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HYDROGEN TRANSFER REACTIONS CATALYSED BY COBALT COMPLEXES

I. HYDROGEN TRANSFER BETWEEN CYCLOHEXANONE AND ISOPROPYL ALCOHOL CATALYZED BY A DERIVATIVE OF TRIS(TRIPHENYLPHOSPHINE)COBALT TRIHYDRIDE

E. MAŁUNOWICZ, S. TYRLIK*
Laboratory of Homogeneous Catalysis, Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warszawa (Poland)

and Z. LASOCKI
Institute of Polymers, Technical University, ul. Zwirki 36, 90-539 Łódź (Poland)

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Summary

Tris(triphenylphosphine)cobalt trihydride (I) is a direct precursor of a catalyst complex for a hydrogen transfer between cyclohexanone and isopropyl alcohol. During the reaction polymeric cobalt alkoxides are formed. The mechanism of the catalytic reaction is discussed. I is also found to be a useful reducing agent of carbonyl groups in organic compounds.

Introduction

In contrast to the hydrogenation of olefins, homogeneous hydrogenation of the carbonyl group has received little attention, until recently, when there has been a growing interest in the homogeneous hydrogen transfer reaction:

$$RR'CO + i\text{-}PrOH \overset{cat}{\rightleftharpoons} RR'CHOH + Me_2CO \quad (1)$$

The reaction is catalyzed by complexes such as (a) those formed from $IrCl_4$ and $R''R''SO$ or H_3PO_3 (or phosphites), and (b) some phosphine complexes of Ir, Ru and Re [1]. In this paper we report our observation that tris(triphenylphosphine)cobalt trihydride $(PPh_3)_3CoH_3$ (I) is a direct precursor of a catalyst for the above reaction (1).

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*To whom correspondence should be addressed.

Results

The stoichiometry of the reduction of ketones with I

Tris(triphenylphosphine)cobalt trihydride can reduce the carbonyl groups of ketones stoichiometrically, as is shown in Table 1. A hydrolysing agent is necessary to isolate the free alcohol; this indicates that alkoxides are probably formed during the reaction.

The reduction of ketones by isopropyl alcohol catalyzed by the complex formed from I

When a ketone/isopropanol mixture in the appropriate ratio is added to a benzene solution of I the colour changes from yellow to dark brown and subsequently to reddish-brown. After about 1 h the colloidal substance III starts to precipitate from the solution, precipitation being complete after about 10 h. After decanting, the benzene phase contains practically no cobalt and all the cobalt used is present in the colloid. The interaction of I with isopropyl alcohol itself does not produce any such compound. The reaction mixture contains alcohol derived from the parent ketone, and acetone from isopropyl alcohol. Figure 1 shows the effect of changing the order in which reagents are added on the rate of formation of cyclohexanol. The reactivity of the system with respect to various ketones is illustrated in Table 2.

The catalytic reaction was studied using the cyclohexanone/isopropanol couple. The catalytic reaction can be divided into three phases:

(1). Reaction of I to give the actual catalyst II. Under the temperature and concentration conditions given in Table 2, this phase lasts for a few minutes.

(2). Catalytic hydrogen transfer from isopropyl alcohol to the ketone effected by II, whose probable structure will be discussed later.

(3). A period of decreasing catalytic activity up to the point of complete cessation, undoubtedly caused by the precipitation of the cobalt compound from benzene solution. The structure of III and the reaction which produces it will be discussed later.

It is quite obvious that there is no sharp division between these three phases of the reaction.

Catalysis by II starts immediately its first molecules are formed and takes

TABLE 1

STOICHIOMETRIC REDUCTION OF KETONES WITH $(PPh_3)_3CoH_3$

[Solvent: benzene; reaction time 5 h; t. = 25±1°; [I] = 0.025 *M*]

Ketone	Molar ratio I/ketone	Product	Yield (%)
Cyclohexanone	1/1	Cyclohexanol	100
Cyclohexanone	1/5	Cyclohexanol	20
Acetone	1/1	Propan-2-ol	20
Cyclopentanone	1/1	Cyclopentanol	90
Acetophenone	1/1	α-Phenylethanol	100
Benzophenone	1/1	Benzhydrol	80
1-Acetylcyclohexene	1/1	1-Acetylcyclohexane	5
5α-Cholestan-3-one	1/1	5α-Cholestan-3β-ol	90

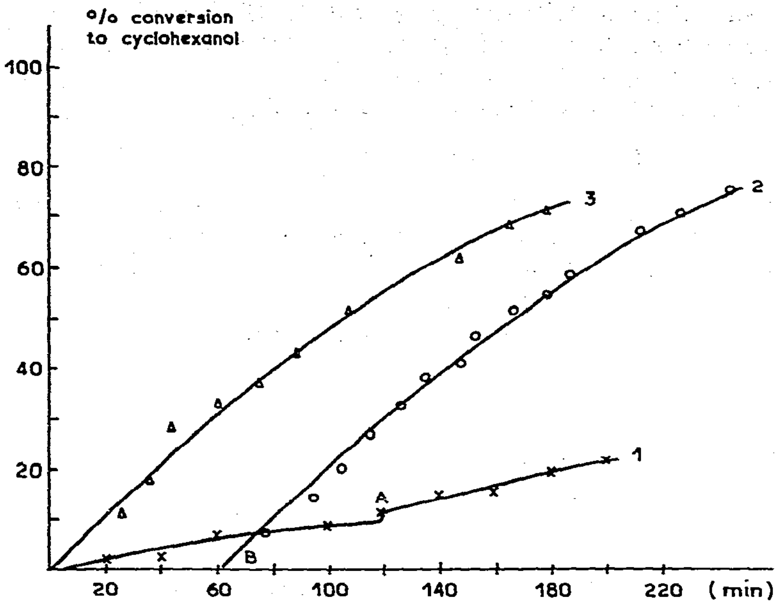


Fig. 1. The influence of the order of addition on the rate of formation of cyclohexanol. (1) The alcohol added at point A. Prior to this only ketone was present in the reaction mixture (2) At B cyclohexanone was added to a mixture of isopropanol + I. Cyclohexanol was detected without any additional hydrolysing agent being needed. (3). Cyclohexanone and isopropanol were added together at the start.

TABLE 2

ACTIVITY OF THE CATALYTIC SYSTEM IN THE REDUCTION OF KETONES

[t. = 25 ± 1°; reaction time 5 h; solvent = benzene]

Ketone	Molar ratio		Product	Yield (%)
	I/ketone	I/alcohol		
Cyclohexanones	1/10	I/i-PrOH = 1/20	Cyclohexanol	93
Cyclopentanone	1/10	I/i-PrOH = 1/20	Cyclopentanol	60
Acetophenone	1/10	I/i-PrOH = 1/20	α-Phenylethanol	65
1-Methylcyclohexan-3-one	1/10	I/i-PrOH = 1/20	None	
1-Acetylcyclohexene	1/10	I/i-PrOH = 1/20	1-Acetylcyclohexane	5
Acetone	1/5	I/α-phenylethanol 1/10	Isopropanol	50
Acetone	1/10	I/cyclohexanol 1/20	Isopropanol	8
5α-Cholestan-3-one	1/10	I/i-PrOH = 1/20	5α-Cholestan-3α-ol	60
			5α-Cholestan-3β-ol	40
5β-Andrestan-3,17-dione	1/10	I/i-PrOH = 1/20	5β-Andrestan-3β-ol-17-one	50
			5β-Andrestan-3β-ol-17-one	40
3β-Acetoxy-pegn-5-en-20-one	1/10	I/i-PrOH = 1/20	None	
3β-Acetoxy-cholestan-7-one	1/10	I/i-PrOH = 1/20	Alcohol product	traces

place concurrently with formation of III, the concentration of II reaching a maximum concentration and then decreasing. The entire system presents a complicated set of simultaneous and consecutive reactions.

Catalytic hydrogen transfer proceeds according to the equation:

$$\mathrm{II} + \mathrm{RR'C{=}O} + \mathrm{{>}CHOH} \rightleftharpoons \mathrm{RR'CHOH} + \mathrm{{>}C{=}O} + \mathrm{II} + \mathrm{III} \qquad (2)$$

II in reaction (2) refers to an active catalyst and transfer of the cobalt from II to III decreases the concentration of active species and so it is responsible for the cessation of the hydrogen transfer reaction.

In this paper we are concerned with the study of substances II and III, as well as with reaching some conclusions regarding the mechanism of hydrogen transfer.

Compound II

II has not been isolated so far in a pure state. All methods making use of precipitation, evaporation or freezing techniques lead to an oil which is extremely sensitive to water and air. II is formed in reactions with ketones but not with alcohols, as shown by:

(1). When an alcohol is added as the first reactant the following reaction probably takes place:

$$\mathrm{(PPh_3)_3CoH_3} + \mathrm{{>}CHOH} \rightarrow \mathrm{(PPh_3)_xCoH}\cdots\mathrm{{>}CHOH} + \mathrm{H_2} \qquad (3)$$

The following observations tend to confirm this supposition: (a), there is hydrogen evolution; (b), the IR spectra of the reaction mixture, exhibiting a band at 2100 cm^{-1} attributable to ν(Co—H) in a monohydride [2]; (c), there is no acetone in the reaction mixture and therefore no dehydrogenation of isopropanol has taken place; (d), there is no colloidal precipitate and cobalt remains in solution in benzene for a very long time; (e), the addition of ketone causes the band at 2100 cm^{-1} to disappear immediately, indicating the uptake of hydric hydrogen.

(2). When a ketone is added as the first reactant hydrogen is evolved and the colour changes from yellow to reddish-brown. Addition of a hydrolysing agent liberates the alcohol. Evaporation without a hydrolysing agent gives a residue whose IR spectrum shows ν(C—O) bands attributable to an alkoxide. In the reaction of I with ketones the product is a mixture of II and III. II still contains coordinated PPh_3 molecules but III is a polymeric alkoxide.

Compound III

We tried to isolate III using several preparative procedures. That most frequently used was the reaction of I with ketone and alcohol in benzene at room temperature. For a molar ratio of reactants 1/10/20 there was no cobalt in the benzene solution after about 10 h. Colloidal substance III was very difficult to filter; IR spectra showed an absence of PPh_3 and OH groups, and strong C—O bands, indicating an alkoxide structure. When III was obtained from cyclohexanone and isopropanol, cyclohexanol and isopropanol were detected in the molar ratio 1/1 after hydrolysis of III with acetic acid; when III was synthesized from cyclohexanone then only cyclohexanol was detected after hydrolysis.

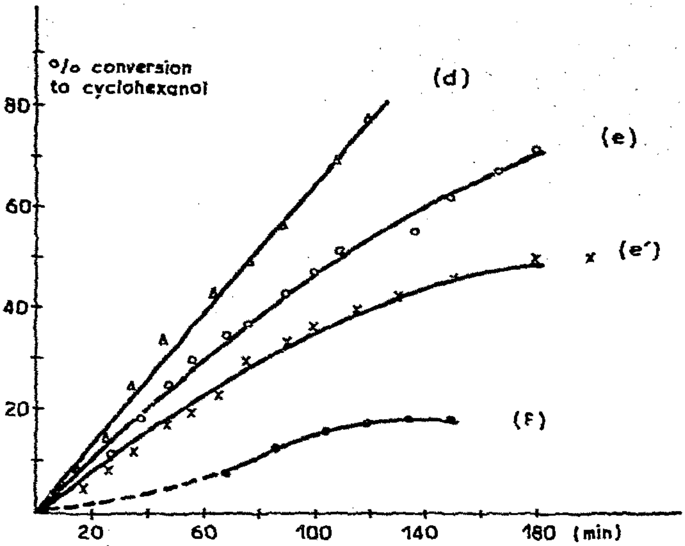


Fig. 2. Influence of cyclohexanone concentration on the rate of cyclohexanol formation. [I] = 0.0083 *M*; [Isopropanol] = 0.166 *M*; Solvent = benzene; t = 25°; [Cyclohexanone] = 0.0415 *M* (d); 0.083 *M* (e); 0.166 *M* (f); 0.029 *M* PPh_3 added (e').

Elemental analysis of the latter substances indicated a formula $[C_6H_{11}O\text{—}Co]_n$ and the complete insolubility of III in any organic solvent indicated its polymeric nature. On exposure to air a 0.5 g sample of III changed colour after 10-20s. After 10 min of contact with air and subsequent drying under high vacuum there was no carbon present in the residue.

We introduced the following modifications to the standard preparative procedure: reaction in boiling benzene; reaction in THF, both at 25° and at

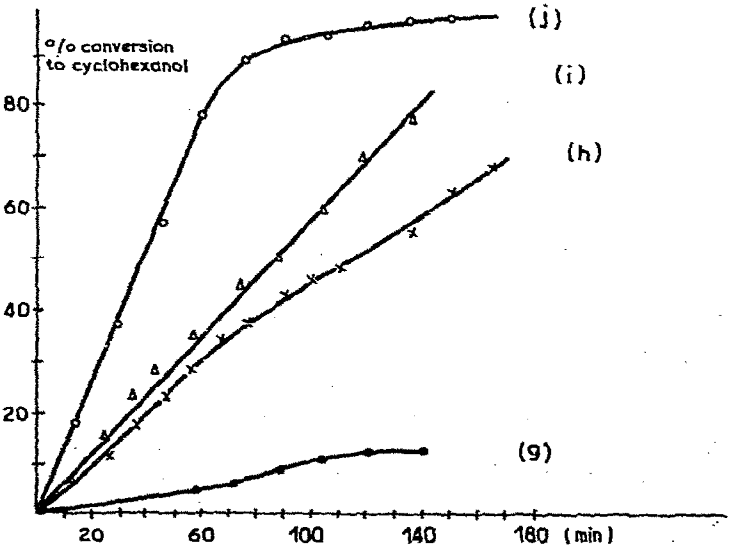


Fig. 3. Influence of complex concentration on the rate of cyclohexanol formation. [Cyclohexanone] = 0.083 *M*; [Isopropanol] = 0.166 *M*; Solvent = benzene; t = 25°; [I] = 0.00415 *M* (g); 0.0083 *M* (h); 0.0166 *M* (i); 0.0249 *M* (j).

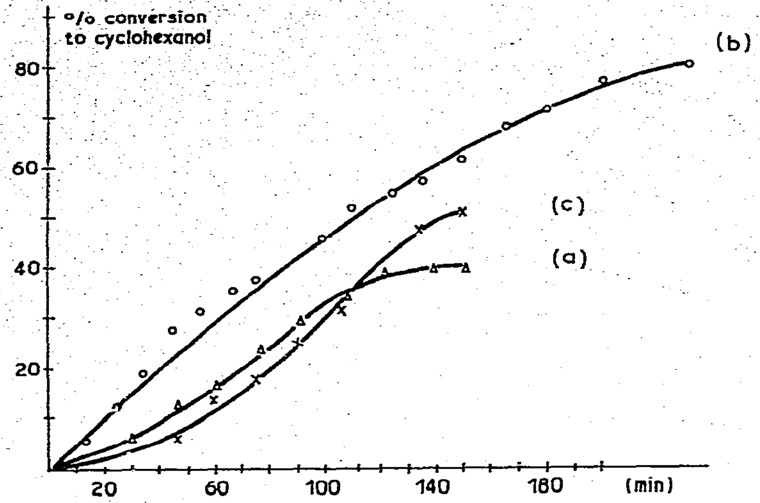


Fig. 4. Influence of isopropanol concentration on the rate of cyclohexanol formation. [I] = 0.0083 *M*; [Cyclohexanone] = 0.083 *M*; Solvent = benzene; t = 25°; [Isopropanol] = 0.083 *M* (a); 0.166 *M* (b); 0.332 *M* (c).

reflux; reaction with the substrate pairs: cyclohexanone/cyclohexanol and benzophenone/benzhydrol, but the compounds obtained during these procedures gave very unsatisfactory elemental analyses.

Influence of concentration on the rate of reaction

Figures 2—4 show the effect of changes in ketone, isopropanol and complex concentrations on the reaction rate. With increasing concentration of complex there is a systematic increase in reaction rate but increased isopropanol and ketone concentrations caused an initial increase and then a decrease in the rate of reaction.

Discussion and conclusions

In proposing a reaction mechanism the following observations must be taken into account:

(1). $(PPh_3)_3CoH_3$ is only a catalyst precursor.

(2). I in the reaction with ketones gives in the first instance $L_xCo—OR$ and in the reaction with alcohols it gives $L_xCoH\cdots ROH$.

(3). $L_xCo—OR$ is the most probable catalyst for hydrogen migration.

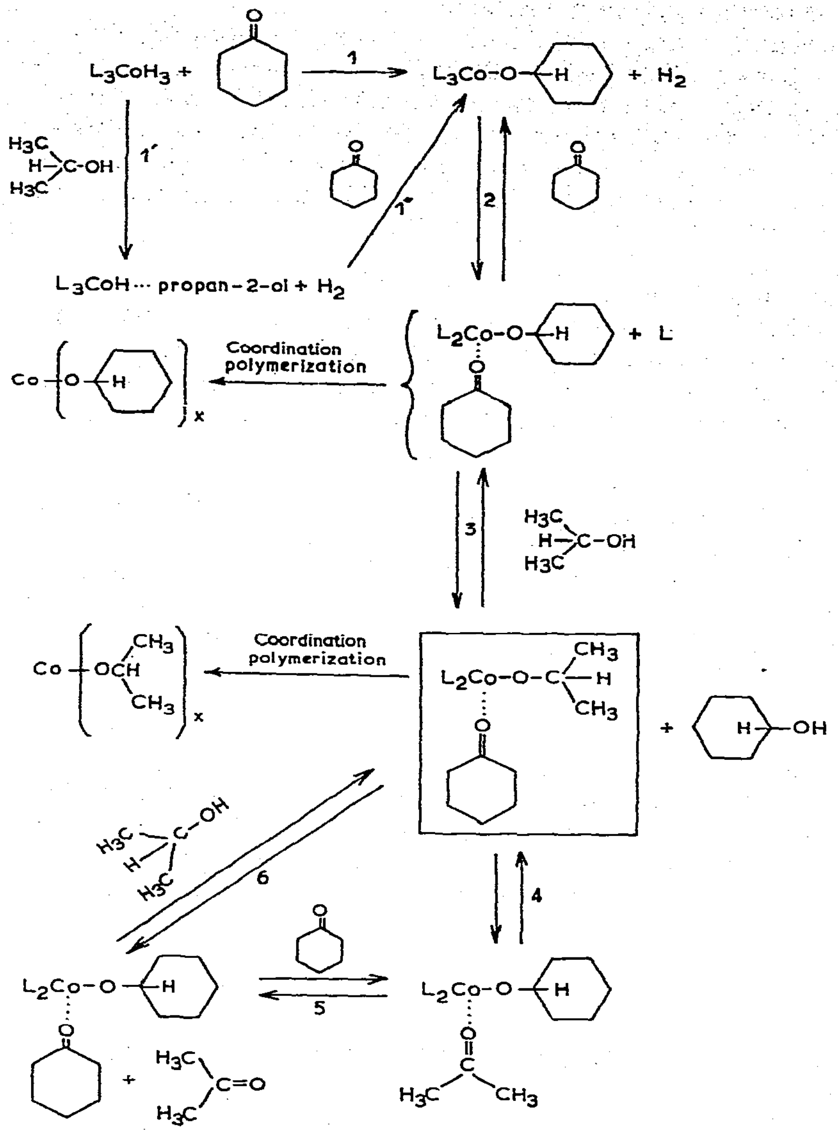
(4). The reaction is reversible.

(5). The reaction is inhibited by addition of phosphine (Fig. 2e').

(6). Stoichiometric reaction of I with 5α-cholestan-3-one gives a 3β-equatorial alcohol in 90% yield and catalytic reaction leads to the mixture of epimeric alcohols in the ratio $3\alpha/3\beta = 3/2$. This observation indicates that the hydride $L_xCoH\cdots ROH$ is not formed as a distinct compound and the hydride transfer does not take place via this species.

(7). Increase of ketone and alcohol concentrations facilitates the formation of polymeric alkoxides.

SCHEME 1



All these observations lead to the following reaction scheme (Scheme 1) where step 4 is the actual catalytic hydrogen transfer and the reactions responsible for the cessation of the catalysis are the coordination polymerizations. Undoubtedly the cobalt orbitals participate in hydrogen transfer from the $-Co-O-CH(CH_3)_2$ unit to the coordinated ketone.

Experimental

All reactions were carried out under purified argon. The solvents were distilled from sodium and were deoxygenated prior to use.

IR spectra were recorded with a Unicam SP-200 using Nujol, KBr pellets or a 5% solution in benzene, with compensation.

The GC of the reaction products and solutions were performed with a Chromatoprep 503 apparatus, fitted with a FID detector, argon being the carrier gas. A 3 m steel column, 4 mm in diameter, filled with 60/80 mesh chromosorb W with 10% Carbowax 20M was used. Optical rotation was measured with a Hilger—Watts polarimeter ($c = 1$ g/100 ml of $CHCl_3$). For separations by column chromatography silica gel (Merck) was used. The complex I was prepared according to Rinze [2].

The stoichiometry of reactions of I with ketones

The appropriate ketone (0.5 mmoles) was added to a solution of 0.47 g of I in 20 ml of benzene, inducing a change in colour from orange to dark-brown, which then turned reddish-violet. After 4 h a 1 ml sample of solution was withdrawn, distilled under reduced pressure and the products identified by GC.

Isolation of the cobalt(III) alcoholate

The reaction of I with cyclohexanone gave a violet, colloidal suspension after 6 to 8 h, while the supernatant liquid remained colourless.

The colloidal precipitate was filtered off with much difficulty, was washed with 10 ml benzene and dried under vacuum for 1 h at ambient temperature to give 0.08 g of a rose-violet solid which was very unstable when exposed to air, identified as complex III. (Found: C, 43.39; H, 8.69. (III) calcd.: C, 45.6; H, 6.39%.)

Hydrogen transfer from the $(PPh_3)_3CoH_3$—propan-2-ol system to ketones

Kinetic data were obtained for the systems indicated in Figs. 1—4 as follows: 1 ml samples of solution were transferred to small round-bottomed flasks, containing ca. 0.01 ml glacial acetic acid. After neutralisation with sodium carbonate the solution was distilled under vacuum and the yield of products was determined by GC.

Acknowledgements

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