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SYNTHESIS, REACTIONS AND CATALYTIC ACTIVITY OF SOME MIXED TRIFLUOROPHOSPHINE(TRIPHENYLPHOSPHINE)HYDRIDO COMPLEXES OF COBALT(I)

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Summary

The complexes $CoH(PF_3)_{4-n}(PPh_3)_n$ (n = 1—3) have been prepared by low pressure routes and the π-allylic complex $Co(\pi\text{-}C_4H_7)(C_4H_6)(PF_3)$ has been obtained from the reaction between $CoH(PF_3)(PPh_3)_3$ and butadiene. The hydrido complexes are active catalysts for the isomerisation of 1-octene to 2-octene under hydrogen or nitrogen.

Introduction

We have recently synthesised the hydridorhodium(I) complexes $RhH(PF_3)(PPh_3)_3$ and $RhH(PF_3)_2(PPh_3)_2$ by treating $RhH(PPh_3)_4$ with either equimolar or excess amounts of trifluorophosphine [1]:

$$RhH(PPh_3)_4 \xrightarrow[-PPh_3]{+PF_3} RhH(PF_3)(PPh_3)_3 \xrightarrow[-PPh_3]{+PF_3} RhH(PF_3)_2(PPh_3)_2$$

In view of the high catalytic activity of these compounds for the hydrogenation and isomerisation of terminal olefins, the analogous cobalt complexes were investigated.

The only reported hydrido mixed trifluorophosphine(triphenylphosphine)-cobalt(I) complex is $CoH(PF_3)_3(PPh_3)$, prepared by treatment of $CoH(PF_3)_4$ with triphenylphosphine at 135° [2]. The carbonyl compounds $CoH(CO)_{4-n}(PPh_3)_n$ (where n = 1 or 2) have been obtained by acidification of the corresponding carbonylmetallates [3—5], while the mono- and dicarbonyl complexes have been prepared by displacement of nitrogen from $CoH(N_2)(PPh_3)_3$ [6]:

$$CoH(N_2)(PPh_3)_3 + CO \longrightarrow CoH(CO)(PPh_3)_3 + N_2 \xrightarrow{+CO} CoH(CO)_2(PPh_3)_2 + PPh_3$$

The monocarbonyl complex has also been prepared by displacement of cyclo-octadiene from a π-cyclooctenyl ligand, with transfer of a hydrogen atom to the metal [7].

$$Co(\pi\text{-}C_8H_{13})(C_8H_{12}) + CO \xrightarrow{-60^\circ} Co(\pi\text{-}C_8H_{13})(C_8H_{12})(CO) \xrightarrow{+3PPh_3} CoH(CO)(PPh_3)_3 + 2C_8H_{12}$$

Results and discussion

Passage of trifluorophosphine through a benzene solution of $CoH(N_2)(PPh_3)_3$ for 15 min leads to the displacement of molecular nitrogen and the formation in good yield of hydrido(trifluorophosphine)tris(triphenylphosphine)cobalt(I), $CoH(PF_3)(PPh_3)_3$ *:

$$CoH(N_2)(PPh_3)_3 + PF_3 \longrightarrow CoH(PF_3)(PPh_3)_3 + N_2$$

The product is an orange, crystalline solid which decomposes only slowly in air, but rapidly in solution, to give triphenylphosphine oxide. $CoH(PF_3)(PPh_3)_3$ is insoluble in hexane and other aliphatic solvents, but is reasonably soluble in benzene. Although it is soluble in chloroform, there is rapid decomposition to a cobalt(II) complex.

When PF_3 is passed through a solution of $CoH(N_2)(PPh_3)_3$ for longer than thirty minutes, hydridobis(trifluorophosphine)bis(triphenylphosphine)cobalt(I), $CoH(PF_3)_2(PPh_3)_2$, can be crystallised in low yield from the mother liquors after precipitation of $CoH(PF_3)(PPh_3)_3$. The same compound is obtained in high yield when a benzene solution of $CoH(PF_3)(PPh_3)_3$ is treated with an excess of PF_3 in a sealed ampoule for a few days at room temperature.

$$CoH(PF_3)(PPh_3)_3 + PF_3 \longrightarrow CoH(PF_3)_2(PPh_3)_2 + PPh_3$$

The product is a yellow, crystalline solid which is slightly soluble in hexane, but readily soluble in benzene. Further treatment of $CoH(PF_3)_2(PPh_3)_2$ with an excess of PF_3 does not give any appreciable amount of $CoH(PF_3)_3(PPh_3)$, even on heating for a day at 60°.

The low-pressure synthesis of hydridotris(trifluorophosphine)(triphenylphosphine)cobalt(I), $CoH(PF_3)_3(PPh_3)$, is achieved by passing PF_3 through a benzene solution of chlorotris(triphenylphosphine)cobalt(I), $CoCl(PPh_3)_3$ [8,9] for about two hours. Free triphenylphosphine and dichlorobis(triphenylphosphine)cobalt(II), $CoCl_2(PPh_3)_2$, are also formed in large amounts.

The source of the hydrogen atom attached to the metal was not elucidated, but possible explanations are an intramolecular hydride-abstraction from a triphenylphosphine ligand [10] or abstraction from the solvent [11]. The product is a colourless, crystalline solid, fairly soluble in hexane and very soluble in benzene, which appears to be identical with $CoH(PF_3)_3(PPh_3)$ prepared from $CoH(PF_3)_4$. No $CoH(PF_3)_4$ is formed when a benzene solution of $CoH(PF_3)_3$-(PPh_3) is heated at 60° with an excess of PF_3 for a day.

The mixed phosphine hydrides listed in Table 1 were characterised by elemental analysis, IR, ^{1}H NMR, ^{19}F NMR and mass spectroscopy. All the complexes

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* This reaction was first studied by R. Peppiatt, but the product was not fully characterised [M.Sc. Thesis, University of Sussex, (1969)].

are air sensitive, especially in solution, but resistance to oxidation increases with PF_3 substitution, solid $CoH(PF_3)_3(PPh_3)$ being practically air-stable.

IR spectra

The IR spectrum of a strong mull of $CoH(PF_3)(PPh_3)_3$ has a very weak band at 2046 cm^{-1} which is absent from the spectra of the other trifluorophosphinecobalt hydrides studied, but comparable to a band at 2066 cm^{-1} in the spectrum of $RhH(PF_3)(PPh_3)_3$ [1]. Assignment of the Co—H stretching frequencies for the analogous carbonyl—phosphine hydrido complexes is complicated because the absorptions are obscured by the very strong carbonyl bands in the same region. It has been suggested that interaction with the aryl groups of the phosphine ligands renders the Co—H stretching mode IR inactive in this type of system [12]. A weak band at 2013 cm^{-1} in the IR spectrum of $CoH(CO)(PPh_3)_3$, however, has been tentatively assigned to ν(Co—H) [7].

Three strong bands at 830, 803 and 797 cm^{-1} in the P—F stretching region are consistent with the presence of a single PF_3 ligand and a similar pattern has also been reported for the rhodium complexes $RhH(PF_3)(PPh_3)_3$ [1] and $Rh(\pi\text{-}C_3H_5)(PF_3)(PPh_3)_2$ [13]. A further strong absorption at 521 cm^{-1} is assigned to P—F bending vibrations, while other bands are due to vibrational modes of the triphenylphosphine ligands.

$CoH(PF_3)_2(PPh_3)_2$ has a weak, broad band at 1964 cm^{-1} in the IR spectrum which is assigned to the metal hydride stretching vibration [cf. 1986 cm^{-1} for $RhH(PF_3)_2(PPh_3)_2$] [1].

Coordination of two PF_3 ligands is indicated by three broad P—F stretching bands at 872, 825 and 804 cm^{-1}, which are similar to those observed for $RhH(PF_3)_2(PPh_3)_2$. Other bands are assigned to P—F bending modes and vibrational modes of the triphenylphosphine ligands.

The Co—H stretching vibration of $CoH(PF_3)_3(PPh_3)$ gives a sharp band of medium intensity at 1938 cm^{-1}, while the P—F stretching region shows four very strong bands at 910, 875, 846 and 822 cm^{-1}. A further very strong band at 520 cm^{-1} is assigned to the P—F bending vibration. The bands due to the single triphenylphosphine molecule are in the expected positions, but are much sharper than those found in either the free ligand or in compounds containing more than one PPh_3 group. This spectrum is in good agreement with published data [2].

^1H NMR spectra

NMR studies are restricted by the low solubility of the complexes, and by the need to avoid chlorinated solvents in which the compounds decompose. A saturated benzene solution of $CoH(PF_3)(PPh_3)_3$ shows only the resonances of the three triphenylphosphine ligands and no high field signal assignable to a hydride is detectable, even in a time-averaged spectrum. The reported resonances of the similar compounds $CoH(CO)(PPh_3)_3$ (τ 23) [6,7] and $RhH(PF_3)(PPh_3)_3$ (τ 19.8) [1] have only been detected with difficulty.

The increased solubility of $CoH(PF_3)_2(PPh_3)_2$ in benzene allows the observation of a very weak, broad multiplet at τ 22.5 in the ^1H NMR spectrum. The width of the signal (ca. 100 Hz) is an indication of the extensive coupling to the phosphorus and fluorine nuclei of the phosphine ligands. There is also the posibility of quadrupole broadening by the cobalt nucleus ($I = 7/2$ for ^{59}Co) [12]. The

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA FOR MIXED PHOSPHINE HYDRIDO COMPLEXES OF COBALT(I), $CoH(PF_3)_{4-n}(PPh_3)_n$ (n = 1—3)

Compound	M.p.[a] (°C)	Mol. wt.[b] found (calcd.)	Analysis found (calcd.) (%)		ν(Co—H) (cm^{-1})	τ(Co—H)	δ[c] (KHz)	ϕ[d] (ppm)	J[f] (Hz)
			C	H					
$CoH(PF_3)(PPh_3)_3$	147—149 (dec.)	[e] (934)	69.2 (69.4)	5.1 (4.9)	2046vw	[e]	−15.244	+0.8	J_1 1239 (d) J_2 20.6 (qn)
$CoH(PF_3)_2(PPh_3)_2$	200 (dec.)	760 (760)	56.2 (56.8)	4.1 (4.1)	1964w	22.5	−14.738	+6.2	J_1 1265 (d) J_2 17.0 (t) J_3 13.0 (d)
$CoH(PF_3)_3(PPh_3)$	175—176 (sublm.)	586 (586)	36.9 (36.9)	2.8 (2.7)	1938m	24.3	−14.569	+8.0	J_1 1231 (d) J_2 7.5 (d) J_3 5.0 (d)

[a] Under nitrogen. [b] Mass spectroscopic. [c] ^{19}F chemical shift rel. internal C_6F_6 standard. [d] ^{19}F chemical shift calculated rel. $CFCl_3$ standard. [e] Not obtained.
[f] J_1, J_2 and J_3 are ^{19}F line separations.

reported hydride shifts for the analogous $CoH(CO)_2(PPh_3)_2$ are τ 20.0 [6] and τ 20.4 [5].

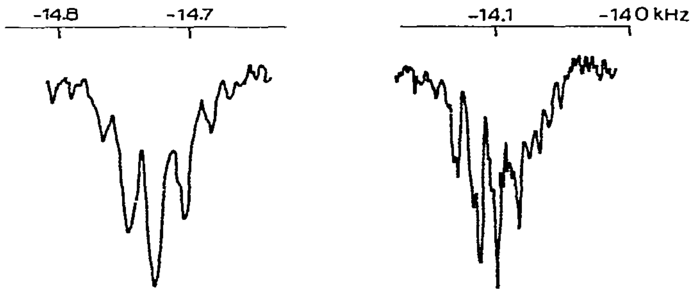
A broad multiplet (width ca. 150 Hz) centered at τ 24.3 in the spectrum of $CoH(PF_3)_3(PPh_3)$ is assigned to the hydride ligand, in reasonable agreement with the value of τ 24.8 reported by Kruck [2]. The published chemical shift for the carbonyl complex $CoH(CO)_3(PPh_3)$ is τ 20.7 [5].

^{19}F *NMR spectra*

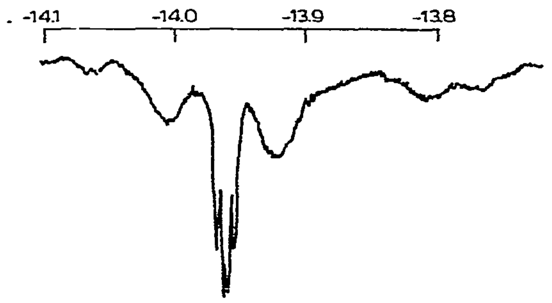
The low solubility of the complexes again makes it difficult to obtain good ^{19}F NMR spectra, but the spectrum of $CoH(PF_3)(PPh_3)_3$ averaged by computer over several hours shows signals assignable to the complex, as well as others due to $CoH(PF_3)_2(PPh_3)_2$, present as an impurity. The spectrum shows two quintets (Fig. 1) at a separation, $J_1 = {}^1J(PF)$, of 1239 Hz. The quintet splitting of 20.6 Hz (J_2) is due to coupling to the three phosphorus nuclei, $^3J(PF)$, of the triphenylphosphine ligands and the hydrogen atom, $^3J(FH)$.

The time-averaged ^{19}F NMR spectrum of $CoH(PF_3)_2(PPh_3)_2$ shows only two complex multiplets at a separation, J_1, of 1265 Hz, equal to $|{}^1J(PF) + {}^3J(PF')|$ if the spin system is classified as $[AX_3]_2$ [14,15]. Each multiplet is a doublet (J_3 13.0 Hz) of triplets (J_2 17.0 Hz) with a broad, weak multiplet outside the main lines [Fig. 1(b)].

The equivalence of the two PF_3 ligands can arise either from a rigid trigonal-bipyramidal structure with both PF_3 groups in either axial or equatorial



(a). $CoH(PF_3)(PPh_3)_3$ (b). $CoH(PF_3)_2(PPh_3)_2$



(c). $CoH(PF_3)_3(PPh_3)$

Fig. 1. ^{19}F NMR spectra of $CoH(PF_3)_{4-n}(PPh_3)_n$ complexes (n = 1—3) (high field parts).

positions or alternatively the apparent equivalence may result from an intramolecular ligand exchange process. A similar mechanism has been proposed to explain the temperature dependent ^{1}H NMR spectrum of $IrH(CO)_2(PPh_3)_2$ [16]. Another possible averaging process involves the rapid hydrogen-atom traversal of the faces of a tetrahedral molecule, as postulated for $CoH(PF_3)_4$ [17], $CoH[P(OPh)_3]_4$ [12] and $CoH[P(OPh)Et_2]_4$ [18].

The ^{19}F NMR spectrum of $CoH(PF_3)_3(PPh_3)$ [Fig. 1(c)] shows a pair of complex multiplets with a separation J_1 1231 Hz between the strongest lines, corresponding to $|^1J(PF) + 2^3J(PF')|$ in an $[AX_3]_3$ spin system [19]. The main lines are surrounded by weak, broad multiplets of total width 290 Hz. The strong multiplets are doublets (J_2 7.5 Hz) of doublets (J_3 5.0 Hz) due to coupling to the single triphenylphosphine ligand, $^3J(P''F)$, and the hydride, $^3J(FH)$. The coupling constants cannot be assigned specifically to either since the ^{1}H NMR signal of the hydride is too broad for meaningful measurements to be made.

The magnetic equivalence of the three trifluorophosphine ligands is readily explained by a trigonal bipyramidal structure with the PF_3 groups in equatorial positions. An intramolecular ligand exchange process would also explain the observed spectrum, although no change is noted on cooling a solution of $CoH(PF_3)_3(PPh_3)$ in toluene to −30°.

Chemical shifts and coupling constants for the complexes $CoH(PF_3)_{4-n}(PPh_3)_n$ ($n = 1$—3) are listed in Table 1.

Reactions of $CoH(PF_3)_{4-n}(PPh_3)_n$ ($n = 1$—3)

(a) With trifluorophosphine. As noted earlier, only $CoH(PF_3)(PPh_3)_3$ reacts with an excess of PF_3 to give $CoH(PF_3)_2(PPh_3)_2$. It seems likely that the tris(triphenylphosphine) complex dissociates in solution, allowing substitution by PF_3, while $CoH(PF_3)_2(PPh_3)_2$ and $CoH(PF_3)_3(PPh_3)$ do not readily dissociate.

$$CoH(PF_3)(PPh_3)_3 \rightleftharpoons CoH(PF_3)(PPh_3)_2 + PPh_3 \xrightarrow[-PPh_3]{+PF_3} CoH(PF_3)_2(PPh_3)_2$$

No evidence for displacement of PF_3 by an excess of PPh_3 is noted for any of the complexes. Kruck has interpreted similar observations on the basis of the differing donor—acceptor properties of the two ligands [20].

(b) With butadiene. When $CoH(PF_3)(PPh_3)_3$ and a large excess of butadiene are mixed together in a sealed tube at room temperature, there is little evidence of reaction, although there is a slow yellow colouration of the butadiene. If the mixture is heated at 60° for about two hours, the hydrido complex dissolves in the butadiene to give an orange solution from which the volatile complex *anti*-1-methyl-π-allylbutadiene(trifluorophosphine)cobalt(I), $Co(\pi\text{-}C_4H_7)(C_4H_6)(PF_3)$, is obtained in good yield. The involatile residue contains a red compound thought to be $Co(\pi\text{-}C_4H_7)(PF_3)(PPh_3)_2$ on the basis of its IR spectrum [21] and by analogy with the known rhodium system [13]. $CoH(PF_3)(PPh_3)_3$ thus inserts a butadiene molecule into the metal—hydride bond, but an excess of butadiene displaces the remaining triphenylphosphine ligands.

$$CoH(PF_3)(PPh_3)_3 + C_4H_6 \rightarrow Co(\pi\text{-}C_4H_7)(PF_3)(PPh_3)_2 + PPh_3 \xrightarrow{+C_4H_6} Co(\pi\text{-}C_4H_7)(C_4H_6)(PF_3) + 2\ PPh_3$$

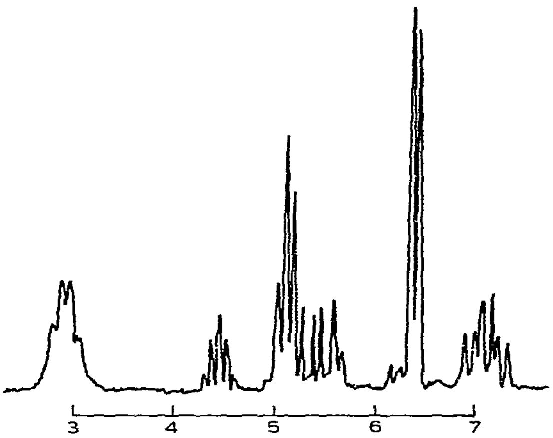
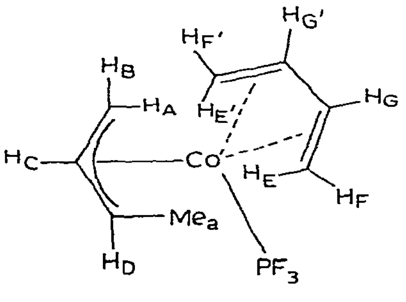


Fig. 2. ^{1}H NMR spectrum of Co(π-C_4H_7)(C_4H_6)(PF_3).

When the reaction mixture is heated for several days, the organometallic product is not isolated, but small amounts of the butadiene dimers, 1,5-cyclooctadiene and vinylcyclohexene, are formed.

The insertion product, Co(π-C_4H_7)(C_4H_6)(PF_3), is a volatile yellow solid which decomposes over a few hours at room temperature, both in the solid state and in solution. Its mass spectrum exhibits a molecular ion at *m/e* 256. The complex is not sufficiently volatile for examination in the vapour phase, but the infrared spectrum of a benzene solution shows a strong band at 838 cm^{-1} and weaker absorptions at 921 and 949 cm^{-1}, assigned to P—F stretching vibrations. The spectrum of a nujol mull shows weak bands assignable to the π-allylic [22, 23] and butadiene [24] groups, similar to those noted for Co(π-C_4H_7)(C_4H_6)-(PPh_3) [25], in addition to the usual P—F stretching and bending vibrations.

The ^{1}H NMR spectrum of Co(π-C_4H_7)(C_4H_6)(PF_3) (Fig. 2) is complex, but can be interpreted by comparison with that of *anti*-Co(π-C_4H_7)(C_4H_6)(PPh_3) [26].



A complex multiplet centred at 2.92 ppm (3H) (rel. C_6H_6) is assigned to the overlapping signals of the internal protons of the butadiene ligand, H_G and $H_{G'}$, and the central proton of the allylic group, H_C. The distinctive quintet at 4.44 (1H) is

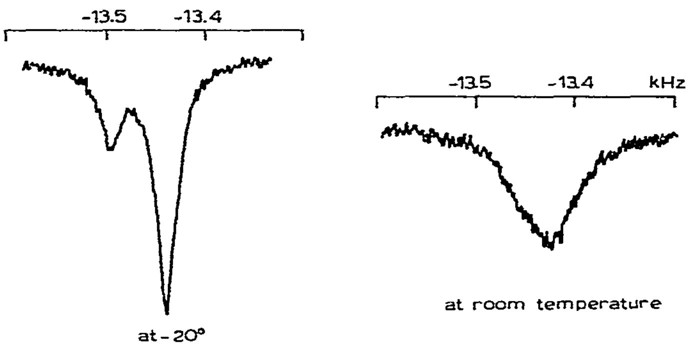
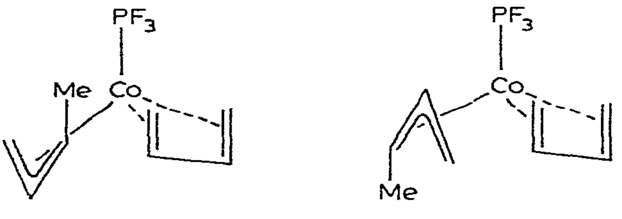


Fig. 3. ^{19}F NMR spectra of $Co(\pi\text{-}C_4H_7)(C_4H_6)(PF_3)$.

due to a *syn*-proton, H_D, adjacent to the methyl group, with equal couplings to both this and H_C [$J(H_DH_C) = J(H_DMe_a) = 6.8$ Hz]. The remaining terminal allylic protons, H_A and H_B, give a complex triplet resonance at 5.10 (2H) with a basic splitting of about 7.0 Hz. Two doublets at 5.32 (1H) and 5.51 (1H) are due to the *syn*-protons, H_F and $H_{F'}$, of the butadiene group, with $J(H_GH_F) = J(H_{G'}H_{F'}) = 12.0$ Hz. The methyl group, Me_a, gives a doublet [$J(Me_aH_D)$ 6.8 Hz] at 6.39 (3H), which shows a further small doubletting, presumably from phosphorus coupling [$J(Me_aP)$ 1.9 Hz]. The *anti*-protons of the butadiene, H_E and $H_{E'}$, give overlapping doublets [$J(H_GH_E) = J(H_{G'}H_{E'}) = 16.0$ Hz] of doublets [$J(H_EP) = J(H_{E'}P) = 9.5$ Hz] at 7.03 (1H) and 7.21 (1H).

The ^{19}F NMR spectrum shows only two broad, weak multiplets at room temperature, but on cooling below −20°, the signal changes to give two doublets of different intensities (Fig. 3). Since there is no change in the ^1H NMR spectrum over the same temperature range, it is concluded that intermolecular phosphine exchange is not responsible for this variation. Some form of intramolecular isomerisation seems likely, probably involving rotation of either or both the organic groups. Two of several possible isomers [25] are illustrated in Fig. 4. By analogy with $Co(\pi\text{-}C_4H_7)(C_4H_6)(PPh_3)$ [27] the most stable structure would be expected to be (a), with the organic groups in a '*cis*' configuration.



(a) (b)

Fig. 4. Two possible structures of $Co(\pi\text{-}C_4H_7)(C_4H_6)(PF_3)$.

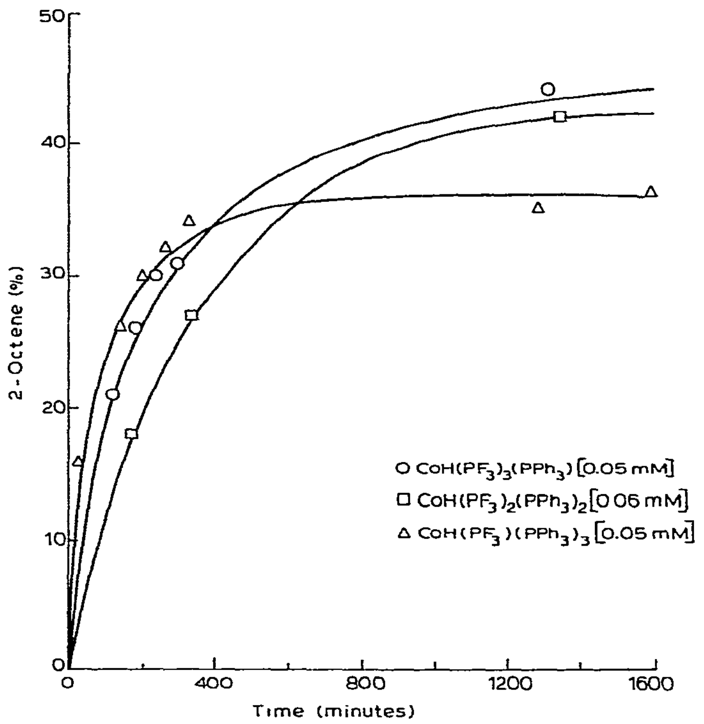


Fig. 5. Isomerisation of 1-octene with $CoH(PF_3)_{4-n}(PPh_3)_n$ ($n = 1—3$) in benzene at 50°.

Treatment of $CoH(PF_3)_2(PPh_3)_2$ and $CoH(PF_3)_3(PPh_3)$ with a large excess of butadiene at room temperature over several days gives no reaction. When the mixtures are heated at 60° for a week, trace amounts of vinylcyclohexene and an unidentified polymeric material are formed.

(c) With tetrafluoroethylene. No isolable product is obtained by heating $CoH(PF_3)(PPh_3)_3$ with C_2F_4 at 60° for two days, unlike the rhodium carbonyl system which gives $Rh(C_2F_4H)(CO)(PPh_3)_2$ [28] and the rhodium trifluorophosphine complex which also gives an insertion product [1].

(d) Catalytic activity of $CoH(PF_3)_{4-n}(PPh_3)_n$ complexes ($n = 1—3$). Unlike the highly active rhodium complexes $RhH(CO)(PPh_3)_3$ and $RhH(PF_3)(PPh_3)_3$, the hydridotrifluorophosphinecobalt complex $CoH(PF_3)(PPh_3)_3$ is found to be inactive as a hydrogenation catalyst at atmospheric pressure, but a benzene solution acts as a catalyst for the slow isomerisation of 1-octene to a mixture of *cis*- and *trans*-2-octene at 50°. The solution becomes inactive after about four hours, due to decomposition (Fig. 5). Like the rhodium analogue, the bis(trifluorophosphine) complex $CoH(PF_3)_2(PPh_3)_2$ is found to be active only for isomerisation, under either hydrogen or nitrogen in benzene solution at 50°, although the rate for nitrogen is about half that for hydrogen. The initial rate of isomerisation is slower than for $CoH(PF_3)(PPh_3)_3$, but the activity lasts longer, indicating a slower decomposition. Addition of free triphenylphosphine greatly reduces the rate of reaction (Fig. 6).

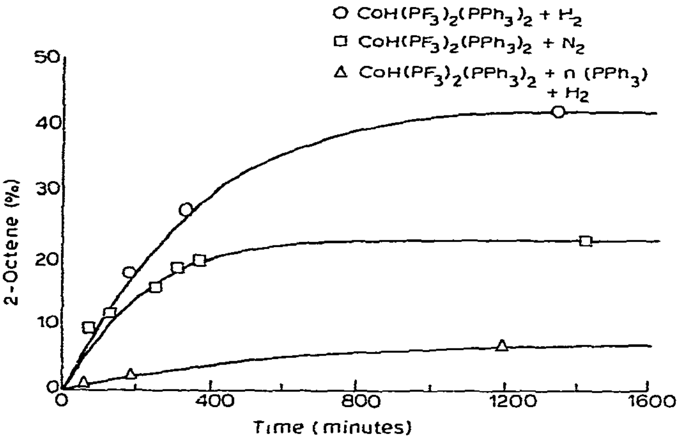


Fig. 6. Isomerisation of 1-octene with $CoH(PF_3)_2(PPh_3)_2$ at 50° in benzene under various conditions.

The tris(trifluorophosphine) complex $CoH(PF_3)_3(PPh_3)$ is also active as an isomerisation catalyst in benzene solution at 50°, with the longest lasting activity of all the hydrido complexes studied.

The activity of $CoH(PF_3)_2(PPh_3)_2$ under both hydrogen and nitrogen suggests that a hydrido complex is the active species, while the inhibition by free phosphine implies the involvement of a dissociative step. A similar mechanism is proposed for the other hydrido compounds.

The lack of hydrogenation probably reflects the difficulty of the required oxidative addition of molecular hydrogen to the metal—alkyl species. The presence of strongly electron-withdrawing trifluorophosphine ligands is expected to increase the polarity, $M^{\delta-}$—$H^{\delta+}$, of the metal—hydrogen bond. This polarity is, however, apparently of minor importance in determining the rate of isomerisation, since there is little difference in activity between the complexes $CoH(PF_3)_{4-n}(PPh_3)_n$ (n = 1—3) with different numbers of trifluorophosphine ligands.

The observation of a faster initial rate for $CoH(PF_3)(PPh_3)_3$ is consistent with the known ease of displacement of triphenylphosphine in benzene solution, while the loss of activity of the solutions is in the same order as that of the decomposition of the solid compounds.

Experimental

Reactions were carried out and complexes handled either in vacuo or under an atmosphere of dry nitrogen gas. Solvents were dried and freshly distilled under nitrogen before use.

^1H NMR spectra were recorded in benzene solutions on a Varian HA 100 spectrometer operating at 100 MHz using benzene as internal standard. ^{19}F NMR spectra were recorded at 94.1 MHz with C_6F_6 as internal standard. [$\Phi(C_6F_6)$ = + 162.8 ppm rel. CCl_3F]. IR spectra in the 4000—400 cm^{-1} range were recorded on a Perkin Elmer 457 spectrometer; volatile complexes were studied in the vapour phase, involatile compounds in nujol mulls between KBr plates. Elemental analyses were carried out by Mrs. A.E. Olney of this department and A. Bernhardt, Elbach über Engelskirchen, W. Germany. Mass spectra were recorded on an AEI MS9 spectrometer.

Preparation of $CoH(PF_3)(PPh_3)_3$ and $CoH(PF_3)_2(PPh_3)_2$

$\mathrm{CoH(N_2)(PPh_3)_3}$ was prepared by a modified version of the literature method [29], by bubbling nitrogen rapidly through a stirred suspension of cobalt(III) acetylacetonate (9.010 g, 25 mmol) and triphenylphosphine (20.147 g, 82 mmol) in diethyl ether (150 ml) at room temperature, while triethylaluminium (12 ml) was slowly added. The resulting orange-red precipitate was washed with dry, nitrogen-purged ether (5 × 100 ml portions) and dried under high vacuum. The product $\mathrm{CoH(N_2)(PPh_3)_3}$ was identified by IR spectroscopy and elemental analysis.

Trifluorophosphine was bubbled into a stirred solution of $\mathrm{CoH(N_2)(PPh_3)_3}$ (3.970 g, 4.5 mmol) in benzene (25 ml) at room temperature for 10 min, the colour changing from red-brown to yellow-brown. The solution was concentrated to 15 ml and hexane (60 ml) added to precipitate a brownish solid which was filtered off. The crude porduct was reprecipitated from a benzene solution (30 ml) by the addition of hexane (60 ml). The solid was filtered off, washed with hexane (20 ml) and dried under high vacuum to give *hydrido(trifluorophosphine)-tris(triphenylphosphine)cobalt(I)*, $\mathrm{CoH(PF_3)(PPh_3)_3}$, as an orange crystalline powder (2.825 g, 3.0 mmol; 67% yield based on the dinitrogen complex; m.p. 147—149° dec.). IR spectrum: 3060mw, 2046vw, 1955vw, 1890vw, 1810vw, 1586w, 1480m, 1433s, 1309w, 1185w, 1157w, 1088s, 1028w, 1000w, 876w, 860w, 848m(sh), 830vs, 803vs, 797vs, 750s, 723w, 698vs, 685m(sh), 624w(sh), 609mw,545w(sh), 531s, 521vs, 512s, 497w(sh), 452w(br), 420m $\mathrm{cm^{-1}}$ (nujol mull). Mass spectrum: Only peaks assignable to triphenylphosphine at *m/e* 262, $\mathrm{PPh_3^+}$; 183, $\mathrm{P(C_6H_4)_2^+}$ and 108, $\mathrm{PPh^+}$ were observed.

The supernatant liquid from the initial precipitation of $\mathrm{CoH(PF_3)(PPh_3)_3}$ was concentrated and cooled to give yellow crystals which were filtered off. This product was washed with hexane (5 ml) and recrystallised from a benzene/hexane solution (20 ml) to give *hydridobis(trifluorophosphine)bis(triphenylphosphine)cobalt(I)*, $\mathrm{CoH(PF_3)_2(PPh_3)_2}$, (0.201 g, 0.26 mmol; 6% yield based on dinitrogen complex; m.p. 200° dec.). IR spectrum: 3062w, 1968w, 1890vw, 1810vw, 1583vw, 1480m, 1432s, 1309w, 1185w, 1158w, 1090s, 1071w, 1027w, 1000mw, 873vs, 860s(sh), 828vs, 806vs, 751ms(sh), 745s, 700vs, 695s(sh), 615vw, 537s, 520vs, 509s, 492m, 452mw, 425w(br) $\mathrm{cm^{-1}}$ (nujol mull). Mass spectrum (*m/e*, ion, rel. abundance): 760, $\mathrm{CoH(PF_3)_2(PPh_3)_2^+} = M^+$; 672, $(M-\mathrm{PF_3})^+$, 2; 585, 2; 584, $(M-2\mathrm{PF_3})^+$, 7; 583, $(M-2\,\mathrm{PF_3}-\mathrm{H})^+$, 4; 506, unknown, 2; 398, unknown, 2; 322, $(M-2\mathrm{PF_3}-\mathrm{PPh_3})^+$, 5; 321, $(M-2\mathrm{PF_3}-\mathrm{PPh_3}-\mathrm{H})^+$, 27; 320, 4; 264, 1; 263, 14; 262, $\mathrm{PPh_3^+}$, 39; 261, 5; 243, 7; 242, unknown, 6; 201, unknown, 21; 199, 13; 185, $\mathrm{PPh_2^+}$, 13; 184, 19; 183, $\mathrm{P(C_6H_4)_2^+}$, 100; 152, unknown, 14; 108, $\mathrm{PPh^+}$, 18; 107, 19; 88, $\mathrm{PF_3^+}$, 2; 78, unknown, 18; 77, 35; 69, $\mathrm{PF_2^+}$, 21; 59, $\mathrm{Co^+}$, 2.

Reaction of $CoH(PF_3)(PPh_3)_3$ with trifluorophosphine

A mixture of $\mathrm{CoH(PF_3)(PPh_3)_3}$ (0.156 g, 0.16 mmol) trifluorophosphine (0.167 g, 1.9 mmol) and benzene (2 ml) was shaken at room temperature for 6 days to give a yellow solution and precipitate. The tube was opened on the vacuum line and the volatile components were removed. The involatile residue was washed with hexane (20 ml) and dried to give a yellow crystalline powder (0.103 g, 0.14 mmol; 87% yield based on the hydridocobalt complex) identified as $CoH(PF_3)_2(PPh_3)_2$ by elemental analysis, melting point and IR spectrum.

Preparation of $CoH(PF_3)_3(PPh_3)$

Trifluorophosphine was bubbled through a stirred suspension in benzene (15 ml) of $CoCl(PPh_3)_3$ [2.193 g, 2.5 mmol; prepared as described in ref.8]. The brown suspension rapidly became green and a bright blue precipitate was slowly deposited. After 3 h hexane (30 ml) was added to precipitate more blue solid and the mixture was filtered. The residue was washed with hexane (10 ml) and dried to give $CoCl_2(PPh_3)_2$ (0.935 g, 1.4 mmol), which was identified by IR spectroscopy. The yellowish filtrate was evaporated to dryness under vacuum and extracted with hexane (50 ml). The resulting solution was stirred with a saturated solution of $CoCl_2$ in ethanol (5 ml) for ca. 1 h to remove free triphenylphosphine. The precipitate formed was filtered off and the filtrate evaporated to dryness. The greenish residue was extracted with hexane (20 ml) and concentrated slowly to give a yellowish crystalline solid identified as *hydridotris(trifluorophosphine)(triphenylphosphine)cobalt(I)*, $CoH(PF_3)_3(PPh_3)$ [2], (0.204 g, 0.35 mmol; 28% yield based on cobalt complex, assuming a bimolecular disproportionation reaction; m.p. 175—176°).

The product was further purified by sublimation at 80° and 10^{-3} mm pressure to give small, white crystals of $CoH(PF_3)_3(PPh_3)$. IR spectrum: 3076w, 3058w, 1938m, 1584vw, 1481m, 1438s, 1410w(br), 1186mw, 1150w(br), 1096s, 1071vw, 1023w(br), 1000m, 925w(sh), 911w(sh), 879vs, 850vs, 826vs, 750vs, 705m, 694s, 542w(sh), 523w(sh), 515vs, 451m, 443m, 408w cm^{-1} (nujol mull). Mass spectrum (*m/e*, ion, rel. abundance): 586, $CoH(PF_3)_3(PPh_3)^+ = M^+$, 6; 498, $(M-PF_3)^+$, 3; 479, $(M-PF_3-F)^+$, 3; 411, 18; 410, $(M-2PF_3)^+$, 100; 391, $(M-2PF_3-F)^+$, 3; 323, 6, 322, 46; 321, $(M-3PF_3-H)^+$, 100; 320, 64; 319, 3; 318, 9; 264, 3; 263, 22; 262, PPh_3^+, 100; 261, 3; 243, 30; 242, unknown, 36; 213, unknown, 6; 184, 6; 183, $P(C_6H_4)_2^+$, 51; 108, PPh^+, 9; 107, 4; 88, PF_3^+, 6; 69, PF_2^+, 9; 59, Co^+, 9.

Treatment of $CoH(PF_3)_2(PPh_3)_2$ with trifluorophosphine

$CoH(PF_3)_2(PPh_3)_2$ (0.177 g, 0.23 mmol), PF_3 (0.127 g, 1.4 mmol) and benzene (3 ml) were heated at 60° for 22 h in a sealed ampoule. The volatile components were removed in vacuo, leaving a greenish-yellow solid residue which was washed with hexane (20 ml) and dried. The IR spectrum of the powder was identical with that of $CoH(PF_3)_2(PPh_3)_2$. Evaporation of the washings gave a small amount of a yellow solid which was found by IR spectroscopy to be a mixture of $CoH(PF_3)_2(PPh_3)_2$ and a trace of $CoH(PF_3)_3(PPh_3)$.

Treatment of $CoH(PF_3)_3(PPh_3)$ with trifluorophosphine

$CoH(PF_3)_3(PPh_3)$ (0.040 g, 0.07 mmol), PF_3 (0.275 g, 3.1 mmol) and benzene (2 ml) were heated at 60° for 24 h in a sealed ampoule. The volatile components were removed and fractionated in the vacuum line, leaving an off-white residue in the tube. The IR spectrum of this solid was identical with that of $CoH(PF_3)_3(PPh_3)$. No $CoH(PF_3)_4$ was detected in the condensate.

Reaction of CoH(PF$_3$)(PPh$_3$)$_3$ with butadiene

(a) CoH(PF$_3$)(PPh$_3$)$_3$ (0.151 g, 0.16 mmol) and butadiene (5 ml) were shaken together for three days at room temperature. The cobalt complex was only very slightly soluble in the butadiene and there was no evidence of reaction. The excess butadiene was removed into the vacuum line and the orange residue examined. The spectrum showed a broadening in the ν(P—F) region, but no new compound was identifiable.

(b) The experiment was repeated on a larger scale with CoH(PF$_3$)(PPh$_3$)$_3$ (0.366 g, 0.39 mmol) and butadiene (5 ml), but this time the mixture was heated at 60° for 4 h to give a clear orange solution. The ampoule was opened and the volatile components were fractionated in the vacuum line, *anti-1-methyl-π-allyl-1,3-butadiene(trifluorophosphine)cobalt(I)*, Co(π-C$_4$H$_7$)(C$_4$H$_6$)(PF$_3$) collecting as a yellow crystalline solid at —78° (0.048 g, 0.19 mmol; 48% yield based on cobalt complex; m.p. 85—87°) (Found: C, 34.2; H, 4.7. C$_8$H$_{13}$CoF$_3$P calcd.: C, 37.5; H, 5.1%). Analytical results are poor because of the low stability of the compound at ambient temperature, but it was characterised spectroscopically. IR spectrum: *(a)* 3060w, 1480m, 1431m, 1393m, 1378w, 1365w, 1221w, 1189w, 1172w, 1068w, 1058w, 1036ms, 999w, 950ms, 918s, 840vs(br), 770w, 654vw, 610w, 579vw, 530vs, 525s(sh), 487vw, 472w, 388w cm^{-1} (nujol mull). *(b)* 949w, 921w, 838vs cm^{-1} (benzene solution). Mass spectrum (*m/e*, ion, rel. abundance): 256, Co(C$_4$H$_7$)(C$_4$H$_6$)(PF$_3$)$^+$ = M^+, 3; 237, (M—F)$^+$, 2; 202, (M—C$_4$H$_6$)$^+$, 2; 183, (M—C$_4$H$_6$—F)$^+$, 2; 169, 7; 168, (M—PF$_3$)$^+$, 85; 138, unknown, 5; 126, unknown, 7; 124, 5; 115, 5; 114, (M—C$_4$H$_6$—PF$_3$)$^+$, 100; 113, 22; 112, 12; 111, 5; 99, unknown, 3; 98, 5; 88, PF$_3^+$, 22; 86, unknown, 35; 69, PF$_2^+$, 25; 59, Co$^+$, 40.

^{19}F NMR spectrum. *(a)* at RT: weak, broad doublet at —14.080 kHz (ϕ +13.2), ^1J(PF) 1308 Hz. *(b)* at —20°: two doublets, (A) at —14.097 kHz (ϕ +13.0), ^1J(PF) 1313 Hz (strong); (B) at —14.154 kHz (ϕ +12.4), ^1J(PF) 1316 Hz (weak).

The involatile orange residue in the ampoule was largely displaced triphenylphosphine, but a red trifluorophosphine complex with bands at 847, 827 and 810 cm^{-1} in the ν(P—F) region of the IR spectrum was also present in small amounts. This is thought to be Co(π-C$_4$H$_7$)(PF$_3$)(PPh$_3$)$_2$.

(c) A mixture of CoH(PF$_3$)(PPh$_3$)$_3$ (0.108 g, 0.11 mmol) and butadiene (5 ml) was heated at 60° for a week. Fractionation of the volatile components produced no solid product at —78°, only a trace of oily liquid, identified as a mixture of 4-vinyl-1-cyclohexene (VCH) and 1,5-cyclooctadiene (COD) by ^{1}H NMR spectroscopy. An unidentified oily orange residue was left in the ampoule.

Reaction of CoH(PF$_3$)$_2$(PPh$_3$)$_2$ with butadiene

(a) A suspension of CoH(PF$_3$)$_2$(PPh$_3$)$_2$ (0.080 g, 0.11 mmol) and butadiene (5 ml) was heated in a sealed tube at 60° for 2 h, then left at room temperature for 3 days. The excess butadiene was removed on the vacuum line and no other volatile component was detected. The solid residue was identified as CoH(PF$_3$)$_2$(PPh$_3$)$_2$ by IR spectroscopy.

(b) In a similar experiment, CoH(PF$_3$)$_2$(PPh$_3$)$_2$ (0.130 g, 0.17 mmol) and butadiene (5 ml) were heated at 60° for one week. Fractionation of the volatile components gave a small amount of a colourless liquid at —78° (0.066 g, 0.61

mmol) identified as VCH by ^{1}H NMR spectroscopy. An unidentified oily yellow residue remained in the ampoule.

Reaction of $CoH(PF_3)_3(PPh_3)$ with butadiene

(a) $CoH(PF_3)_3(PPh_3)$ (0.053 g, 0.09 mmol) and butadiene (5 ml) were warmed to 60° for 5 min in a sealed ampoule to give a colourless solution which was left at room temperature for 4 days. Fractionation of the volatile components gave only unreacted butadiene while the involatile residue was found by IR spectroscopy to be unreacted $CoH(PF_3)_3(PPh_3)$.

(b) In a repeat experiment $CoH(PF_3)_3(PPh_3)$ (0.045 g, 0.08 mmol) and butadiene (5 ml) were heated at 60° for a week. The volatile components were fractionated in the vacuum line and a small amount of yellowish liquid collected at —78° (0.080 g, 0.74 mmol). This was identified as VCH by ^{1}H NMR spectroscopy. An oily yellow residue was left in the ampoule.

Reaction of $CoH(PF_3)(PPh_3)_3$ with tetrafluoroethylene

(a) $CoH(PF_3)(PPh_3)_3$ (0.190 g, 0.20 mmol), C_2F_4 (0.630 g, 7.2 mmol) and benzene (25 ml) were shaken in a large, sealed ampoule at room temperature for a day to give an orange solution. The excess C_2F_4 was removed on the vacuum line and hexane (30 ml) was added to the solution, precipitating an orange solid, identified as unreacted $CoH(PF_3)(PPh_3)_3$ by IR spectroscopy.

(b) The experiment was repeated, heating $CoH(PF_3)(PPh_3)_3$ (0.197 g, 0.21 mmol), C_2F_4 (0.126 g, 1.4 mmol) in benzene (5 ml) for 2 days at 60°. Treatment of the solution after removal of C_2F_4 with hexane (20 ml) gave a yellow precipitate. The IR spectrum showed it to be largely unreacted starting material, but a new band at 872 cm^{-1} was observed. The system was not investigated further.

Catalytic studies

All experiments were carried out under similar conditions using an Engelhard Hydrogenation Control Unit to maintain a constant hydrogen pressure of 1 atmosphere in the reaction vessel, and to record gas uptake on a chart recorder. The unit has a calibrated reservoir which holds 1.12 litres of gas at S.T.P., equivalent to 50 mmol hydrogen.

The reactions were carried out in a 200 ml glass bulb which was surrounded by a constant temperature water jacket and which could be connected to either the hydrogen supply or a vacuum pump.

A removable spoon with a ground glass seal was used to introduce the solid complex into the system. A rubber serum cap on a sidearm allowed samples of the reaction mixture to be extracted by a syringe for GLC examination which was carried out at room temperature on an Aerograph Autoprep chromatograph with a 10′ × $\frac{1}{8}$″ column, packed with 5% oxypropionitrile/chromasorb G.

In a typical reaction the dried solvent (40 ml) and freshly dried and distilled 1-octene (10 ml, 7.2 g, 64 mmol, 1.60 *M*) were introduced into the reaction vessel which was then evacuated and flushed with hydrogen 3 times. The weighed catalyst (about 0.05 g) was introduced against a flow of hydrogen and dissolved with rapid stirring. The reaction was monitored automatically for hydrogen uptake by the control unit and conversion of 1-octene to octane or 2-octene was determined by GLC analysis.

Activity of $CoH(PF_3)_2(PPh_3)_2$

(a) Under hydrogen. $CoH(PF_3)_2(PPh_3)_2$ (0.053 g, 0.07 mmol) was investigated in benzene solution at 50°, but no hydrogenation occurred. Examination of the reaction mixture by GLC analysis showed a slow isomerisation of 1-octene to 2-octene. Percentage 2-octene: 180 min, 18%; 340 min, 27%; 1350 min, 42%.

(b) Under nitrogen. The experiment was repeated with $CoH(PF_3)_2(PPh_3)_2$ (0.050 g, 0.07 mmol) under a nitrogen atmosphere. Isomerisation occurred, but at a rate slower than that under hydrogen. Percentage of 2-octene: 75 min, 10%; 130 min, 12%; 255 min, 16%; 315 min, 19%; 375 min, 20%; 1430 min, 23%.

(c) Under hydrogen with added triphenylphosphine. The experiment was repeated with $CoH(PF_3)_2(PPh_3)_2$ (0.040 g, 0.05 mmol) under hydrogen with triphenylphosphine (0.100 g, 0.38 mmol) in solution. The rate of isomerisation was greatly decreased. Percentage of 2-octene: 60 min, 1%; 180 min, 2%; 1200 min, 7%.

Activity of $CoH(PF_3)(PPh_3)_3$

$CoH(PF_3)(PPh_3)_3$ (0.047 g, 0.05 mmol) was investigated at 50° in benzene solution under hydrogen. No hydrogen uptake was observed, but there was a slow isomerisation of 1-octene to 2-octene. Percentage of 2-octene: 10 min, 5%; 30 min, 16%; 150 min, 26%; 210 min, 30%; 270 min, 32%; 330 min, 34%; 1290 min, 35%.

Activity of $CoH(PF_3)_3(PPh_3)$

$CoH(PF_3)_3(PPh_3)$ (0.030 g, 0.05 mmol) was investigated at 50° in benzene solution under hydrogen. No hydrogenation occurred, but there was isomerisation of 1-octene to 2-octene. Percentage of 2-octene: 120 min, 21%; 180 min, 26%; 240 min, 30%; 300 min, 31%; 1320 min, 44%.

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