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CATALYSIS BY PHOSPHINE COBALT CARBONYL COMPLEXES
III. THE SYNTHESIS AND CATALYTIC PROPERTIES OF A NEW SERIES OF COBALT(0) CLUSTERS*

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SUMMARY

The preparation and properties of a series of paramagnetic green compounds are reported. A probable formula for these complexes is $[Co(CO)_2PR_3]_3$, where $PR_3 = P(n\text{-}C_4H_9)_3, P(n\text{-}C_4H_9)_2(C_6H_5), P(C_6H_5)_3$. Their catalytic activity towards hydrogenation of monoolefins, diolefins, and aldehydes has been studied and is discussed. The isomerisation of olefins by these compounds is also reported.

INTRODUCTION

During our investigations on olefin hydroformylation catalyzed by the system $Co_2(CO)_8$/tributylphosphine, we prepared hydrides of formula $CoH(CO)_n[P(n\text{-}C_4H_9)_3]_{4-n}$ ($n=2, 3$) by stoichiometric hydroformylation of olefins with $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$[1,2]. The $Co_2(CO)_8/P(n\text{-}C_4H_9)_3$ system shows remarkable hydrogenating properties[3,4], which are dependent on the hydroformylating conditions, and which can be related to the presence of these hydrides. However, on changing the experimental conditions, it is possible to isolate green clusters[5] which are probably trimeric. These clusters also show hydrogenating properties and are probably similar to the complex formulated by Sacco[6] as $[Co(CO)_2P(C_6H_5)_3]_m$. Trimeric carbonyl derivaties of cobalt have been described by other authors: for example, the reaction between $Co_2(CO)_8$ and tetramethyldiphosphine has been reported[7] to result in the formation of a dark-green compound, which is probably a trimer with bridging phosphido ligands.

A trimeric, diamagnetic cyclopentadienylcobalt(I) carbonyl of formula $[C_5H_5Co(CO)]_3$ has also been synthesized[8] by ultraviolet irradiation of $C_5H_5Co(CO)_2$. Finally, other authors have recently reported[9] the preparation of the anion $[Co_3(CO)_{10}]^-$.

Here, we report in detail the preparation and the properties of $[Co(CO)_2PR_3]_m$ (probably $m=3$), discussing in particular their catalytic behaviour.

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* The following paper is to be regarded as Part II, see ref. 17.

RESULTS

Preparation and properties of $[Co(CO)_2PR_3]_3$ species

Paramagnetic compounds of general stoichiometry $[\mathrm{Co(CO)_2PR_3}]_m$, where $\mathrm{PR_3}$ is tributyl- or dibutylphenylphosphine, can be obtained during the stoichiometric hydroformylation of linear α-olefins, according to the reaction:

$$m\,\mathrm{CoH(CO)_3PR_3} + m\,\mathrm{C}_n\mathrm{H}_{2n} + \tfrac{3}{2}\,m\,\mathrm{H_2} \rightarrow [\mathrm{Co(CO)_2PR_3}]_m + m\,\mathrm{C}_n\mathrm{H}_{2n+1}\text{-}\mathrm{CH_2OH} \quad (1)$$

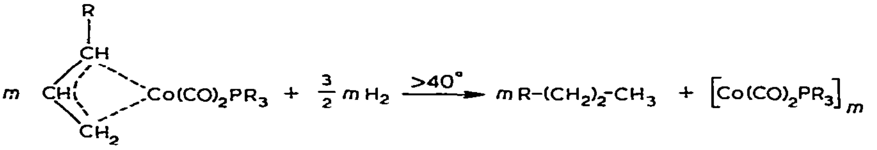
The dimers $[\mathrm{Co(CO)_3PR_3}]_2$ are precursors of the hydridic species. The failure to prepare the triphenylphosphine derivative may be due to the complete insolubility of the initial complex in most organic solvents.

Since high temperatures (> 110°) are necessary to achieve acceptable reaction rates, thermal decomposition of the resulting complexes into $[\mathrm{Co(CO)_3PR_3}]_2$ and metallic cobalt takes place to some extent. However, the use of more reactive olefins reduces the reaction time and higher yields are obtained. In agreement with the results obtained using linear α-olefins[10], ethylene and propylene give much better performances, inasmuch as higher olefins are readily transformed into the less reactive internal isomers in the early stages of the reaction. The main reaction products are alcohols but the formation of alkanes in large quantities has also been observed.

The formation of closed clusters of cobalt(0) by stoichiometric hydroformylation has already been described by other authors[11]; thus dodecacarbonyltetracobalt(0) is formed from hydridotetracarbonylcobalt(I), olefins and hydrogen, as follows:

$$4\,\mathrm{CoH(CO)_4} + 4\,\mathrm{C}_n\mathrm{H}_{2n} + 2\,\mathrm{H_2} \rightarrow \mathrm{Co_4(CO)_{12}} + 4\,\mathrm{C}_n\mathrm{H}_{2n+1}\text{-}\mathrm{CHO} \quad (2)$$

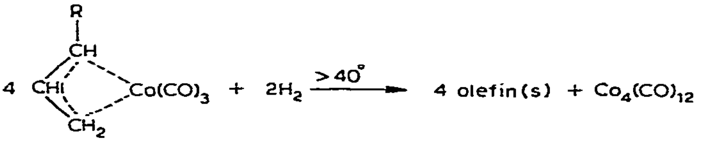
The compounds $[\mathrm{Co(CO)_2PR_3}]_m$ were also obtained by direct hydrogenation of the well known π-allyl(triorganophosphine)cobalt dicarbonyl complexes[12,13]:



(3)

In this way the compounds with tributyl-, dibutylphenyl-, and triphenylphosphine were synthesized in higher yields than by reaction (1).

The unsubstituted initial complex, *i.e.* π-allyltricarbonylcobalt, gives the diamagnetic tetrameric cluster derivative $\mathrm{Co_4(CO)_{12}}$ under the same conditions:



(4)

Likewise, a diamagnetic compound (probably the tetrameric cluster $[\mathrm{Co(CO)_2P(OC_6H_5)_3}]_4$ recently described by other authors[14]) has been obtained by direct hydrogenation of π-allyldicarbonyl(triphenylphosphite)cobalt(I)[12,13]. This shows that $P(OC_6H_5)_3$ behaves much more like carbon monoxide than a tertiary phosphine.

In the investigation of the structure of these phosphine compounds, the presence of hydridic hydrogen (which could not be detected by elemental analysis) could not be excluded *a priori*. We did not find high field signals in the NMR spectra, but, since the materials are strongly paramagnetic, these signals could be too broad to be detected. However, the absence of any Co–H bond has been clearly confirmed in two ways. Hydrogen is absent in the off-gas from the reaction of the triphenylphosphine derivative with carbon monoxide to yield $[Co(CO)_3P(C_6H_5)_3]_2$[15] and with 1,2-bis(diphenylphosphino)ethane (Diphos) to yield $[Co(CO)_2Diphos]_2$[16]; moreover the infrared spectra of the compounds prepared in the presence of either deuterium or hydrogen are identical.

TABLE 1

MAGNETIC DATA FOR THE SPECIES $[Co(CO)_2PR_3]_3$

Compound	Temp. (°K)	χ_{mol} ($\times 10^6$)	Diam. corr. ($\times 10^6$)	$\mu_{eff.}$ (B.M.)
$[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$	292.5	2853	−607	2.86
$[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$	222.2	4241	−607	2.95
$[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$	162.2	5944	−607	2.93
$[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$	128.8	7798	−607	2.95
$[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$	82.0	12268	−607	2.91
$[Co(CO)_2P(C_6H_5)_3]_3$	295.0	3359	−623	3.08
$[Co(CO)_2P(C_6H_5)_3]_3$	272.4	3744	−623	3.10
$[Co(CO)_2P(C_6H_5)_3]_3$	235.0	4388	−623	3.08
$[Co(CO)_2P(C_6H_5)_3]_3$	202.1	5169	−623	3.07
$[Co(CO)_2P(C_6H_5)_3]_3$	172.8	5881	−623	3.01
$[Co(CO)_2P(C_6H_5)_3]_3$	138.4	7623	−623	3.02
$[Co(CO)_2P(C_6H_5)_3]_3$	121.0	9048	−623	3.07
$[Co(CO)_2P(C_6H_5)_3]_3$	79.8	13821	−623	3.05
$[Co(CO)_2P(C_6H_5)_3]_3 \cdot 2\,C_7H_8$	291	3130	−756	3.02
$[Co(CO)_2P(C_6H_5)_3]_3 \cdot 2\,C_6H_6$	291	3385	−733	3.11

In the light of the conclusion that the $[Co(CO)_2PR_3]_m$ compounds are Co^0 species, their structure has been deduced on the basis of magnetic and EPR data, X-ray and molecular weight determinations and infrared spectra. The magnetic moments (2.9–3.1 B.M. per molecule assuming a trimeric structure) are independent of temperature and satisfy the Curie law in the range of temperatures investigated (82–295°K); good reproducibility was always obtained for different samples (Table 1). The compounds are also paramagnetic in solution, a broad ESR signal being detected which could not, however, be resolved, even at low temperatures. The crystals of the triphenylphosphine derivative are triclinic, as shown by an X-ray study of a single crystal obtained from toluene*. The parameters are as follows: $a=25.34$, $b=10.756$,

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* The X-ray and IR-studies were carried out by Dr. J. C. J. Bart and Dr. B. Minasso, respectively of the Centro Richerche di Bollate.

TABLE 2

INFRARED ABSORPTION SPECTRA OF THE SPECIES $[Co(CO)_2PR_3]_3$ IN THE CARBONYL STRETCHING REGION[a]

Compound	Phase	$\nu(CO)$ (cm^{-1})		Compound	Phase	$\nu(CO)$ (cm^{-1})		
$[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$	Oil	1985 m	sharp	$[Co(CO)_2P(C_6H_5)_3]_3$	Nujol mull	1985	m	sharp
		1942 vs	broad			1951	vs	broad
		1827 vw				1835	vw	
		1787 s	broad			1797	s	sharp
						1788	s	sharp
$[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$	Heptane soln.	1988 m	sharp	$[Co(CO)_2P(C_6H_5)_3]_3$	Toluene soln.	2000	m	sharp
		1954 vs	sharp			1967 1960	vs	broad
		1828 vw						
		1790 vs	sharp			1800	vs	broad
		1783 s	sharp			1795	(sh)	
$[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$	Toluene soln.	1985 m	sharp	$[Co(CO)_2P(C_6H_5)_3]_3\cdot 2\,C_6H_6$	Nujol mull	2000	ms	sharp
		1947 vs	broad			1979	ms	sharp
		1826 vw				1951	vs	broad
		1787 s	broad			1836	w	
		1780 (sh)				1800	s	sharp
$[Co(CO)_2P(n\text{-}C_4H_9)_2C_6H_5]_3$	Oil	1985 m	sharp			1790	s	sharp
		1945 vs	broad					
		1828 vw						
		1791 s	sharp					

[a] vs, Very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak; sh, shoulder. $[Co(CO)_2P(C_6H_5)_3]_3\cdot 2\,C_7H_8$ is not included, since the solvent is readily lost during the preparation of the nujol mull or of the KBr pellet.

$c=13.74$ Å, $\alpha=83°46'$, $\beta=76°4'$, $\gamma=63°14'$, space group $P1$ or $P\bar{1}$, $V=3245.6$ Å^3, $D_{calc.}$ $(Z=2)$ 1.346 g/cm^3, $D_{obs.}$ 1.345 g/cm^3. The mass of the unit cell is 2628, in excellent agreement with 2632 required for $[Co(CO)_2P(C_6H_5)_3]_6 \cdot 4\ C_7H_8$; on the basis of these data, both a tetramer and a pentamer can be ruled out. A monomeric form is excluded by the presence of bridging carbonyl groups in the infrared spectrum (Table 2), while a dimer is unlikely due to the temperature invariant paramagnetism of the substances. The remaining possibilities are a trimer or a hexamer, and the former is preferred on the basis of molecular weight measurements (determined cryoscopically in cyclohexane) on the tributylphosphine derivative. Therefore two moles of $[Co(CO)_2P(C_6H_5)_3]_3 \cdot 2\ C_7H_8$ are probably present per unit cell.

The infrared spectra (Table 2) are consistent with a local C_{3v} symmetry, perhaps of the type shown in Fig. 1, in which the steric relative positions of the phosphines is arbitrary.

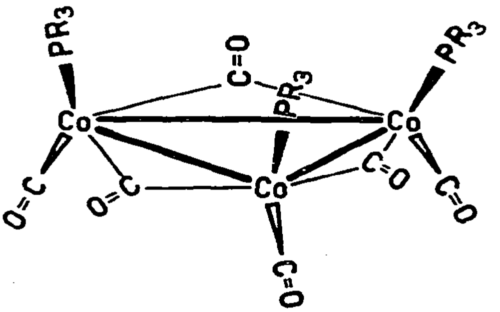


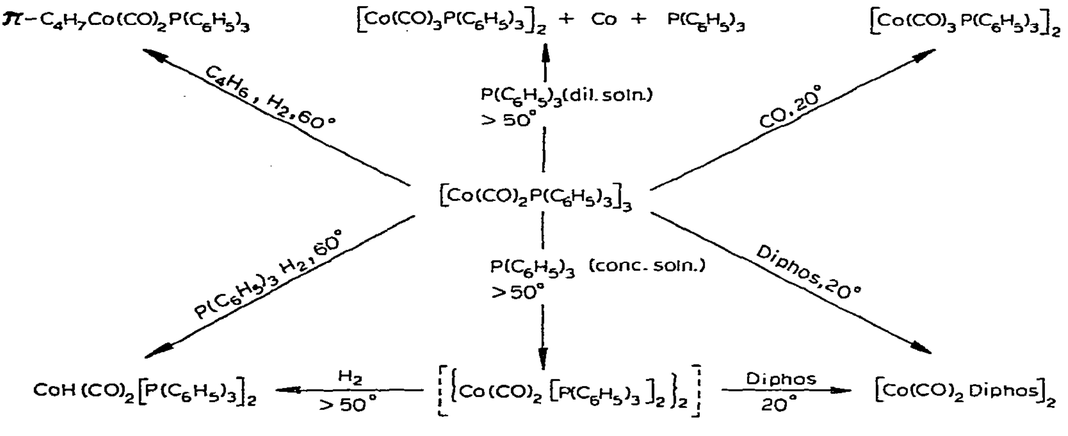
Fig. 1.

In fact, with a local C_{3v} symmetry two terminal carbonyl stretching frequencies (A_1, E) and two bridging carbonyl stretching frequencies (A_1, E) are expected. With the latter absorptions, although the bands of type A_1 have been reported[18] to lie at higher frequencies, uncertainty exists about the assignment, since the two bridging carbonyl absorptions are very close together. Single, very broad bands have been observed in the region of bridging carbonyl groups for the oily tributylphosphine derivative and for the toluene solutions of all the complexes (Table 2) in which a shoulder is also observed. This broadening is probably due to a solvent effect, similar to that observed with several halogenated, aromatic, or polar solvents. However the spectra of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ in heptane solution and of $[Co(CO)_2P(C_6H_5)_3]_3$ in the solid state show clear doublets in the bridging carbonyl stretching region in accordance with a C_{3v} symmetry. Therefore these complexes must be of the 6/6/6 type, involving trimeric clusters in which the formal coordination number of each cobalt atom is six[19].

Reactivity of $[Co(CO)_2PR_3]_3$ species

The green clusters of cobalt show a marked tendency to accept further ligands, this behaviour being typical of coordinative unsaturation. A particularly high reactivity has been observed with respect to soft nucleophilic ligands (Scheme 1); for example, carbon monoxide is absorbed at room temperature and at atmospheric

SCHEME 1



pressure giving $[Co(CO)_3PR_3]_2$ in almost quantitative yield.

In the presence of 1,2-bis(diphenylphosphino)ethane (Diphos), an addition-redistribution reaction [eqn. (5)] takes place slowly under mild conditions (20°) to form a dimeric species, previously described by other authors[16]:

$$2\,[Co(CO)_2PR_3]_3 + 6\ \text{Diphos} \rightarrow 3\,[Co(CO)_2\text{Diphos}]_2 + 6\ PR_3 \qquad (5)$$

$[Co(CO)_2P(C_6H_5)_3]_3$ reacts with excess triphenylphosphine in toluene at $T > 50°$ to give a brown-red solution (which shows only terminal carbonyl absorptions) probably containing $\{Co(CO)_2[P(C_6H_5)_3]_2\}_2$ (Scheme 1). This brown-red compound cannot be purified, since fast decomposition occurs during the removal of the excess of phosphine; clearly, the free ligand stabilizes the dimeric species and dissociation with loss of phosphine seems to be the initial stage of the decomposition. The formation of $\{Co(CO)_2[P(C_6H_5)_3]_2\}_2$ seems to be probable on additional results; *e.g.*, the above solution reacts very fast under mild conditions with Diphos to give $[Co(CO)_2\text{Diphos}]_2$[16] (almost quantitatively at 20°), with HI to give H_2 and $CoI(CO)_2[P(C_6H_5)_3]_2$[6] and with hydrogen (10 atm) to give $CoH(CO)_2[P(C_6H_5)_3]_2$[20] (Scheme 1).

When $[Co(CO)_2P(C_6H_5)_3]_3$ and triphenylphosphine are used in equimolecular quantities (under otherwise identical conditions) the reaction leads to the formation of $[Co(CO)_3P(C_6H_5)_3]_2$, metallic cobalt, and free phosphine as final reaction products. The reaction between $[Co(CO)_2PR_3]_3$ and PR_3 under a hydrogen pressure results in the direct formation of hydrides of formula $CoH(CO)_2(PR_3)_2$. Addition of 1,3-butadiene and hydrogen takes place similarly, giving the known[13] dicarbonyl-(tertiaryphosphine)-π-crotylcobalt(I):

$$[Co(CO)_2PR_3]_3 + 3\ C_4H_6 + \tfrac{3}{2}\ H_2 \rightarrow 3\ \pi\text{-}C_4H_7Co(CO)_2PR_3 \qquad (6)$$

Nucleophilic ligands on the borderline between soft and hard bases show a less pronounced reactivity with respect to the trimeric clusters of cobalt. In the case of pyridine, formation of $[Co(CO)_3PR_3]_2$ and metallic cobalt takes place more slowly than in the presence of tertiary phosphines, possibly through a hypothetical unstable intermediate $[Co(CO)_3PR_3Py]_2$ (Py = pyridine), similar to $\{Co(CO)_2[P$-

$(C_6H_5)_3]_2\}_2$. Finally hard bases such as ROH and R_2O have little or no effect on the decomposition of the trimeric clusters.

All the complexes show a characteristic behaviour to heat, a "ligand disproportionation" taking place as follows:

$$[Co(CO)_2PR_3]_3 \rightarrow [Co(CO)_3PR_3]_2 + Co + PR_3 \quad (7)$$

It is conceivable that the reaction is autocatalytic, due to the formation of free phosphine.

In conclusion, the probably trimeric structure is unstable in the presence of "soft" bases and is transformed easily into dimeric or monomeric species.

Catalytic properties

The cobalt clusters reported in this paper show catalytic properties when used under hydrogen pressure in the hydrogenation and isomerisation of monoolefins, in the selective hydrogenation of conjugated diolefins and in the hydrogenation of aldehydes. Because of the low stability and solubility of the triphenylphosphine derivative, the study has been restricted to $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$.

TABLE 3

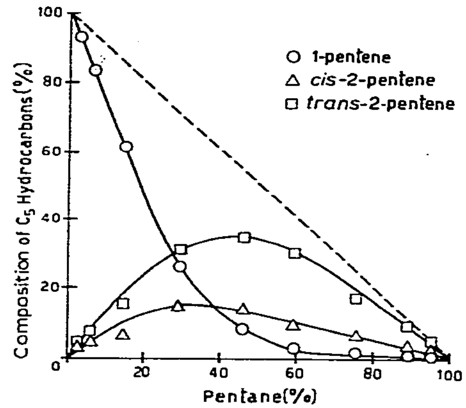
HYDROGENATION AND ISOMERISATION OF MONOENES IN THE PRESENCE OF $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$[a]

Substrate	Initial rate ($mole \cdot l^{-1} \cdot h^{-1}$)	
	Hydrogenation	Isomerisation
Propene	0.46	
1-Pentene	0.39	1.77, 0.31[b]
cis-2-Pentene	0.27	0.51
trans-2-Pentene	0.17	0.22
Cyclohexene	0.15	

[a] The reaction was carried out at 66° in n-heptane with a catalyst concentration of 0.02 moles·l^{-1}, an olefin concentration of 1.0 mole·l^{-1}, and a hydrogen pressure of 15 atm. [b] Under a nitrogen atmosphere.

(*i*). *Hydrogenation and isomerisation of monoolefins.* Olefins are readily hydrogenated in the presence of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$, isomerisation taking place extensively at the same time (Table 3). In Fig. 2, the disappearance of the initial olefin (1-pentene) is reported; the curve lies well below the theoretical (dotted) line which is related to complete absence of isomerisation[21]. Clearly, since the rates of hydrogenation and isomerisation of various olefins are of the same order (Table 3), it is not possible to hydrogenate selectively α-olefins in a mixture of terminal, internal, and cyclic olefins. Comparison of the catalytic activity of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$, $CoH(CO)[P(n\text{-}C_4H_9)_3]_3$[2] and $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$[2] under the conditions reported in Table 3, shows that $CoH(CO)[P(n\text{-}C_4H_9)_3]_3$ hydrogenates α-olefins faster than the trimeric species (negligible isomerisation taking place at the same time), while it is almost inactive towards internal and cyclic olefins. $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ has a lower activity than $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ in the hydrogenation and even lower in the isomerisation of all olefins.

The isomerisation of 1-pentene to *cis* and *trans* isomers of 2-pentene in the



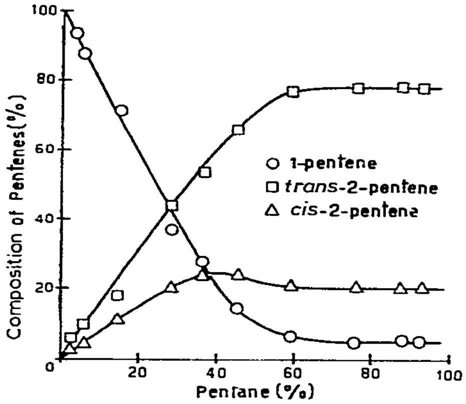


Fig. 2. Composition of C_5 hydrocarbons during the hydrogenation of 1-pentene in the presence of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ (conditions as in Table 3).

Fig. 3. Composition of the olefin fraction during the hydrogenation of 1-pentene in the presence of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ (conditions as in Table 3).

presence of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ is initially stereoselective; in fact the *trans/cis* isomer ratio is considerably lower than the equilibrium figure in the early stages of the reaction (Fig. 3). This *cis* content reaches a maximum and then decreases to the equilibrium value (*cis*-2-pentene 20.2%, *trans*-2-pentene 76.5%, 1-pentene 3.3% at 70°)[22]; evidently, the initial *trans* to *cis* ratio is controlled by kinetic factors. Interestingly, the same behaviour has been reported for the $PdCl_2$ catalyzed isomerisation of 1-pentene[22,23]. A hydridic complex formed *in situ* seems to be mainly responsible for most of the catalytic activity; thus under nitrogen isomerisation takes place at lower rates (Table 3). Nothing can be said with certainty about the nature of the actual catalytic species. However, some information was obtained from hydrogenation experiments using dicarbonyl(tributylphosphine)-π-crotylcobalt as the starting catalyst, which gives $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ under the reaction conditions, according to (3)*. In this case an induction period is observed (decreasing with increasing hydrogen pressure), both hydrogenation and isomerisation taking place at a very slow rate. The end of the induction period corresponds to the appearance of infrared

TABLE 4

HYDROGENATION AND ISOMERISATION OF MONOENES IN THE PRESENCE OF $\pi\text{-}C_4H_7Co(CO)_2P(n\text{-}C_4H_9)_3$[a]

Substrate	Induction (min)	Rate ($mole \cdot l^{-1} \cdot h^{-1}$)	
		Hydrogenation[b]	Isomerisation[b]
1-Pentene	10	3.2	4.0
cis-2-Pentene	9	2.7	3.3

[a] Catalyst concentration of 0.06 $moles \cdot l^{-1}$; other conditions as in Table 3. [b] The figures correspond to the highest rate of disappearance of the initial olefin after the induction period.

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* The hydrogenating properties of π-crotyl(tertiaryphosphine)cobaltdicarbonyl have been briefly reported by other authors[24].

bands characteristic of the trimer; at this point, both hydrogenation and isomerisation take place at a much higher rate than when preformed $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ is used, under otherwise identical conditions (Table 4).

These results seem to indicate that neither the initial π-allyl complex nor the final trimer are the active species. Although direct hydrogen activation by the undissociated trimeric cluster cannot be completely ruled out, the actual active catalyst might be the monomeric unsaturated species $CoH(CO)_2P(n\text{-}C_4H_9)_3$.

Assuming the existence of equilibrium (8), which should lie fairly well to the left,

$$[Co(CO)_2PR_3]_3 \xrightleftharpoons{+H_2} 3\ CoH(CO)_2PR_3 \qquad (8)$$

the concentration of the unsaturated hydrido complex (which cannot be detected at ordinary hydrogen pressure either by IR or NMR spectroscopy) should depend on factors such as hydrogen pressure, concentration of the trimer, and temperature.

Generally speaking, factors favouring the rupture of the cluster enhance the activity of the system. For example, the addition of small amounts of nucleophilic ligands favours the hydrogenation and isomerisation of olefins, the effect being more pronounced in the case of the more reactive soft ligands. In the specific case of tributylphosphine, which has been studied in some detail, the rates reach a maximum at a molar ratio $P(n\text{-}C_4H_9)_3$/trimer$\simeq 1/1$ (Fig. 4). The ascending part of the curve can be tentatively ascribed to the presence of increasing amounts of $CoH(CO)_2P(n\text{-}C_4H_9)_3$, while the descending part corresponds to the disappearance of the active species in favour of the rather inert monomeric species $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ whose presence in the reaction mixtures has been proved. This hypothesis cannot however justify the rather high catalytic activity in olefin isomerisation observed under nitrogen. This fact shows that the catalytic system is very complex, and that more than one active species or other mechanisms are probably involved.

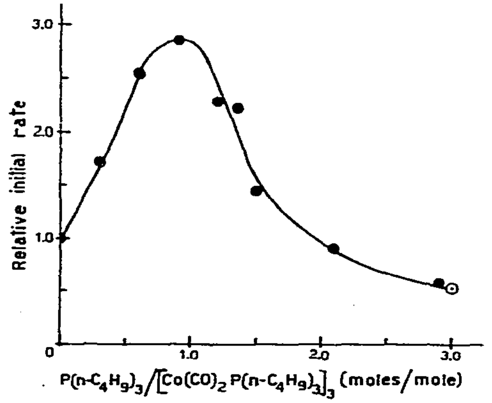


Fig. 4. Effect of $P(n\text{-}C_4H_9)_3$ on the rate of hydrogenation of 1-pentene in the presence of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ (conditions as in Table 3). ⊙ Preformed $CoH(CO)_2[P(n\text{-}C_4H_9)_3]_2$ was used.

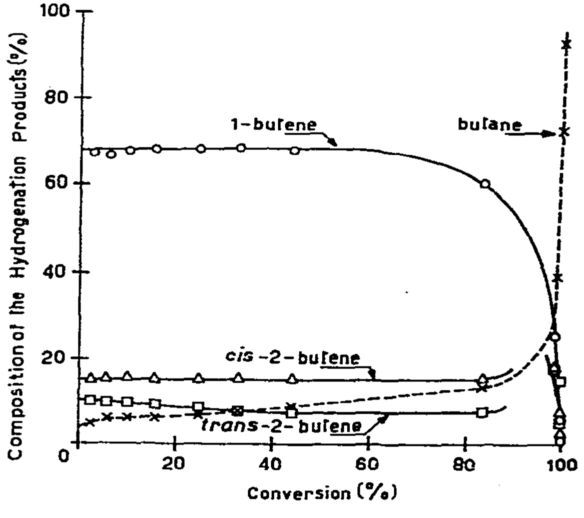


Fig. 5. Hydrogenation of 1,3-butadiene in the presence of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ (conditions as in Table 3).

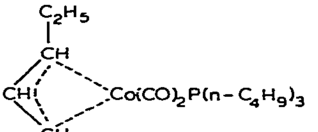
(*ii*). *Hydrogenation of conjugated diolefins*. The hydrogenation of 1,3-butadiene has been carried out using $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ or $\pi\text{-}C_4H_7Co(CO)_2P(n\text{-}C_4H_9)_3$ as the initial complex. In the presence of excess 1,3-butadiene, the former is converted into the latter under the reaction conditions [eqn. (6)]; however a remarkable difference in the kinetic behaviour has been observed. In particular, a zero order reaction in diolefin (up to high conversion) was observed only with $\pi\text{-}C_4H_7Co(CO)_2P(n\text{-}C_4H_9)_3$. This indicates that the formation of the π-allyl intermediate is a slow step, and the behaviour can again be related to the existence of a slow equilibrium (8).

The reaction is highly selective in butenes up to 70–80% conversion. In this range the composition of the reaction products is almost constant (Fig. 5), which indicates that the catalytic system has very low isomerising properties. Consequently, the composition of the olefins appears to be closely connected with the mode of opening of the π-allyl intermediate, in accordance with a model proposed by Bond *et al.*[22]. It is worth pointing out the high stereoselectivity of the reaction, 1-butene being the main reaction product. Significant amounts of butane were found from the early stages of the reduction; in this case a direct path from diolefin to alkane can be invoked, as suggested by other authors[25] for a similar reaction.

At higher conversions (>70–80%), a second stage of the reaction takes place, in which both hydrogen consumption and alkane formation increase sharply and the catalytic system shows very high isomerising properties. As a consequence, 2-butene reaches a maximum concentration which then decreases rapidly at the end of the reaction.

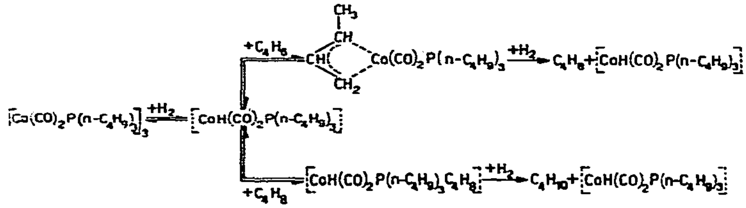
Roughly the same reaction trend is observed for 1,3-pentadiene (73.2% *trans*, 26.8% *cis*), the selectivity to monoene formation being lower (75% for 70% convn.) than in the first case. The *cis*- and *trans*-dienes show the same reactivity, as inferred from their constant ratio throughout the reaction; among the resulting monoenes, 1-pentene is the main reaction product (55%).

These results indicate that 3,4-addition on a Co–H bond takes place preferentially, the following π-allyl being the main intermediate:



In the cases under investigation, the high selectivity can be ascribed only to thermodynamic factors, *i.e.* very strong competition of the diene with respect to the monoene for the catalytic species (Scheme 2)[26]. This overcomes the unfavourable kinetic situa-

SCHEME 2



tion due to the fact that monoenes undergo hydrogenation at a faster rate than conjugated diolefins in presence of the catalytic species described here.

(*iii*). *Hydrogenation of aldehydes.* Aldehydes are reduced in the presence of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$, the rate being lower than in foregoing cases under otherwise identical conditions. Thus tests were run under more drastic conditions but always within the range of the thermal stability of the cobalt complex. For example about 20% of n-butyraldehyde (1 mole $\cdot l^{-1}$, heptane solution), was hydrogenated in 5 h at 80° (catalyst 1.93×10^{-2} moles $\cdot l^{-1}$, hydrogen pressure 150 atm), negligible decomposition of the catalyst being observed.

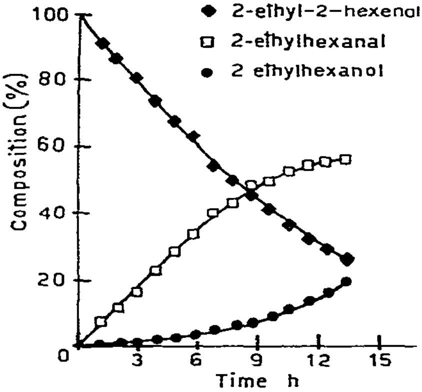


Fig. 6. Hydrogenation of 2-ethyl-2-hexenal (1.0 mole $\cdot l^{-1}$) in the presence of $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ (0.02 moles $\cdot l^{-1}$) at 80° and under 150 atm of hydrogen in heptane.

In contrast with previous results, attempts to obtain 2-ethylhexanal selectively from 2-ethyl-2-hexenal failed, (Fig. 6) because of the equal (slow) rates of reduction of both types of unsaturation. This behaviour could be tentatively ascribed to the steric hindrance of the substituent in α-position to the double bond. To test this hypothesis, hydrogenation was carried out using linear α,β unsaturated aldehydes, such as crotonaldehyde and cinnamaldehyde, under the same experimental conditions. Unfortunately, the trimeric cluster rapidly disappeared in the presence of the above substrates (as inferred from the decrease of the bridging carbonyl band in the IR spectrum), giving rise to the formation of $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$. Surprisingly, no C_3 or C_8 hydrocarbons (respectively) were detected in the reaction mixture, and thus no carbon monoxide abstraction from the substrate seems to take place.

CONCLUSION AND DISCUSSION

The preparation of cobalt(0) carbonyl cluster compounds from Co^I carbonyl complexes by both stoichiometric hydroformylation and hydrogenation of π-allyl species is an interesting new type of synthesis of clusters.

A hydrido intermediate $[CoH(CO)_3$ or $CoH(CO)_2PR_3]$ is probably involved. The former has been assumed[27] as the active species in the conventional hydroformylation reaction, while the latter is reported[24] to be the probable intermediate in diene hydrogenation catalyzed by dicarbonyl(tributylphosphine)-π-allylcobalt. Both hydrides are coordinatively unsaturated; in absence of ligands they therefore tend to condense[19] with themselves (with hydrogen evolution) to yield tetrameric diamagnetic species or paramagnetic, probably trimeric, clusters respectively.

It is interesting to try to explain the tendency to form trimers or tetramers in the above two cases: clearly, in both instances the structures are characterized by high symmetry, which is a general feature of closed metal carbonyl clusters. In the case of the unsubstituted cobalt carbonyl derivative, a noble gas configuration is reached (tetramer) by virtue of the necessity of electronic back-donation to carbon monoxide (this back-bonding being greater when all the low energy orbitals of cobalt are formally filled)[19]. However, in the presence of tertiary phosphines as substituents, the back-donation requirements are met without fulfilling the noble gas rule, due to the high electronic density on the metal and to the decreased number of strong π-acceptor ligands bound to the cobalt atom. Consequently, a certain stability is conferred to a trimeric, paramagnetic structure. When only carbonyl ligands are present, the trimeric structure must be stabilized by a negative charge as in the case of the $[Co_3(CO)_{10}]^-$ anion. In the case of triphenylphosphite derivatives, the tetrameric structure is preferred because of the lower electronic density on the cobalt atoms. However, steric effects cannot be completely ruled out [in fact CO and $P(OR)_3$ ligands have smaller steric requirements than PR_3 ligands] although there is no evidence for their existence.

Despite the proposed analogy with metal surfaces, the metal clusters are generally rather inert and do not show strong catalytic activity. The unusual catalytic activity of $[Co(CO)_2PR_3]_3$ species can be related to the instability of this particular paramagnetic cluster when under hydrogen to form monomeric hydrides according to eqn. (8). The presence of intermediate hydridic species is confirmed by the ready hydrogen–deuterium exchange catalyzed by $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$ under very mild conditions (p_{H_2} 5 atm, p_{D_2} 5 atm, 60°, heptane solution) to give HD. However, at present there is no direct evidence for the existence of such monomeric species under the catalytic conditions used.

Therefore, a direct activity of these "unsaturated" clusters (through hydridic clusters) cannot be excluded. This particularly interesting possibility deserves further investigation since it would represent the first case of homogeneous catalytic activity with a cluster catalyst.

EXPERIMENTAL

Elemental analyses were carried out in the analytical laboratory of the Centro Ricerche Montecatini Edison, Bollate.

ESR spectra were recorded using a Perkin–Elmer instrument. Bulk susceptibility measurements were made using the Faraday method; the χ_g values were found independent of the field strength, so that the presence of ferromagnetic impurities could be ruled out. The results of the magnetic measurements are reported in Table 1.

Infrared spectra were recorded using a Perkin–Elmer 225, grating spectrophotometer: the results are shown in Table 2.

Reactions under pressure were carried out in 100 or 200 ml stainless steel rocking autoclaves, immersed in oil baths and provided with sampling devices for discharging the reaction mixtures.

Hexacarbonyltris(tributylphosphine)tricobalt(0): $[Co(CO)_2P(n\text{-}C_4H_9)_3]_3$

(*a*). *By stoichiometric hydroformylation of α-olefins in the presence of* $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$. A solution of $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$ (4.66 g, 6.75 mmole) in n-heptane (95 ml) was introduced into a 200 ml stainless steel autoclave. Propylene (14 g, 333 mmoles) was then injected from a separate reservoir. After heating to 116°, an autogenous pressure of 16 atm was observed in the reactor; the introduction of hydrogen up to 20–22 atm total pressure, resulted in a very fast gas uptake. The reaction temperature was regulated to within ±2° by gradual replacement of the absorbed gas. When the hydrogen absorption was almost complete (40 min), the reaction mixture was discharged through the sampling device and rapidly cooled to room temperature. Butyl and isobutyl alcohols in a 8/1 ratio were detected in the solution by gas-chromatographic analysis together with propane as the main reaction product.

A dark green tarry residue was obtained by evaporation of the solvent under vacuum; the complex was purified by column chromatography, using silica as the stationary phase and a 90/5/5 heptane/ethyl ether/methanol mixture as the eluent. Yield 62.4%.

(*b*). *By hydrogenation of dicarbonyl(tributylphosphine)-π-crotylcobalt.* A solution of the complex (4.25 g, 11.45 mmoles) in n-heptane (45 ml) was introduced into a 100 ml stainless steel autoclave. The temperature was raised to 85° and hydrogen was pumped in to a total pressure of 130 atm. Gas absorption was observed; after 25 min, the reaction mixture was discharged with quenching. Butane was detected in the solution by gas chromatographic analysis. The purification was carried out as before and a dark-green oil was obtained, similar to that reported above. Yield 78.5%. (Found: (*a*): C, 53.1; H, 8.5; P, 9.6; Co, 18.4; CO, 18.2. (*b*): C, 53.4; H, 8.5; P, 9.7; Co, 18.3; CO, 18.1. $Co(CO)_2P(n\text{-}C_4H_9)_3$ calcd.: C, 53.0; H, 8.5; P, 9.8; Co, 18.6; CO, 17.7%.)

The complex is paramagnetic; in the pure state it is fairly stable to air, whereas in solution it is very sensitive to oxidation. The molecular weight (cryoscopically in cyclohexane) is 852 (calcd. 951). Hydrocarbon solutions of the complex are stable at 80–85° for many hours in nitrogen atmosphere; at higher temperatures decomposition takes place, giving metallic cobalt and bis[tricarbonyl(tributylphosphine)-cobalt(0)], identified by means of its melting point and infrared spectrum.

Hexacarbonyltris(dibutylphenylphosphine)tricobalt(0) $[Co(CO)_2P(n\text{-}C_4H_9)_2C_6H_5]_3$

This compound was similarly prepared starting from $[Co(CO)_3P(n\text{-}C_4H_9)_2C_6H_5]_2$ (*a*) or from $C_4H_7Co(CO)_2P(n\text{-}C_4H_9)_2C_6H_5$ (*b*). The product is a dark-green paramagnetic oil. (Found: (*a*): C, 56.8; H, 6.7; Co, 17.2; CO, 17.7. (*b*): C, 56.9; H, 6.8; Co, 17.1; CO, 17.6. $Co(CO)_2P(n\text{-}C_4H_9)_2C_6H_5$ calcd.: C, 57.0; H, 6.8; Co, 17.5; CO, 16.6%.)

Hexacarbonyltris(triphenylphosphine)tricobalt(0) $[Co(CO)_2P(C_6H_5)_3]_3$

A solution of dicarbonyl(triphenylphosphine)-π-crotylcobalt (11.4 g, 26.3 mmoles) in benzene (90 ml) was introduced into a 200 ml stainless steel autoclave. At 65°, as soon as hydrogen was added (110 atm), gas absorption was observed. After 15 min, a dark-green mixture was discharged from which a residue consisting of $[Co(CO)_3P(C_6H_5)_3]_2$ and metallic cobalt was separated by centrifugation.

$[Co(CO)_2P(C_6H_5)_3]_3 \cdot 2\ C_6H_6$ was precipitated by addition of light petroleum

(200 ml) and was recrystallized from benzene/light petroleum. The benzene could be removed by crushing the product in the presence of light petroleum. Yield 40.7%. (Found: C, 63.6; H, 4.1; P, 8.1; Co, 15.2; CO, 14.6. $Co(CO)_2P(C_6H_5)_3$ calcd.: C, 63.7; H, 4.0; P, 8.2; Co, 15.6; CO, 14.8%.)

Dark-green paramagnetic crystals, dec. 141°, soluble in benzene and toluene, from which recrystallization takes place with retention of the solvent, insoluble in aliphatic solvents. The complex is very sensitive to air in solution, but the pure complex is not altered on exposure to air for several hours. Solutions of the complex decompose slowly at 60°, giving bis[tricarbonyl(triphenylphosphine)cobalt(0)] and metallic cobalt.

Hydrogenation of tricarbonyl-π-crotylcobalt

Tricarbonyl-π-crotylcobalt (0.98 g, 5 mmoles) dissolved in n-hexane (40 ml), was treated at 75° with hydrogen (75 atm) for 15 min, during which gas absorption was observed. After evaporation of the solvent under vacuum, black crystals were obtained, whose infrared spectrum was identical to that of an authentic sample of $Co_4(CO)_{12}$. Yield 92%. (Found: C, 25.4; Co, 41.0. $Co_4(CO)_{12}$ calcd.: C, 25.2; Co, 41.3%.)

Hydrogenation reactions

The catalyst and the solvent were introduced (operating in a nitrogen atmosphere) into a 100 ml stainless steel autoclave, provided with a sampling device.

After heating to the desired temperature, the substrate was added under pressure from a reservoir, together with hydrogen (the total liquid volume amounted to about 50 ml).

Sampling was made at suitable time intervals.

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