The behaviour of *n*- and *iso*-propylcobalt tricarbonyl tributylphosphine complexes under hydroformylation conditions

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Abstract

Tributylphosphine *n*-propyl- (**Ia**) and *iso*-propyl (**Ib**) cobalt tricarbonyl have been prepared from $NaCo(CO)_3(PBu_3)$ and the proper alkyl halide. The behaviour of **Ia** and **Ib** under hydroformylation conditions ($T = 120–180\,°C$, $p_{CO} = 5\,atm$, $p_{H_2} = 50\,atm$ in the presence or absence of an excess of an olefin or PBu_3) has been tested. **Ia** and **Ib** gave the expected isomeric alcohols with a selectivity higher than 95%. The role of these complexes in the hydroformylation reaction has been discussed. © 1997 Elsevier Science S.A.

1. Introduction

The behaviour of alkyl- and acylcobaltcarbonyl complexes, accepted intermediates in the hydroformylation of olefins catalyzed by $Co_2(CO)_8$, has been studied by several authors in an attempt to rationalize the factors affecting the isomeric composition of the reaction products [1–13]. Extensive work has been done on alkyl and acylcobaltcarbonyls prepared from alkyl [1,2] or acyl halides and potassium or sodium tetracarbonylcobaltate [2–5,10] as well as acylic derivatives of $HCo(CO)_4$ and ketenes [11,13] under N_2 or CO at temperatures up to 45 °C. Some experiments were also made in the presence of an olefin [13]. Extensive isomerization of the alkyl and acyl derivatives with an inhibiting effect of CO under pressure was generally found and considered responsible for the low regioselectivity of the oxo reaction.

This explanation, however, does not hold in the case of the hydroformylation of simple olefins, like propene, carried out under typical oxo conditions ($p_{CO} = p_{H_2} = 80\,atm$, $T = 80\,°C$).

It has in fact been shown that in these conditions not only C4 acyl- but also *n*-propyl- and *iso*-propylcobalt tetracarbonyls, synthesized by reacting sodium tetracarbonylcobaltate with the appropriate alkyl iodide, even in the presence of an olefin, produce respectively only *n*-butanal or *iso*-butanal [6–9,12].

The isomeric composition of the products of the hydroformylation of propene catalyzed by $Co_2(CO)_8$ must therefore be determined by the regioselectivity of the addition of the H–Co bond to the C=C double bond of the activated olefin.

When using the $Co_2(CO)_8/PBu_3$ catalytic system instead of $Co_2(CO)_8$ alone, the regioselectivity of the reaction changes and the *n*/*iso* ratio of the isomeric reaction products increases from 80/20 in the latter case to 90/10 even though the temperature used when working in the presence of the phosphine ligand is decidedly higher (150–180 °C) [14–22].
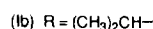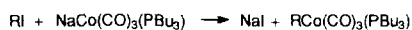
In order to find out if the regioselectivity is determined also in this case by the initial step of the reaction, the addition of the hydride to the olefin, or is due to subsequent isomerization phenomena involving alkyl and/or acyl intermediates, we have investigated the behaviour of *n*-propyl and *iso*-propylcobalt tricarbonyl tributylphosphine complexes under appropriate conditions.

2. Results and discussion

2.1. Synthesis, characterization and behaviour of $RCo(CO)_3(PBu_3)$ derivatives

N- and *iso*-propylcobalt tricarbonyl tributylphosphine derivatives were prepared according to known procedures [20] from $NaCo(CO)_3(PBu_3)$ and the appropriate

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RI + NaCo(CO)₃(PBu₃) ⟶ NaI + RCo(CO)₃(PBu₃)

(Ia) R = CH₃CH₂CH₂–

(Ib) R = (CH₃)₂CH–

Scheme 1.

$$NaCo(CO)_3(PBu_3) + RX \xrightarrow{CO, H_2} NaX + RCH_2OH + [Co]$$

(V)

[Co] = HCo(CO)₃(PBu₃) + Co₂(CO)₆(PBu₃)₂ mixture

Scheme 3.

alkyl iodide in diethylether solution, under nitrogen (Scheme 1).

The reaction occurs already at temperatures as low as −80 °C. At 0 °C it is practically complete in a few minutes. The complexes were recovered from the solution by evaporation of the solvent under reduced pressure. No attempts were made to crystallize them. Their IR and ^{31}P NMR data are in agreement with those appropriate for the expected formulation. The ^{31}P NMR chemical shifts of the *n*- and *iso*-species occur at 43.9 and 41.5 ppm respectively, thus permitting the detection of each of them in an eventual mixture. The isomeric identity of the alkyl derivatives was confirmed by their conversion into the corresponding acyl species by reaction with CO and then, by a known procedure [23], into the corresponding methyl esters by treatment with iodine in methyl alcohol. The GLC of the solution showed the presence of the sole ester expected.

A *n*-heptane solution of CH₃CH₂CH₂Co(CO)₃-(PBu₃) (Ia) retained the same IR spectrum when heated up to 25 °C under nitrogen. By a further increase of the temperature to 40 °C, the solution became red and gas was evolved (H₂ and propene). The IR spectrum of this solution indicated the presence, in addition to Ia, of Co₂(CO)₆(PBu₃)₂ and of an acyl species (band at 1600 cm⁻¹). By subsequent chemical treatment, this acyl was shown to be CH₃CH₂CH₂COCo(CO)₃(PBu₃) (IIa). At 40 °C Ia decomposes with formation of HCo(CO)₃(PBu₃) (III) and propene (Scheme 2). This hydride in turn, as is known [20], decomposes to Co₂(CO)₆(PBu₃)₂ (IV) and H₂, giving rise also to other species with evolution of CO which immediately transforms the residual alkyl (Ia) into the corresponding acyl derivative (IIa) (Scheme 2).

At 60 °C Ia decomposes completely in a short time. A similar behaviour is shown by (CH₃)₂CHCo(CO)₃(PBu₃) (Ib): the ester recovered by its treatment with iodine and CH₃OH is solely methyl
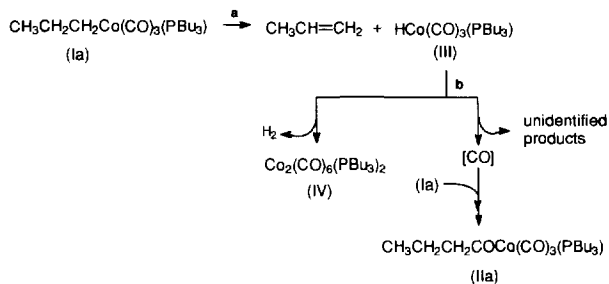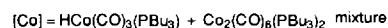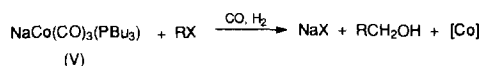
iso-butyrate. The decomposition of the alkyl derivative however in this case begins at a lower temperature (10 °C).

These results agree with our previous findings: the step (a) in Scheme 2 is irreversible to all practical effects under the conditions explored and it is followed by the decomposition of the hydride III [20].

It may then be stated that the alkyl species tested, when heated under nitrogen, decompose but do not isomerize.

2.2. Synthesis and behaviour of the alkyl derivatives under oxo conditions

In order to explore the behaviour of the above alkyl species under oxo conditions, the reaction between C3 alkyl halides and NaCo(CO)₃(PBu₃) (V) was carried out under a CO + H₂ (1:1) mixture using the technique described for the analogous experiments on the unsubstituted cobalt derivatives [7,8] (Scheme 3).
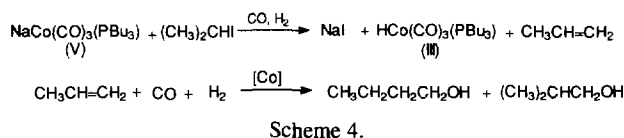
The solution of V in diethylether was placed in an autoclave under vacuum which was then pressurized with 5 atm of CO and heated up to 165 °C. The halide was then introduced and then hydrogen under pressure was added up to 50 atm. The autoclave was then rocked and after 5 h the crude was analysed by GLC. Alcohols were the sole carbonylation products; V was no longer present (IR monitoring) (Table 1). From *n*-propyl iodide, *n*- and *iso*-butanol were obtained, the first in high prevalence (97%); from *iso*-propyl iodide, *iso*-butanol was 75% of the mixture of the two alcohols.

This last result suggests that rather relevant isomerization phenomena take place in this last case. An alternative explanation may, however, be offered (Scheme 4) by admitting an elimination reaction of the halide giving rise to propene, which in turn is hydroformylated yielding a mixture of *n*- and *iso*-butanol with a high prevalence of the first. This hypothesis has

CH₃CH₂CH₂Co(CO)₃(PBu₃) ⟶ᵃ CH₃CH=CH₂ + HCo(CO)₃(PBu₃)

(Ia)   (III)

↓ b

H₂ ←┘   └→ unidentified products

Co₂(CO)₆(PBu₃)₂   [CO]

(IV)   (Ia) ⟶

↓

CH₃CH₂CH₂COCo(CO)₃(PBu₃)

(IIa)

Scheme 2.

Table 1
Reaction of RX and NaCo(CO)₃(PBu₃) under CO and H₂

RX	Reaction products CH₃CH₂CH₂CH₂OH	Composition % (CH₃)₂CHCH₂OH
CH₃CH₂CH₂–I	96.6	3.4
CH₃CH₂CH₂–Br	98.0	2.0
(CH₃)₂CH–I	25.2	74.8
(CH₃)₂CH–Br	3.6	96.4

Diethylether 75 ml; NaCo(CO)₃(PBu₃) 2.03 mmol; RX 2.20 mmol; p_{CO} = 5 atm at r.t.; p_{H_2} = 45 atm; T = 165 °C, reaction time 5 h.

$$NaCo(CO)_3(PBu_3) + (CH_3)_2CHI \xrightarrow{CO, H_2} NaI + HCo(CO)_3(PBu_3) + CH_3CH=CH_2$$
$$\text{(V)} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(III)}$$

$$CH_3CH=CH_2 + CO + H_2 \xrightarrow{[Co]} CH_3CH_2CH_2CH_2OH + (CH_3)_2CHCH_2OH$$

Scheme 4.

been confirmed by the results obtained by using *iso*-propyl bromide instead of the iodide derivative in the same reaction: 96.6% of *iso*-butanol was the result. It is known [24] that alkyl bromides undergo elimination reaction less easily than the corresponding iodides when reacted with a nucleophile, and therefore the relevance of the substitution with them is higher. This is in keeping with the results obtained.

The elimination/substitution ratio decreases as the temperature is reduced [24]. The results of a series of experiments carried out on *iso*-propyl bromide at temperatures in the 120–180 °C range are in line with the above suggestion: the percentage of *iso*-butanol formed decreases from 100% at 120 °C to 94.5% at 180 °C (Table 2).

For a more realistic simulation of the oxo conditions we have finally synthesized the alkyl derivatives from *iso*-propyl bromide and V, in the presence not only of CO, H_2 but also of a free olefin. No significant effect was noticed on the selectivity of this reaction due to the presence of hex-1-ene even if in large excess compared with the amount of the alkyl bromide (Table 3).

The influence of the presence of free phosphine was also tested. Unfortunately the experiments performed using a PBu_3/RI molar ratio of 10 gave very low yield due to the formation of tetralkylphosphonium salts $(RPBu_3)^+I^-$. An experiment carried out using *n*-butyryl chloride/PBu_3 in the same ratio gave the same result as in the absence of PBu_3: *n*-butyl alcohol was formed with 97.0% selectivity (Table 4).

In conclusion, both the *n*- and *iso*-$C_3H_7Co(CO)_3(PBu_3)$ complexes and the corresponding acyl species under the conditions used for the standard hydroformylation of olefins in the presence of the $Co_2(CO)_8/PBu_3$ catalytic system do not isomerize to an extent sufficient to justify the observed composition of the products obtained from propene. Such composition must therefore be determined also in this case by the selectivity of the addition of the H–(Co) bond to the

C=C double bond of the olefin, giving rise to the alkyl species.

3. Experimental

3.1. IR spectra

Recorded with an FT-IR Perkin-Elmer mod. 1760 instrument using KBr or CaF_2 windows for solutions and KBr pellets for solid samples.

3.2. NMR spectra

^{1}H NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 or at 199.975 MHz on a Varian Gemini-200 spectrometer, using tetramethylsilane as external reference. A Varian VXR 300 instrument was used to record the ^{31}P NMR spectra at 121.421 MHz. All ^{31}P NMR spectra were acquired as proton decoupled using H_3PO_4 (85%) as external reference. Downfield values are reported as positive.

3.3. GLC analyses

Usually performed using a GLC apparatus for packed columns Shimadzu mod. GLC-14A with a computer Shimadzu C-R4A and a GLC instrument for capillary columns Perkin-Elmer mod. 8320. All instruments had

Table 3
Reaction of $(CH_3)_2CHBr$ and $NaCo(CO)_3(PBu_3)$ under CO and H_2; effect of added hex-1-ene [a]

Hex-1-ene $(CH_3)_2CHBr$ molar ratio	Reaction products $(CH_3)_2CHCH_2OH$ % [b]	Composition $CH_3CH_2CH_2CH_2OH$ %
0	96.4	3.6
5	95.5	4.5
50	95.6	4.4

Diethylether 75 ml; $NaCo(CO)_3(PBu_3)$ 2.03 mmol; $(CH_3)_2CHBr$ 2.20 mmol; $p_{CO} = 5$ atm at r.t.; $p_{H_2} = 45$ atm; $T = 165\,°C$; reaction time 5 h.
[a] The pressure was kept constant during the reaction by adding a CO/H_2 (1:2) mixture.
[b] C_7 alcohols were also present.

Table 2
Reaction of $(CH_3)_2CHBr$ and $NaCo(CO)_3(PBu_3)$ under CO and H_2 at various temperatures

T	Reaction products %		RCHO composition %		RCH_2OH composition %	
	RCHO	RCH_2OH	$(CH_3)_2CHCHO$	$CH_3CH_2CH_2CHO$	$(CH_3)_2CHCH_2OH$	$CH_3CH_2CH_2CH_2OH$
120	90.0	10.0	100	0	100	0
150	35.1	64.9	96.8	3.2	97.1	2.9
165	0	100	—	—	96.4	3.6
180	0	100	—	—	94.5	5.5

Diethylether 75 ml; $NaCo(CO)_3(PBu_3)$ 2.03 mmol; $(CH_3)_2CHBr$ 2.20 mmol; $p_{CO} = 5$ atm at r.t.; $p_{H_2} = 45$ atm; reaction time 5 h.

Table 4

Reaction of $CH_3CH_2CH_2COCl$ with $NaCo(CO)_3(PBu_3)$ under CO and H_2; effect of added PBu_3

PBu_3 $CH_3CH_2CH_2COCl$ molar ratio	Reaction products $CH_3CH_2CH_2CH_2OH$ %	Composition $(CH_3)_2CHCH_2OH$ %
0	97.5	2.5
10	97.1	2.9

Diethylether 75 ml; $NaCo(CO)_3(PBu_3)$ 2.03 mmol; $CH_3CH_2CH_2COCl$ 2.20 mmol; $p_{CO} = 5$ atm at r.t.; $p_{H_2} = 45$ atm; $T = 165\,°C$; reaction time 5 h.

FID detectors. The following columns were used: a packed (2 m) column PPG ("Polipropylenglicol" LB-550-X 15% supported on Chromosorb W) and a capillary column Al_2O_3 PLOT containing alumina (50 m, internal diameter 0.32 mm). Quantitative analyses of isomeric compounds were performed assuming that all products had the same response factors. The identification of hydrogen by GLC was carried out using a Perkin-Elmer Sigma 1 instrument with a Sigma 10 computer, equipped with a conductivity detector, using a packed Porapak Q column (2 m).

3.4. GLC-MS analyses

Performed using a GLC apparatus for capillary columns Shimadzu mod. GLC-14A equipped with a capillary column SPB-1™ (30 m, i.d. 0.25 mm) and a mass detector Shimadzu QP2000.

3.5. Materials

$Co_2(CO)_8$ was prepared as described by Natta and Ercoli [25], crystallized by n-hexane and had m.p. 56 °C. $Co_2(CO)_6(PBu_3)_2$ (IV) was prepared according to Piacenti et al. [20] and had m.p. 121–122 °C.

N-propyl iodide, iso-propyl iodide, n-propyl bromide, n-butyryl chloride, iso-butyryl chloride, tributylphosphine were commercial products and distilled under nitrogen prior to use. Iso-propyl bromide [26] was synthesized as reported in the literature.

3.6. Reaction of alkyl halides with $NaCo(CO)_3(PBu_3)$ (V)

3.6.1. Under nitrogen: preparation of $RCo(CO)_3(PBu_3)$

To a solution of V, prepared by reacting IV (500 mg) in 50 ml diethylether with Na/Hg 0.5% (100 g), C_3H_7I (2.20 mmol) in 10 ml of diethylether was added under stirring at 0 °C. The reaction was followed through the IR spectra of samples of the solution. The formation of solid NaI occurs immediately, and is accompanied by the decrease in intensity of the bands due to V (bands at 1933(w), 1901(w), 1847(s) cm^{-1}). After 2 h at room temperature using n-propyl iodide, or after half an hour at 0 °C using the iso-propyl iodide, the reaction is complete. The solution, after separation of NaI, was evaporated to dryness under reduced pressure at $-10\,°C$. IR and NMR spectra, taken on the complex present as residue, showed the characteristics reported in Table 5.

3.6.2. Under CO: preparation of $RCOCo(CO)_3(PBu_3)$ (II)

The same synthetic procedure described above was performed in the presence of CO at room pressure. An oily material was recovered which gave IR and NMR spectra in keeping with the $RCOCo(CO)_3(PBu_3)$ formulation (Table 5). The same product was obtained by treating a solution of preformed $RCo(CO)_3(PBu_3)$ with CO at atmospheric pressure, or by reacting RCOX with V as described above.

Table 5

IR and ^{31}P NMR characteristics of $RCo(CO)_3(PBu_3)$ and $RCOCo(CO)_3(PBu_3)$ derivatives

Complex	IR [a] ν (cm^{-1})	^{31}P NMR [b] δ (ppm)
$Co_2(CO)_6(PBu_3)_2$	1967(sh), 1949(vs), 1924(sh)	53.9(s)
$NaCo(CO)_3(PBu_3)$	1933(w), 1901(w), 1847(s)	41.5(s)
$CH_3CH_2CH_2Co(CO)_3(PBu_3)$	2027(w), 1970(w), 1948(vs)	43.9(s)
$(CH_3)_2CHCo(CO)_3(PBu_3)$	n.d.	41.5(s)
$CH_3CH_2CH_2COCo(CO)_3(PBu_3)$	2041(w), 1971(s), 1950(vs), 1680(m)	34.9(s)
$(CH_3)_2CHCOCo(CO)_3(PBu_3)$	1968(s), 1949(vs), 1678(m)	34.2(s)

[a] Diethylether solution: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.
[b] Octadeuterofurane solution: s, singlet.

The solution of the acyl complex reacted with I_2 and MeOH [23] gave the expected methyl ester RCOOMe. The reaction mixture was analyzed by GLC; the identification of the products was made by GLC-MS.

3.6.3. Under CO and H₂

Compound **V** (2.03 mmol) in diethylether (50 ml) was introduced into a 125 ml rocking autoclave and CO was then added up to a pressure of 5 atm at room temperature. The autoclave was heated at the desired temperature (120–180 °C) for 30 min and a solution of the alkyl halide (2.20 mmol) in diethylether (25 ml) was then introduced through an injection system operated by a hydrogen pressure of 50 atm which therefore entered into the autoclave. After 5 h the autoclave was cooled to 0 °C, the gas vented and the crude mixture analyzed by IR and GLC techniques. The identity of the products was confirmed by GLC-MS analysis.

3.6.4. Under CO, H₂ and hex-1-ene

The experiment was carried out as described in Section 3.6.3. The olefin (11 or 110 mmol, see Table 3) was introduced into the autoclave together with the $NaCo(CO)_3(PBu_3)$ solution. The gas pressure was kept constant during the reaction, supplying a carbon monoxide–hydrogen mixture (1:2) from a high pressure cylinder.

The reaction products were analyzed as reported above.

3.7. Thermal behaviour of RCo(CO)₃(PBu₃)

n-Heptane solutions of $RCo(CO)_3(PBu_3)$ were heated under nitrogen at a fixed temperature (in the range 0–80 °C) and monitored by IR and GLC techniques. THF-d_8 solutions of **I** were placed under N_2 in sealed tubes capable of withstanding 3 atm of pressure and monitored by NMR spectroscopy. We could follow the formation of $Co_2(CO)_6(PBu_3)_2$ [bands at 1967(sh), 1949(vs), 1924(sh) cm^{-1} in the IR spectrum, resonances at δ 53.9 ppm in the ^{31}P NMR], hydrogen (by GLC using the Porapak column), propene (by GLC) and $RCOCo(CO)_3(PBu_3)$ [for $R = CH_3CH_2CH_2-$ bands at 2041(w), 1971(s), 1950(vs), 1680(m) cm^{-1} in the IR spectrum, resonances at δ 34.9 ppm in the ^{31}P NMR; for $R = (CH_3)_2CH-$ bands at 1968(s), 1949(vs), 1678(m) cm^{-1} in the IR spectrum, resonances at δ 34.2 ppm in the ^{31}P NMR] and the disappearance of the starting material $RCo(CO)_3(PBu_3)$.

No isomeric mixtures of $RCo(CO)_3(PBu_3)$ or $RCOCo(CO)_3(PBu_3)$ were ever detected.

3.8. Reaction of acyl halides with NaCo(CO)₃(PBu₃)

A solution of RCOCl (2.20 ml) in 10 ml diethylether was added at 0 °C under nitrogen to a solution of **V** in

the same solvent prepared as described in Section 3.6.1. The mixture was stirred until **V** was completely converted (IR control monitorage). The solution, after separation of NaCl, was evaporated to dryness under reduced pressure. The residue, analyzed by IR and NMR spectroscopy, showed the characteristics reported in Table 5.

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