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CATALYSIS BY PHOSPHINE COBALT CARBONYL COMPLEXES
I. SYNTHESIS AND CATALYTIC PROPERTIES OF (TRIBUTYLPHOSPHINE)COBALT (I) HYDRIDE CARBONYL COMPLEXES*

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SUMMARY

The synthesis of the cobalt hydrides of formula $CoH(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_n$ ($n=2, 3$) are described and their chemical and spectroscopic properties are discussed. The complexes homogeneously catalyze the hydrogenation of alkynes and aldehydes and isomerization of olefins. These reactions are discussed in relation to the aldehyde hydrogenation catalyzed under hydroformylation conditions by the $Co_2(CO)_8$ system modified with $P(n\text{-}C_4H_9)_3$.

INTRODUCTION

Recent research has shown that catalytic systems such as $Co_2(CO)_8+PR_3$ or preformed $[Co(CO)_3PR_3]_2$ complexes[1] catalyze the hydroformylation of propylene and other olefins. These systems are reported to be more selective than $Co_2(CO)_8$ in reducing the formation of branched-products, and show strong hydrogenating properties which result in the formation of alcohols. Several authors[2-5] have discussed the nature of the effective catalytic species in the modified hydroformylation catalyst, and despite some controversy about the action of the tertiary phosphine, have proposed that the hydrido complex of formula $CoH(CO)_3PR_3$, is the actual catalyst. During our studies on the cobalt carbonyl–tertiary phosphine catalytic system[6,7] we have isolated some hydrido carbonyl complexes of cobalt(I) with $P(n\text{-}C_4H_9)_3$**, and we describe their synthesis and catalytic properties below.

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* Part of this paper has been presented at 4th Int. Conf. of Organometal. Chem., Bristol (1969) and at Biennal Meeting C.N.R. on Coordination Compounds, Rome (1970).

** The hydrogenating properties of phosphine containing cobalt carbonyl hydrides have been claimed also by others[8].

SYNTHESIS, PROPERTIES AND REACTIONS OF $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ AND $CoH(CO)[P(n\text{-}C_4H_9)_3]_3$

Synthesis and stability

Although many complexes of formula $CoH(CO)_3PR_3$, have been reported, including the complex with $R = n\text{-}C_4H_9$[9], only very few examples are known of bis- and monocarbonyl hydrido complexes of Co^I containing tertiary phosphines. Thus $CoH(CO)_2(PPh_3)_2$ has been obtained by Hieber and coworkers[10] by reduction of $CoX(CO)_2(PPh_3)_3$ ($X = Cl$, Br) with sodium amalgam, and $CoH(CO)(PPh_3)_3$ has been also reported[11]. No detailed studies on the catalytic properties of these complexes have been made* .

Two different methods were developed for the synthesis of the tributylphosphine complexes; thus the bisphosphine complex (I) can be obtained from the known cobalt (0) derivate $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$ [eqn. (1)] or directly from cobalt(II) salts [eqn. (2)]:

$$\tfrac{1}{2}[Co(CO)_3P(n\text{-}C_4H_9)_3]_2 + P(n\text{-}C_4H_9)_3 + \tfrac{1}{2}\,H_2 \rightarrow$$
$$\rightarrow \underset{(I)}{CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2} + CO \qquad (1)$$

$$(RCOO)_2Co + 2\,P(n\text{-}C_4H_9)_3 + 2\,CO + 1\tfrac{1}{2}H_2 \rightarrow$$
$$\rightarrow \underset{(I)}{CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2} + 2\,RCOOH \qquad (2)$$

Reaction (1) was carried out in heptane at 120–180° under 30 atm of hydrogen and with a ratio of free phosphine to cobalt of 1.25 to 1. Carbon monoxide was found in the discharged gas but some starting cobalt(0) dimer was still present in the solution (red colour and characteristic IR absorption at 1949 cm^{-1} with shoulder at 1971 cm^{-1})[9]. In order force the reaction to completion this operation must be repeated several times by repeatedly discharging the gas mixture and pumping in pure hydrogen.

Complex (I) was more simply prepared according to eqn. (2) at 110° under 40–50 atm of hydrogen with the reagents $(CH_3COO)_2Co$, $P(n\text{-}C_4H_9)_3$ and CO in the stoichiometric ratios.

The hydrido complex (I) is obtained as a dark yellow oil, which cannot be crystallized even at −60°, and is fairly stable under pure nitrogen. It is thermally stable in n-heptane up to 160° and it is stable in presence of aldehydes, alcohols, ketones and dimethylformamide at least up to 110°. Above 130° in the presence of aldehydes, $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$ is slowly formed.

To bring about further replacement of carbon monoxide by tributylphosphine a new method using stoichiometric hydroformylation was applied:

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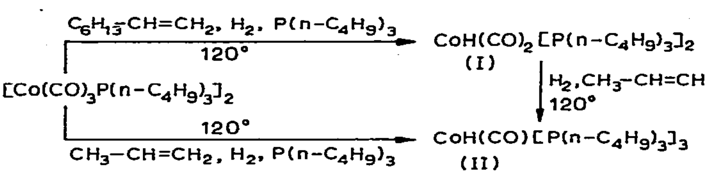
* However, when this work was being written-up a brief preliminary communication appeared dealing with hydrogenating properties of $CoH(CO)(PPh_3)_3$[12].



(3)

Long chain α-olefins readily gave (I) even at 120°, but it was necessary to use ethylene or propylene as carbon monoxide acceptors in order to obtain $CoH(CO)[P(n\text{-}C_4H_9)_3]_3$ (II). Hydrogenation of the olefin took place together with the stoichiometric hydroformylation and so additional quantities of propylene and hydrogen were supplied. The lower activity of long chain α-olefins compared with propylene and ethylene can be ascribed to their easy isomerization to internal olefins (see later), which give the hydroformylation reaction less easily[4].

Complex (II) was isolated as a yellow-green air sensitive oil; it is stable in n-heptane solution up to 80° and up to 140° in the presence of hydrogen and free tributylphosphine. However, it is rather reactive towards linear aldehydes, such as butyraldehyde, and carbon monoxide abstraction[13], a well known reaction for rhodium[14] and ruthenium[15] phosphine complexes, takes place at about 60°:

$$(II)+R\text{-}CH_2\text{-}CH_2\text{-}CHO \rightleftarrows (I)+R\text{-}CH{=}CH_2+H_2+P(n\text{-}C_4H_9)_3 \quad (4)$$

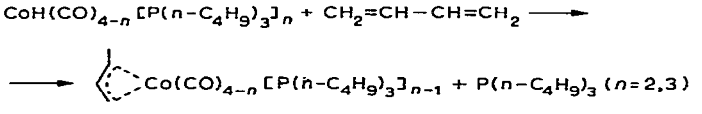
By comparing (4) with (3) we can see that the formation of (II) through hydroformylation takes place because the aldehyde is reduced under the reaction conditions.

IR, NMR and reactivity

The presence of the hydridic hydrogen in the complexes (I) and (II) is indicated by the ^1H NMR spectra (Tables 2 and 3) and by some typical reactions of the hydrogen–metal bond:

$$(I)+HI \rightarrow CoI(CO)_2[P(n\text{-}C_4H_9)_3]_2+H_2 \quad (5)$$
$$(I)+CHI_3 \rightarrow CoI(CO)_2[P(n\text{-}C_4H_9)_3]_2+CH_2I_2 \quad (6)$$

π-Allyl complexes of cobalt, containing two phosphines per metal atom, which cannot be obtained by addition of phosphine to a preformed π-allyl complex[16,17], are easily obtained according to the following equation:



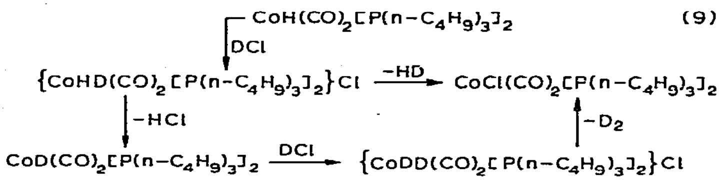
(7)

In the presence of carbon monoxide a series of reversible reactions takes place at room temperature and can be easily followed by IR spectroscopy (eqn. 8).

$$(II) \underset{+P(n\text{-}C_4H_9)_3}{\overset{+CO}{\rightleftarrows}} (I) \underset{+P(n\text{-}C_4H_9)_3}{\overset{+CO}{\rightleftarrows}} CoH(CO)_3P(n\text{-}C_4H_9)_3 \underset{+P(n\text{-}C_4H_9)_3}{\overset{+CO}{\rightleftarrows}} CoH(CO)_4 \quad (8)$$

The first equilibrium is completely shifted to the right at atmospheric pressure, while the others, and especially the last, require higher carbon monoxide pressures.

Both (I) and (II) undergo hydrogen–deuterium exchange with gaseous deuterium: in heptane solution (I) reacts in 3 h at 120° under 22 atm of D_2; (II) reacts in 1 h at 60° under 15 atm of D_2. The hydrogen–deuterium exchange with both hydrides is more easily carried out at room temperature using DCl–D_2O. In the case of (II), $CoD(CO)[P(n\text{-}C_4H_9)_3]_3$ and HCl are obtained whilst $CoCl(CO)_2[P(n\text{-}C_4H_9)_3]_2$, HD, and some D_2 are observed in the case of (I). The presence of acid is absolutely necessary and for this reason an initial $d^8 \rightarrow d^6$ oxidative addition is suggested to occur in both cases, probably forming an ionic intermediate[18], $\{CoHD(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_n\}Cl$ ($n=2, 3$), which undergoes loss of HCl in the case of $n=3$, while in the case of $n=2$ reactions (9) take place:



$$\begin{tikzcd}
CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2 \arrow[d, "DCl"] & \\
\{CoHD(CO)_2[P(n\text{-}C_4H_9)_3]_2\}Cl \arrow[r, "-HD"] \arrow[d, "-HCl"] & CoCl(CO)_2[P(n\text{-}C_4H_9)_3]_2 \\
CoD(CO)_2[P(n\text{-}C_4H_9)_3]_2 \arrow[r, "DCl"] & \{CoDD(CO)_2[P(n\text{-}C_4H_9)_3]_2\}Cl \arrow[u, "-D_2"]
\end{tikzcd} \qquad (9)$$

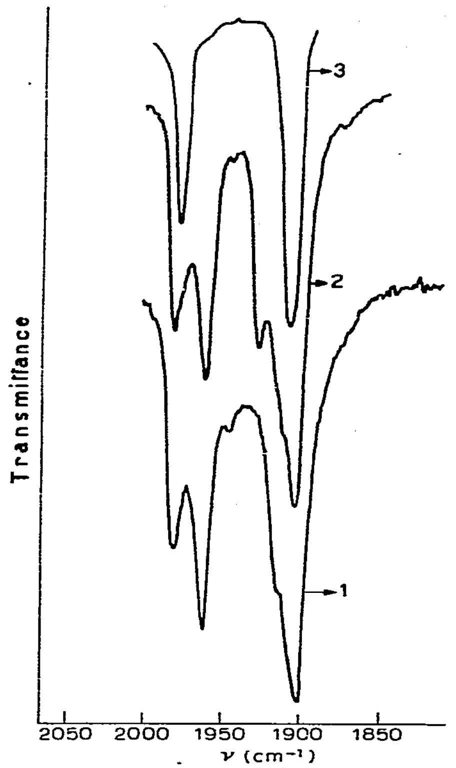
The different behaviour of the two hydrides lies in the differing basic properties of the cobalt atom; the basic strength is higher for (II) as the non-bonding metal electronic density is less involved in back-donation to carbon monoxide.

Both complexes (I) and (II) show remarkable properties in solution. Like the homologous $IrH(CO)_2(PPh_3)_2$ compound[19], (I) appears to exist in solution as a mixture of two or more different stereoisomers which interchange very quickly. This as-

TABLE 1

IR ABSORPTIONS (REGION 2200–1800 cm^{-1}) OF DICARBONYLBIS(TRIBUTYLPHOSPHINE)COBALT(I) COMPLEXES

Compound	Phase	ν (cm^{-1})					
$CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$	Heptane	1978–1976	s	sharp	1958	s	sharp
		1942	w		1912	(sh)	
		1902	vs	sharp			
	Toluene	1968	w		1948	s	sharp
		1932	(sh)		1902	(sh)	
		1891	vs	sharp			
	Acetone	1964	w		1945	s	sharp
					1898	(sh)	
		1887	vs	sharp			
	Methyl ethyl ketone	1964	w		1946	s	sharp
					1900	(sh)	
		1883	vs	sharp			
$CoD(CO)_2[P(n\text{-}C_4H_9)_3]_2$	Heptane	1977	s	sharp	1959	s	sharp
		1940	w		1924	m	
		1913	(sh)		1903	vs	sharp
$CoI(CO)_2[P(n\text{-}C_4H_9)_3]_2$	Heptane	1973	s	sharp			
		1908	vs	sharp			



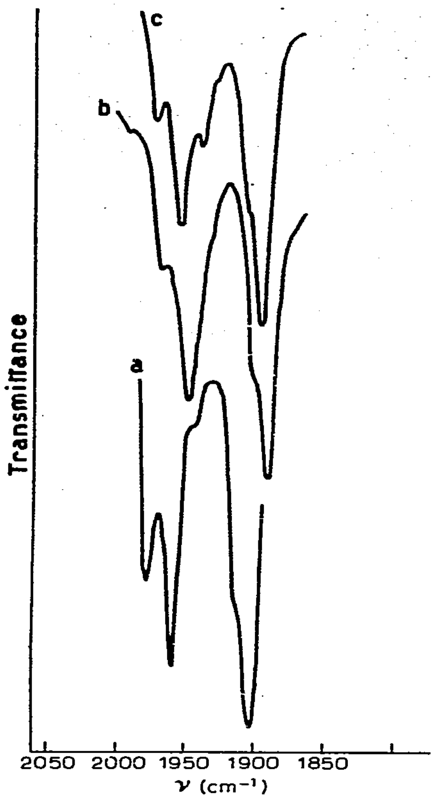


Fig. 1. IR spectra of (1) $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$, (2) $CoD(CO)_2[P(n\text{-}C_4H_9)_3]_2$, (3) $CoI(CO)_2[P(n\text{-}C_4H_9)_3]_2$ at 25° in heptane as a solvent.

Fig. 2. IR spectra of $CoH(CO)_2$ $[P(n\text{-}C_4H_9)_3]_2$ (a) at 25° in heptane, (b) at 25° in toluene, (c) at 160° in toluene.

sumption is based mainly on IR and NMR spectra. The IR spectrum in the region between 1800 and 2200 cm^{-1} shows more adsorption bands (Table 1 and Fig. 1) than expected for only one isomer, the number of absorptions and their intensities being strongly dependent on both solvent (Table 1) and temperature (Fig. 2). This clearly indicates the existence of two or more stereoisomers in equilibrium which makes difficult the assignment of the absorption bands to ν(CO) or ν(Co–H) respectively. Assignment of ν(Co–H) is uncertain despite a previous temptative assignment[7], as, for this purpose, comparison with $CoD(CO)_2[P(n\text{-}C_4H_9)_3]_2$ and $CoI(CO)_2[P(n\text{-}C_4H_9)_3]_2$ spectra (Fig. 1) is not adequate. It is possible that the Co–H stretching is hidden by some ν(C=O) adsorption bands around 1950 cm^{-1}. Moreover, in one stereoisomer at least, the hydridic atom is in a *trans* position with respect to a CO ligand whose stretching frequency shifts to higher frequencies (1924 cm^{-1}) after deuteration[20] (see Fig. 1).

The NMR spectrum confirms the presence in solution of two or more species in rapid equilibrium. Thus the high-field signal of (I), which is a symmetrical triplet, confirms the presence of two or more stereoisomers, the chemical shift being dependent on solvent and temperatures (Table 2). J(P–H) also strongly depends on the

TABLE 2

NMR DATA FOR $CoH(CO)_2 [P(n\text{-}C_4H_9)_3]_2$ AT 100 MHz IN SOME SOLVENTS AT 25°

Solvent	τ(Co–H) (TMS as standard)	J(P–H) (Hz)
Hexane	21.15	49.1
Benzene	20.52	48.6
THF	20.96	47.6
Ethyl acetate	20.96	47.5
Methanol 70% Acetone 30%	20.94	46.5
Methyl-isobutyl-ketone	20.77	46.9
Pyridine	20.55	46.7
Acetone	20.90	45.9
DMF	20.83	45.3

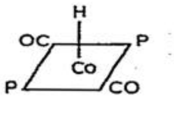
polarity of the solvent; the higher the polarity, the lower is the J(P–H). This high field peak, which shifts to lower fields at lower temperatures (Table 3), transforms into a rather broad peak at about −80° in toluene and at about −110° in propane; these values correspond probably to a coalescence temperature determined by the rates of interchange of the several species.

TABLE 3

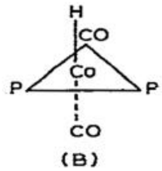
NMR DATA FOR $CoH(CO)_2 [P(n\text{-}C_4H_9)_3]_2$ AT 100 MHz AT DIFFERENT TEMPERATURES

Solvent	Temp. (°C)	τ(Co–H) (TMS as standard)	J(P–H) (Hz)
Toluene	+20	20.78	48.8 sharp triplet
	−30	20.66	48.7 sharp triplet
	−80	20.14	collapse
Propane	−95	20.54	46.7 broad triplet
	−112	20.44	collapse
Tridecane	+20	21.21	48 sharp triplet
	+100	21.78	49 sharp triplet
	+140	21.90	49 broad triplet
	+180	22.04	collapse

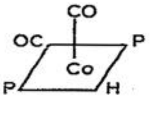
As the hydridic NMR signal is a symmetrical triplet, the phosphines must be equivalent, and thus the possible structures present in solution are the following:



(A)



(B)



(C)

Structure (B) or (C) must certainly be present, since in these the hydrogen is in a *trans* position to a carbon monoxide ligand. Moreover, as shown in Fig. 3, the hydridic

NMR signal of (I) in tridecane is a well-defined sharp triplet up to 140° and only at this temperature does it begin to broaden reversibly, complete collapse occurring at 170°. This behaviour is in accordance with occurrence of the dissociation (10):

$$CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2 \rightleftharpoons [CoH(CO)_2P(n\text{-}C_4H_9)_3] + P(n\text{-}C_4H_9)_3 \qquad (10)$$

which involves formation of a coordinatively unsaturated cobalt hydride; this reaction does not take place in tridecane at an observable NMR rate below 140°. Interestingly the coalescence temperature is lowered by olefins (such as 1-dodecene) and increased by phosphine by about 5–10°.

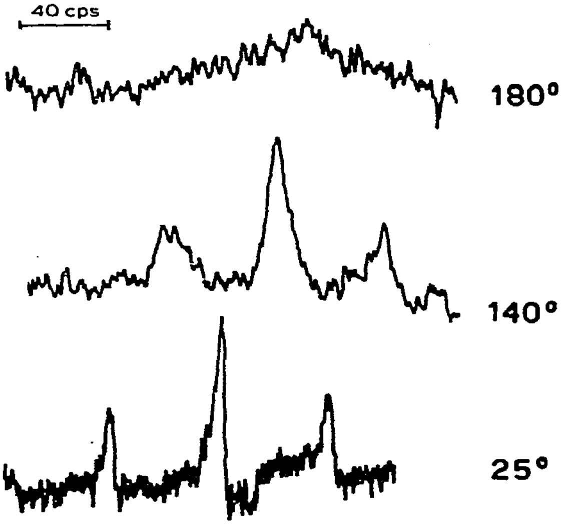
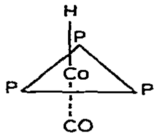


Fig. 3. NMR spectra of $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ at different temperatures in tridecane as a solvent.

The hydride (II) seems to exist in solution as only one isomer, having a trigonal pyramidal structure (D) similar to that of the related rhodium[21] and iridium[20] triphenylphosphine compounds:



(D)

The equivalence of the three phosphorus nuclei (the hydridic signal is split into a symmetrical quartet) and the expected shift of ν(CO) to higher wavelengths by deuteration[20] (Table 4) are in agreement with this structure. The hydride does not show any sign of appreciable dissociation in tridecane solution up to 120°, the temperature of complete decomposition.

In conclusion, as observed in other aspects of the chemistry of low valent phosphine cobalt complexes, the behaviour in solution of the hydrides (I) and (II) is related more to that of the homologous iridium derivatives than to that of the homologous

TABLE 4

IR AND NMR DATA FOR CARBONYLTRIS(TRIBUTYLPHOSPHINE)COBALT(I) COMPLEXES

Compound	ν(C=O) (cm^{-1})^a	ν(Co–H) (cm^{-1})	τ(Co–H)^b	J(P–H) (Hz)
CoH(CO)[P(n-C$_4$H$_9$)$_3$]$_3$	1883 s sharp	1908 ms sharp	23.9	48
CoD(CO)[P(n-C$_4$H$_9$)$_3$]$_3$	1890 vs sharp			

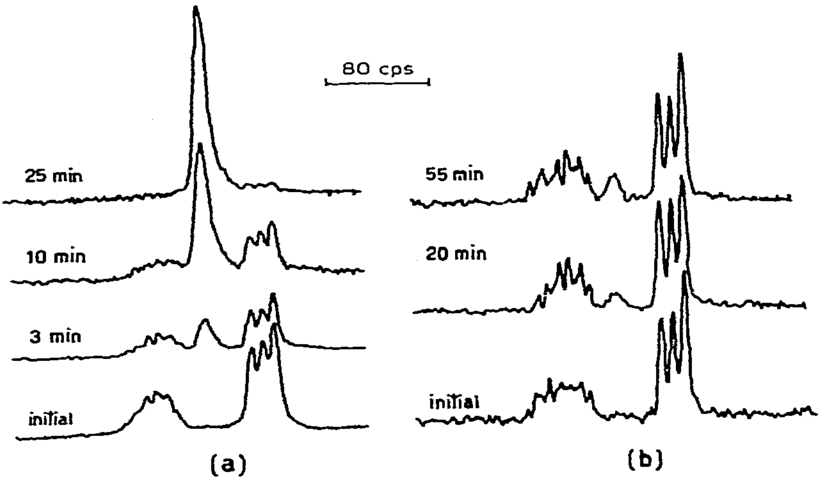
^{a} In heptane solution. ^{b} C$_6$D$_6$ soln.; TMS as internal standard.

rhodium complexes; thus, RhH(CO)$_2$(PPh$_3$)$_2$, unlike CoH(CO)$_2$[P(n-C$_4$H$_9$)$_3$]$_2$, easily loses hydrogen[22] and RhH(CO)[P(n-C$_4$H$_9$)$_3$]$_3$ is dissociated in solution[23] even at room temperature.

CATALYTIC PROPERTIES

Olefin isomerization

Both the hydrido complexes (I) and (II) catalyze the isomerization of the double bond. For instance, at 120° (I) brings about the isomerization of α-olefins at a reasonable rate; the reaction is easily followed by NMR spectroscopy (Fig. 4), the disappearance of the peaks due to the vinylic protons being easily detected along the simultaneous appearance of the protons of *cis* and *trans* internal olefins.



(a) (b)

Fig. 4. NMR spectra (100 MHz) of olefinic protons on solutions: (a) dodecane, 1-dodecene, CoH(CO)$_2$-[P(n-C$_4$H$_9$)$_3$]$_2$ (7/7/1 ratios) at 120°; (b) P(n-C$_4$H$_9$)$_3$, 1-dodecene, CoH(CO)$_2$[P(n-C$_4$H$_9$)$_3$]$_2$ (7/7/1 ratios) at 120°.

Table 5 lists the approximate* initial rates of hydrogenation and isomeriza-

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* To obtain reproducible initial rates, the presence in the catalysts of small amounts of [Co(CO)$_3$P-(n-C$_4$H$_9$)$_3$]$_2$ must be avoided, otherwise [Co(CO$_2$P(n-C$_4$H$_9$)$_3$]$_3$, which shows strong hydrogenating and isomerizing properties[24], is formed.

tion of several olefins in presence of (I) at 115° and of (II) at 45°, the other reaction conditions being identical. (I) is moderately active towards isomerization of both α-olefins and internal *cis* olefins;the activity increases sharply under hydrogen pressure. (II) is active at much lower temperatures and catalyzes the isomerization of internal *cis* olefins more than that of α-olefins; hydrogen does not have much effect in this case.

TABLE 5

HYDROGENATION AND ISOMERIZATION RATES FOR SEVERAL OLEFINS IN THE PRESENCE OF $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ OR $CoH(CO)[P(n\text{-}C_4H_9)_3]_3$.

Solvent heptane; olefin concn. 1.0 mole·l^{-1}; catalyst concn. 28.8 mmoles·l^{-1}.

Olefin	Hydrogen pressure (atm)	$CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ at 115° Initial rate (mole·l^{-1}·h^{-1})		$CoH(CO)[P(n\text{-}C_4H_9)_3]_3$ at 45° Initial rate (mole·l^{-1}·h^{-1})	
		Hydrogenation	Isomerization	Hydrogenation	Isomerization
1-Pentene[a]	30	~1	8–10	2.6	~0.3
1-Pentene[a]			~1.7		0.3
1-Pentene[b]	30	0.8	0.7	2×10^{-2}	7×10^{-3}
1-Pentene[c]	30	~0.9	7–8	1.9	~0.2
cis-2-Pentene[a]	30	~0.6	4–5	$\sim10^{-2}$	1.1
cis-2-Pentene			0.8		1.5
trans-2-Pentene	30	0.3	1.5	10^{-3}	~0.2
Cyclohexene	30	0.2		0	
Isobutene	30	0.4		10^{-2}	

[a] Similar results were obtained when deuterides were used. [b] In the presence of free phosphine (free phosphine/Co=7/1). [c] In the presence of pyridine (pyridine/Co=7/1).

For both hydrides the presence of free phosphine drastically lowers the catalytic activity, while pyridine has only a small effect. In both cases there is no appreciable effect on the isomerization rate when the hydride complexes are replaced with the corresponding deuterides. The scrambling of deuterium with the olefins (followed by IR or NMR spectroscopy) is rather slow, and there is still a large amount of the deutero complex when the molar ratio of converted olefin to cobalt complex is more than 17/1 and 8/1 for (I) and (II), respectively, in the absence of gaseous hydrogen (Table 6). These quite unexpected results suggest that isomerization can proceed also by a

TABLE 6

H–D SCRAMBLING ON COBALT DEUTERIDES DURING HYDROGENATION AND ISOMERIZATION OF 1-PENTENE

Deuteride	Hydrogen pressure (atm)	Temp. (°C)	Reaction time (min)	1-Pentene concn. (mmoles·l^{-1})	1-Pentene concn. (mmoles·l^{-1})	Deuteride to hydride concn. (mmoles·l^{-1})
$CoD(CO)_2[P(n\text{-}C_4H_9)_3]_2$		115	22	1000	485	< 28.8
	30	115	17	1000	910	< 28.8
	30	115	90			< 28.8
$CoD(CO)[P(n\text{-}C_4H_9)_3]_3$		45	90	1000	233	~20
	30	45	45	1000	765	~15
	30	45	180			~25

mechanism different from the classical olefin insertion into the metal–hydrogen bond[25]; similar results have been reported for $CoD(CO)_4$ by Orchin and Roos[26]. In no other way can the unusually high rate of isomerization of *cis*-2-pentene with (II) compared with that of 1-pentene be explained.

In examination of non-hydrocarbon substrates, the allyl alcohol isomerization was studied; propionaldehyde was obtained, probably via formation and isomerization of a vinyl alcohol. The compound (II) catalyzes this reaction even at 60° but its activity quickly decreases because of its transformation into the dicarbonyl complex (I) (active only at 100°) by carbon monoxide abstraction from the aldehyde initially formed.

Olefin, diolefin and alkyne hydrogenation

Both hydrido complexes catalyze olefin hydrogenation under relatively mild conditions. As expected, the monocarbonyl hydride (II) is more active than the dicarbonyl complex (I), but both hydrogenate terminal and internal olefins (Table 5). With (I) the reactivity of olefins decreases in the order terminal > internal > cyclic, which corresponds to that observed for other transition metal complexes[27]. Free ligands such as tributylphosphine or pyridine lower the catalytic activity of (I) and (II).

The initial rates with deutero complexes do not show an appreciable difference from those of the corresponding hydrides (Table 5). Moreover the exchange of the deuterium bonded to cobalt under hydrogenating conditions (30 atm of hydrogen) is still incomplete when the molar ratio of converted olefin to cobalt complex is more than 32/1 and 26/1 for (I) and (II) respectively (Table 6). The deuterium–hydrogen exchange occurs at much the same rate when the olefin is absent. It follows that there is very little deuterium scrambling between the preformed cobalt–deuterium bond and the olefin, the substitution of the deuterium atom by hydrogen being probably due mainly to the previously mentioned exchange with molecular hydrogen.

The hydrogenation of a diene such as 1,3-butadiene or 1,3-pentadiene can be carried out with (I) or (II); initially (I) or (II) adds to the diolefin to form the corresponding [(eqn. (7)] π-allyl complex, which is probably the active species in the hydrogenation. The selectivity to monoenes is not high, substantial amounts of alkane being formed even at low conversions; moreover, due to the isomerizing properties of the catalysts, the α-olefins initially formed are converted into the internal isomers.

Alkyne hydrogenation is catalyzed by both complexes (I) and (II), and it is rather selective under very mild reaction conditions; thus 1-pentyne is hydrogenated to 1-pentene with a selectivity of 90–95% up to very high conversion. The subsequent reduction of the olefin to the corresponding alkane takes place slowly with time (Fig. 5). The reaction conditions [60° and 30 atm of hydrogen for (I)] are milder in the case of (II), 95% conversion being obtained in 45 min at 40° and 30 atm of hydrogen. Because the reaction conditions are very mild, isomerization is very low, and the concentration of internal olefins never rises above 1%.

High selectivity is also obtained in the hydrogenation of 2-pentyne, but in this case the reaction rate is lower [4 h at 40° with (II): Fig. 6], and *cis*-2-pentene is obtained as the main product (yield 85%). The high selectivity to specific formation of olefin in the hydrogenation of alkynes using conditions similar to those employed in the olefin hydrogenation [at least in the case of (II)] can be ascribed to the competition for the catalyst between the alkynes and olefins[28].

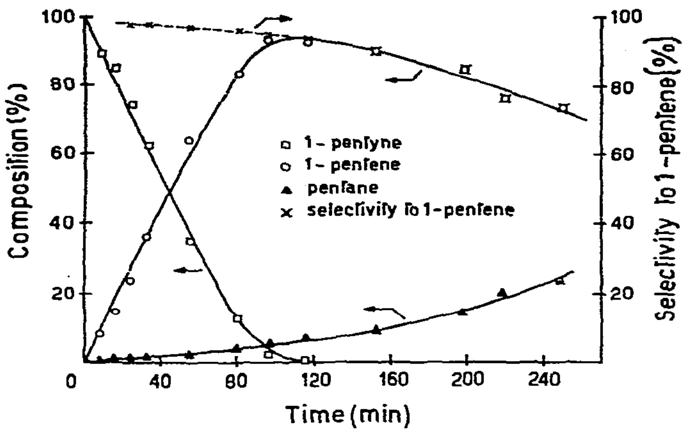


Fig. 5. Hydrogenation of 1-pentyne with $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$. Solvent: heptane; 1-pentyne concn. 1 mole·l^{-1}; catalyst concn. 28.8 mmoles·l^{-1}; hydrogen pressure 30 atm; temp. 60°.

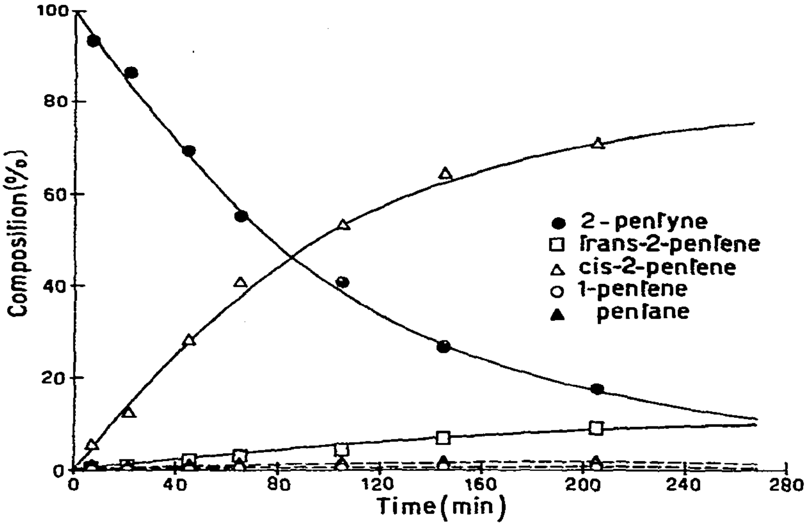


Fig. 6. Hydrogenation of 2-pentyne with $CoH(CO)[P(n\text{-}C_4H_9)_3]_3$. Solvent tridecane; 2-pentyne concn. 1 mole·l^{-1}; catalyst concn. 28.8 mmoles·l^{-1} hydrogen pressure 30 atm; temp. 40°.

Aldehyde hydrogenation

Generally speaking aldehyde hydrogenation is of particular interest as it is a difficult reaction to carry out homogeneously[27]. For instance, when unsubstituted cobalt or rhodium carbonyls are used, relatively high pressures of carbon monoxide are required to stabilize the catalysts[27,29,30] and high temperatures and hydrogen pressures are also necessary. Since it has been reported that addition of tertiary phoshines to the cobalt carbonyl during the hydroformylation of olefins favours the formation of alcohols[1], it was interesting to study the hydrogenation of aldehydes in presence of (I) and (II). The results (Table 7) show that alcohols can be obtained under

TABLE 7

INITIAL RATE OF HYDROGENATION OF SOME ALDEHYDES

Solvent heptane; substrate concn. 1 mole·l^{-1}; catalyst concn. 28.8 mmoles·l^{-1}; hydrogen pressure 30 atm.

Substrate	$CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ Initial rate at 130° (moles·l^{-1}·h^{-1})	$CoH(CO)[P(n\text{-}C_4H_9)_3]_3$ Initial rate at 60° (moles·l^{-1}·h^{-1})
n-Butanal	0.72[a]	1.01[b]
n-Pentanal	0.54	0.93
Isobutanal	0.50	0.83
Pivalaldehyde	0.32	0.36

[a] Conversion after 35 min: 33%. [b] Conversion after 35 min: 30%.

relatively mild conditions; linear aldehydes being reduced faster than those branched at the β-position. (II) shows a higher activity than (I), but because of carbon monoxide abstraction from the aldehyde, it is slowly transformed into the dicarbonyl complex (I).

The effect of the presence of excess phosphine on the rate of aldehyde hydrogenation catalyzed by (I) is shown in Fig. 7. An unexpected increase of the hydrogenation rate is observed up to a ratio of phosphine to cobalt complex of 5 to 1. At higher ratios, the hydrogenation decreases rapidly. It is difficult to explain this behaviour fully, but clearly phosphine dissociation from (I), to form a vacant site of coordination, is not very important.

To add to the knowledge of the hydrogenating properties of the hydroformylation catalyst formed by $Co_2(CO)_8$ and $P(n\text{-}C_4H_9)_3$, we have studied the hydrogenation of n-butanal under different conditions of carbon monoxide pressure and

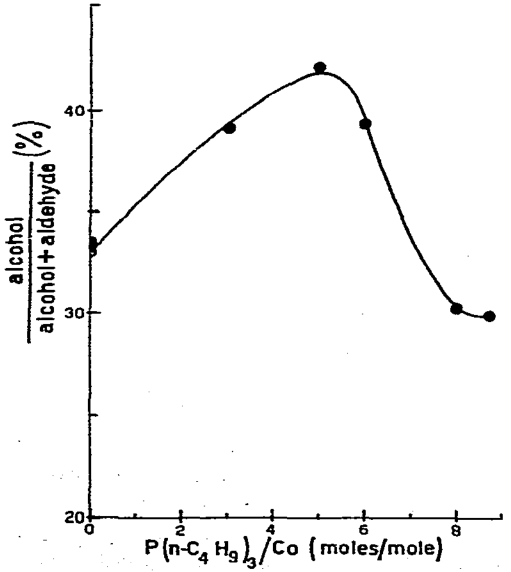


Fig. 7. Hydrogenation of n-butanal with $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ in the presence of free phosphine. Solvent heptane; substrate concn. 1 mole·l^{-1}; cobalt concn. 28.8 mmoles·l^{-1}; hydrogen pressure 30 atm; temp. 130°; time 36 min.

free tributylphosphine concentration. Because of the effect of carbon monoxide on the nature of the catalysts [as reported in eqn. (8), and pointed cut by Piacenti and coworkers[5,9]], our results refer to catalytic mixtures formed *in situ*.

When the reduction is studied as a function of the phosphine concentration (Fig. 8), a steeply rising conversion to alcohol is first observed at very low carbon monoxide pressures (2 atm), but further increase of the amount of tributylphosphine brings about a slow fall in the activity. At higher carbon monoxide pressures ($\geqslant$15 atm) the activity drops very rapidly with increasing phosphine concentration and soon reaches an almost constant value. We conclude that at high carbon monoxide pressures ($\geqslant$15 atm), only one catalytic complex, probably $CoH(CO)_3P(n\text{-}C_4H_9)_3$, is formed when the phosphine to cobalt ratio is greater than 2/1. The activity of this hydride, which not influenced by free phosphine, slightly decreases with increasing carbon monoxide pressure showing that in these conditions carbon monoxide dissociation must be the important step in the reduction.

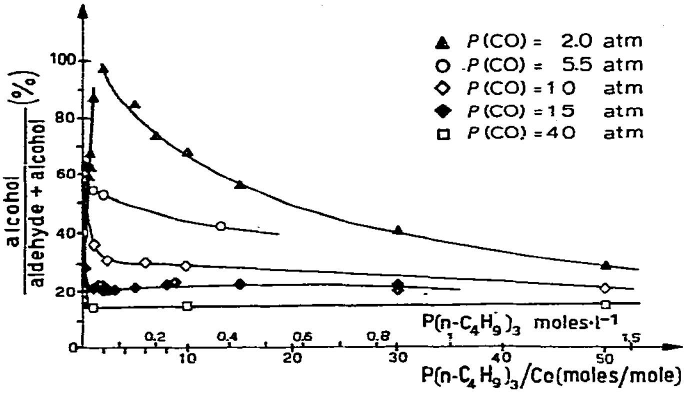


Fig. 8. Hydrogenation of n-butanal with $CoH(CO)_4+P(n\text{-}C_4H_9)_3$ as catalyst system. Solvent heptane; substrate concn. 1 mole·l^{-1}; cobalt concn. 28.8 mmoles·l^{-1}; hydrogen pressure 30 atm; temp. 160°; time 36 min.

Conversely at low carbon monoxide pressure (*e.g.* 2 atm.), mixtures of coordinatively unsaturated species containing one or more phosphines must be involved. The activity of these species decreases with increasing phosphine to cobalt ratios (2/1), which indicates that coordinatively saturated species are formed.

When the results are plotted in a different way (Fig. 9), it can be seen that the activity of simple $Co_2(CO)_8$ is very low under conditions in which the phosphine-containing system shows the highest activity (carbon monoxide pressure 2–5 atm). This is attributable to the large amount of decomposition and cluster formation with free $Co_2(CO)_8$ at low carbon monoxide pressures[31]. The addition of tributylphosphine prevents these processes and increases the stability of the catalytic system.

Interestingly, the hydrogenating properties of simple $Co_2(CO)_8$ decrease rapidly (after a maximum at 10–20 atm) with increasing carbon monoxide pressure. This is in accord with the formation of small amounts of hydrogenated products in the conventional oxo process, in which higher carbon monoxide partial pressures (90–130 atm) and lower temperatures (130–150°) are used than was the case in the reactions represented in Fig. 9.

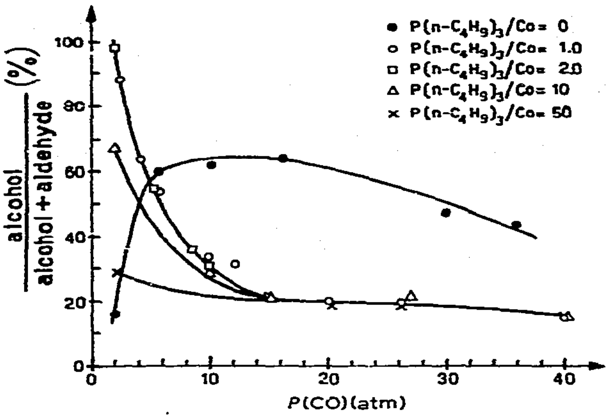


Fig. 9. Hydrogenation of n-butanal with $CoH(CO)_4 + P(n\text{-}C_4H_9)_3$ as catalytic system. Solvent heptane; substrate concn. 1 mole·l^{-1}; cobalt concn. 28.8 mmoles·l^{-1}; hydrogen pressure 30 atm; temp. 160°; time 36 min.

Conversely the activity of the phosphine containing system, which strongly depends upon carbon monoxide pressure up to 15 atm, is not greatly modified between 15 and 40 atm. Thus the extensive formation of alcohols in the modified oxo process is easily explained since the reaction conditions used were similar to those concerned in the reactions represented in Figs. 8 and 9, except for the hydrogen pressure which is normally higher.

CONCLUSIONS AND DISCUSSION

Our investigations into the catalytic properties of the hydrides $CoH(CO)_{4-n}$-$[P(n\text{-}C_4H_9)_3]_n$ ($n=2, 3$) have shown that the overall rates of hydrogenation and isomerization of olefins and alkynes are depressed by the presence of excess free phosphine. This is consistent with a dissociative pathway of type (10) in which "vacant sites" for coordination are formed.

$$CoH(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_n \rightleftharpoons$$
$$\rightleftharpoons CoH(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_{n-1} + P(n\text{-}C_4H_9)_3 \quad (n=2, 3)$$

However the phosphine dissociation which has also been suggested in explanation of the catalytic activities of some analogous Rh and Ir hydride carbonyl phosphine complexes[27], takes place more slowly and to a smaller extent than for the analogous rhodium catalysts; this is in accordance with the general trends found in kinetic investigations of reactions occurring by dissociative mechanisms with analogous carbonyl complexes, the elements of the second transition row always showing the lowest activation parameters[32]. Probably for these reasons higher temperatures are required for catalysis by the cobalt complexes. Some rather distinctive aspects of the cobalt catalysis are evident in our studies; the bis(tributylphosphine)-derivative (I) shows a lower selectivity than the analogous (triphenylphosphine)-rhodium and -iridium complexes, which hydrogenate only terminal olefins. As suggested by Wilkinson and coworkers this is probably attributable to the smaller steric hindrance in the unsaturated species $CoH(CO)[P(n\text{-}C_4H_9)_3]_2$ than in $MH(CO)(PPh_3)_2$ (M=Rh,Ir)[27].

The second and more important trend is the unusually low mobility of the cobalt–hydrogen bond in the presence of olefins and hydrogen. This seems to exclude the possiblity that the olefin insertion into the metal–hydrogen bond of the complexes (I) and (II) is the only important step of catalytic reactions such as hydrogenation and isomerization, as is generally accepted for processes catalyzed by analogous rhodium (and iridium) complexes. The possibility that the reaction proceeds via a Co^{III} trihydride complex (path A of Fig. 10) seems to be excluded by the rate of hydrogen exchange with gaseous deuterium. This reaction, which probably takes place via an oxidative addition of deuterium to form a cobalt(III) complex, is much slower than the olefin hydrogenation. Although we have no direct evidence for it, the mechanism could involve a direct hydrogenation of the olefin π-complexed to the cobalt hydride (path B of Fig. 10).

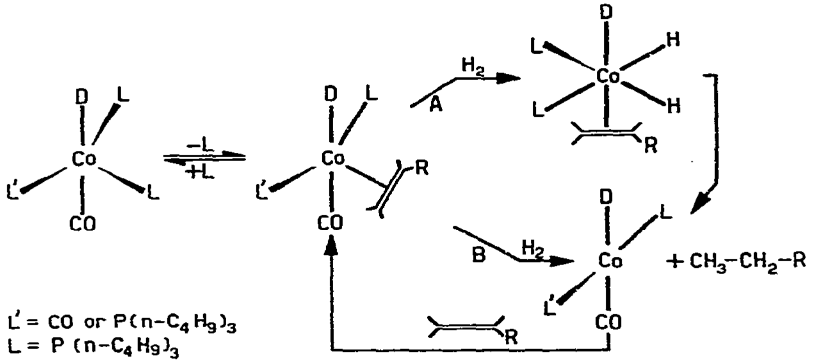
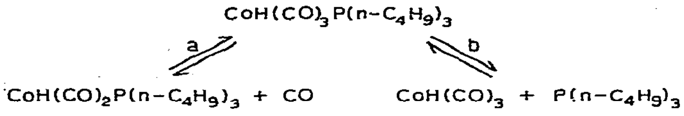


Fig. 10. Suggested scheme for the hydrogenation catalyzed by tributylphosphine cobalt(I) deuterido (or hydrido) carbonyl complexes.

Any kind of activation of hydrogen atoms of the n-butyl radicals of the tertiary phosphine by the cobalt atom to form labile cobalt–hydrogen bonds must be ruled out, since there is no deuterium incorporation into the n-butyl radicals even under 30 atm of deuterium. Only a kinetic investigation, which is in progress, will give more information on the unusual pathway of catalysis by these cobalt hydrides.

The isomerization also fails to fit into the usual pattern. Although the classical mechanisms of olefin insertion into the metal–hydrogen bond cannot be completely excluded, they are probably less relevant than other, as yet unclarified, pathways.

Aldehyde hydrogenation proceeds via coordination of the aldehyde to the cobalt atom in the free sites formed by loss of ligand. Thus when $Co_2(CO)_8 + P(n\text{-}C_4H_9)_3$ is used as the catalytic system, the activity is strongly dependent upon both the carbon monoxide pressure (in all the range of our experiments) and the free phosphine concentration at carbon monoxide pressures lower than 15 atm. The experiments at carbon monoxide pressures higher than 15 atm and at phosphine to cobalt ratio higher than 2, have shown that the dominant species present is the hydride $CoH(CO)_3P(n\text{-}C_4H_9)_3$; the features of the activity of this complex, which depends on carbon monoxide pressure but not on the free phosphine concentration, suggests that a dissociative mechanism to form an active unsaturated species by loss of carbon monoxide [eqn. (11), path a] rather than phosphine (path b) is operative:



(11)

When (I) is used in the absence of carbon monoxide, a similar pathway involving loss of carbon monoxide must be invoked. The results reported here do not support Tucci's point of view[2] that the strong hydrogenating properties of the phosphine modified oxo catalyst in comparison with those of the simple cobalt carbonyl, must be attributed only to the increased hydridic character of the cobalt–hydrogen bond arising from the coordination of phosphine to the metal atom. We suggest that the most important feature accounting for the different overall rate of hydrogenation consists in the different reaction conditions, namely carbon monoxide pressure. As a rule, the conventional oxo reaction is carried out under 80–150 atm of carbon monoxide partial pressure while the hydroformylation by means of the phosphine modified catalytic system is normally carried out at 20–30 atm of carbon monoxide. Furthermore, in the latter case, when reaction was carried out under 300 atm of 1/1 carbon monoxide/hydrogen mixture, aldehydes are the main products[33], alcohols being formed in small amounts. When similar conditions are employed for both the systems within the range of their stabilities (carbon monoxide pressure 20–30 atm) the activity of $Co_2(CO)_8$ alone is higher than that of the phosphine-containing system. It appears that under industrial oxo conditions the phosphine-modified catalyst has stronger hydrogenating properties because of the low carbon monoxide pressure.

The high activity observed for the complexes containing 2 or 3 phosphine molecules (see the activity of the catalyst with CO pressure of only 2 atm in Fig. 8) could reflect an easier phosphine dissociation and cannot be definitely related simply to a different hydridic character of the cobalt–hydrogen bond.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 225 spectrometer and PMR spectra on a Varian HA 100 Instrument.

Analyses

VPC analyses were carried out with a C. Erba C-ATC/T apparatus. Aldehyde–alcohol separations (and also cyclohexene–cyclohexane) were achieved using Carbowax 1500 (25%) on silanized Chromosorb 7 with helium as the transport gas (copper column 2 m × 4 mm). The separation of C_4 and C_5 hydrocarbons was achieved with triallyl citrate (25%) on celyte (60–80 mesh) (copper column 4 m × 4 mm) again using helium as the transport gas.

The determination of carbon monoxide in cobalt complexes was carried out by thermal decomposition of the complexes at 500° in nitrogen. The gas evolved was collected after condensation of liquid products [$P(n\text{-}C_4H_9)_3$, etc.] and analyzed by VPC using molecular sieves (5 Å) with helium as the transport gas (steel column 2 m × 4 mm).

Carbon, hydrogen, and cobalt analyses were carried out in the analytical laboratory of the Bollate Research Center.

Reagents

Tributylphosphine (Fluka) was distilled before use. Propylene (Montecatini Edison S.p.A., 99%), isobutene (Phillips Petroleum, 99.3%), and 1-pentyne (Schuchardt, 97%) were used without further purification. 1-Pentene (Phillips Petroleum, 99.4%), *cis*-2-pentene (Schuchardt, 94.7%), *trans*-2-pentene (Fluka, 99.9%), and cyclohexene (Fluka, 99%) were distilled from Na–K alloy (44% Na) before use. Aldehydes (C. Erba) were distilled before use. Hydrogen and carbon monoxide had an oxygen content of less than 20 ppm. Deuterium was 99.5% pure. Peroxides were removed from solvents when necessary.

Preparation of hydrides (I) and (II)

(I), $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$

(*a*). 4.67 g (6.77 mmoles) of $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$ and 2.76 g (13.7 mmoles) of tributylphosphine were dissolved in 100 ml of n-heptane (or n-hexane). The solution was maintained under 30 atm of hydrogen at 160° in a 250 ml steel autoclave for 4–5 h, the hydrogen being repeatedly changed in order to remove the carbon monoxide formed during the reaction. The complex (I) was obtained by evaporation of the solvent under vacuum; it is a diamagnetic yellow-orange oil, unstable to the air and rather soluble in many organic solvents. The small excess of free tributylphosphine was removed by evaporation under high vacuum (60°, 10^{-4} mm) or by extraction with a solution of HCOOH (20–30%). The residue corresponded to compound (I) (quantitative yield).

Found: C,60.26; H, 10.60; Co, 10.90; CO, 1035. $C_{24}H_{55}\,Co(CO)_2P_2$ calcd.: C, 60.20; H, 10.57; Co, 11.37; CO, 10.79%.

(*b*). 4.6 g (6.67 mmoles) of $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$, 14.1 g of 1-octene (126 mmoles), and 2.82 g (14 mmoles) of tributylphosphine in 95 ml of n-heptane were maintained under a constant pressure of 30–35 atm of hydrogen at 120°. After 30 min the olefin was almost completely isomerized to internal olefins, the reaction was stopped after 8 h. From the solution 13 mmoles of nonyl alcohol and a quantity of n-octane were recovered. Compound (I) was isolated as in (*a*).

(*c*). 4.66 g (13.5 mmoles) of 2-ethylhexanoate of cobalt(II), 5.45 g (27 mmoles) of tributylphosphine and 95 ml of n-heptane were introduced into a 250 ml steel autoclave and brought to a temperature of 110°, 605 N ml (27 mmoles) of carbon monoxide were introduced (the gas was initially in a pressurized vessel of 40 ml and the amount of gas introduced in the autoclave was calculated by the loss of pressure in this vessel). 35 atm of hydrogen were then added and a fast reaction ensued which was almost complete in 10 min. From the solution, after washing with a 5% alkaline solution to remove the 2-ethylhexenoic acid, compound (I) was isolated as in (*a*).

(II), $CoH(CO)[P(n\text{-}C_4H_9)_3]_3$

A n-heptane solution (95 ml) of 5.5 g (7.97 mmoles) of $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$

and 19.6 g (97.3 mmoles) of tributylphosphine was introduced into a steel autoclave (250 ml). Compound (I) was then prepared as in (*a*); when the gases had been removed, the solution was cooled to room temperature and 15 g of propylene were introduced into the autoclave. The temperature was then raised to 115° and 30 atm of hydrogen was introduced. The pressure was maintained at 30 atm by continuous addition of hydrogen since gas absorption occurred. The addition of propylene and hydrogen was repeated 4 times. (If the first operation at 160° is omitted the same final result can be obtained by further repeating the reaction with propylene.) From the final solution 15 to 31 mmoles of n-butyl alcohol were recovered, the amount depending on the method used. After centrifuging and evaporation of the solvent, the residue was freed from the excess of free tributylphosphine by treatment at 0° with 1 molar solution of H_2SO_4 in methanol/water (50/50); the insoluble residue was extracted with heptane and the hydrocarbon solution washed with water until the washings were neutral. Evaporation of the n-heptane gave the pure hydride (II) as a green-yellow oil, fairly soluble in the common organic solvents.

An alternative method was also used to remove the excess of free tributylphosphine: the solution obtained from the autoclave was treated with 13 g (91.5 mmoles) of CH_3I; after 1 h at +5° the insoluble quaternary salt of tributylphosphine was filtered of and evaporation of the solvent gave the pure complex (II).

Found: C, 64.05; H, 11.75; Co, 8.10; CO, 3.95. $C_{36}H_{82}Co(CO)P_3$ calcd.: C, 64.00; H, 11.81; Co, 8.51; CO, 4.04%.

Preparation of deutero complexes

(*a*). A solution of 1.8 g (3.46 mmoles) of (I) in 43 ml of n-heptane was maintained at 120° under 22 atm of deuterium for 3 h. At the end of this time the NMR spectrum showed that the hydrogen–deuterium exchange was complete. A 1.2 g (1.73 mmoles) of solution of (II) in 50 ml of n-heptane was maintained at 60° under 15 atm of deuterium for 100 min until hydrogen–deuterium exchange was complete (confirmed by NMR).

(*b*). (I) or (II) treated with D_2O in the absence of acids did not exchange. When 0.62 g (0.89 mmole) of (II) was dissolved in 0.6 ml of D_2O containing 0.2 mmole of HCl, a rapid exchange took place; the exchange was complete in 30 min, as shown by the NMR spectrum. The same reaction carried out on (I) gave $CoCl(CO)_2[P(n\text{-}C_4H_9)_3]_2$ [ν(CO) 1966 and 1899 vs cm^{-1}; ν(Co–Cl) 272 cm^{-1}], a mixture of HD and small amounts of D_2 (analyzed by mass spectroscopy) being evolved.

Hydrogenation and isomerization reactions

Hydrogenations and isomerizations were carried out in steel autoclaves with stirring and automatic control of temperature and pressure; reagents could be added from a pressurized lateral vessel into the autoclaves. Using special devices, samples could be collected from the autoclaves during the reaction.

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