A Novel Paramagnetic Cobalt(0) Carbonylphosphine Cluster showing Catalytic Properties

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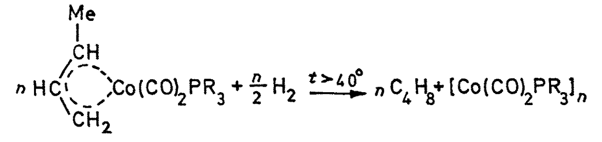
COBALT CARBONYL–TERTIARY PHOSPHINE systems[1] catalyse olefin hydroformylation, giving very high yields of linear alcohols, and have useful hydrogenating properties.

During studies on the catalytic properties of hydrido-compounds of formula $HCo(CO)_n(PBu^n{}_3)_{4-n}$ (n = 3, 2, 1)[2,3] (some of which could be present in the hydroformylation catalyst) we have found that a deep green compound is formed during the hydrogenation of some olefins with $HCo(CO)_3(PBu^n{}_3)$. This compound, which analyses as $[Co(CO)_2PBu^n{}_3]_n$, is formed by stoicheiometric hydroformylation of the olefins, *e.g.* propene, according to the reaction:

$$n HCo(CO)_3PR_3 + n CH_3{\cdot}CH{:}CH_2 + \tfrac{3}{2}n H_2 \xrightarrow{120^\circ} [Co(CO)_2PR_3]_n + n C_4H_9OH.$$

$$(PR_3 = PBu^n{}_3,\ PPh_2Bu^n).$$

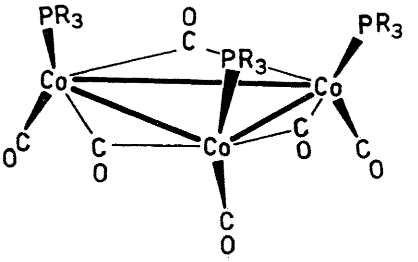
Similar compounds are obtained in better yield by direct hydrogenation of the π-allylcobalt dicarbonyl phosphine complexes:[4]



$$n\,(\pi\text{-}MeCH{\cdot}CH{\cdot}CH_2)Co(CO)_2PR_3 + \tfrac{n}{2}H_2 \xrightarrow{t > 40^\circ} n\,C_4H_8 + [Co(CO)_2PR_3]_n$$

$$PR_3 = PBu^n{}_3,\ PPh_3$$

The compounds, which are air sensitive, are generally oily but in the case of triphenylphosphine the compound can be crystallised, from benzene or toluene, with some molecules of solvent of crystallisation. The absence of hydridic hydrogen is confirmed by the reaction with carbon monoxide to yield $[Co(CO)_3PR_3]_2$[5] and with 1,2-bisdiphenylphosphinoethane (dpe) to $[Co(CO)_2dpe]_2$;[6] no hydrogen was produced. All the green complexes $[Co(CO)_2PR_3]_n$ are paramagnetic both in the solid state and in solution, and do not show any magnetic anomaly down to −170°. The paramagnetism suggests a trimeric cluster structure, similar to that of a Ni^I d^9 paramagnetic cluster;[7] assuming a trimeric structure, the molecular magnetic moments are around 3 B.M. (R = Ph, Bu^n). The molecular weight of the triphenylphosphine complex determined by X-ray study† of a single crystal from toluene is 1314, in excellent agreement with the 1316 required for $[\{Co(CO)_2PPh_3\}_3],2C_7H_8$, and that of the tributylphosphine complex (cryoscopically in benzene) is 852 (Calc. 951). The i.r. spectra show terminal and bridging carbonyls. All this evidence suggests the structure shown in the Figure (in which, however, the relative positions of the phosphines are arbitrary).



FIGURE

The cluster compounds catalyse olefin hydrogenation and isomerisation (Table 1), the latter process taking place also in the absence of hydrogen. With these complexes no induction period is detected; moreover under a hydrogen atmosphere the initial rate of isomerisation is greater than the initial rate of hydrogenation. The hydrogenation is not selective between terminal and internal olefins, though

TABLE 1

Catalytic activity of $[Co(CO)_2PBu^n{}_3]_3$

Olefin	Initial rate of hydrogenation[a] (mole l.$^{-1}$ hr.$^{-1}$)	Initial rate of isomerisation[b] (mole l.$^{-1}$ hr.$^{-1}$)
Propene	0·46	—
Pent-1-ene	0·39	1·77; 0·31[c]
cis-Pent-2-ene . .	0·27	0·51
trans-Pent-2-ene . .	0·17	0·22
Cyclohexene	0·15	—

[a] The reaction has been carried out at 66° in n-heptane with a catalyst concentration of $1{\cdot}93 \times 10^{-2}$ moles l.$^{-1}$, an olefin concentration of 1 mole l.$^{-1}$, and a hydrogen pressure of 15 atm.
[b] The reaction conditions were similar to that of (a).
[c] Under a nitrogen atmosphere.

TABLE 2

Catalytic activity of π-$C_4H_7Co(CO)_2(PBu^n{}_3)$[a]

Olefin	Initial rate of hydrogenation[b] (mole l.$^{-1}$ hr.$^{-1}$)	Initial rate of isomerisation[b] (mole l.$^{-1}$ hr.$^{-1}$)
Pent-1-ene	3·17	3·96
Pent-2-ene	2·70	3·30

[a] The reaction was carried out at 66° in n-heptane with a catalyst concentration of $5{\cdot}79 \times 10^{-2}$ mole l.$^{-1}$, an olefin concentration of 1 mole l.$^{-1}$, and a hydrogen pressure of 15 atm.
[b] The rates correspond to the highest values after the induction period.

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† An X-ray investigation of the molecular structure is in progress (Dr. J. Bart).

selective hydrogenation occurs during the hydrogenation of conjugated dienes. In the hydrogenation of butadiene up to a conversion of 70%, butenes are formed selectively (they correspond to nearly 90% of the hydrogenation products).

Parallel studies of olefin hydrogenation and isomerisation using the π-allyl complex π-$C_4H_7Co(CO)_2(PBu^n{}_3)$ (Table 2) suggest the existence of the same catalytic species formed from the trimeric cluster. After an induction period, probably due to the slow formation of the catalytic species, the rates of hydrogenation and isomerisation are higher than in the case of the cluster $[Co(CO)_2PR_3]_3$ catalysts. The catalytic species is probably a solvated monomer $Co(CO)_2PR_3$ formed by dissociation of the cluster or by hydrogenation of the π-allyl compound. With the π-allyl complex the concentration of this active species is probably higher, which explains the higher catalytic activity.

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