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Functionalized phosphine substituted cobalt carbonyls. Synthesis, characterization and catalytic activity in the hydroformylation of olefins

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Abstract

Four tertiary phosphines containing functionalized alkyl groups $P(CH_2CH_2CN)_3$, $P(CH_2CH_2CO_2CH_3)_3$, $P(CH_2CH_2CH_2OCH_3)_3$ and $P(CH_2CH_2CH_2OCH_2CH_3)_3$ have been synthesized and used as ligands in $Co_2(CO)_6(L)_2$ complexes which were fully characterized. The catalytic activity of these cobalt complexes in the hydroformylation of hex-1-ene and propene was tested. The influence of several parameters such as type of solvent, reaction temperature, carbon monoxide partial pressure, excess of free phosphine in solution, on the chemio- and regioselectivity of the reaction were investigated. These results are compared with those obtained when using $Co_2(CO)_8$ or $Co_2(CO)_6(PBu_3)_2$ as catalytic precursors. The hydroformylation of hex-1-ene in the presence of the above complexes has been rationalized on the basis of the mechanism suggested for the hydroformylation of propene in the presence of $Co_2(CO)_6(PBu_3)_2$.

Keywords: Hydroformylation; Cobalt; Carbonyl; Functionalized phosphine; Catalysis; Homogeneous; Olefin

1. Introduction

In the hydroformylation of linear olefins in the presence of cobalt catalysts the best chemioselectivity to aldehydes is obtained with $Co_2(CO)_8$ at $T < 150°C$. The best regioselectivity (91%) to linear isomers, mainly one alcohol (98.5%), is reached, on the other hand, in the presence of $Co_2(CO)_6(L)_2$ derivatives (mainly $L = PBu_3$), working at relatively high temperatures (> 150°C) in the presence of a considerable excess of the phosphinic ligand (ligand/Co ratio = 2) [1].

The highest percentage of the straight chain isomer (85%), as aldehyde, was obtained with the same catalytic precursor, working at 150°C, 40 atm of hydrogen, 3.5 atm of carbon monoxide [2]. In these conditions, however, nearly 16.6% of the olefin is hydrogenated and alcohols represent 44.3% of the hydroformylation products. Since the hydroformylation and hydrogenation activity of cobalt catalysts strongly depend on the coordinated ligands we have prepared cobaltcarbonyl complexes of the type $Co_2(CO)_6(L)_2$ where the tertiary phosphines contain the following functionalized alkyl groups: $-CH_2CH_2CN$, $-CH_2CH_2COOCH_3$, $-CH_2CH_2COOCH_2CH_3$,

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$-CH_2CH_2CH_2OCH_3$. We have tested their performance as hydroformylation and hydrogenation catalysts and compared their behavior with that of $Co_2(CO)_8$ and $Co_2(CO)_6(PBu_3)_2$.

The presence of polar functional groups in the phosphinic ligands coordinated to the metal improves the hydrophylicity of these complexes compared to that of $Co_2(CO)_6(PBu_3)_2$. We thought therefore worth trying the use of such complexes as catalytic precursors in the hydroformylation of olefins in polar solvents or in water containing solvents, a goal of considerable interest from an industrial point of view [3–6].

2. Results and discussion

2.1. Synthesis of the tertiary phosphines

2.1.1. $P(CH_2CH_2CN)_3$

Tris(propionitril)phosphine has been synthesized according to the method reported by Rauhut et al. [7] by addition of phosphine (PH_3) to acrylonitrile in the presence of a base. Due to the difficulty of the phosphine dosage, mono-, di- and trialkyl phosphines are formed (Scheme 1).

By reacting the phosphines mixture with an excess of acrylonitrile, the trialkyl derivative was obtained as the only product (Scheme 2). The spectroscopic data of this phosphine are reported in Tables 1–4.

2.1.2. $P(CH_2CH_2COOCH_3)_3$ and $P(CH_2CH_2COOCH_2CH_3)_3$

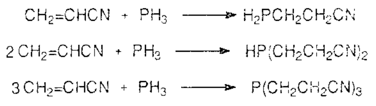
The above phosphines have been synthesized following the method suggested for the synthesis of the corresponding ethyl ester (Scheme 3), by hydrolysis of $P(CH_2CH_2CN)_3$ in ethanol or methanol solution in the presence of gaseous hydrogen chloride [7]. The hydrochloride of the imino ester is formed as intermediate. After treatment with an alkaline solution the desired $P(CH_2CH_2COOCH_3)_3$ is obtained which is then purified by distillation. The ethyl ester is obtained in the same way. The spectroscopic characteristics of these phosphines are reported in Tables 1–4.

Table 1
IR data of the phosphinic ligands

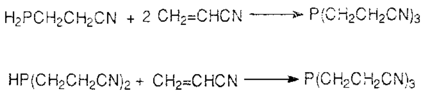
L	ν CH	ν OCH_2, ν OCH_3	ν CN	ν CO	δ OCH_2 δ OCH_3	ν C–OR	$\nu CH_2–OCH_2$
$P(CH_2CH_2CN)_3$ [a]	2965(m) 2952(m) 2936(m) 2919(s)		2247(s)		1425(s)		
$P(CH_2CH_2COOCH_3)_3$ [b]	2997(m) 2953(m) 2916(vw) 2848(w)			1738(vs)	1437(s)	1237(s)	
$P(CH_2CH_2COOCH_2CH_3)_3$ [b]	2981(m) 2937(w) 2908(w)			1734(vs)	1425(w)	1232(s)	
$P(CH_2CH_2CH_2OCH_3)_3$ [b]	2979(m) 2925(m) 2894(m) 2871(m)	2826(m)			1461(m)		1117(vs)

[a] Mulled with KBr.

[b] Neat.



Scheme 1.



Scheme 2.

2.1.3. $P(CH_2CH_2CH_2OCH_3)_3$

The synthesis of this phosphine is not reported in the literature. We have prepared it through a modification of the method suggested by Stiles for the synthesis of $P(CH_2CH_2OCH_3)_3$ [8]. We have carried out the addition of 3-methoxypropene to the phosphine (PH_3) in the presence of azo-bis-(2-methylpropionitrile) (AIBN) using a strong excess of allyl ether with respect to the phosphine, in order to reduce the formation of partially substituted mono- and dialkylphosphine (Scheme 4). Since 3-methoxypropene is not commercially available it has been prepared according to the procedure suggested by Henry [9] (Scheme 5). The trialkylphosphine obtained was purified by fractional distillation. Its spectroscopic data are reported in Tables 1–4.

2.2. Synthesis of cobalt complexes

The synthesis of the $Co_2(CO)_6L_2$ complexes where L is one of the above phosphines has been done according to the same procedure described for the analogous trialkyl- and triarylphosphines derivatives [10,11] (Scheme 6). The substitution of carbon monoxide appears to proceed through the intermediate formation of $Co_4(CO)_{12}$ which was in fact detected by IR spectroscopy in samples taken during the reaction, in agreement with the findings of Calderazzo et al. [12] and Kemmitt et al. [13] in similar $Co_2(CO)_8$ substitution reactions (Scheme 7). This sequence however is different from that one found for the tributylphosphine derivative, which involves the preliminary formation of an ionic Co carbonyl species [10].

In the conditions adopted we have always obtained disubstituted derivatives as final product, with a Co/L ratio equal to 1, even when using an excess of ligand. This is in agreement with the fact that the phosphines synthesized have similar cone angle values (near 132°). The difference between the chemical shifts of the

Table 2
^{1}H-NMR data of the phosphinIC ligands

L	Solvent	CH_2^α	CH_2^β	CH_2^γ	CH_3^δ	OCH_2	OCH_2CH_3	OCH_3
$P(CH_2CH_2CH_2OCH_3)_3$	$CDCl_3$	1.19 m $^3J_{HH}$ 6.0	1.43 ps $^3J_{HH}$ 6.0	3.15 pt				3.07 s
$P(CH_2CH_2COOCH_3)_3$	$CDCl_3$	1.66 t $^3J_{HH}$ 8.2	2.37 pq $^3J_{HH}$ 8.2 $^3J_{HP}$ 8.8					3.60 s
$P(CH_2CH_2COOCH_2CH_3)_3$	$CDCl_3$	1.68 t $^3J_{HH}$ 8.3	2.37 td $^3J_{HH}$ 8.3 $^3J_{PH}$ 8.5			4.08 q $^3J_{HH}$ 7.1	1.20 t $^3J_{HH}$ 7.1	
$P(CH_2CH_2CN)_3$	CD_3COCD_3	1.99 t $^3J_{HH}$ 7.8	2.70 dt $^3J_{HH}$ 7.8 $^3J_{PH}$ 9.9					
$P(CH_2CH_2CH_2CH_3)_3$	C_6D_6	1.41 m	1.41 m	1.33 m	0.90 t $^3J_{HH}$ 6.8			

Chemical shifts (ppm) with respect to TMS as external standard, coupling constants in Hz; α, β, γ, δ are referred to as the position with reference to the phosphorous atom; s:singlet, d:doublet, t:triplet, q:quartet, m:multiplet, p:pseudo.

Table 3
^{13}C-NMR data of the phosphinIC ligands

L	Solvent	CH$_2^\alpha$	CH$_2^\beta$	CH$_2^\gamma$	CH$_3^\delta$	CO	OCH$_2$	OCH$_2$CH$_3$	OCH$_3$	CN
$P(CH_2CH_2CH_2OCH_3)_3$	$CDCl_3$	26.0 d	23.3 d	73.5 d					58.1 s	
		J_{CP} 33.1	J_{CP} 12.1	J_{CP} 12.2						
$P(CH_2CH_2COOCH_3)_3$	$CDCl_3$	30.2 d	21.3 d			173.4 d			51.7 s	
		J_{CP} 17.2	J_{CP} 13.7			J_{CP} 11.7				
$P(CH_2CH_2COOCH_2CH_3)_3$	$CDCl_3$	30.6 d	21.4 d			173.4 d	61.1 s	14.0 s		
		J_{CP} 16.6	J_{CP} 12.9			J_{CP} 11.7				
$P(CH_2CH_2CN)_3$	CD_3COOD	14.2 d	23.3 d							120.2 d
		J_{CP} 21.3	J_{CP} 15.7							J_{CP} 11.2
$P(CH_2CH_2CH_2CH_3)_3$	C_6D_6	28.7 d	24.9 d	27.8 d	14.1 s					
		J_{CP} 13.8	J_{CP} 13.8	J_{CP} 11.5						

Chemical shifts (ppm) with respect to TMS as external standard, coupling constant in Hz; α, β, γ are referred to as the position with reference to the phosphorous atom; s: singlet, d: doublet.

coordinated and the free phosphine (Δ) (Table 5) is positive in all cases. This is an indication that the cone angle and the SPS angle are higher due to the coordination to cobalt [14]. The stretching frequency of the main absorption of the carbonyl groups decreases in the order $P(CH_2CH_2CN)_3$, $P(CH_2CH_2CH_2CH_3)_3$, $P(CH_2CH_2CH_2OCH_3)_3$, $P(CH_2CH_2COOCH_3)_3$, $P(CH_2CH_2COOCH_2CH_3)_3$, indicating that the stability of the various complexes decreases in the same order. These complexes are soluble in most of the usual organic solvents. Their spectroscopic data are reported in Tables 5–8.

There is no difference between the stretching frequencies of the nitrile or carboxylic groups in the free ligands and in the corresponding coordinated phosphines. This fact may be taken as an indication that the phosphine acts as monodentate ligand through the phosphor atom. This indication is confirmed by the NMR spectra where signals due to the atoms of phosphor, carbon or hydrogen in no equivalent positions are lacking.

The IR spectra of these complexes lead to exclude the presence of a bridging carbonyl group; it is possible to assign to these complexes a D_{3d} symmetry [15] and a structure analogous to that one of $Co_2(CO)_6(PPh_3)_2$.

2.3. Catalytic activity of cobalt complexes in the hydroformylation of olefins

The hydroformylation experiments in the presence of preformed $Co_2(CO)_6[P(CH_2CH_2CN)_3]_2$ **1** $Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3)_3]_2$ **2**, and $Co_2(CO)_6[P(CH_2CH_2COOCH_3)_3]_2$ **3** were carried out on hex-1-ene, a linear olefin which may undergo isomerization phenomena. The influ-

Table 4
^{31}P NMR data of the phosphinIC ligands

L	Solvent	δ (ppm)
$P(CH_2CH_2CH_2OCH_3)_3$	$CDCl_3$	−30.5
$P(CH_2CH_2COOCH_3)_3$	$CDCl_3$	−25.4
$P(CH_2CH_2COOCH_2CH_3)_3$	$CDCl_3$	−25.6
$P(CH_2CH_2CN)_3$	CD_3COOD	−22.0
$P(CH_2CH_2CH_2CH_3)_3$	C_6D_6	−29.9

Chemical shifts (ppm) with respect to H_3PO_4 (85%) as external standard; downfield values are taken as positive.

Table 5
^{31}P NMR data of the complexes $Co_2(CO)_6(L)_2$

L	Solvent	δ (ppm)	Δ (ppm)
$P(CH_2CH_2CH_2OCH_3)_3$	$CDCl_3$	54.2	84.7
$P(CH_2CH_2COOCH_3)_3$	CD_3OD	56.8	88.4
$P(CH_2CH_2COOCH_2CH_3)_3$	C_6D_6	53.8	79.4
$P(CH_2CH_2CN)_3$	CD_3COCD_3	46.1	66.1
$P(CH_2CH_2CH_2CH_3)_3$	C_6D_6	53.1	83.0

Chemical shifts (ppm) with respect to H_3PO_4 (85%) as external standard; downfield values are taken as positive. Δ is the difference between the chemical shift of coordinated and free phosphine.

Table 6
IR data of the complexes $Co_2(CO)_6(L)_2$ in the 2300–1700 cm^{-1} range

L	Solvent	ν_{CN}	ν_{CO} [a]	ν_{CO} [b]
$P(CH_2CH_2CH_2OCH_3)_3$	pentane		2031 (vw), 1970 w), 1951 (vs), 1928 (sp)	
$P(CH_2CH_2COOCH_3)_3$	C_6H_6		1990 (w), 1946 (s)	1742 (vs)
$P(CH_2CH_2COOCH_2CH_3)_3$	C_6H_6		1990 (w), 1970 (sh), 1946 (s), 1920 (w)	1742 (vs)
$P(CH_2CH_2CN)_3$	acetone	2243 (vw)	2037 (vw), 1975 (sh), 1955 (vs), 1928 (sh)	
$P(CH_2CH_2CH_2CH_3)_3$	pentane		2031 (vw), 1995 (vw), 1970 (m), 1952 (vs), 1926 (w)	

[a] Carbonyl group linked to the metal.
[b] Carbonyl group of the ligand.

Table 7
^{1}H-NMR data of the complexes $Co_2(CO)_6(L)_2$

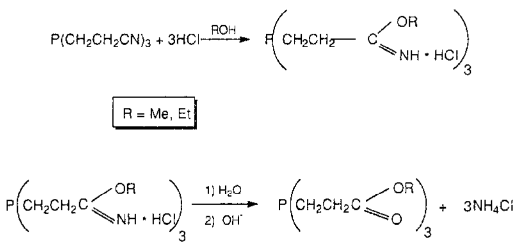
L	Solvent	CH_2^{α}	CH_2^{β}	CH_2^{γ}	CH_3^{δ}	OCH_2CH_3	OCH_2CH_3	OCH_3
$P(CH_2CH_2CH_2OCH_3)_3$	$CDCl_3$	1.82 ps	1.82 ps	3.45 ps				3.35 s
$P(CH_2CH_2COOCH_3)_3$	C_6D_6	1.80 td $^3J_{HH}$ 9.2 $^2J_{HP}$ 7.2	2.41 td $^3J_{HH}$ 9.2 $^3J_{HP}$ 6.3					3.29 s
$P(CH_2CH_2COOCH_2CH_3)_3$	C_6D_6	2.08 m	2.58 m			3.30 m	0.86 m	
$P(CH_2CH_2CN)_3$	CD_3COCD_3	2.08 ps	2.86 ps					
$P(CH_2CH_2CH_2CH_3)_3$	C_6D_6	1.54 ps	1.54 ps	1.22 psx $^3J_{HH}$ 6.5 $^3J_{HH}$ 7.2	0.82 t $^3J_{HH}$ 7.2			

Chemical shifts (ppm) with respect to TMS as external standard; α, β, γ, δ are referred to as the position with reference to the phosphorous atom; s: singlet, d: doublet, t: triplet, q: quartet, sx: sextet, m: multiplet, p: pseudo.

Table 8
^{13}C-NMR data of the complexes $Co_2(CO)_6(L)_2$

L	Solvent	CH_2^{α}	CH_2^{β}	CH_2^{γ}	CH_3^{δ}	CO [a]	OCH_2	OCH_2CH_3	OCH_3	CN	CO [b]
$P(CH_2CH_2CH_2OCH_3)_3$	C_6D_6	26.6 m	24.4 s	72.5 m					58.1 s		203.5 pt J_{CP} 9.8
$P(CH_2CH_2COOCH_3)_3$	C_6D_6	24.6 m	28.6 s			172.0 m			51.5 s		202.4 pt J_{CP} 9.7
$P(CH_2CH_2COOCH_2CH_3)_3$	C_6D_6	23.0 m	29.4 s			172.9 s	52.0 s	14.2 s			208.2 m
$P(CH_2CH_2CN)_3$	CD_3COCD_3	16.4 s	18.9 s							126.0 s	207.7 m
$P(CH_2CH_2CH_2CH_3)_3$	C_6D_6	29.2 m	26.1 s	24.4 m	13.7 s						203.7 pt J_{CP} 10.0

Chemical shifts (ppm) with respect to TMS as external standard and coupling constant in Hz; α, β, γ, δ, are referred to the position with reference to the phosphorous atom; s: singlet, t: triplet, m: multiplet, p: pseudo.
[a] Carbonyl groups present in the phosphinic ligands.
[c] Carbonyl groups linked to cobalt.



Scheme 3.

$CH_2{=}CHCH_2Br + CH_3ONa \longrightarrow CH_2{=}CHCH_2OCH_3 + NaBr$

Scheme 5.

ence on the reaction course of the nature of the phosphinic ligand in the catalytic precursor was then studied. Also the influence of the reaction variables such as temperature, carbon monoxide pressure, nature of the solvent, including the presence of water, and the addition of free phosphine in the solution were investigated.

Reaction conditions were chosen to make possible to compare our results with those reported by Piacenti et al. [2] on the hydroformylation of propene in the presence of $Co_2(CO)_6(PBu_3)_2$ **4**. The experiments were performed under CO (5 atm) and H_2 (40 atm), using a 100/1 substrate/catalyst ratio.

2.3.1. *Influence of temperature*

The experiments were performed in the presence of **2** in toluene in the 100–150°C temperature range. The results are reported in Table 9.

When the reaction temperature is increased the hydroformylation rate increases appreciably: the conversion changes from 36.2% at 100°C to 87.3% at 150°C, aldehydes being always the main product. Alcohols are also present among the products when the reactions are carried out at 120 (14.6%) and 150°C (34.2%) and their amount increases when increasing the temperature; even the hydrogenation of the substrate increases when the temperature rises (2.2% at 100°C and 8.9% at 150°C).

In the temperature range explored the percentage of linear isomers formed (aldehydes and alcohols) decreases from 77.6% at 100°C to 56.8% at 150°C. These results are similar to those reported by Piacenti et al. [2] on the hydroformylation of propene in the presence of $Co_2(CO)_6(PBu_3)_2$ **4**. We can moreover observe that the behavior of these catalytic systems with temperature is analogous to that of $Co_2(CO)_8$ **5** under the same conditions. We have also noticed that the reaction time does not appreciably influence the isomeric distribution of the aldehydes, but obviously the amount of the products obtained.

The residual olefin is a mixture of isomeric hexenes with prevalence of the terminal ones working at low temperature (Table 9).

2.3.2. *Influence of the solvent*

The effect of the solvent on the yield and on the isomeric composition of the products has been examined carrying out two sets of reactions in a few solvents at 120 and 150°C in the presence of **2** as catalyst. The results are reported in Table 10. Experiments were done in toluene, dioxane, diethyl ether, methyl orthoformate, and a dioxane/water mixture. The nature of the solvent, with the exception of the dioxane/water case, does not have a large effect on the isomeric distribution of the aldehydes and alcohols while it has a considerable influences on the reaction rate. Toluene and dioxane provide the best conversions. The behaviour of this catalytic system with different solvents is analogous to that of **5** [16,17].

The activity of the complex in a dioxane/water mixture (1:1) is very low and it was therefore not possible to get reproducible results. Using a high ratio of dioxane/water (10:1) we can observed a drastic decrease of the yield of the hydroformylation products (5.3%) when compared with the results obtained in neat

$3\,CH_2{=}CHCH_2OCH_3 + PH_3 \xrightarrow{AIBN} P(CH_2CH_2CH_2OCH_3)_3$

Scheme 4.

$Co_2(CO)_8 + 2L \longrightarrow Co_2(CO)_6L_2 + 2CO$ where $L{=}PBu_3, PPh_3$

Scheme 6.

Table 9
Hydroformylation of hex-1-ene in the presence of $Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3)_3]_2$, influence of the reaction temperature

Temp. (°C)	React. time (h)	Heptanal (%)	2-Methy-hexanal (%)	2-Ethyl-pentanal (%)	Heptanol (%)	2-Methyl-hexanol (%)	2-Ethyl-pentanol (%)	Hexane (%)	Hexenes (%)	Linear products/ hydrofor- mylation products (%)	Aldehydes/ hydroformyla- tion products (%)
80	24	50.3	11.4	3.5	—	—	—	2.1	32.7	77.1	100
100	24	58.1	14.1	4.8	1.5	0.3	0.2	3.9	17.1	75.4	88.3
100	3	28.1	6.2	1.9	—	—	—	2.2	61.6	77.6	100
120	3	36.6	11.9	4.2	7.0	5.2	2.4	7.1	25.6	64.8	78.3
150	3	31.7	13.6	7.8	17.9	11.1	5.2	8.9	3.8	56.8	60.8

Residual olefins composition (as % of the total products)

Temp. (°C)	Hexenes (%)	Hex-1-ene (%)	*cis*-Hex-2-ene (%)	*trans*-Hex-2-ene (%)	*trans*-Hex-3-ene (%)	*cis*-Hex-3-ene (%)
80 [a]	32.7	23.1	2.4	4.9	1.9	0.4
100	61.6	44.2	4.3	10.5	2.1	0.5
100 [a]	17.1	1.1	3.3	9.5	3.2	traces
120	25.6	2.7	4.7	13.1	5.1	traces
150	3.8	1.6	1.1	0.8	0.3	—

Olefin 2 mmol, catalyst 0.02 mmol, toluene 25 ml, $p(CO)$ 5 atm, $p(H_2)$ 40 atm, reaction time 3 h.

[a] Reaction time 24 h.

Table 10

Hydroformylation of hex-1-ene in the presence of $Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3)_3]_2$, influence of the solvent

Solvent	*T* (°C)	Heptanal (%)	2-Methyl-hexanal (%)	2-Ethyl-pentanal (%)	Heptanol (%)	2-Methyl-hexanol (%)	2-Ethyl-pentanol (%)	Hexane (%)	Hexenes (%)	Linear products/ hydroformylation products (%)	Aldehydes/ hydroformylation products (%)
Toluene	120	36.6	11.9	4.2	7.0	5.2	2.4	7.1	25.6	64.8	78.3
Methyl orthoformate	120	34.4	11.2	3.8	—	—	—	3.2	47.4	69.6	100
Diethyl ether [a]	120	27.6	9.0	2.8	0.5	0.2	—	4.4	55.5	70.1	98.2
1,4-Dioxane	120	50.0	16.4	5.5	0.4	traces	—	3.2	24.5	69.7	98.4
Toluene	150	31.7	13.6	7.8	17.9	11.1	5.2	9.0	3.7	56.8	60.8
Methyl orthoformate	150	19.2	9.8	3.7	—	—	—	6.3	61.0	58.7	100
Diethyl ether [a]	150	18.5	9.6	3.5	3.0	1.6	0.4	7.8	55.6	58.7	86.3
1,4-Dioxane	150	41.2	18.0	7.5	12.4	6.8	2.1	8.5	3.5	60.9	75.8
1,4-Dioxane/water (10:1) [b]	150	4.2	0.8	0.3	—	—	—	3.7	91.0	79.2	100

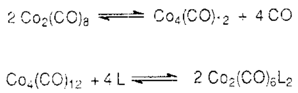
Residual olefins composition (as % of the total products)

Solvent	T (°C)	Hexenes (%)	Hex-1-ene (%)	*cis*-Hex-2-ene (%)	*trans*-Hex-2-ene (%)	*trans*-Hex-3-ene (%)	*cis*-Hex-3-ene (%)
Toluene	120	25.5	2.6	4.7	13.1	5.1	traces
Methyl orthoformate	120	47.4	25.5	5.4	11.8	4.2	0.5
Diethyl ether [a]	120	55.5	18.4	8.6	20.6	7.7	0.2
1,4-Dioxane	120	24.5	6.6	4.4	9.7	3.6	0.3
Toluene	150	3.7	1.6	1.1	0.8	0.3	—
Methyl orthoformate	150	61.0	7.5	12.9	29.3	11.3	—
Diethyl ether [a]	150	55.6	6.0	10.0	27.9	11.7	—
1,4-Dioxane	150	3.5	0.6	0.6	1.2	1.1	—
1,4-Dioxane/water (10: 1) [b]	150	91.0	30.1	21.7	31.1	7.4	0.7

Olefin 2 mmol, catalyst 0.02 mmol, solvent 25 ml, $p(CO)$ 5 atm, $p(H_2)$ 40 atm, reaction time 3 h.

[a] Hexanol was employed as internal standard.

[b] $p(H_2)$ 50 atm.



Scheme 7.

dioxane (88.0%), and at the same time a very significant increase of the heptanal/total aldehydes ratio (79.2%) with respect to those observed in other solvents (56.8–60.9%).

These results suggest a reduced solubility of CO in dioxane when containing water. The higher regioselectivity obtained in dioxane–water may indicate that the active catalyst still contains the phosphinic ligand.

A further support to this hypothesis are the results of hydroformylation experiments carried out in the presence of an excess of free phosphine, which are analogous to those obtained in solvents containing water.

The residual olefin was extensively isomerized, especially at higher conversions (Table 10).

2.3.3. *Influence of carbon monoxide pressure*

To test the influence of the carbon monoxide partial pressure we have performed experiments in the presence of **2** using a dioxane/water mixture (10:1) as solvent and propene as substrate. These results (Table 11), if compared with those reported by Piacenti et al. [2] for propene hydroformylation in the presence of **4**, using toluene as solvent, suggest that the presence of water reduces considerably the influence of the carbon monoxide partial pressure on the isomeric distribution of the aldehydes. In fact the amount of the straight chain isomer decreases from 86.0% to 76.9% (9.1% difference) when p_{CO} is increased from 7 to 80 atm using a water containing solvent; when using toluene, in the same range of p_{CO}, the decrease in the linear aldehyde formation is higher: from 82.2% to 68.5% (13.7% difference).

2.3.4. *Influence of the ligand*

The effect of the ligand has been evaluated by performing experiments at 150°C in dioxane. The results obtained are reported in Table 12.

The yield and the isomeric distribution of the products obtained working with **2**, **3**, and **4** are practically the same and similar to those observed in the presence of **5**. In this last case a greater amount of alcohols is obtained.

When the hydroformylation was carried out in the presence of **1** we had a poorer yield and a lower heptanal/total aldehydes ratio; the different behaviour of this complex may be connected at least in part to its lower solubility in the solvents used.

The catalytic activity of **2** has also been studied in the presence of the free ligand, at various concentrations (Table 13). The presence of the free phosphine causes a decrease in the conversion and, at the same time, an increase in the amount of the straight chain products; furthermore it does inhibit the isomerization of the substrate.

A molar ratio $P(CH_2CH_2CH_2OCH_3)_3/Co$ (mol free phosphine/mol of cobalt complex) equal to 1.3 is sufficient to cause a strong

Table 11
Hydroformylation of propene in the presence of $Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3)_3]_2$: influence of the carbon monoxide pressure

p(CO) (atm)	Butanal (%)	2-Methylpropanal (%)	Butanol (%)	Total aldehydes yield (%)	Hydroformylation products yield (%)	Butanal/2-methylpropanal (%)	Butanal/total aldehydes (%)
7	11.9	1.9	2.3	13.8	16.1	6.3	86.2
10	14.8	2.4	2.4	17.2	19.6	6.2	86.0
20	14.7	3.3	1.5	18.0	19.5	4.5	81.7
40	11.9	3.2	0.81	15.1	15.9	3.7	78.8
80	6.0	1.8	0.34	7.8	8.1	3.3	76.9

Olefin 1.3 g (30.89 mmol), catalyst 0.02 mmol, solvent: dioxane 22 ml, water 2.2 ml, $p(H_2)$ 40 atm, reaction temperature 150°C, reaction time 3 h. 2-Methylpentanol was employed as internal standard.

Table 12
Hydroformylation of hex-1-ene in the presence of $Co_2(CO)_6L_2$: influence of the nature of the ligand.

L	Heptanal (%)	2-Methyl-hexanal (%)	2-Ethyl-pentanal (%)	Heptanol (%)	2-Methyl-hexanol (%)	2-Ethyl-pentanol (%)	Hexane (%)	Hexenes (%)	Liner products/ hydroformylation products (%)	Aldehydes/ hydroformylation products (%)
CO	29.6	13.3	6.2	24.7	14.8	1.9	8.4	1.1	60.0	54.2
$P(CH_2CH_2CH_2CH_3)_3$	41.5	18.8	7.4	11.2	6.1	1.8	9.6	3.6	60.7	78.0
$P(CH_2CH_2CH_2OCH_3)_3$	41.2	18.0	7.5	12.4	6.8	2.1	8.5	3.5	60.9	75.8
$P(CH_2CH_2COOCH_3)_3$	37.6	16.8	6.7	14.7	8.0	3.4	9.3	3.5	60.0	70.1
$P(CH_2CH_2CN)_3$	26.4	17.4	6.5	5.9	4.6	0.4	10.3	28.5	52.8	82.2

Residual olefins composition (as % of the total products)

L	Hexenes (%)	Hex-1-ene (%)	*Cis*-hex-2-ene (%)	*Trans*-hex-2-ene (%)	*Trans*-hex-3-ene (%)	*Cis*-hex-3-ene (%)
CO	1.1	0.7	0.2	0.2	traces	traces
$P(CH_2CH_2CH_2CH_3)_3$	3.6	0.7	0.8	1.6	0.5	traces
$P(CH_2CH_2CH_2OCH_3)_3$	3.5	0.6	0.6	1.2	1.1	—
$P(CH_2CH_2COOCH_3)_3$	3.5	1.5	0.4	1.2	0.4	traces
$P(CH_2CH_2CN)_3$	28.5	3.1	5.7	14.3	5.4	traces

Olefin 2 mmol, catalyst 0.02 mmol, dioxane 25 ml, $p(CO)$ 5 atm, $p(H_2)$ 40 atm, temperature 150°C, reaction time 3 h.

Table 13

Hydroformylation of hex-1-ene in the presence of $Co_2(CO)_6L_2$ and free phosphine: influence of the phosphine

L	L/Co [a] molar ratio	Heptanal (%)	2-Methyl-hexanal (%)	2-Ethyl-pentanal (%)	Heptanol (%)	2-Methyl-hexanol (%)	2-Ethyl-pentanal (%)	Hexane (%)	Hexenes (%)	Linear/ hydroformyulation products (%)	Aldehydes/ hydroformylation products (%)
$P(CH_2CH_2CH_2OCH_3)_3$	—	41.2	18.0	7.5	12.4	6.8	2.1	8.5	3.5	60.9	75.8
$P(CH_2CH_2CH_2OCH_3)_3$	1.3	10.2	2.3	0.7	0.7	0.4	—	4.4	81.3	76.2	92.3
$P(CH_2CH_2CH_2OCH_3)_3$	2.6	7.4	0.9	0.2	0.3	—	—	5.0	86.2	87.5	96.6
$P(CH_2CH_2CH_2OCH_3)_3$	6.5	7.1	0.7	0.1	0.9	—	—	5.0	86.2	90.9	89.8
$P(CH_2CH_2CH_2OCH_3)_3$ [b]	6.5	10.3	1.4	0.6	11.1	1.6	0.7	15.3	59.1	83.6	48.0
$P(CH_2CH_2CH_2OCH_3)_3$	10	2.3	0.3	—	0.4	—	—	4.6	92.4	90	86.6
$P(CH_2CH_2CN)_3$	—	26.4	17.4	6.5	5.9	4.6	0.4	10.3	28.5	52.8	82.2
$P(CH_2CH_2CN)_3$	10	0.18	0.06	—	—	—	—	0.5	99.26	75.0	100
$P(CH_2CH_2CN)_3$ [c]	10	traces	—	—	1.0	0.6	—	7.8	90.6	62.5	0.0
$P(CH_2CH_2COOCH_3)_3$	—	37.6	16.8	6.7	14.7	8.0	3.4	9.3	3.5	60.0	70.1
$P(CH_2CH_2COOCH_3)_3$	10	0.3	0.17	traces	—	—	—	4.5	95.0	63.8	100

Residual olefins composition (as % of the total products)

L	L/Co [a] molar ratio	Hexenes (%)	Hex-1-ene (%)	*Cis*-hex-2-ene (%)	*Trans*-hex-2-ene (%)	*Trans*-hex-3-ene (%)	*Cis*-hex-3-ene (%)
$P(CH_2CH_2CH_2OCH_3)_3$	—	3.5	0.6	0.6	1.2	1.1	—
$P(CH_2CH_2CH_2OCH_3)_3$	1.3	81.3	15.1	20.6	35.2	10.0	0.4
$P(CH_2CH_2CH_2OCH_3)_3$	2.6	86.2	17.0	22.1	37.1	9.6	0.4
$P(CH_2CH_2CH_2OCH_3)_3$	6.5	86.2	16.7	22.6	36.7	9.5	0.7
$P(CH_2CH_2CH_2OCH_3)_3$ [b]	6.5	59.1	6.4	12.5	28.6	11.6	—
$P(CH_2CH_2CH_2OCH_3)_3$	10	92.4	24.9	23.5	35.2	8.3	0.5
$P(CH_2CH_2CN)_3$	—	28.5	3.0	5.7	14.3	5.4	traces
$P(CH_2CH_2CN)_3$	10	99.3	95.8	1.5	1.0	0.26	0.7
$P(CH_2CH_2CN)_3$ [b]	10	90.6	9.2	19.3	45.5	16.6	—
$P(CH_2CH_2COOCH_3)_3$	—	3.5	1.5	0.4	1.2	0.4	traces
$P(CH_2CH_2COOCH_3)_3$	10	95.0	33.0	22.0	32.0	7.4	0.6

Olefin 2 mmol, catalyst 0.02 mmol, dioxane 25 ml, $p(CO)$ 5 atm, $p(H_2)$ 40 atm, reaction time 3 h, $T = 150°C$.

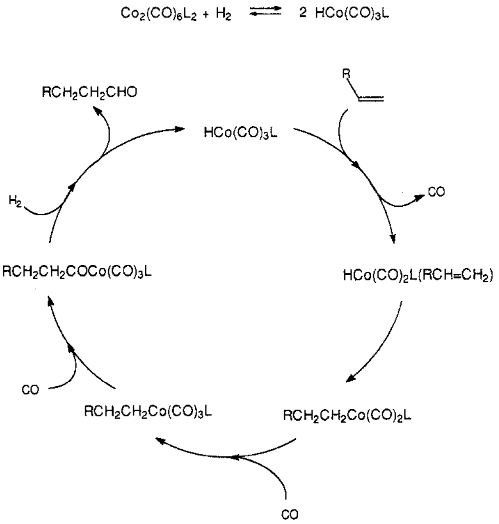
[a] L/Co = free phosphine/catalyst.

[b] $T = 180°C$.

[c] $T = 180°C$.

reduction of the catalytic activity of the system and at the same time to enhance its selectivity. The conversion to aldehydes and alcohols goes down from 88.0 to 14.3% while the ratio linear/total hydroformylation products rises from 60.9 to 76.2%. When the molar ratio free phosphine/catalyst has a value of 2.6 the yield in hydroformylation products further decreases (8.8%), and the ratio normal aldehyde/total aldehydes reaches 87.5%. Higher concentrations of the free phosphine do not cause significant improvements of the selectivity. The highest regioselectivity reached towards linear products has been 90.9%. In the course of this investigation on the influence of the free ligand in solution (P/Co = 6.5), it has also been observed that an increase of the reaction temperature from 150 to 180°C causes a decrease of the amount of straight chain products formed and an increase of the alcoholic fraction, in agreement with the data already reported [2].

The effect of the $P(CH_2CH_2CH_2OCH_3)_3$/Co ratio on the isomeric distribution of the reaction products is analogous to that found by Piacenti and Tucci in the hydroformylation of propene in the presence of $Co_2(CO)_6(PBu_3)_2$ [2,18]. Also the decrease in reaction rate when increasing the P/Co ratio is in the range of the data reported in the literature [2,19,20].



Scheme 8.

$$Co_2(CO)_6L_2 + CO \rightleftharpoons Co_2(CO)_7L + L$$

$$Co_2(CO)_7L + CO \rightleftharpoons Co_2(CO)_8 + L$$

$$Co_2(CO)_7L + H_2 \rightleftharpoons HCo(CO)_3L + HCo(CO)_4$$

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\ HCo(CO)_4$$

Scheme 9.

The influence of the free phosphine in solution has also been studied using cobalt complexes containing different phosphine ligands, in the molar ratio P/Co = 10 (Table 13). The effect of the free phosphine is to hinder dramatically the hydroformylation rate (in both cases conversions lower than 0.5%); in the light of an insignificant conversion, the increased selectivity clearly loses any interest.

An attempt to interpret these results, could be done taking into account the mechanism reported for the hydroformylation of propene in the presence of **4** [2] (Scheme 8). The data collected point out that with a P/Co ratio below 2.6 the effect of two catalytic species should be operative: $HCo(CO)_4$ and $HCo(CO)_3P(CH_2CH_2CH_2OCH_3)_3$. An increase in the free phosphine concentration causes an increase in the percentage of phosphine substituted hydridic complexes (Scheme 9).

It appears therefore that the presence of the bulky $P(CH_2CH_2CH_2OCH_3)_3$ molecule coordinated to the cobalt is presumably responsible, for steric reasons, of the high selectivity shown. When the P/Co ratio increases the amount of the phosphine substituted species increases compared with that of $HCo(CO)_4$. At the same time, since $HCo(CO)_3P(CH_2CH_2CH_2OCH_3)_3$ is less active than $HCo(CO)_4$, we observe a decrease in the reaction rate when the concentration of the phosphine substituted species increases.

3. Conclusion

Taking into account the data collected we may conclude that the mechanism of the hydroformylation (Scheme 8) and the activity of the catalysts tested are analogous to those previously reported for **4**. At high p_{CO} the phosphine is displaced to some extent from the complex and $HCo(CO)_4$ is the real catalyst involved in the reaction. The phosphine substituted catalysts play the main role only in the presence of free phosphine in solution. In these conditions, however, the selectivity is analogous to that reported when using $Co_2(CO)_6(PBu_3)_2$.

These catalysts are active both in polar solvents and in a water containing solvent but in the last case the activity is strongly reduced. These results show the possibility of reaching 100% chemio- and about 80% regioselectivity (79.2% with hexene, 86.4% with propene).

4. Experimental section

4.1. Materials

Reagents and solvents were purified and dried as reported. Hex-1-ene was passed through activated Al_2O_3 (70–230 mesh) and rectified under nitrogen (bp 64°C). Tri-*n*-butylphosphine was distilled under nitrogen prior to its use (bp 158–160°C (60 mm Hg)). Toluene was dried by refluxing on sodium metal, then it was refluxed and distilled on $LiAlH_4$. All reactions and manipulations were routinely performed under nitrogen. Acetonitrile (Aldrich): distilled before use, bp 82°C. Acrylonitrile: distilled before use, bp 76°C. Dioxane: treated as reported by Vogel, bp 101–102°C. AIBN (Janssen). Methyl orthoformate (Aldrich): distilled before use, bp 101°C. Methanol: dried as reported by Vogel, bp 65°C. Tetrahydrofuran: dried on $LiAlH_4$ and distilled under hydrogen immediately before use, bp 64°C. Diethyl ether: dried on $LiAlH_4$. Phosphine PH_3 (Rivoira): used as received. All other products: supplied by the usual commercial suppliers, used without further purification.

4.2. Instruments

Elemental analyses were performed with a Perkin-Elmer 240 C system. Gas chromatographic analyses (GLC) were performed with a Shimadzu GC-14A chromatographic system, coupled with a computer Shimadzu C-R4A, equipped with a packed column (2m, i.d. $\frac{1}{8}''$) PPG ('Polipropylenglicol' LB-550-X on Chromosorb W at 15%) or with a Perkin-Elmer 8320 system equipped with a capillary column Al_2O_3 PLOT (alumina on fused silica, 50 m, i.d. 0.32 mm). Both apparatus were equipped with an FID.

No correction factors due to responses were introduced. In some experiments, as reported in the tables, hexan-1-ol was used as internal standard.

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

Infrared spectra were recorded on an FTIR spectrophotometer Perkin Elmer model 1760-X. Liquid products and solutions were analyzed using a KBr or CaF_2 cell having a 0.1 mm path. Solid samples were mulled with KBr.

Multinuclear NMR spectra were registered using a Varian VXR300 spectrometer operating at 299.944 MHz for ^1H, at 75.429 MHz for ^{13}C and at 121.421 MHz for ^{31}P.

Peak positions were relative to tetramethylsilane as an external reference for ^1H- and ^{13}C-NMR spectra. H_3PO_4 (85%) was employed as external standard in the ^{31}P-NMR spectra; downfield values were taken as positive. ^{13}C- and ^{31}P-NMR spectra were recorded as proton decoupled spectra.

4.3. Synthesis of tertiary phosphines

4.3.1. $P(CH_2CH_2CN)_3$

A solution of $CH_2{=}CH{-}CN$ (26.5 ml), CH_3CN (30 ml) and KOH (10 M, 5 ml), was introduced by suction into an evacuated stainless steel Parr autoclave (150 ml). The autoclave was cooled at −50°C and then gaseous PH_3 (4.5 g, 0.13 mol) was added. The resulting suspension was left to stir for 26 h at room temperature. The organic layer was separated, washed with water and analyzed by GLC and ^{31}P-NMR. The presence of mono- and disubstituted phosphines was shown by GLC and confirmed by GC-MS spectroscopy. The solution was therefore transferred into a Schlenk flask (100 ml) and a solution of $CH_2=CH-CN$ (26.5 ml), CH_3CN (30 ml) and KOH (10 M, 5 ml) was added again and the resulting mixture stirred for 10 h at room temperature. At the end the bright orange mixture was transferred into a beaker containing water and ice; a yellow solid was separated, filtered, washed with cold water, then with cold methanol, then recrystallized from a solution of CH_3COOH–water (1:1). The $P(CH_2CH_2CN)_3$ was obtained as white needles having a melting point of 96°C. The amount of product was 18.5 g, (0.096 mol, yield 73.84%).

Spectroscopic data are reported in Tables 1–4. The mass spectrum shows peaks at *m/e* 193 $[M]^+$, 165 $[M-C_2H_4]^+$, 153 $[M-CH_2CN]^+$, 138 $[M-CH_3CH_2CN]^+$, 125 $[165-CH_2CN$ or $153-C_2H_4]^+$, 112 $[138-CN]^+$, 86 $[HP(CN)CH_2CH_2CN]^+$, 59 $[H_2PCN]^+$, 57 $[PCN]^+$, and 54 (100%) $[CH_2CH_2CN]^+$.

Anal. Calcd for $C_9H_{12}N_3P$: %C 55.94, %H 6.26, %N 21.76. Found: %C 56.12, %H 6.43, %N 21.54.

4.3.2. $P(CH_2CH_2CO_2CH_3)_3$

This compound was prepared for methanolysis of $P(CH_2CH_2CN)_3$. In a round bottom flask with three necks (50 ml) equipped with a thermometer, refrigerator and a capillary coil to bubble gaseous HCl, 5 g of $P(CH_2CH_2CN)_3$ (2.59×10^{-2} mol), 17.6 ml of methanol and 1.26 ml of H_2O were introduced under nitrogen. The flask was placed in a water–ice bath in order to keep the temperature below 50°C while gaseous HCl was bubbled through the solution for about 10 min. The resulting mixture was then stirred for 24 h. The solid formed (NH_4Cl) was filtered and the solvent was distilled in vacuo. Degassed H_2O (25 ml) was added, followed by a solution of NaOH 40% to reach pH 14. The organic layer was separated, washed with water, dried over magnesium sulfate and then distilled under vacuum. A dense, pale yellow liquid with bp 206–207°C (5 mm Hg) was obtained (1.27 g, 4.345×10^{-3} mol, yield 16.71%).

The spectroscopic data are reported in Tables 1–4. The mass spectrum shows peaks at *m/e* 277 $[M-CH_3]^+$, 261 $[M-OCH_3]^+$, 205 $[M-CH_2CH_2COOCH_3]^+$ and 55 (100%) $[CH_2=CHCO]^+$.

Anal. Calcd for $C_{12}H_{21}O_6P$: %C 49.31, %H 7.24. Found: %C 49.17, %H 7.37.

4.3.3. $P(CH_2CH_2CO_2CH_2CH_3)_3$

This compound was prepared for ethanolysis of $P(CH_2CH_2CN)_3$ following the procedure described above for the methyl derivative.

In a round bottom flask with three necks (50 ml) equipped with a thermometer, a refrigerator and a capillary coil to bubble gaseous HCl, 5 g of $P(CH_2CH_2CN)_3$ (2.59×10^{-2} mol), 17.6 ml of ethanol and 1.26 ml of H_2O were introduced under nitrogen. The flask was placed in a water–ice bath in order to keep the temperature below 50°C while gaseous HCl was bubbled through the solution for about 10 min. The resulting mixture was then stirred for 24 h. The solid formed (NH_4Cl) was separated by filtration and the solvent was distilled in vacuo. Degassed H_2O (25 ml) was added, then a solution of NaOH 40% was added up to pH 14. The organic layer was separated, washed with water, dried over magnesium sulfate and distilled under vacuum. A dense, pale yellow liquid with bp 221°C (5 mm Hg) was obtained (2.36 g, 7.06×10^{-3} mol, yield 27.15%).

The spectroscopic data are reported in Tables 1–4. The mass spectrum shows peaks at *m/e* 277 $[M-CH_3]^+$, 261 $[M-OCH_3]^+$, 205 $[M-CH_2CH_2COOCH_3]^+$ and 55 (100%) $[CH_2=CHCO]^+$.

Anal. Calcd for $C_{12}H_{21}O_6P$: %C 49.31, %H 7.24. Found: %C 49.17, %H 7.37.

4.3.4. $P(CH_2CH_2CH_2OCH_3)_3$

This phosphine was prepared using the method reported by Stiles et al. [8,9] for $P(CH_2CH_2OCH_3)_3$.

4.3.4.1. Synthesis of $CH_2=CHCH_2OCH_3$. This compound was prepared by a modification of the method reported by Henry [10]. Allylbromide (439.5 g, 3.63 mol) was added dropwise to MeONa (216 g, 4 mol) at 0°C. The solution was then brought to room temperature and distilled. The product collected had the following composition: allylmethylether (75.3%), methanol (1.5%) allylbromide (23.2%). By rectification a fraction containing allylmethylether (97.0%) and methanol (3.0%) was collected. This fraction was washed with water and dried over calcium chloride. GLC pure allylmethylether (160.0 g, 2.22 mol; yield 61.2% to allylbromide) was then obtained by distillation.

4.3.4.2. Synthesis of $P(CH_2CH_2CH_2OCH_3)_3$. Azo-bis-(2-methylpropionitrile) (1 g) was introduced into a stainless steel autoclave (125 ml). Air was then evacuated and a solution of allylmethylether (40 g) was introduced in pentane (50 ml). The autoclave was cooled at −80°C and then gaseous PH_3 (3.15 g, 9.3×10^{-2} mol) was added. The autoclave was heated at room temperature and then placed in a thermostatic oil bath set at 80°C for 13 h. After cooling at room temperature the unreacted gas was evacuated through a $CuSO_4$ solution. The solution recovered from the autoclave was distilled and the phosphine collected (colorless liquid) had a bp of 155°C (6 mm Hg).

The spectroscopic data are reported in Tables 1–4. The mass spectrum shows peaks at m/e 250 $[M]^+$; 235 $[M-CH_3]^+$, 205 $[M-CH_2OCH_3]^+$, 192 $[M-CH_2=CHOCH_3]^+$, 177 $[M-CH_2CH_2CH_2OCH_3]^+$, 134 $[M-2CH_2=CHOCH_3]^+$, 119 $[177-CH_2=CHOCH_3]^+$, 76 (100%) $[P(CH_3)_3]^+$, 73 $[CH_2CH_2CH_2OCH_3]^+$, 71 $[C_4H_7O]^+$ and 45 $[CH_2OCH_3]^+$.

Anal. Calcd for $C_{12}H_{27}O_3P$: %C 57.56, %H 10.88. Found: %C 57.12, %H 11.00.

4.4. Synthesis of the cobalt complexes

4.4.1. $Co_2(CO)_6[P(CH_2CH_2CN)_3]_2$

In a round bottom flask $P(CH_2CH_2CN)_3$ (0.368 g, 2.0×10^{-3} mol) was introduced under nitrogen. The phosphine was dissolved in methanol (10 ml) under reflux; then a solution of $Co_2(CO)_8$ (0.2 g, 5.8×10^{-4} mol) in methanol (10 ml) was added. A red-brick solid separated immediately, insoluble in most organic solvents. By recrystallization from acetone red crystals of the complex were obtained (0.110 g, 2.08×10^{-4} mol, yield 35.9%).

The spectroscopic data are reported in Tables 5–8.

Anal. Calcd for $C_{24}H_{24}O_6Co_2N_6P_2$: %C 42.86, %H 3.60, %N 12.50. Found: %C 42.71, %H 3.79, %N 12.27.

4.4.2. $Co_2(CO)_6[P(CH_2CH_2COOCH_3)_3]_2$

In a round bottom flask with three necks equipped with a magnetic stirrer and a reflux condenser, a solution of $Co_2(CO)_8$ (0.2 g, 5.8×10^{-4} mol) in n-hexane (10 ml) and a solution of $P(CH_2CH_2COOCH_3)_3$ (0.58 g, 2.0×10^{-3} mol) in n-hexane (10 ml) were introduced. The solution was stirred under reflux for 6 h. The formation of the complex was revealed by an IR spectrum. The solvent was then removed in vacuo from this solution and the oily residue was dissolved in benzene. By addition of n-heptane, a brick-red solid was obtained (0.250 g 2.87×10^{-4} mol, yield 49.5%), very soluble in toluene.

The spectroscopic data are reported in Tables 5–8.

Anal. Calcd for $C_{30}H_{24}O_{18}Co_2P_2$: %C 41.40, %H 4.86 found: %C 41.70, %H 5.16.

4.4.3. $Co_2(CO)_6[P(CH_2CH_2CH_2OCH_3)_3]_2$

In a round bottom flask, equipped with a magnetic stirrer and a reflux condenser, a solution of $Co_2(CO)_8$ (0.2 g, 5.8×10^{-4} mol) in *n*-heptane (10 ml) and another solution of $P(CH_2CH_2CH_2OCH_3)_3$ (0.5g, 2×10^{-3} mol) in the same solvent (10 ml) were introduced under nitrogen. The flask was heated at reflux for 3 h. A brown–red solution was formed. Nitrogen was slowly bubbled while heating in order to remove the CO evolved. An IR spectrum of a sample of the mixture showed the presence of the bands due to the carbonyl groups of the desired complex. The solvent was then removed in vacuo and the residue was recrystallized from *n*-pentane at −20°C, obtaining brown red needles (0.14 g, 1.78×10^{-4} mol, yield 30.7%) having a mp of 84–85°C. This complex is very soluble in pentane, hexane, benzene, toluene and also in methanol/water 1:1 and dioxane/water 1:1.

The spectroscopic data are reported in Tables 5–8.

Anal. Calcd for $C_{30}H_{54}O_{12}Co_2P_2$: %C 45.81, %H 6.92. Found: %C 45.85, %H 7.16.

4.4.4. $Co_2(CO)_6[P(CH_2CH_2CH_2CH_3)_3]_2$

This complex was prepared as reported by Piacenti et al. [10]. Its IR spectrum is in agreement with that reported in the literature [11].

The spectroscopic data are reported in Tables 5–8.

4.5. Catalytic hydroformylation

4.5.1. Hex-1-ene experiments

The catalytic experiments were carried out in a Parr model 4759 stainless steel autoclave (150 ml), electrically heated, with a magnetic drive stirrer. Air was evacuated from the vessel by a vacuum pump, then the solution containing the complex, substrate and solvent was introduced by suction. Hydrogen and carbon monoxide were added up to the desired pressure.

When the complex was only slightly soluble at room temperature in the solvent used, it was introduced as first component into the autoclave and then the vessel was closed, the air removed, and the solution of the substrate added. The autoclave was pressurized with the gases and heated at the selected temperature for the fixed time.

All experimental conditions adopted, are reported in the tables.

The analysis of the hydroformylation products present at the end of the reaction was performed by GLC using a PPG column (35°C for 15 min, then heated up to 50°C at a rate of 5°C/min, kept at 50°C for 2 min, then heated at a rate of 1°C/min up to 100°C and kept at this temperature for 60 min). The peaks due to hexane, hexenes, *n*-heptanal, 2-methylhexanal, 2-ethylpentanal, *n*-heptanol, 2-methylhexanol and 2-ethylpentanol could be separated under these conditions.

In order to get an evaluation of the isomeric composition of the olefins present among the reaction products, samples of the solution were analyzed on an Al_2O_3 PLOT capillary column kept at 130°C for 25 min, then heated up to 200°C at a rate of 30°C/min, and kept at this temperature for 45 min. Under these conditions the peaks due to hexane, hex-1-ene, *cis*- and *trans*-hex-2-ene, *cis*- and *trans*-hex-3-ene could be observed.

4.5.2. Propene experiments

The catalytic experiments were carried out in a Parr model 4759 stainless steel autoclave (150 ml), electrically heated, with a magnetic drive stirrer. Air was evacuated from the vessel, then the solution containing the complex and solvent was introduced by suction. The propene, contained in a cylinder, was introduced. The amount of olefin was determined weighing the autoclave before and after the olefin introduction. Hydrogen and carbon monoxide were added to the desired pressure.

All experimental conditions adopted are reported in Table 11.

The analysis of the hydroformylation products present at the end of the reaction was performed by GLC using a PPG column (50°C for 5 min, then heated up to 120°C at a rate of 5°C/min, kept at 120°C for 30 min). The peaks due to butanal, 2-methylpropanal, butanol, and 2-methylpropanol could be separated under these conditions.

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