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Oligomerization of aldehydes catalyzed by cobalt carbonyl complexes

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Abstract

The catalytic activity of $Co_2(CO)_6L_2$ complexes (L = carbon monoxide, phosphines) has been tested in the oligomerization of aldehydes under the conditions adopted for hydroformylation of olefins. The influence of the type of substrate, phosphinic ligand and reaction temperature has been investigated. The products formed are β-hydroxyaldehydes, α,β-unsaturated aldehydes and β-hydroxyesters. Very poor catalytic activity was shown by cobalt complexes in the oligomerization of ketones. The role of cobalt carbonyl complexes in the aldehyde oligomerization has been rationalized by a mechanism, in which acylcobalt intermediates are involved.

Keywords: Oligomerization; Cobalt; Carbonyl; Phosphine; Catalysis; Homogeneous; Aldehydes

1. Introduction

In the hydroformylation of olefins catalyzed by dicobalt octacarbonyl or its phosphine substituted derivatives [$Co_2(CO)_6L_2$ (L = carbon monoxide, phosphines)] aldols formation, by dimerization of aldehydes, usually occurs to a small extent and it is often followed by dehydration and hydrogenation of the double bond [1,2]. Trimerization of aldehydes has also been reported in some cases.

The one step production of 2-ethylhexanol from propene, CO and H_2, the so-called Aldox process [3–5], requires the presence of KOH and a Ni complex, in addition to a cobalt catalyst; 2-ethylhexanol were also obtained by Tian et al. in a one-pot reaction using $Co_2(CO)_5(PBu_3)_2N$ (N = 2-aminopyridine) as catalyst [6]. In both processes the catalytic activity of cobalt complexes in the aldolization has not been proven since the strong base (KOH) or the strong basic groups (NH_2) present on the nitrogen containing ligand may be responsible of the aldolization.

We have investigated the transformation of typical aldehydes in the presence or in the absence of the cobalt complexes $Co_2(CO)_6L_2$ under hydroformylation conditions used to produce aldehydes in order to distinguish the relevance of the cobalt catalyzed and/or of the pure thermal reactions. Attempts to oligomerize ketones have been also made.

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2. Results and discussion

The same experimental conditions used for the hydroformylation of olefins to aldehydes catalyzed by phosphine substituted cobalt carbonyls (150°C, p_{CO} 5 atm, p_{H_2} 40 atm) [7] were adopted to investigate the dimerization and trimerization of aldehydes, i.e., the oligomerization process. [We use the generic term oligomerization instead of aldolization because the products formed, dimers and trimers of the substrate employed, are aldols, their derivatives (α,β-unsaturated aldehydes) and β-hydroxyesters.] Pure aldehydes (acetaldehyde, propanal, butanal, 2-methylpropanal, 2-methylbutanal, benzaldehyde and phenylacetaldehyde) were used as substrates, normally without solvent, in order to improve the formation of high boiling materials. Dicobalt octacarbonyl and its phosphine substituted derivatives [$Co_2(CO)_6L_2$ (L = carbon monoxide, phosphines)] were used as catalysts.

Series of isocronous experiments were carried out on different substrates in an autoclave heated at the appropriate conditions, using the same catalyst concentration. The results are compared with those obtained in the absence of catalyst. The data are reported in Tables 1–5.

2.1. Nature of the oligomerization products

Whatever the substrate and the catalytic precursor, the conversions of the aldehydes were decidedly higher than those obtained in the absence of a catalyst. Also the nature and the isomeric distribution of the products were different thus supporting the indication of a catalytic reaction. The aldehyde dimerizes first giving an aldol which then may either dehydrate giving the α,β-unsaturated aldehyde or may

Table 1
Acetaldehyde oligomerization

Catalyst	Conv. (%)	Dim[a] (%)	Trim A[a] (%)	Trim B[a] (%)	Trim-OH[a] (%)	Tish[a] (%)
$Co_2(CO)_8$	53.8	43.6	0.3	0.8	2.2	6.9
$Co_2(CO)_6[P(CH_2CH_3)_3]_2$	58.8	46.3	2.4	2.4	3.5	4.2
$Co_2(CO)_6[P(CH_2CH_2CH_2CH_3)_3]_2$	66.8	48.6	4.2	5.2	4.5	4.3
$Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3)_3]_2$	56.3	40.0	3.8	3.0	4.6	4.9
$Co_2(CO)_6[P(CH_2CH_2COOCH_3)_3]_2$	54.7	40.0	0.2	0.2	2.6	11.7
$Co_2(CO)_6[P(CH_2CH_2CN)_3]_2$	59.7	44.0	1.1	1.3	4.0	9.3
Absent	11.5	11.5	0.0	0.0	0.0	0.0

Acetaldehyde 25 ml, catalyst 0.02 mmol, p_{CO} = 5 atm, p_{H_2} = 40 atm, temperature 150°C, reaction time 3 h.
[a]Dim: but-2-enal; Trim A: 2-ethenylbut-2-enal; Trim B: hex-2,4-dienal; Trim-OH: 2-(1-hydroxyethyl)but-2-enal; Tish: mixture of 1- and 3-acetate of 1,3-butandiol.

Table 2
Propanal oligomerization

Catalyst	Conv. (%)	Dim[a] (%)	Dim-OH[a] (%)	Tish[a] (%)
$Co_2(CO)_8$	47.7	6.1	10.6	31.0
$Co_2(CO)_6[P(CH_2CH_3)_3]_2$	40.3	6.0	4.8	29.5
$Co_2(CO)_6[P(CH_2CH_2CH_2CH_3)_3]_2$	24.0	2.2	4.2	17.6
$Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3]_3)_2$	25.0	3.4	5.2	16.4
$Co_2(CO)_6[P(CH_2CH_2COOCH_3)_3]_2$	46.4	10.2	7.6	28.6
$Co_2(CO)_6[P(CH_2CH_2CN)_3]_2$	51.9	11.2	9.4	31.3
Absent	19.3	1.1	5.8	12.4

Propanal 25 ml, catalyst 0.02 mmol, p_{CO} = 5 atm, p_{H_2} = 40 atm, temperature 150°C, reaction time 3 h.
[a]Dim: 2-methylpent-2-enal; Dim-OH: 3-hydroxy-2-methylpentanal; Tish: mixture of 1- and 3-propanoate of 2-methyl-1,3-pentandiol.

Table 3
Butanal oligomerization

Catalyst	Conv. (%)	BuOH[a] (%)	Dim[a] (%)	Dim-H[a] (%)	Dim-OH[a] (%)	Tish[a] (%)
$Co_2(CO)_8$	63.6	0.0	51.8	0.0	0.4	11.4
$Co_2(CO)_6[P(CH_2CH_3)_3]_2$	55.9	0.0	39.1	0.3	1.0	15.5
$Co_2(CO)_6[P(CH_2CH_2CH_2CH_3)_3]_2$	26.6	0.0	8.8	0.0	2.9	14.9
$Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3]_3)_2$	65.9	0.6	31.9	0.6	5.6	27.2
$Co_2(CO)_6[P(CH_2CH_2COOCH_3)_3]_2$	39.7	0.0	24.8	0.0	1.2	13.7
$Co_2(CO)_6[P(CH_2CH_2CN)_3]_2$	43.5	0.0	28.0	0.0	1.0	14.5
Absent	23.3	0.0	4.8	0.0	3.1	15.4

Butanal 25 ml, catalyst 0.02 mmol, $p_{CO} = 5$ atm, $p_{H_2} = 40$ atm, temperature 150°C, reaction time 3 h.
[a]BuOH: 1-butanol; Dim: 2-ethylhex-2-enal; Dim-H: 2-ethylhexanal; Dim-OH: 2-ethyl-3-hydroxyhexanal; Tish: mixture of 1- and 3-butanoate of 2-ethyl-1,3-hexandiol.

Table 4
2-Methylpropanal oligomerization

Catalyst	Conv. (%)	*i*-BuOH[a] (%)	Dim-OH[a] (%)	Trim-OH[a] (%)	Tish[a] (%)
$Co_2(CO)_8$	49.1	0.0	0.0	0.0	49.1
$Co_2(CO)_6[P(CH_2CH_3)_3]_2$	8.9	1.4	0.4	3.0	4.1
$Co_2(CO)_6[P(CH_2CH_2CH_2CH_3)_3]_2$	10.8	2.7	0.4	3.8	3.9
Absent	4.9	0.1	0.7	4.1	0.0

2-Methylpropanal 12.5 ml, catalyst 0.01 mmol, $p_{CO} = 5$ atm, $p_{H_2} = 40$ atm, temperature 150°C, reaction time 3 h.
[a]*i*-BuOH: 2-methylpropanol; Dim-OH: 3-hydroxy-2,2,4-trimethylpentanal; Trim-OH: 3,5-dihydroxy-2,2,4,4,6-pentamethylheptanal; Tish: mixture of 1- and 3-(2-methylpropanoate) of 2,2,4-trimethyl-1,3-pentandiol.

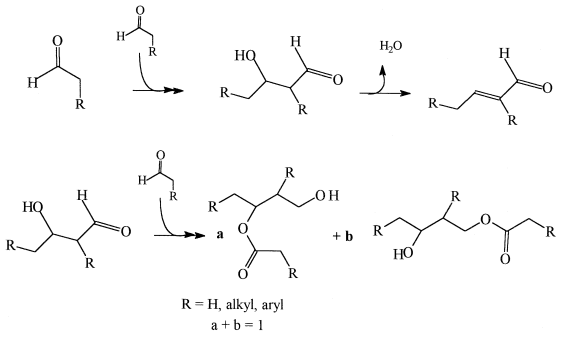
react with another molecule of the substrate giving a β-hydroxyester (Scheme 1). Trimeric aldol are also formed by reaction of the aldols or the α,β-unsaturated aldehydes with another molecule of the substrate. These trimeric products are usually unsaturated aldehydes. They are mainly formed when acetaldehyde is the substrate.

The synthesis of β-hydroxyesters by reaction of an aldehyde and a β-hydroxyaldehyde is reported in literature as the Tishchenko's reaction. Usually it is catalyzed by alkoxydes such as $Mg[Al(OEt_4)]_2$ or $Ca(OEt)_2$ [8,9] if the reaction is carried out between an aldehyde and a β-hydroxyaldehyde or by $Al(OEt)_3$ or $Al(O\text{-}iPr)_3$ if the starting material are only aldehydes [8,9]. Our results are an indication that this reaction occurs also in the presence of cobalt complexes. In fact using acetaldehyde and 2-methylpropanal, in the absence of cobalt com-

Table 5
Phenylacetaldehyde oligomerization

Catalyst	Conv. (%)	Dim[a] (%)	Dim-OH[a] (%)	Trim[a] (%)	Tish[a] (%)
$Co_2(CO)_8$	79.9	48.5	4.4	0.0	27.0
$CCo_2(CO)_6[P(CH_2CH_3)_3]_2$	86.5	51.0	5.5	13.0	17.0
$Co_2(CO)_6[P(CH_2CH_2CH_2CH_3)_3]_2$	88.3	67.6	4.3	5.8	10.6
Absent	41.6	6.9	1.7	0.0	33.0

Phenylacetaldehyde 12.5 ml, catalyst 0.01 mmol, $p_{CO} = 5$ atm, $p_{H_2} = 40$ atm, temperature 150°C, reaction time 3 h.
[a]Dim-OH: 2,4-diphenyl-3-hydroxybutanal; Dim: 2,4-diphenylbut-2-enal; Tish: mixture of 1- and 3-phenylacetate of 2,4-diphenyl-1,3-butandiol; Trim: 2,4,6-triphenylhexa-2,4-dienal.



Scheme 1.

plexes, Tishchenko type products are not formed. A catalytic action by cobalt complexes, at least in these cases, can be claimed. Interestingly Co naphtenato compounds have been reported to be efficient catalysts in the formation of β-hydroxyesters from aldehydes [10]; furthermore the hydrido ruthenium complex $H_2Ru(PPh_3)_4$ catalyzes the dimerization of aldehydes to the corresponding esters [11,12] through a process analogous to the Tishchenko reaction. An oxidative addition of the aldehyde to the ruthenium atom to form an acyl ruthenium complex is reported, followed by an addition of a second mole of aldehyde to form an alkoxy acyl ruthenium complex. The ester and the initial catalyst are formed by reductive elimination.

The presence of a β-hydroxyaldehyde seems to be necessary to obtain the Tishchenko's reaction catalyzed by our cobalt complexes: in fact the relevance of this reaction is higher when the dehydration of the aldol formed, due to its structure, is reduced (Table 5) or avoided (Table 4).

2.2. Influence of substrate

The conversion of the aldehyde decreases when the molecular weight of the substrate is increased (Tables 1–3).

Straight chain aldehydes give higher conversions than the branched ones, in agreement with the data reported by Piacenti and Neggiani [13,14] for the secondary reactions of the hydroformylation; *n*-butanal (Table 3) gives higher conversion than 2-methylpropanal (Table 4) and 2-methylbutanal does not react confirming that steric factors play an important role in these reactions.

Aldol dehydration is favoured by the presence of a phenyl group in β-position with respect to the aldehydic group, because the double bond formed is conjugated to the phenyl ring. As a consequence, low yields of β-hydroxyester are obtained in the phenylacetaldehyde oligomerization. An opposite trend was observed with 2-methylpropanal. The β-hydroxyaldehyde from 2-methylpropanal can not dehydrate, and its high concentration in solution increases the formation of β-hydroxyester.

Benzaldehyde can not aldolize, and consequently aldol and β-hydroxyesters are not formed.

2.3. Influence of the ligand

$Co_2(CO)_8$ provides higher conversion than the other cobalt complexes tested containing two phosphinic ligands. The only exception is the oligomerization of acetaldehyde. These results seem to indicate that the steric demand of the substrate plays a very important role. In fact the substitution of carbonyl groups with phosphine ligands while increasing the electron density on the metal would increase the catalytic activity in the oligomerization. This is the case of acetaldehyde but when the substrate has a higher molecular weight or a branching in the alkyl moiety the steric hindrance due to the phosphine reduce the catalytic activity of the cobalt complexes. These results are in agreement with the data reported for the hydroformylation reaction: Lower amounts of high boiling materials were obtained using phosphine substituted cobalt catalysts.

The role played by phosphines containing polar groups on alkyl chains can not be easily rationalized with respect to that one of simple trialkyl phosphines.

Table 6
Oligomerization of butanal. Influence of reaction temperature

Temp. (°C)	Catalyst	Time (h)	Conv. (%)
150	$Co_2(CO)_8$	3	63.6
150	Absent	3	23.3
142	$Co_2(CO)_8$	3	25.0
142	Absent	3	0.0
135	$Co_2(CO)_8$	3	20.0
135	Absent	3	0.0
120	$Co_2(CO)_8$	3	8.2
120	Absent	3	0.0
100	$Co_2(CO)_8$	24	34.9
100	Absent	24	11.2

Butanal 25 ml, catalyst 0.02 mmol, $p_{CO} = 5$ atm, $p_{H_2} = 40$ atm.

2.4. Influence of temperature

The influence of temperature was tested on *n*-butanal in the 100-150°C temperature range using $Co_2(CO)_8$ as catalyst. As expected, a decrease of the reaction temperature results in a considerable decrease of the rate (Table 6): The conversion, after 3 h, was 63.6% working at 150°C and 8.2% at 120°C.

It is interesting to note that at temperature below 150°C the thermal oligomerization does not occur at any detectable extent with a reaction time of 3 h.

However, working at 100°C, with a reaction time of 24 h, a 11.2% conversion was obtained without catalyst, but in the presence of $Co_2(CO)_8$ the conversion is 34.9%.

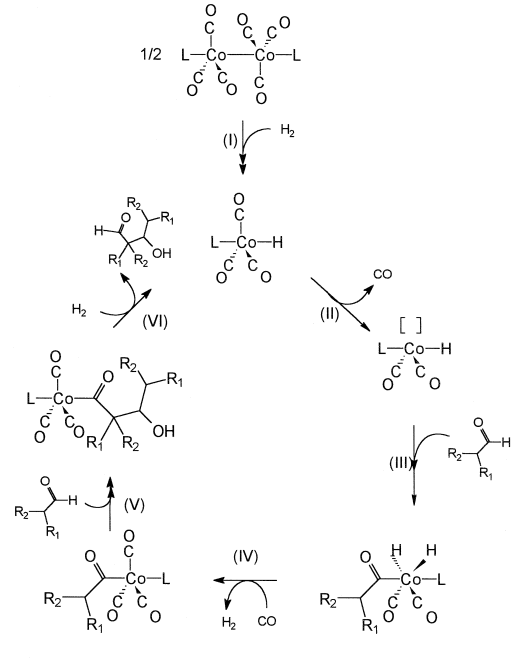
2.5. Oligomerization of ketones

The catalytic activity of the cobalt complexes in the oligomerization of ketones has been tested using acetone and methylethylketone as substrates. Acetone hardly reacts (total yield ~ 2%, whatever the catalyst) giving 4-hydroxy-4-methylpentan-2-one and 4-methyl-3-penten-2-one while methylethylketone does not oligomerize at all. No reaction occurs in the absence of the catalyst.

Evidently the catalytic activity of the cobalt carbonyl complexes involving a carbonylic compound is practically lost when the aldehydic hydrogen is replaced by an alkyl group.

2.6. Mechanism

The very low catalytic activity shown by the cobalt complexes in the oligomerization of ketones and the remarkable one displayed in the case of aldehydes, seem to indicate that the activation of the substrate by the cobalt center involves the CH bond of the formyl group. An hypothesis for the mechanism of the aldehydes aldolization is reported in Scheme 2. The key step is the formation of an acyl cobalt carbonyl through the oxidative addition of the aldehydic C–H bond to cobalt. This step is the reverse of the final step of the hydroformylation reaction were aldehydes are formed from an acylcobalt carbonyl in the presence of hydrogen. The oxidative addition of an aldehyde to a transition metal has been reported in the literature: It is the first step of the decarbonylation of aldehydes catalyzed by VIII group transition metal complexes [15–27] and it is involved in the



Scheme 2.

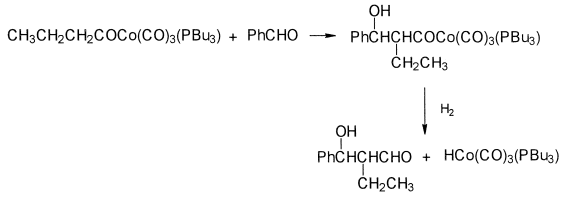
synthesis of ketones through the addition of an aldehyde to an olefin [28–31].

In a subsequent step a nucleophilic attack of the acyl cobalt carbonyl species on the free aldehyde occurs with formation of a 3-hydroxy-acylcobalt carbonyl.

Step V requires that the carbon atom in the α-position, with respect to the carbonyl group of the acyl cobalt complex, must be more nucleophilic than the analogous carbon atom of the free aldehyde.

To verify this hypotheses the tributylphosphine substituted butanoyl cobalt carbonyl was prepared according to Rosi et al. [32] and its ^{1}H- and ^{13}C-NMR spectra registered. The CH_2 group present in the α position with respect to the carbonyl group has chemical shifts of 3.1 and 67.2 ppm (for ^{1}H- and ^{13}C-NMR, respectively), while the chemical shifts of the same group in butanal are 2.4 and 45.8 ppm (for ^{1}H- and ^{13}C-NMR, respectively) [33]. These differences in the chemical shifts indicate a greater acidity of the hydrogen in the α-position of the acylcobalt complex and a greater nucleophilicity of the corresponding carbon atom. It, therefore, appears reasonable to attribute to the acyl species a pronounced reactivity in the aldolization reaction.

A test was also performed to verify the role played by the acylcobalt carbonyls in this connection. The reaction between a sample of $CH_3CH_2CH_2COCo(CO)_3(PBu_3)$ [32], and an excess of benzaldehyde was carried out at 150°C under carbon monoxide pressure, adding hydrogen at the end. The mixed aldol $PhCH(OH)CH(C_2H_5)CHO$ (Scheme 3) was identified in the reaction crude strongly indicating that acylcobalt carbonyls may be a reactive



Scheme 3.

intermediate in the aldolization process catalyzed by cobalt complexes under hydroformylation conditions. When reacting butanal and an excess of benzaldehyde, in the same conditions, but in the absence of a cobalt complex, the mixed aldol is not formed.

Finally, in the last step of the reaction the hydrogenolysis of the acyl intermediate takes place restoring the catalytic species. This step is largely reported in literature [1,32,34–37].

The entropic data of the reaction give a further support to this mechanism. A negative value of $\Delta S^{\#} = -14$ J K^{-1} mol^{-1}, evaluated from the experiments carried out in the 120–150°C temperature range, suggests that an associative step is involved in the rate determining step, probably steps III or V of the cycle proposed.

No hypothesis can be done for the role played by cobalt complexes in the Tishchenko type reaction.

3. Conclusion

The data collected show that the oligomerization of aldehydes is catalyzed by cobalt carbonyl complexes. Olefins may, therefore, be transformed into aldehydes and subsequently into their oligomers using cobalt carbonyls as catalytic precursors. Due to the higher reactivity of linear aldehyde, with respect to the branched one, the high boiling materials formed are enriched in the products arising from linear aldehydes.

Acylcobalt carbonyls seem to be the intermediates both in the hydroformylation and oligomerization reaction. In the course of the hydroformylation acylcobalt complexes react with molecular hydrogen giving aldehydes, while during oligomerization a nucleophilic attack onto free aldehyde gives the aldol derivatives. If hydrogenolysis prevails on the nucleophilic attack, the aldolization can be limited. The hydrogenolysis prevails when the reaction is carried out in dilute solution. In fact when a solvent is present, it is possible to eliminate or

at least to reduce the oligomerization of aldehydes in the course of the hydroformylation. Furthermore, in the presence of $Co_2(CO)_6L_2$, working in appropriate conditions [1,2,37–42], the direct syntheses of alcohols from olefins can be obtained and consequently the oligomerization of aldehydes suppressed.

4. Experimental

4.1. Materials

$Co_2(CO)_8$ was synthesized as reported by Natta and Ercoli [43], recrystallized from hexane had m.p. 56°C. Complexes $Co_2(CO)_6[P(CH_2CH_3)_3]_2$ [44], $Co_2(CO)_6[P(CH_2CH_2CH_2CH_3)_3]_2$ [45] $Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3)_3]_2$, [32] $Co_2(CO)_6[P(CH_2CH_2COOCH_3)_3]_2$[32], $Co_2(CO)_6[P(CH_2CH_2CN)_3]_2$ [32] were synthesized as reported.

Aldehydes, ketones, diethylether, and *n*-butanoylchloride, were commercial products and distilled under nitrogen prior to use.

4.2. Instruments

Elemental analyses were performed with a Perkin–Elmer 240 C system.

Gas chromatographic analyses were performed with a Shimadzu GC-14A, chromatographic system, coupled with a computer Shimadzu C-R4A, equipped with a FID and a packed column (2 m, i.d. 1/8′) OV1 (silicon on Chromosorb G AW-DMCS at 2.5%). No corrections due to response factors were introduced.

GC-MS spectra were collected using a Shimadzu QP2000 equipment, having a gas-chromatograph GC-14A, equipped with a CP-SIL 8 capillary column (50 m), coupled with a mass detector and a computer.

IR spectra were recorded with a FT-IR Perkin–Elmer mod. 1760 instrument using KBr or CaF_2 windows for solutions and KBr pellets for solid samples.

Multinuclear NMR spectra were recorded using a Varian VXR300 or a Varian Gemini 200 spectrometer operating respectively at 299.944 MHz or 199.975 MHz for ^1H, at 75.429 MHz or 50.286 MHz for ^{13}C and 121.421 MHz for ^{31}P (Varian VXR300). Peak positions were relative to tetramethylsilane as an external reference for ^1H and ^{13}C-NMR spectra; ^{31}P-NMR spectra were referred to H_3PO_4 (85%), downfield values are reported as positive. ^{13}C- and ^{31}P-NMR experiments were acquired as proton decoupled spectra. COSY, HETCOR, ATP and DEPT spectra were acquired according to the standard Varian pulse sequences for each of these experiments.

4.3. Catalytic oligomerization

Oligomerization experiments were carried out in a Parr model 4758 stainless steel autoclave (150 ml), electrically heated, equipped with a magnetic drive stirrer. Air was evacuated from the vessel, then the solution containing the complex (0.02 mmol) and substrate (25 ml) was introduced under nitrogen by suction. Hydrogen (40 atm) and carbon monoxide (5 atm) were then added. The vessel was heated for 3 h at 150°C. At the end of the reaction the autoclave was rapidly cooled, the gas vented and the solution analyzed.

Oligomerization experiments using phenylacetaldehyde, 2-methylpropanal and 2-methylbutanal as substrates were carried out using the same procedure with the exception that 12.5 ml of substrate and 0.01 mmol of cobalt complex were used.

4.4. Analysis of the reaction products

The analysis of the reaction products was performed by GLC using an OV1 column, as follows:

Acetaldehyde: the oven was kept at 40°C for 5 min, then heated at a rate of 6°C min^{-1} up to 220°C and kept at this temperature for 10 min; the peaks due to acetaldehyde, but-2-enal, 2-ethenylbut-2-enal, hex-2,4-dienal, 2-(1-hydroxyethyl)but-2-enal and a mixture of 1- and 3-acetate of 1,3-butandiol could be separated.

Propanal: using the same glc conditions adopted for acetaldehyde the peaks due to propanal, 2-methylpent-2-enal, 3-hydroxy-2-methylpentanal and a mixture of 1- and 3-propanoate of 2-methyl-1,3-pentandiol were separated.

Butanal: the oven was kept at 50°C for 5 min, then heated at a rate of 6°C min^{-1} up to 220°C and kept at this temperature for 30 min; the peaks due to butanal, butan-1-ol, 2-ethylhexanal, 2-ethylhex-2-enal, 2-ethyl-3-hydroxyhexanal and a mixture of 1- and 3-butanoate of 2-ethyl-1,3-hexandiol could be separated.

2-Methylpropanal: the oven was kept at 40°C for 2 min, then heated at a rate of 10°C min^{-1} up to 280°C and kept at this temperature for 10 min; the peaks due to 2-methylpropanal, 2-methylpropanol, 3-hydroxy-2,2,4-trimethylpentanal, 3,5-dihydroxy-2,2,4,4,6-pentamethylheptanal and a mixture of 1- and 3-(2-methylpropanoate) of 2,2,4-trimethyl-1,3-pentandiol were separated.

Phenylacetaldehyde: the reaction products were dissolved in CH_2Cl_2 and analyzed by GLC using the oven kept at 80°C for 2 min, then heated up to 220°C at a rate of 30°C min^{-1}, kept at this temperature for 1 min, then heated at a rate of 5°C min^{-1} up to 280°C and kept at this temperature for 10 min. The peaks due to phenylacetaldehyde, 2,4-diphenyl-3-hydroxybutanal, 2,4-diphenylbut-2-enal, a mixture of 1- and 3-phenylacetate of 2,4-diphenyl-1,3-butandiol and 2,4,6-triphenylhex-2,4-dienal could be separated.

4.5. Identification of oligomerization products

4.5.1. Acetaldheyde

But-2-enal has been isolated from the crude by distillation and spectroscopically identified. ^{1}H-NMR spectrum ($CDCl_3$) had signals at: 9.5 (d, 1H, CHO, $^3J_{H,H} = 8.0$ Hz), 6.9 (dq, 1H, $CH_3CH=$, $^3J_{H,H} = 18.0$ Hz, $^3J_{H,H} = 7.0$ Hz), 6.1 (ddq, 1H, *CH*CHO, $^3J_{H,H} = 18.0$ Hz, $^3J_{H,H} = 9.0$ Hz, $^4J_{H,H} = 1.5$ Hz) and 2.0 (dd, 3H, CH_3, $^3J_{H,H} = 7.0$ Hz, $^4J_{H,H} = 1.5$ Hz) ppm; the mass spectrum was in agreement with that reported in literature [46].

2-Ethenylbut-2-enal and hex-2,4-dienal were identified in a fraction, obtained by distillation of the crude at reduced pressure (50 mm Hg). The mass spectra of the two products are very similar and confirm their presence but can not be used to discriminate among them. These products were identified through their ^{1}H-NMR spectra ($CDCl_3$): the signals of 2-ethenylbut-2-enal were attributed to: 9.4 (d, 1H, CHO, $^4J_{H,H} = 1.5$ Hz), 6.6 (q, 1H, $CH_3CH=$, $^3J_{H,H} = 7.0$ Hz), 6.4 (ddd, 1H, $CH=CH_aH_b$, $^3J_{H,H} = 18.0$ Hz, $^3J_{H,H} = 12.0$ Hz, $^4J_{H,H} = 1.5$ Hz), 5.9 (dd, 1H, $CH=CH_aH_b$ *trans* to CH=, $^3J_{H,H} = 18.0$ Hz, $^2J_{H,H} = 2.0$ Hz), 5.4 (dd, 1H, $CH=CH_aH_b$ *cis* to CH=, $^3J_{H,H} = 12.0$ Hz, $^2J_{H,H} = 2.0$ Hz) and 2.1 (d, 3H, $CH_3CH=$, $^3J_{H,H} = 7.0$ Hz) ppm; the COSY spectrum showed the following correlation: signal at 5.4 ppm with those at 5.9 and 6.4 ppm; signal at 5.9 ppm with those at 6.4 and 5.4 ppm, signal at 6.4 ppm with those at 5.9 and 5.4 ppm and signal at 2.1 ppm with that one at 6.6 ppm; the mass spectrum was in agreement with that one reported in the literature [46]. Hex-2,4-dienal: ^{1}H-NMR and mass spectra were the same of those reported in the literature [46,47].

2-(1-Hydroxyethyl)but-2-enal, 1-acetate of 1,3-butandiol and 3-acetate of 1,3-butandiol: By distillation of the crude at reduced pressure (0.5 mm Hg) a fraction containing these products was obtained; ^{1}H-NMR spectrum ($CDCl_3$) of 2-(1-hydroxyethyl)but-2-enal had signals at: 9.3 (d, 1H, CHO, $^4J_{H,H} = 2.0$ Hz), 6.5 (q, 1H, $CH_3CH=$, $^3J_{H,H} = 7.0$ Hz), 4.7 (qd, 1H, *CH*OH, $^3J_{H,H} = 7.0$ Hz, $^4J_{H,H} = 2.0$ Hz), 1.9 (d, 3H, $CH_3CH=$, $^3J_{H,H} = 7.0$ Hz) and 1.3 (d, 3H, CH_3CHOH, $^3J_{H,H} = 7.0$ Hz) ppm; a COSY spectrum confirmed the attributions above reported because the signal at 6.5 ppm correlated with that one at 1.9 ppm and the signal at 4.7 ppm correlated with those at 1.3 ppm and 9.3 ppm; the presence of 2-(1-hydroxyethyl)but-2-enal was further confirmed by the ^{13}C-NMR spectrum. It shows signals at: 196.1 (CHO),

150.5 (CH=), 145.3 (C=), 64.7 (CHOH), 22.8 (CH_3CH=) and 14.6 (CH_3CHOH) ppm; these attributions were confirmed by an ATP and a DEPT spectra and furthermore supported by an HETCOR spectrum: in fact the following correlation between carbon and hydrogen signals, respectively, were evidentiated: 196.1 ppm with 9.3 ppm, 150.5 ppm with 6.5 ppm, 64.7 ppm with 4.7 ppm, 22.8 ppm with 1.3 ppm and 14.6 ppm with 1.9 ppm. The ^{1}H-NMR spectrum ($CDCl_3$) of 1-acetate of 1,3-butandiol had signals at: 4.3 (m, 1H, one diastereotopic CH_2OCO), 4.1 (m, 1H, one diastereotopic CH_2OCO), 3.8 (m, 1H, *CH*OH), 2.0 (s, 3H, CH_3COO), 1.7 (m, 2H, CH_2CH_2O) and 1.2 (d, 3H, CH_3CHOH, $^3J_{H,H} = 7.0$ Hz) ppm in agreement with that one reported in the literature [47]; a COSY spectrum confirms the attribution above reported; the ^{13}C-NMR spectrum had signals at: 171.4 (COO), 64.7 (CHOH), 61.7 (CH_2OCO), 37.8 (CH_2CH_2OCO), 23.3 (CH_3CHOH) and 20.8 (CH_3COO) ppm; these attributions were confirmed by an ATP and a DEPT spectra and furthermore supported by an HETCOR spectrum: in fact the following correlation between carbon and hydrogen signals, respectively, were evidentiated: 64.7 ppm with 3.8 ppm, 61.7 ppm with 4.3 and 4.1 ppm, 37.8 ppm with 1.7 ppm, 23.3 ppm with 1.2 ppm and 20.8 ppm with 2.0 ppm. ^{1}H-NMR spectrum ($CDCl_3$) of 3-acetate of 1,3-butandiol had signals at: 5.0 (m, 1H, CHOCO), 3.6 (m, 2H, CH_2OH), 2.0 (s, 3H, CH_3COO), 1.7 (m, 2H, CH_2CH_2OH) and 1.2 (d, 3H, CH_3CHOCO, $^3J_{H,H} = 7.0$ Hz) ppm in agreement with that one reported [47]; the COSY spectrum confirms the attribution above reported; the ^{13}C-NMR spectrum had signals at: 171.4 (COO), 68.2 (*CH*OCO), 58.6 (CH_2OH), 38.8 (CH_2CH_2OH), 21.1 (CH_3COO) and 20.2 (CH_3CHOCO) ppm; these attributions were confirmed by an ATP and a DEPT spectra and furthermore supported by an HETCOR spectrum: in fact the following correlation between carbon and hydrogen signals, respectively, were evidentiated: 68.2 ppm with 5.0 ppm, 58.6 ppm with 3.6 ppm, 38.8 ppm with 1.7 ppm, 21.1 ppm with 2.0 ppm and 20.2 ppm with 1.2 ppm.

4.5.2. Propanal

3-Hydroxy-2-methylpentanal has been identified by gc-ms analysis on the reaction crude, which showed peaks at m/e: 98 $[M-H_2O]^+$,70 $[CH_2=C(CH_3)CHO]^+$, 58 (100%) $[CH_3CH_2$-$CHO]^+$, 55 $[70\text{-}CH_3]^+$ and 41 $[CH_3CH=CH]^+$.

2-Methylpent-2-enal: was separated by fractional distillation at reduced pressure (115 mm Hg). The mass and ^{1}H-NMR spectra ($CDCl_3$) are in agreement with those reported in the literature [46,47].

1- and 3-Propanoate of 2-methyl-1,3-pentandiol: the mixture was separated by fractional distillation at reduced pressure (1.5 mm Hg). The mass spectrum of the mixture of these esters showed peaks at m/e: 174 $[M]^+$, 156 $[M-H_2O]^+$, 100 $[M-CH_3CH_2COOH]^+$, 83 (100%) $[156\text{-}CH_3CH_2COO]^+$ and 56 $[C_4H_8]^+$. The ^{1}H-NMR spectrum ($CDCl_3$) of 1-propanoate of 2-methyl-1,3-pentandiol had signals at: 4.2–3.8 (m, 2H, CH_2OCOCH_2), 3.5–3.2 (m, 1H, *CH*OH), 2.6 (s, 1H, OH), 2.3 (q, 2H, CH_3CH_2COO, $^3J_{H,H} = 7.5$ Hz), 1.7 (m, 1H, $CHCH_3$), 1.5 (m, 2H, CH_3CH_2CHO), 1.1 (t, 3H, CH_3CH_2COO, $^3J_{H,H} = 7.5$ Hz) and 0.8 (m, 6H, CH_3CH and CH_3CH_2) ppm. Fine structure of the hydrogen signals on carbon atoms linked to oxygen was due to the presence of two diastereoisomers in solution. ^{1}H-NMR spectrum ($CDCl_3$) of 3-propanoate of 2-methyl-1,3-pentandiol had signals at: 5.0–4.6 (m, 1H, $CHOCOCH_2$), 3.5–3.2 (m, 2H, CH_2OH), 2.6 (s, 1H, OH), 2.3 (q, 2H, CH_3CH_2COO, $^3J_{H,H} =$ 7.5 Hz), 1.7 (m, 1H, $CHCH_3$), 1.5 (m, 2H, CH_3CH_2CHO), 1.1 (t, 3H, CH_3CH_2COO, $^3J_{H,H}$ = 7.5 Hz) and 0.8 (m, 6H, CH_3CH and CH_3CH_2) ppm. The fine structure of signals due to hydrogen on carbon atoms linked to oxygen was due at the presence of two diastereoisomers in solution. The COSY spectrum of the mixture of 1- and 3-propanoate of 2-methyl-1,3-pentandiol are in agreement with the attribution reported. The ^{13}C-NMR spectrum of

the mixture of 1- and 3-propanoate of 2-methyl-1,3-pentandiol had main characteristic signals at: 175.0 and 174.0 (*COO*CH_2), 76.4, 74.8, 74.0 and 72.4 (*CH*OCO and *CH*OH), 66.8, 66.2, 64.1 and 63.9 (CH_2O), 38.6, 38.4, 38.0 and 37.0 (*CH*CH_3) ppm. All carbons of the main chain give two signals because two diastereoisomers are present; it doesn't occurred for carbons of the propanoate moiety. The attributions were supported by an ATP and an HETCOR spectra.

4.5.3. Butanal

2-Ethylhexanal: its mass spectrum, on the reaction crude, was in agreement with that reported in literature [46]; the other reaction products were isolated from the crude by fractional distillation at reduced pressure.

2-Ethylhex-2-enal had b.p. 123–125°C/1 mm Hg; the mass spectrum was in agreement with that reported in literature [46]; ^{1}H-NMR spectrum ($CDCl_3$) had signals at: 9.3 (s, 1H, CHO), 6.4 (t, 1H, CH=C, $^3J_{H,H} = 7.5$ Hz), 2.2 (m, 4H, CH_2C= and *CH_2*CH=), 1.5 (m, 2H, *CH_2*CH_3) and 0.9 (m, 6H, CH_3) ppm.

2-Ethyl-3-hydroxyhexanal: had the same gc retention time and ms spectrum of an authentic sample obtained by butanal condensation with KOH [48].

1- and 3-Butanoate of 2-ethyl-1,3-hexandiol: a mixture of these hydroxyesters were separated by fractional distillation b.p. 135°C/1 mm Hg; elemental analyses: for $C_{12}H_{24}O_3$: found % (calcd %), C: 66.22 (66.63), H: 11.50 (11.18); IR spectrum (neat) shows characteristic absorptions at: 3453 (m, ν_{OH}), 2963 (vs, ν_{CH}), 2936 (s, ν_{CH}), 2876 (s, ν_{CH}), 1736 (vs, $\nu_{C=O}$), 1718 (sh, $\nu_{C=O}$), 1464 (m, δ_{CH}), 1383 (m, δ_{CH}), 1260 (m, ν_{C-O}), 1187 (s, ν_{C-O}) cm^{-1}; the mass FAB spectrum had peaks at m/e: 217 (100%) $[MH]^+$; 199 $[MH-H_2O]^+$; 147 $[MH-C_4H_6O]^+$; 129 $[MH-C_3H_7COOH]^+$; 111 [129-H_2O or 199-C_3H_7COOH $]^+$; the mass and ^{1}H-NMR spectra of 1-butanoate of 2-ethyl-1,3-hexandiol are in agreement with those reported by Fouquet et al. [49]. ^{1}H-NMR spectrum ($CDCl_3$) of 3-butanoate of 2-ethyl-1,3-hexandiol had signals at: 4.9 (m, 1H, *CH*OCOCH_2), 3.6 (m, 2H, *CH_2*OH), 2.4 (s, 1H, OH), 2.2 (t, 2H, CH_2COO, $^3J_{H,H} = 7.5$ Hz), 1.7–1.0 (m, 9H, CH_3*CH_2*-CH_2COO, *CHCH*$_2$ and *CH_2CH_2*CH_3) and 0.9 (t, 9H, CH_3, $^3J_{H,H} = 7.4$ Hz) ppm.

4.5.4. 2-Methylpropanal

3-Hydroxy-2,2,4-trimethylpentanal: the mass spectrum had peaks at m/e: 101 $[M-CH(CH_3)_2]^+$, 98 $[M-OH-CHO]^+$, 83 $[98-CH_3]^+$,72 $[C_4H_8O]^+$ and 55 $[72-OH]^+$.

1- and 3-(2-Methylpropanoate) of 2,2,4-trimethyl-1,3-pentandiol: these esters were identified by ^{1}H-NMR spectroscopy on the crude of the test catalyzed by $Co_2(CO)_8$ where these compounds are the main products. The following signals in the ^{1}H-NMR spectrum ($CDCl_3$) were attributed to 1-(2-methylpropanoate) of 2,2,4-trimethyl-1,3-pentandiol: 4.1 (s, 1H, one diasteromeric *CH_2*OCOCH), 4.0 (s, 1H, one diasteromeric *CH_2*OCOCH), 3.4 (d, 1H, *CH*OH, $^3J_{H,H} = 3.0$ Hz), 2.6 (m, 1H, CHCOO), 1.8 (std, 1H, CH(OH)*CH*$(CH_3)_2$, $^3J_{H,H} = 7.0$ Hz, $^3J_{H,H} = 3.0$ Hz) ppm and finally four signals due to the four CH_3 groups are present near to 1 ppm. The following signals in the ^{1}H-NMR spectrum ($CDCl_3$) were attributed to 3-(2-methylpropanoate) of 2,2,4-trimethyl-1,3-pentandiol: 4.7 (d, 1H, *CH*OCOCH, $^3J_{H,H} = 3.0$ Hz), 3.7 (s, 1H, one diastereotopic *CH_2*OH), 3.6 (s, 1H, one diastereotopic *CH_2*OH), 2.6 (m, 1H, CHCOO), 2.0 (std, 1H, CH(OH)*CH*$(CH_3)_2$, $^3J_{H,H} = 7.0$ Hz, $^3J_{H,H} = 3.0$ Hz) ppm and four signals around 1 ppm were attributed to four CH_3 groups. Mass spectrum of the mixture of the esters had peaks at m/e: 173 $[M-CH(CH_3)_2]^+$, 143 $[M-CH(OH)CH(CH_3)_2]^+$, 89 $[C_4H_9O_2]^+$, 71 $[COCH(CH_3)_2]^+$, 56 $[CH=CH(CH_3)_2]^+$ and 43 (100%) $[CH(CH_3)_2]^+$.

2-Methylpropanol and 3,5-dihydroxy-2,2,4,4,6-pentamethylheptanal were identified, by ^{1}H-NMR spectrum, on the crude of the test catalyzed by $Co_2(CO)_6[P(CH_2CH_3)_3]_2$ after separation of the starting 2-methylpropanal by distillation at reduced pressure. The ^{1}H-NMR

spectrum ($CDCl_3$) of 2-methylpropanol was in agreement with that reported [47]. In the ^{1}H-NMR spectrum ($CDCl_3$) the signals at: 9.6 (s, 1H, CHO), 3.5 (d, 1H, CH*CH*OH, $^3J_{H,H} = 3.0$ Hz), 3.2 (s, 1H, C*CH*OH), 1.8 (std, 1H, CH*CH*$(CH_3)_2$, $^3J_{H,H} = 7.0$ Hz $^3J_{H,H} = 3,0$ Hz) ppm were attributed to 3,5-dihydroxy-2,2,4,4,6-pentamethylheptanal. The resonances of the methyl groups are covered by analogous signals of other products; mass spectrum had peaks at m/e: 173 $[M–CH(CH_3)_2]^+$, 143[M–CH(OH)CH$(CH_3)_2]^+$, 98 $[COC(CH_3)_2CHO]^+$, 83 [98-$CH_3]^+$, 71 $[(CH_3)_2$ CHO$]^+$, 56[CH=CH$(CH_3)_2]^+$ and 43 (100%) $[CH(CH_3)_2]^+$.

^{13}C-NMR spectrum of a solution containing all products of 2-methylpropanal oligomerization, shows characteristics signals at 207.1 and 206.2 ppm attributed to CHO of 2-methylpropanal and trimeric aldehyde, and at 179.0 and 178.1 ppm attributed to COO of the esters.

4.5.5. Phenylacetaldheyde

2,4-Diphenylbut-2-enal: the mass spectrum shows peaks at m/e: 222 $[M]^+$, 221 $[M–H]^+$, 204 $[M–H_2O]^+$, 193 $[M–CHO]^+$, 145 $[M–C_6H_5]^+$, 131 $[M–C_7H_7]^+$, 115 (100%) $[PhC_3H_2]^+$, 103 $[PhCH=CH]^+$ and 91 $[C_7H_7]^+$; ^{1}H-NMR spectrum ($CDCl_3$) shows characteristic signals at: 9.6 (s, 1H, CHO), 6.8 (t, 1H, CH=, $^3J_{H,H} = 8.0$ Hz), 3.8 (d, 2H, CH_2, $^3J_{H,H} = 8.0$ Hz) ppm; the signals of the hydrogen of the phenyl ring were covered by those of phenylacetaldheyde.

2,4-Diphenyl-3-hydroxybutanal: mass spectrum shows peaks at m/e: 210 $[M–HCHO]^+$, 119 $[PhCHCHO]^+$ and 91 (100%) $[C_7H_7]^+$.

1- and 3-Phenylacetate of 2,4-diphenyl-1,3-butandiol and 2,4,6-triphenylhex-3,5-dienal were identified in a preparative tlc obtained using SiO_2 as support and CH_2Cl_2 as solvent. The ^{13}C-NMR spectrum of the two esters showed two sets of signals of different intensities. The strong signals are attributed to 1-phenylacetate ester and the others to 3-phenylacetate ester. Mass spectrum of mixture of 1- and 3-phenylacetate of 2,4-diphenyl-1,3-butandiol had peaks at m/e: 269 $[M–C_7H_7]^+$, 193 $[PhC=CH-CH_2Ph]^+$, 133 $[M–C_7H_7–PhCH_2COOH]^+$, 104 $[CHCH_2Ph]^+$ and 91 (100%) $[C_7H_7]^+$. ^{1}H-NMR spectrum ($CDCl_3$) of 1-phenylacetate of 2,4-diphenyl-1,3-butandiol shows signals at: 7.5–7.0 (m, 15H, C_6H_5), 4.59 (d, 1H, one diastereotopic CH_2OCO, $^3J_{H,H} = 7.0$ Hz), 4.5 (d, 1H, one diastereotopic CH_2OCO, $^3J_{H,H} = 5.0$ Hz), 4.0 (td, 1H, *CH*OH, $^3J_{H,H} = 7.0$ Hz, $^3J_{H,H} = 3.0$ Hz), 3.6 (s, 2H, CH_2COO), 3.0–2.3 (m, 5 H, C_6H_5CH, $C_6H_5CH_2$) ppm; ^{13}C-NMR spectrum shows characteristic signals at: 171.2 (COO), 140–132 (C_{ipso}), 130–126 ($CH_{aromatic}$), 73.4 (CHOH), 65.9 (CH_2OCO), 51.0 (*CH*Ph), 41.6 and 41.5 (CH_2COO and CH_2Ph) ppm. ^{1}H-NMR spectrum ($CDCl_3$) of 3-phenylacetate of 2,4-diphenyl-1,3-butandiol had signals at: 7.5–7.0 (m, 15H, C_6H_5), 5.5 (td, 1H, *CH*OCO, $^3J_{H,H} = 6.0$ Hz $^3J_{H,H} = 3.0$ Hz), 4.63 (d, 1H, one diastereotopic CH_2OH, $^3J_{H,H} = 7.0$ Hz), 4.4 (d, 1H, one diastereotopic CH_2OH, $^3J_{H,H} = 5.0$ Hz), 3.6 (s, 2H, CH_2COO), 3.0–2.3 (m, 5 H, C_6H_5CH, $C_6H_5CH_2$) ppm; ^{13}C-NMR spectrum shows characteristic signals at: 171.2 (COO), 140–132 (C_{ipso}), 130–126 ($CH_{aromatic}$), 74.9 (*CH*OCO), 63.8 (CH_2OH), 52.2 (*CH*Ph), 41.6 and 39.0 (CH_2COO and CH_2Ph) ppm. A COSY spectrum of the mixture of the two esters confirmed the above attributions.

2,4,6-Triphenylhex-2,4-dienal were identified through its mass and ^{1}H-NMR spectra. Mass spectrum shows only one peak at 306 m/e attributed to $[1,3,5\text{-triphenylbenzene}]^+$; the presence of 1,3,5-triphenylbenzene in solution was excluded by gc of an authentic sample. The mass spectrum may be attributed to the dienal compound that during ionization gave 1,3,5-triphenylbenzene. Between 2,4,6-triphenylhex-2,4-dienal and 2,4,6-triphenylhex-3,5-dienal the presence of the second product could be ruled out because ^{1}H-NMR spectrum shows signals at 7.0, 5.6 and 3.7 ppm and these resonances are attributed to: 7.0 (m, 1H, *CH*=C(Ph)CHO), 5.6 (m, 1H, $PhCH_2CH=$), 3.7 (m, 2H, $PhCH_2$) ppm.

4.5.6. Acetone

4-hydroxy-4-methylpentan-2-one and 4-methylpent-3-en-2-one were identified on the crude of the reaction products. Their gc-ms spectra were in agreement with those reported in the literature [46].

4.6. Synthesis of $CH_3CH_2CH_2COCo(CO)_3(PBu_3)$

$CH_3CH_2CH_2COCo(CO)_3(PBu_3)$ was synthesized according to the procedure reported by Rosi et al. [32]. To a diethylether solution of $NaCo(CO)_3(PBu_3)$, prepared by reacting $Co_2(CO)_6(PBu_3)_2$, (500 mg) in diethylether (50 ml) with Na/Hg 0.5% (100 g), C_3H_7COCl (2.20 mmol) in 10 ml of diethylether was added at 0°C under a nitrogen atmosphere. The ^{1}H-NMR spectrum of the oily material, dissolved in C_6D_6 shows a signal at 3.1 ppm (t, 2H, CH_2CO, $^3J_{H,H} = 7.0$ Hz), 1.6 (ss, 2H, CH_2CH_2CO, $^3J_{H,H} = 7.0$ Hz), 1.4 (m, 12H, CH_2CH_2P), 1.2 (m, 6H, $CH_2CH_2CH_2P$), 0.8 (m, 12H, $CH_3CH_2CH_2CH_2P$ and $CH_3CH_2CH_2CO$. The ^{31}P-NMR (CD_2Cl_2) shows a singlet at 36.8 ppm. The ^{13}C-NMR (C_6D_6) shows signals at 238.3 (d, CH_2CO, $^2J_{CP} = 29.3$ Hz), 201.1 (m, COCo), 67.2 (d, CH_2CO, $^3J_{CP} = 22.0$ Hz), 28.0 (d, CH_2P, $^1J_{CP} = 24.4$ Hz), 25.8 (s, CH_2CH_2P), 24.4 (d, $CH_2CH_2CH_2P$, $^3J_{CP} = 12.2$ Hz), 19.4 (s, CH_2CH_2CO), 13.6 (s, CH_3). The IR spectrum (C_6H_6) shows bands, in the 2200–1500 cm^{-1} region, at: 2040(w), 1971(s), 1950(vs), 1680(m) cm^{-1}.

4.7. Reaction between $CH_3CH_2CH_2COCo(CO)_3(PBu_3)$ and PhCHO

A diethylether solution of $CH_3CH_2CH_2COCo(CO)_3(PBu_3)$, prepared as above reported, was placed in the Parr model 4758 stainless steel autoclave, previously described, where the air was evacuated. The solvent was evaporated to dryness at room temperature under reduced pressure, then the benzaldehyde (12.5 ml) and carbon monoxide (5 atm) were introduced. The reactor was heated at 150°C for 3 h then hydrogen up to 45 atm was added and the vessel heated at 150°C for 1.5 h. The gas was vented and the gc-ms analysis of the solution recovered, shows a peak, attributed to $PhCH(OH)CH(C_2H_5)CHO$ having characteristic fragments at m/e: 178$[M]^+$, 108 $[PhCH_2OH]^+$, 107 $[PhCHOH]^+$, 91 (100) $[C_7H_9]^+$, 71 $[C_2H_5CHCHO]^+$, 43 $[C_3H_7]^+$. The ^{31}P-NMR spectrum of the solution recovered shows a total conversion of the starting complex.

4.8. Reaction between $CH_3CH_2CH_2CHO$ and PhCHO

A solution of $CH_3CH_2CH_2CHO$ (0.14 ml) and benzaldehyde (12.5 ml) was placed in the autoclave previously described, where the air was evacuated and carbon monoxide (5 atm) were introduced. The reactor was heated at 150°C for 3 h than hydrogen up to 45 atm was added and the vessel heated at 150°C for 1.5 h. The gas was vented and the solution recovered, analyzed by gc-ms, as reported in 4.7. The croxed aldol $PhCH(OH)CH(C_2H_5)CHO$ was not present.

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