly-prepared mixture does so giving $C_2H_5COCo(CO)_4$. Pasynkiewicz [10] has investigated the reaction of $CoAA_3$ with Me_3Al and has postulated that metallic cobalt is formed during this process.

The results of all the studies carried out so far on the structure of compounds formed during the reaction of $CoAA_3$ with R_3Al leave the following questions unanswered:

(1). Are cobalt hydride and metallic cobalt (Co_{met}) the only main products of this reaction and what are their proportions?

(2). What is the dependence of the composition of the reaction product on the $CoAA_3/R_3Al$ molar ratio, atmosphere and reaction time?

(3). What is the ratio of cobalt present in the precipitate to that present in the solution?

The product of reaction between $CoAA_3$ and R_3Al is a hydrogenation catalyst but no kinetic studies on catalytic hydrogenation have been published and it is not known whether, in the presence of this catalyst, reproducible hydrogenation rates can be obtained.

In the present work we are reporting the results of investigations of the reactions of the catalytic solutions with $PhCH_2Br$, Ph_2Hg and styrene under argon and hydrogen atmosphere.

Results

Relative rates of hydrogenation of cis-pent-2-ene in various aromatic hydrocarbons

The hydrogenation catalyst was prepared from cobalt(III) acetylacetonate and $i\text{-}Bu_3Al$ in various aromatic hydrocarbons under hydrogen:

$$CoAA_3 + i\text{-}Bu_3Al \xrightarrow[H_2]{\text{aromatic hydrocarbon}} I \qquad (1)$$

I stands for the post-reaction mixture having the catalytic properties. Under the temperature and concentration conditions given in the Experimental part the synthesis of the catalyst takes place in a few minutes. Then the ageing of the catalyst begins. During this process cobalt compounds precipitate. The structure of these compounds will be discussed later in this work.

Fig. 1 shows the rates of catalytic hydrogenation of *cis*-pent-2-ene in the presence of catalyst I prepared in various aromatic hydrocarbons. It can be seen from Fig. 1 that in several hydrocarbons the hydrogenation rate is relatively high. These data are the mean values of series of 6 determinations. The reproducibility of the rate of hydrogen consumption is not satisfactory and is equal to ~50%. For this reason the data presented have only preliminary character, nevertheless it is certain that cumene is one of the solvents in which a relatively active catalyst is formed and therefore we decided to investigate this system. Another reason for this choice was the presence of the active isopropyl group, since it was of interest to observe the reactivity of this group under the influence of compounds resulting from the reaction of $CoAA_3$ with $i\text{-}Bu_3Al$.

Reactions of I with $PhCH_2Br$

I_C stands for mixture I prepared in cumene. If it contains reactive Co—H or Al—H bonds its reaction with $PhCH_2Br$ should lead to the formation of toluene. In the presence of cobalt in the metallic or some similar state, $PhCH_2Br$ should give the coupling product $PhCH_2CH_2Ph$. Friedel—Crafts reaction with the solvent and reaction with unreacted organoaluminium compound present in the solution are also possible.

The products of the reactions of I_C with $PhCH_2Br$ which are of interest to us are toluene and dibenzyl:

$$I_C + PhCH_2Br \rightarrow PhCH_3 + PhCH_2CH_2Ph + ... \qquad (2)$$

Table 1 shows the results of our investigation of this reaction for I_C prepared at

TABLE 1

RATIOS $PhCH_3/CoAA_3$ AND $PhCH_2CH_2Ph/CoAA_3$ IN THE REACTION OF $PhCH_2Br$ WITH I_C AS A FUNCTION OF MOLAR RATIO i-$Bu_3Al/CoAA_3$

i-$Bu_3Al/CoAA_3$	$PhCH_3/CoAA_3$ [a]	$PhCH_2CH_2Ph/CoAA_3$ [a]	$PhCH_3/CoAA_3$ [b]	$PhCH_2CH_2Ph/CoAA_3$ [b]
2	0.10	0.15		
3	0.13	0.22	0.10	0.12
4	0.26	0.27		
5	0.40	0.35	0.21	0.35
6	0.45	0.40		
8	0.50	0.47	0.60	0.50
10	0.90	0.50	1.00	0.74
20	1.55	0.53	1.43	0.96

[a] Under hydrogen. [b] Under argon.

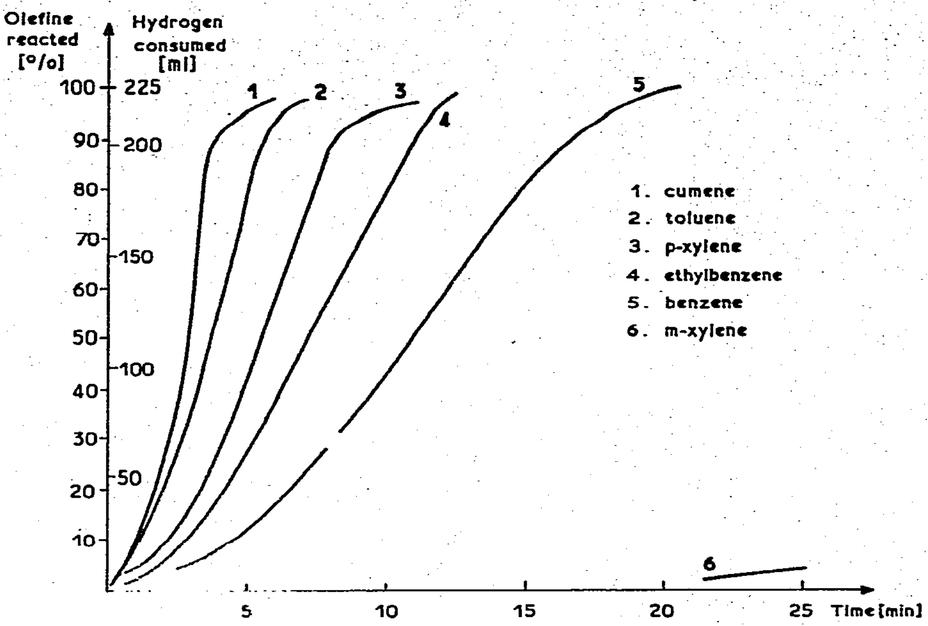


Fig. 1. The rate of hydrogenation of *cis*-pent-2-ene by I. Conditions of synthesis of I: [Co] = 20 × 10^{-3} mol l^{-1}; molar ratio $i\text{-Bu}_3\text{Al/CoAA}_3$ = 5/1; molar ratio Co/pentene = 1/100; temperature 20-25°C; time of reaction 1 15 min; hydrogen pressure 1 atm.

various $\text{CoAA}_3/i\text{-Bu}_3\text{Al}$ molar ratios. Table 2 shows the results for this reaction in which the time of reaction of I_C with hydrogen was varied.

The reaction of I_C with $PhCH_2Br$ takes place during several minutes (under the temperature and concentration conditions described in the Experimental part). This is shown by the change of colour of mixture I_C which is observed after 5 to 6 min; subsequently the colour of the reaction mixture remains unchanged. The ratios $PhCH_3/Co$ and $PhCH_2CH_2Ph/Co$ also remain unchanged after 5 to 6 min; this indicates that the reaction of $PhCH_2Br$ with I_C takes place during 5 to 6 min.

TABLE 2

RATIOS $PhCH_3/CoAA_3$ AND $PhCH_2CH_2Ph/CoAA_3$ IN THE REACTION OF $PhCH_2Br$ WITH I_C AS A FUNCTION OF TIME OF INTERACTION OF I_C WITH CUMENE AND HYDROGEN

Time of interaction of I_C (h)	$PhCH_3/CoAA_3$
0.33	0.45
0.80	0.43
2.00	0.40
4.00	0.44
25.00	0.40
46.00	0.40
76.00	0.47
120.00	0.40
150.00	0.44

TABLE 3

RATIO OF THE AMOUNT OF PRODUCTS OF REACTION 4 TO $CoAA_3$ AS A FUNCTION OF MOLAR RATIO $Et_3Al/CoAA_3$ IN REACTION 3

$Et_3Al/CoAA_3$	$PhCH_3/CoAA_3$	$PhCH_2CH_2Ph/CoAA_3$	$Ph_2CH_2/CoAA_3$	$PhCH_2CH_2CH_3/CoAA_3$
2	0,10	0,19		0,52
3	0,20	0,23		0,94
4	0,27	0,10	0,04	
5	0,50	0,45	0,32	
6	0,52	0,50	0,10	0,70
8	0,95	0,45	0,01	0,56
10	0,98	0,37	0,01	0,48
15	0,90	0,37		
20	1,06	0,21		

We have also prepared the catalytic mixture by carrying out the reaction of Et_3Al with cobalt(III) acetylacetonate in benzene:

$$CoAA_3 + Et_3Al \xrightarrow[H_2]{\text{benzene}} I_B \qquad (3)$$

and we have investigated its reactions with $PhCH_2Br$:

$$I_B + PhCH_2Br \rightarrow PhCH_3 + PhCH_2CH_2Ph + PhCH_2CH_2CH_3 + Ph_2CH_2 \qquad (4)$$

The results are shown in Table 3.

In the synthesis of the catalyst, organoaluminium compounds containing Al—H bonds can be formed which, with $PhCH_2Br$, would lead to $PhCH_3$. For this reason we have carried out the following series of reactions:

(1) the catalytic micture was prepared from $i\text{-}Bu_2AlH$:

$$CoAA_3 + i\text{-}Bu_2AlH \xrightarrow[H_2]{\text{cumene}} I'_C \qquad (5)$$

(2) the catalytic mixture was prepared from an equimolar mixture of $i\text{-}Bu_3Al$ and $i\text{-}Bu_2AlH$:

$$CoAA_3 + \{i\text{-}Bu_2AlH + i\text{-}Bu_3Al\} \rightarrow I''_C \qquad (6)$$

(3) $i\text{-}Bu_2AlH$ was added to the catalytic mixture I_C.

The results of reactions of the above mixtures with $PhCH_2Br$ are shown in Table 4. This Table shows also the dependence of the yield of the toluene on Co/Al ratio.

Reactions of I with Ph_2Hg

The reaction of I with $PhCH_2Br$ causes complete disappearance of the catalytic properties of I for the hydrogenation of olefines. This is not surprising since, after the formation of the Co—Br bond, cobalt is oxidised and the low valence states

TABLE 4

RATIOS $PhCH_3/CoAA_3$, $PhCH_2CH_2Ph/CoAA_3$ AND $Ph_2CH_2/CoAA_3$ AS A FUNCTION OF KIND AND AMOUNT OF ORGANOALUMINIUM COMPOUND USED IN REDUCTION OF COBALT(III) ACETYLACETONATE

Al/Co	$PhCH_3/CoAA_3$	$PhCH_2CH_2Ph/CoAA_3$	$Ph_2CH_2/CoAA_3$
Reducing agent $i\text{-}Bu_3Al$			
5	0.44	0.26	0.40
10	1.51	0.46	0.02
20	1.49	0.35	0.01
Reducing agent $i\text{-}Bu_2AlH$			
5	0.79	0.38	0.12
10	1.41	0.59	0.01
20	0.84	0.30	0.01
Reducing agent $i\text{-}Bu_3Al/i\text{-}Bu_2AlH$ (1/1)			
10	1.61	0.43	0.01
Reducing agent $i\text{-}Bu_3Al/i\text{-}Bu_2AlH$ (1/3)			
20	1.03	0.30	0.01

of cobalt, which are active in the catalytic processes, cease to exist. It was of interest to find out whether reactions of I with organometallic compounds of metals of the main groups (e.g. Ph_2Hg and Ph_4Pb) lead to the formation of benzene and whether after these reactions cobalt retains its properties as a hydrogenation catalyst.

The considered reactions could lead to the following products: metallic cobalt in addition to metallic mercury or phases consisting of [Co,Hg] and [Co,Pb]. These formulae stand for compounds which contain Co—Hg or Co—Pb bonds.

We have found that benzene is not formed as a result of the reaction of I with Ph_4Pb, whereas it is formed as a result of its reaction with Ph_2Hg:

$$I_C + Ph_2Hg \xrightarrow[H_2]{\text{cumene}} C_6H_6 + [Co,Hg] \text{ or } [Co] + [Hg] \qquad (7)$$

The results of reaction 7 are shown in Table 5.

Cobalt-containing products of reaction 7 catalyse the hydrogenation of olefines and also the reaction of Ph_2Hg with hydrogen gas.

Reactions of I with $PhCH{=}CH_2$

The reaction of I_C with styrene in a hydrogen atmosphere is a catalytic hydrogenation but if this reaction were carried out under argon the determination of the amount of the resulting ethylbenzene could provide informations regarding the number of reactive Co—H bonds in the mixture I_C. For this reason we have carried out the following reactions:

$$I_C + PhCH{=}CH_2 \xrightarrow[Ar]{\text{cumene}} I_C''' + PhCH_2CH_3 \qquad (8)$$

$$I_C''' + PhCH_2Br \xrightarrow[Ar]{\text{cumene}} [Co{-}Br] + PhCH_3 \qquad (9)$$

The results of these reactions are shown in Table 6.

TABLE 5

RATIO $C_6H_6/CoAA_3$ (REACTION 7) AS A FUNCTION OF MOLAR RATIO $R_3Al/CoAA_3$
Molar ratio Co/Hg = 1/1.5

i-$Bu_3Al/CoAA_3$	$C_6H_6/CoAA_3$[a]	$C_6H_6/CoAA_3$[b]
2	0.15	0.10
3	0.35	0.17
4	0.50	
5	0.73	0.52
6	0.95	
8	1.32	0.70
10	0.94	1.45
20	0.99	1.13

[a] Under hydrogen. [b] Under argon.

TABLE 6

DEPENDENCE OF MOLAR RATIOS $PhCH_3/CoAA_3$ AND $PhCH_2CH_3/CoAA_3$ ON THE TIME OF REACTION 8

Other conditions of reaction 8: $[Co] = 20 \times 10^{-3}$ mol l^{-1}; $i\text{-}Bu_3Al/CoAA_3 = 5/1$; Co/styrene = 1/2

Time of reaction 8 (h)	$PhCH_3/CoAA_3$	$PhCHCH_2/CoAA_3$	$PhCH_2CH_3/CoAA_3$
0.00	0.21	2.00	0.00
0.75	0.13	1.86	0.15
2.00	0.12	1.81	0.17
30.00	0.15	1.69	0.39

Reactions of I_C with S, CH_3OH and K_{met}

We have carried out reactions of I_C with S, CH_3OH and K_{met}. Each of these reagents caused disappearance of the catalytic properties of I_C. It was also of interest to find out whether these reactions affect the activity of I_C in reduction of $PhCH_2Br$ to $PhCH_3$ and its coupling property. The results of these studies are shown in Table 7.

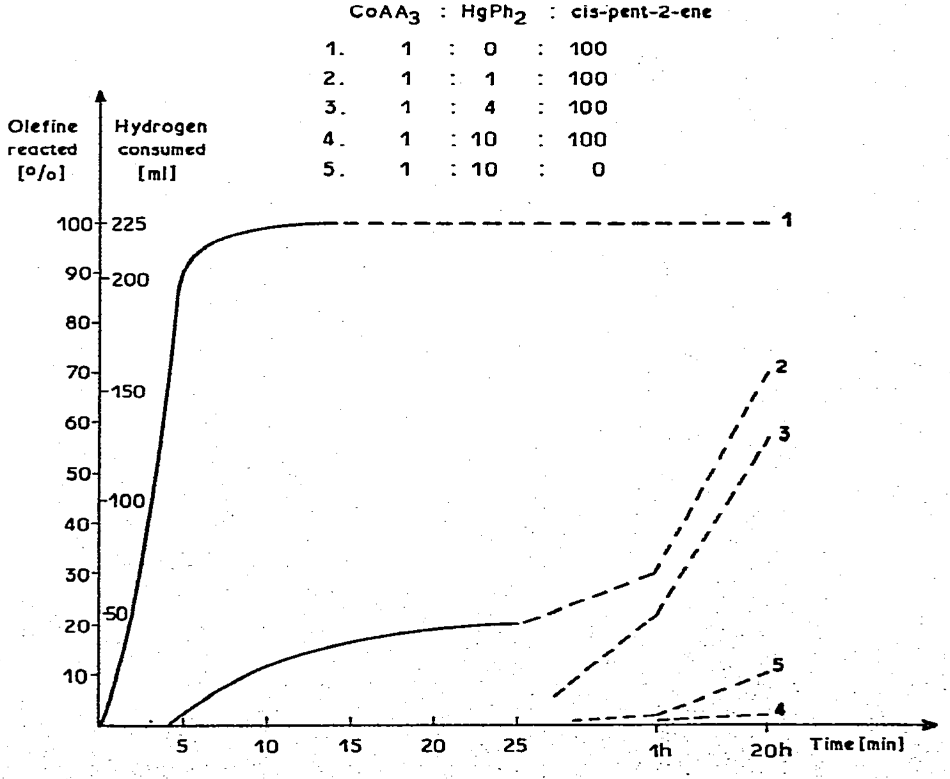


Fig. 2. Inhibited catalysis of hydrogenation of *cis*-pent-2-ene and Ph_2Hg by [Co,Hg] or [Co] + [Hg] product of reaction 7. Conditions the same as on Fig. 1.

TABLE 7

RATIOS $PhCH_3/CoAA_3$ AND $PhCH_2CH_2Ph/CoAA_3$ IN THE SEQUENCE OF REACTIONS:
(1) I_C + S, CH_3OH, K_{met} (potassium sand, great excess)
(2) Reaction with $PhCH_2Br$

$i\text{-}Bu_3Al/CoAA_3$	$S/CoAA_3$	$CH_3CH/CoAA_3$	$K_{met}/CoAA_3$	$PhCH_3/CoAA_3$	$PhCH_2CH_2Ph/CoAA_3$
Reaction with S					
	1				
7	2			0.30	0.60
10	2			0.74	0.72
Reaction with CH_3OH					
5		0		0.52	0.36
5		1		0.41	0.37
5		2		0.26	0.35
5		5		0.38	0.25
Reaction with K_{met}					
5			great excess	0.26	0.15

Discussion

The appearance of toluene as a product of the reaction of I with $PhCH_2Br$ and the formation of benzene as a product of the reaction of I with Ph_2Hg indicate that reactive hydrogen (H_{react}) is present in mixture I. This hydrogen could have the following origins:

(1). The reaction of hydrogen transfer from H_2 via cobalt i.e. catalytic reduction of $PhCH_2Br$ and Ph_2Hg by hydrogen gas.

(2). Hydrogenation by means of organoaluminium compounds which are present in solution I via cobalt. Stoichiometric hydrogenation with organoaluminium compounds is also possible but this reaction gives toluene in a low yield (about 5%).

(3). Dehydrogenation of cumene. This is a stoichiometric reaction which must be accompanied by the formation of α-methylstyrene or $PhC(CH_3)_2C(CH_3)_2Ph$ which are the products of dehydrogenation and coupling, respectively.

(4). [Co—H] bonds.

The results of our experiments rule out the first three possibilities. Toluene and benzene were formed during the reactions of $PhCH_2Br$ and Ph_2Hg carried out under argon after pumping off hydrogen. Also, the reaction of $CoAA_3$ and i-Bu_3Al carried out under argon gave the hydrogenation products. This rules out the first possibility. The ratios $PhCH_3/Co$ and PhH/Co increase up to a certain value of R_3Al/Co (usually 8) and then they remain constant even at large values of R_3Al/Co so the presence of R_2AlH and certain cobalt compounds in the reaction mixture is insufficient for hydrogenation of $PhCH_2Br$ and Ph_2Hg. This excludes the second possibility. The third possibility is ruled out by the fact we did not observe cumene dehydrogenation products or the coupling product $PhC(CH_3)_2C(CH_3)_2Ph$. Thus the only source of the hydrogen necessary for the formation of toluene from $PhCH_2Br$ and benzene from Ph_2Hg is hydrogen combined in some way with cobalt [Co—H]. The formation of dibenzyl observed during the reaction with $PhCH_2Br$ indicates that I contains cobalt in an active state which makes possible the coupling of $PhCH_2^{\cdot}$. The results shown in Table 1 can be interpreted as follows:

(1). All the hydrogen participating in the reactions of $PhCH_2Br$ and Ph_2Hg is obtained from [Co—H] bonds and dibenzyl is formed during the subsequent reaction:

$$[Co{-}H] + PhCH_2Br \rightarrow PhCH_3 + [CoBr] \tag{10}$$

$$[CoBr] + PhCH_2Br \rightarrow 0.5\ PhCH_2CH_2Ph + [CoBr_2] \tag{11}$$

$$\underline{\overline{[Co{-}H] + 2\ PhCH_2Br \rightarrow PhCH_3 + 0.5\ PhCH_2CH_2Ph + [CoBr_2]}} \tag{12}$$

(2). The source of hydrogen participating in the reactions of $PhCH_2Br$ and Ph_2Hg is the hydride $[CoH_2]$:

$$[CoH_2] + 2\ PhCH_2Br \rightarrow 2\ PhCH_3 + [CoBr_2] \tag{13}$$

whereas dibenzyl is formed due to the presence of "active" cobalt:

$$[Co]_{act} + 2\ PhCH_2Br \rightarrow PhCH_2CH_2Ph + [CoBr_2] \tag{14}$$

These observations indicate that mixture I contains either one cobalt compound [Co—H] or two such compounds [CoH_2] and $[Co]_{act}$.

However, the amount of cobalt calculated according to eqns. 10-14 is considerably smaller than that taken for reaction 1 in the form of $CoAA_3$. This can be interpreted in two ways: either not all the cobalt taken for reaction 1 reacts with the organoaluminium compounds some remaining in the form of $CoAA_3$ or some other inactive compound, or the reaction took place and cobalt was converted to the inactive form $[Co]_{inact}$.

According to the work published by Tamai et al. [6] all the cobalt reacts even at the molar ratio $CoAA_3/R_3Al = 1/1.5$ and in the post reaction mixture it is present in the form of a compound not containing acetylacetone ligands. Thus the second possibility is more probable: a fraction of the cobalt present in the post reaction mixture does not participate in the formation of toluene and dibenzyl during the reaction of $PhCH_2Br$.

The composition of mixture I prepared at low molar ratios: $R_3Al/CoAA_3 = 2, 3$

Cobalt is present mainly in the form which is inactive in the reaction with $PhCH_2Br$, $[Co]_{inact}$. If the remaining cobalt were present in the form [CoH_2] we would not observe the formation of $PhCH_2CH_2Ph$. The formation of dibenzyl indicates that the mixture I contains either $[Co]_{act}$ or [Co—H]. The possibility of the existence of the product of interaction between $[Co]_{act}$ and [Co—H]:

$$[Co]_{act} + [Co\text{—}H] \rightarrow [Co_2H]$$

should also be taken into account. The presence of the last compound in mixture I seems to be quite probable and it appears that at small molar ratios most of the cobalt present in the products of reaction $CoAA_3$ and i-Bu_3Al is in the forms $[Co]_{inact}$ + [Co—H].

The composition of mixture I prepared at intermediate molar ratios $R_3Al/CoAA_3 = 4, 5$

This mixture also contains $[Co]_{inact}$ and [Co_2H] but their relative amounts are different. The mixture contains more [Co_2H] and the [Co—H] species begins to appear.

The composition of mixture I prepared at high molar ratios $R_3Al/CoAA_3 = 6, 8, 10$

At these molar ratios the main product is [Co—H]. The inactive cobalt is almost absent. Obviously there is no sharp border between these regions and mixtures I prepared at various molar ratios contain certain amounts of each of the species discussed. This is shown in Fig. 3.

Reaction $CoAA_3$ and i-Bu_3Al in an argon atmosphere

The values of $PhCH_3/Co$ and $PhCH_2CH_2Ph/Co$ ratios obtained for mixture I prepared in an argon atmosphere (Table 1) indicate that the amounts of $[Co]_{inact}$, [Co_2H] and [Co—H] are similar to those observed in the case of the reactions carried out under hydrogen. Hence the source of reactive hydrogen formed during the preparation of mixture I is the organoaluminium compound rather than H_2. The kind of gas under which the reaction is carried out also has no effect on the amount of cobalt participating in the coupling reaction.

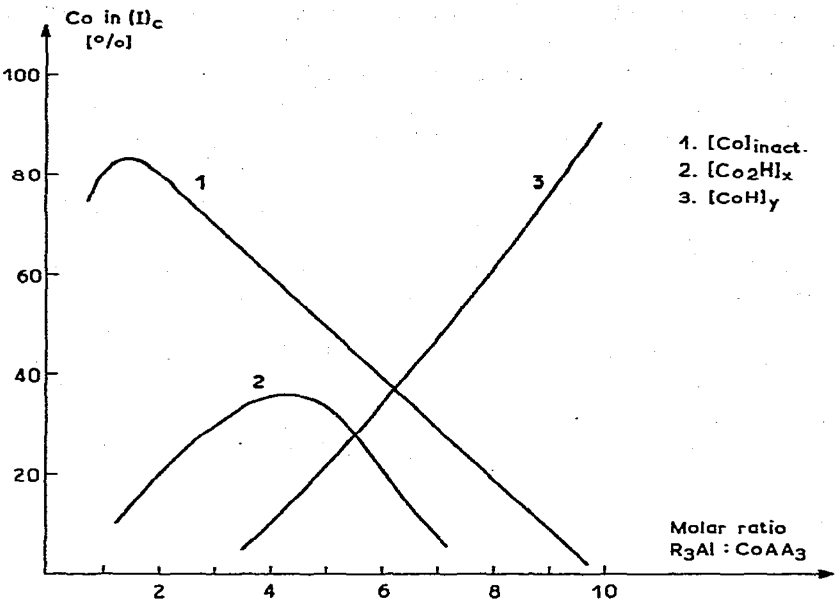


Fig. 3. Proportions of $[Co_2H]_x$, $[Co{-}H]_y$ and $[Co]_{inact}$ as a function of molar ratio i-$Bu_3Al/CoAA_3$.

The dependence of the ratios $PhCH_3/Co$ and $PhCH_2CH_2Ph/Co$ on the time of reaction of I with H_2

We did not observe any time dependence of the ratios $PhCH_3/Co$ and $PhCH_2CH_2Ph/Co$. This means that the number of Co—H bonds and the amount of inactive cobalt formed during the reaction do not change as a result of contact with hydrogen. Since we have observed the slow appearance of precipitates containing cobalt we can say that this process has no effect on the activity of mixture I in the hydrogenation of $PhCH_2Br$ and in the coupling reaction. This observation corroborates our hypothesis that we are dealing with $[Co_2H]$ and $[Co{-}H]$ in which the link between cobalt and hydrogen is a true chemical bond. Compounds $[Co_2H]$ and $[Co{-}H]$ are polymers which should be expressed in the forms $[Co_2H]_x$ and $[Co{-}H]_y$. When x and y become sufficiently large the polymers precipitate from their solutions in hydrocarbons but when x and y are small we are dealing with true solutions. The kinetics of agglomeration and precipitation is very complex and probably depends on the amounts of traces of impurities, which can catalyse or inhibit the formation of aggregates.

Solvation, formation of complex compounds of cobalt with the organoaluminium compounds, and catalytic hydrogenation

There is no doubt that the solvents interact with the products of reaction of $CoAA_3$ with R_3Al which contain cobalt and it appears that this interaction is stronger in the case of small values of x and y. When the aggregates are large cobalt atoms present in the bulk of the microcrystallites do not contact the solvent molecule. We suggest that the same is true also in the case of the reaction of cobalt with R_3Al leading to the formation of $Co \rightarrow AlR_3$. In the case of cobalt atoms or small aggregates the bond shown by the arrow is stronger and the number of such bonds is larger.

We have observed the fastest rates of hydrogenation in the case of I prepared at the ratio $CoAA_3/R_3Al$ = 4 to 5. In this case the amount of the $[Co_2H]_x$ species was also the largest. If we accept the hypothesis that in hydrogenation of olefines the active centres are first of all Co atoms situated irregularly in the $[Co_2H]_x$ species we come to the conclusion that the hydrogenation rate should be a function of the amount of this phase and the number of active cobalt atoms in this phase. At the present time we are not yet able to give the method of preparation of $[Co_2H]_x$ containing the maximum amount of the active centres.

As a result of reactions of I with S, CH_3OH and K the catalytic properties of I disappear. The products of the reactions of I with CH_3OH and K retain the property of stoichiometric reduction of $PhCH_2Br$ and coupling of $PhCH_2^{\cdot}$. This observation is in agreement with the concept of active centres in catalytic hydrogenation which are analogous to the centres participating in heterogeneous catalysis.

Experimental part

Reagents

Cobalt acetylacetonate ($CoAA_3$) manufactured by Koch—Light Lab. was used without further purification. Organoaluminium compounds i-Bu_3Al (i-Bu_2AlH and Et_3Al) of Fluka AG were also used without purification. Cumene (POCh, Gliwice) was dried over sodium and was distilled immediately before use in an argon atmosphere. Then it was degassed and saturated with hydrogen. Hydrogen and argon were freed from oxygen by means of BTS and were dried with 5A molecular sieves.

Procedure

The preparation of I and the reactions of I with $PhCH_2Br$ and with Ph_2Hg were carried out under hydrogen or argon at room temperature.

The glass apparatus used in these reactions (100 ml three necked flasks) was previously heated at about 150°C in vacuo (P = 1 mmHg) and was rinsed several times with hydrogen.

The solutions of $CoAA_3$, R_3Al and Ph_2Hg in cumene were transferred to the reactor by means of hypodermic syringes. The reagents were added in the following order: cumene, organoaluminium compound, $CoAA_3$ solution. The last reagent was added to the reactor dropwise and very slowly with constant stirring by means of a magnetic stirrer.

An example of the reaction

Solutions in cumene having the concentrations: $[CoAA_3]$ 16.75 mmol l^{-1}, [i-Bu_3Al] 500.00 mmol l^{-1}, $[Ph_2Hg]$ 75.5 mmol l^{-1} were added in the following amounts: cumene 5.6 ml, i-Bu_3Al 2.4 ml, $CoAA_3$ 12.0 ml.

The change of the green colour of $CoAA_3$ to a dark brown colour characteristic of catalyst I took place immediately (in the case of small Al/Co ratios after a short time).

After 60 min from the start of the reaction of $CoAA_3$ with i-Bu_3Al, benzyl bromide (35 μl = 3 mol/mol Co) or a solution of Ph_2Hg in cumene (2 ml = 1.5 mol/mol Co) was added to the reactor. The reaction mixture was constantly and vigorously stirred.

When the synthesis of I was carried out under hydrogen the catalytic solution was several times degassed and saturated with argon before the reaction with Ph_2Hg.

After the reaction of I with $PhCH_2Br$ and Ph_2Hg, samples of the reaction mixture were collected and evaporated in vacuo, the distillate being condensed at —70°C. The products were analysed by gas chromatography in order to determine the amount of toluene or benzene formed during the reaction. The amount of dibenzyl was also determined chromatographically by injecting a sample of the reaction mixture directly into the chromatographic apparatus (Giede 18.3). Chromatography was carried out under the following conditions: determination of toluene and benzene: 3 m 5% DC-710 on chromosorb GAW, temp. 100°C, pressure N_2 1.1 atm; determination of dibenzyl: 1 m 5% DC-710 on chromosorb GAW, temp. 158°C, pressure N_2 2 atm. In both cases a flame ionisation detector was used.

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