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SYNTHESIS AND CATALYTIC ACTIVITY OF SOME π-ALLYLIC BIS(TRIFLUOROPHOSPHINE)(TRIPHENYLPHOSPHINE)COBALT(I) COMPLEXES

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Summary

The syntheses of Co(π-all)(PF_3)$_2$(PPh_3) complexes (π-all = π-allyl, *anti*-1-Me-π-allyl, *syn*-1-Me-π-allyl, 1,1-dimethyl-π-allyl, *anti*-1,2-diMe-π-allyl, *syn,syn*-1,3-diMe-π-allyl, 2Et-π-allyl, π-cyclooctenyl, h^3-π-cycloheptadienyl) are described. ^1H and ^{19}F NMR data are presented and discussed in relation to the structures of the complexes. The compound Co(π-C_5H_9)(PF_3)(PPh_3)$_2$ is also reported. Several of the π-allylic complexes are found to be active catalysts for the isomerisation of 1-octene to 2-octene under a hydrogen atmosphere.

Introduction

Compounds of the type Rh(π-all)L(PPh_3)$_2$ (where L = CO, PF_3, or Me_2NPF_2) have been prepared by several different routes [1-3]. Analogous bis(trifluorophosphine) and dicarbonyl complexes of rhodium have not been isolated, but there is spectroscopic evidence for the formation of Ir(π-C_4H_7)(CO)$_2$(PPh_3) when solutions of the monocarbonyl iridium complex are treated with carbon monoxide [3].

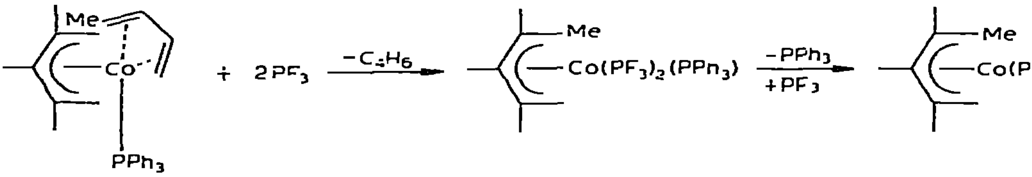
π-Allylic tricarbonylcobalt complexes readily undergo substitution by triphenylphosphine at room temperature to give stable complexes of the type Co(π-all)(CO)$_2$(PPh_3). It was found that substitution is easiest for 2-substituted allylic groups and slowest for 1-substituted groups [4]. The same compounds have also been prepared by the displacement of butadiene from Co(π-C_4H_7)(C_4H_6)(PPh_3) by carbon monoxide under mild conditions [5], while very recently Rinze has reported the *trihapto* cycloheptadienyl complex Co(C_7H_9)(CO)$_2$(PPh_3) [6].

In this paper we describe the syntheses and catalytic activity of some mixed trifluorophosphine-triphenylphosphine π-allylic complexes of cobalt(I).

Results and discussion

Preparation and properties of $Co(\pi\text{-}all)(PF_3)_2(PPh_3)$ *complexes*

We have recently described the synthesis of several tris(trifluorophosphine) complexes $Co(\pi\text{-}all)(PF_3)_3$, by complete displacement of the conjugated diene (CD) and triphenylphosphine from a complex of the type $Co(\pi\text{-}all)(CD)(PPh_3)$ by an excess of PF_3 [7]. It is possible, however, to limit the reaction to removal of the diene only, using a 2:1 molar ratio of trifluorophosphine, e.g.:



Thus treatment of *anti*-$Co(\pi\text{-}C_4H_7)(C_4H_6)(PPh_3)$ [5] in pentane solution with a deficit of PF_3 at room temperature gives *anti*-1-methyl-π-allylbis(trifluorophosphine)(triphenylphosphine)cobalt(I), $Co(\pi\text{-}C_4H_7)(PF_3)_2(PPh_3)$ (II). The product is an orange-red crystalline solid which is stable in air for short periods, but is air-sensitive in solution.

The *syn*-1-methyl (III), 1,1-dimethyl (IV) and *syn,syn*-1,3-dimethyl (VI) π-allylic complexes are similarly formed by treatment of the corresponding diene complex with a slight deficit of PF_3. The products of these reactions are usually slightly contaminated with free triphenylphosphine, since there is always at least a small amount of the tris(trifluorophosphine) complex formed.

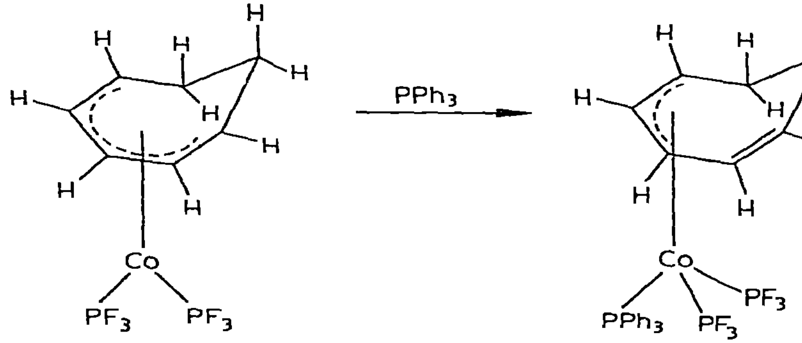
The mixed phosphine complexes of other π-allylic isomers reported here are prepared by treating solutions of the $Co(\pi\text{-}all)(PF_3)_3$ compounds [7] with a large excess of triphenylphosphine:

$$Co(\pi\text{-}all)(PF_3)_3 + PPh_3 \rightarrow Co(\pi\text{-}all)(PF_3)_2(PPh_3) + PF_3$$

The complex containing the cyclooctenyl group, $Co(\pi\text{-}C_8H_{13})(PF_3)_3$, reacts readily with triphenylphosphine at ambient temperature to give VIII. On the other hand, $Co(\pi\text{-}C_3H_5)(PF_3)_2(PPh_3)$ (I) is formed in 50% yield only after heating the reaction mixture at 60° for 4 h, while a similar preparation of the *anti*-1,2-dimethyl isomer (V) requires heating at 60° for a day.

Treatment of crude *anti*-1,2-dimethyl-π-allyltris(trifluorophosphine)cobalt(I) (containing the 2-ethyl-π-allylic isomer as impurity) with triphenylphosphine at 60° for 6 h gives almost pure $Co(2\text{-}Et\text{-}\pi\text{-}all)(PF_3)_2(PPh_3)$ (VII). It is concluded that the 2-ethyl compound is preferentially formed because of the 2-substitution of the π-allylic group, as observed for the $Co(\pi\text{-}all)(CO)_3$ complexes [4]. The ease of PF_3 displacement from the 2-ethyl isomer is further indicated by the isolation of a mono(trifluorophosphine)bis(triphenylphosphine) complex, $Co(2\text{-}Et\text{-}\pi\text{-}all)(PF_3)(PPh_3)_2$ (VIIa), from a mixture of crude 1,1-dimethyl and 2-ethyl-π-allylic bis(trifluorophosphine)mono(triphenylphosphine) complexes with excess triphenylphosphine. The product is a red, crystalline solid which is reasonably air-stable. No evidence of bis(triphenylphosphine) compounds is noted for other Co(π-all)$(PF_3)_2(PPh_3)$ complexes in the presence of a large excess of triphenylphosphine.

The cycloheptadienyl complex Co(π-C_7H_9)$(PF_3)_2$ [7] in which the organic group is behaving as a *pentahapto* ligand readily adds triphenylphosphine at room temperature to give Co(π-C_7H_9)$(PF_3)_2(PPh_3)$ (IX), in which the cycloheptadienyl ligand is now behaving as a *trihapto* ligand, viz.:



(IX)

The Co(π-all)$(PF_3)_2(PPh_3)$ products are red or orange crystalline solids which are stable in air for short periods and are readily soluble in common organic solvents. In oxygenated solvents there is decomposition to triphenylphosphine oxide and an unidentified cobalt species. The formation of triphenylphosphine oxide appears to be catalytic in the presence of an excess of triphenylphosphine.

All compounds have been characterised by elemental analysis, mass spectra, IR, ^1H NMR and ^{19}F NMR spectroscopy and are listed in Table 1.

The mixed phosphine complex of the 1,1-dimethyl-π-allylic isomer undergoes an isomerisation similar to the tris(trifluorophosphine) complex already reported [7]. Thus when a benzene solution of Co(1,1-diMe-π-all)$(PF_3)_2(PPh_3)$ (IV) in a sealed NMR tube is heated at 60° there is a rapid conversion over 3 h to the Co(*anti*-1,2-diMe-π-all)$(PF_3)_2(PPh_3)$ (V) isomer. A mechanism similar to that discussed elsewhere for the isomerisation of the M(1,1-diMe-π-all)$(PF_3)_3$ complexes (M = Co, Rh) seems likely [7-9].

The mixed trifluorophosphine-triphenylphosphine complexes readily react with an excess of PF_3 in solution at room temperature to give the volatile tris(trifluorophosphine) compounds. This route has been employed for the synthesis of the *syn*-1-methyl-π-allyl-, 2-ethyl-π-allyl- and h^3-π-cycloheptadienyl-tris(trifluorophosphine)cobalt(I) complexes as a means of eliminating organic and isomeric impurities present in the crude starting materials [7].

The π-allylic (I), *anti*- and *syn*-1-methyl-π-allylic (II) and (III), 1,1-dimethyl-π-allylic (IV) and *syn,syn*-1,3-dimethyl-π-allylic (VI) complexes are found to be active as catalysts for the isomerisation of 1-octene to 2-octene under a hydrogen atmosphere (see later).

When Co(*anti*-1-Me-π-all)$(PF_3)_2(PPh_3)$ is heated with butadiene at 60° for one week, no extensive polymerisation or insertion products are detected, but a trace amount of the butadiene dimer, vinylcyclohexene, is formed.

TABLE 1

PHYSICAL PROPERTIES OF $Co(\pi\text{-all})(PF_3)_2(PPh_3)$ COMPLEXES

Compound	M.p.[a] (°C)	Mol. wt. found[b] (calcd.)	Elemental analysis found (calcd.) (%)	
			C	H
$Co(\pi\text{-}C_3H_5)(PF_3)_2(PPh_3)$ (π-allyl) (I)	145-147	538 (538)	46.8 (46.8)	3.8 (3.7)
$Co(\pi\text{-}C_4H_7)(PF_3)_2(PPh_3)$ (*anti*-1-Me-π-allyl) (II)	114-115	552 (552)	47.0 (47.8)	4.1 (4.0)
$Co(\pi\text{-}C_4H_7)(PF_3)_2(PPh_3)$ (*syn*-1-Me-π-allyl) (III)	125-126	552 (552)	47.9 (47.8)	4.0 (4.0)
$Co(\pi\text{-}C_5H_9)(PF_3)_2(PPh_3)$ (1,1-diMe-π-allyl) (IV)	153-157	566 (566)	48.7 (48.8)	4.4 (4.2)
$Co(\pi\text{-}C_5H_9)(PF_3)_2(PPh_3)$ (*anti*-1,2-diMe-π-allyl) (V)	150-152	566 (566)	48.8 (48.8)	4.3 (4.2)
$Co(\pi\text{-}C_5H_9)(PF_3)_2(PPh_3)$ (*syn,syn*-1,3-diMe-π-allyl) (VI)	114-115	566 (566)	48.6 (48.8)	4.3 (4.2)
$Co(\pi\text{-}C_5H_9)(PF_3)_2(PPh_3)$ (2-Et-π-allyl) (VII)	96-98	566 (566)	49.1 (48.8)	4.4 (4.2)
$Co(\pi\text{-}C_5H_9)(PF_3)(PPh_3)_2$ (2-Et-π-allyl) (VIIa)	145-152	473 (740—PPh_3)	68.5 (68.5)	5.4 (5.3)
$Co(\pi\text{-}C_8H_{13})(PF_3)_2(PPh_3)$ (π-cyclooctenyl) (VIII)	137-139	518 (606—PF_3)	51.7 (51.5)	4.5 (4.6)
$Co(\pi\text{-}C_7H_9)(PF_3)_2(PPh_3)$ (h^3-π-cycloheptadienyl) (IX)	116-118	328 (590—PPh_3)	50.9 (50.85)	4.3 (4.1)

[a] Under nitrogen. [b] Mass spectroscopy.

Spectroscopic studies

Mass spectra of Co(π-all)(PF$_3$)$_2$(PPh$_3$) complexes

Substitution of triphenylphosphine for trifluorophosphine in the π-allylic complexes greatly reduces their volatility, but it is still possible to observe a weak molecular ion in the mass spectra of the non-cyclic compounds (see Table 1). Subsequent loss of either phosphine ligand or the allylic group gives a stepwise breakdown to cobalt metal. The presence of a second triphenylphosphine ligand reduces the volatility of the π-allylic compounds still further, and no molecular ion is observed in the mass spectrum of $Co(2\text{-}Et\text{-}\pi\text{-}all)(PF_3)(PPh_3)_2$ (VIIa), the highest peak being due to $Co(2\text{-}Et\text{-}\pi\text{-}all)(PF_3(PPh_3)^+$. Similarly, the cyclic π-allylic mixed phosphine complexes are not volatile enough to show molecular ions. The π-cyclooctenyl complex shows a peak due to $Co(\pi\text{-}C_8H_{13})\text{-}(PF_3)(PPh_3)^+$ at 110°, but at 125° the molecule undergoes a rearrangement to give the mixed phosphine hydride, $CoH(PF_3)_2(PPh_3)_2$, by elimination of the cyclooctadiene and combination with free triphenylphosphine:

$$Co(\pi\text{-}C_8H_{13})(PF_3)_2(PPh_3) \rightarrow C_8H_{12} + [CoH(PF_3)_2(PPh_3)] \xrightarrow{+PPh_3} CoH(PF_3)_2(PPh_3)_2$$

The mass spectrum of the cycloheptadienyl complex exhibits a peak assigned to $Co(\pi\text{-}C_7H_9)(PF_3)_2^+$, but even at 108° the molecule undergoes rearrangement to give the mixed phosphine hydride $CoH(PF_3)_3(PPh_3)$ by elimination of cycloheptatriene and combination with free trifluorophosphine in the spectrometer:

$$Co(\pi\text{-}C_7H_9)(PF_3)_2(PPh_3) \rightarrow C_7H_8 + [CoH(PF_3)_2(PPh_3)] \xrightarrow{+PF_3} CoH(PF_3)_3(PPh_3)$$

The reason for the formation of a different hydride in each case may be simply an indication of differing free phosphine concentrations for each compound.

Infrared spectra of Co(π-all)(PF$_3$)$_2$(PPh$_3$) complexes

The infrared spectra of the mixed phosphine π-allylic complexes $Co(\pi\text{-}all)\text{-}(PF_3)_2(PPh_3)$ show several very strong bands between 880 and 790 cm^{-1} in the P—F stretching region, consistent with the presence of two PF_3 ligands. Further strong bands at 540-520 cm^{-1} are assigned to P—F bending vibrations. The positions of the triphenylphosphine absorptions are similar to those of the free ligand. The intensity and sharpness of these bands is a good indication of the purity of the mixed phosphine complexes, since small amounts of free triphenylphosphine cause noticeable broadening of the absorptions, especially those at 750 and 700 cm^{-1}.

The spectrum of $Co(2\text{-}Et\text{-}\pi\text{-}all)(PF_3)(PPh_3)_2$ shows a much narrower absorption band in the P—F stretching region, with strong bands at 826, 794 and 783 cm^{-1}, while the triphenylphosphine bands are relatively stronger.

Bands due to the π-allylic group tend to be very weak compared with other absorptions, but are detectable and assignable for some complexes. A strong band at 1071 cm^{-1} in the spectrum of $Co(1,1\text{-}diMe\text{-}\pi\text{-}all)(PF_3)_2(PPh_3)$ (IV) is assigned to a carbon skeletal vibration of the (Me_2C—) group, since

TABLE 2

^1H NMR DATA FOR THE ALLYLIC GROUPS OF Co(π-all)$(PF_3)_2(PPh_3)$ COMPLEXES
CHEMICAL SHIFTS ARE IN PPM RELATIVE TO THE INTERNAL BENZENE STANDARD. COUPLING CONSTANTS J ARE IN Hz

Compound	H_A	H_B	H_C	H_D	H_E	Me_a	Me_s	Me_c
Co(π-C_3H_5)$(PF_3)_2(PPh_3)$ (I)	5.32 q $J(H_AH_C)$ = 11.0 $J(H_AP)$ = 11.0	4.69 q $J(H_BH_C)$ = 5.2 $J(H_BP)$ = 5.2	2.67m					
Co(π-C_4H_7)$(PF_3)_2(PPh_3)$ (II) (*anti*-1-Me)	4.26-4.05m		2.84m	3.42m		6.02d $J(Me_aH_D)$ = 7.3 $J(Me_aP)$ = 7.3 $J(Me_aP')$ = 4.5		
Co(π-C_4H_7)$(PF_3)_2(PPh_3)$ (III) (*syn*-1-Me)	5.52m	4.84m	2.75m		4.60m		6.69dt $J(Me_sH_E)$ = 6.0 $J(Me_sP)$ = 3.0	
Co(π-C_5H_9)$(PF_3)_2(PPh_3)$ (IV) (1,1-diMe)	4.90m		3.26m			5.00dd $J(Me_aP)$ = 7.0 $J(Me_aP')$ = 4.0	5.63t $J(Me_sP)$ = 3.8	
Co(π-C_5H_9)$(PF_3)_2(PPh_3)$ (V) (*anti*-1,2-diMe)	4.40m			3.64m		5.06d $J(Me_aH_D)$ = 7.0 $J(Me_aP)$ = 7.0 $J(Me_aP')$ = 4.3		5.73dd $J(Me_cP)$ = 7.0 $J(Me_cP')$ = 3.8
Co(π-C_5H_9)$(PF_3)_2(PPh_3)$ (VI) (*syn,syn*-1,3-diMe)			2.80m		5.00m		5.82m	
						CH_2	Me_{Et}	
Co(π-C_5H_9)$(PF_3)_2(PPh_3)$ (VII) (2-Et)	5.63d $J(H_AP)$ = 8.2 $J(H_AP')$ = 6.0	4.42q $J(H_BP)$ = 3.6				5.23q $J(CH_2—Me_a)$ = 7.4	6.16t $J(CH_2—Me_{Et})$ = 7.4	
Co(π-C_5H_9)$(PF_3)(PPh_3)_2$ (VIIa) (2-Et)	5.79s	4.53d $J(H_BP)$ = 3.6				5.22q $J(CH_2—Me_{Et})$ = 7.4	6.10t $J(CH_2—Me_{Et})$ = 7.4	

this does not occur in the spectra of the other allylic complexes. A similar band has been noted in the spectra of Co(1,1-diMe-π-all)$(CO)_3$ and Co(1,1,2-triMe-π-all)$(CO)_3$ which also contain terminal (Me_2C—) groups [10].

The regions where other bands assignable to vibrations of the π-allylic groups might be expected are obscured by strong absorptions of the phosphine ligands. The P—F stretching bands prevent observation of C—Me stretching vibrations at 900-800 cm^{-1} and the C—C—C vibration of the π-allylic skeleton at 550-500 cm^{-1} is also covered by PPh_3 and PF_3 bands [11, 12].

^{1}H NMR spectra of Co(π-all)$(PF_3)_2(PPh_3)$

The ^{1}H NMR spectra of the mixed phosphine complexes are more complicated than those we described previously for the tris(trifluorophosphine) compounds [7], because of different spin—spin coupling constants for the various phosphorus nuclei.

The chemical shifts of the signals for each type of π-allylic proton are similar to those in the Co(π-all)$(PF_3)_3$ complexes and the same notation is used [7]. The main characteristics of the spectra are listed in Table 2 and the details are discussed below.

Co(π-C_3H_5)$(PF_3)_2(PPh_3)$ (I). The central proton, H_C, gives a broad multiplet arising from coupling to both sets of *syn*- and *anti*-protons and to some or all of the phosphorus nuclei. The *syn*-protons, H_B, give rise to a quartet pattern from coupling to H_C [$J(H_BH_C)$ = 5.2 Hz] and to two of the phosphorus atoms [$J(H_BP)$ = 5.2 Hz]. Similarly, the *anti*-protons, H_A, give a quartet at 5.32 [$J(H_AH_C) = J(H_AP)$ = 11.0 Hz].

As in the case of the related tris(trifluorophosphine)cobalt complex Co(π-all)$(PF_3)_3$, no evidence of any intermolecular phosphine exchange process was observed.

Co(anti-1-Me-π-all)$(PF_3)_2(PPh_3)$ (II). The resonance of proton H_C appears as a multiplet from spin coupling to *syn*- and *anti*-protons, and presumably also to phosphorus nuclei. The chemical shift of the *syn* proton, H_D, adjacent to the methyl group is moved downfield to give a broad multiplet (coupling to H_C, the group Me_a and phosphorus nuclei). The remaining protons, H_A and H_B, give complex, overlapping multiplets. The signal of the *anti*-methyl group, Me_a, occurs as a doublet of triplets from coupling to the adjacent proton, H_D, and two phosphorus atoms. By analogy with the values of $J(Me_aH_D)$ noted for the Co(π-all)$(PF_3)_3$ complexes it is assumed that $J(Me_aH_D)$ = 7.3 Hz and that the phosphorus couplings are different [$J(Me_aP)$ = 7.3 Hz, $J(Me_aP')$ = 4.5 Hz].

Co(syn-1-Me-π-all)$(PF_3)_2(PPh_3)$ (III). A broad multiplet at lowest field is assigned to H_C. The *anti*-proton H_E, adjacent to the methyl group, Me_s, appears as a broad multiplet due to coupling to H_C, Me_s and the phosphine ligands. This signal overlaps that of the H_B *syn* proton which is a narrow multiplet from coupling to phosphorus nuclei and H_C. The other *anti*-proton, H_A, gives a signal which appears to be a triplet [$J(H_AH_C) = J(H_AP)$ = 12.0 Hz], but which is obscured by the resonance of the *syn*-methyl group. The latter appears to be a doublet [$J(Me_sH_E)$ = 6.0 Hz] of triplets [$J(Me_sP)$ = 3.0 Hz].

Co(1,1-diMe-π-all)$(PF_3)_2(PPh_3)$ (IV). The central proton, H_C, gives a multiplet at higher field than usually observed. The terminal protons, H_A and H_B, give a complex overlapping multiplet. The *syn*-methyl group, Me_s, appears as a triplet

[$J(\mathrm{Me_sP})$ = 3.8 Hz] while the *anti*-methyl, Me$_a$, gives a doublet of doublets [$J(\mathrm{Me_aP})$ = 7.0 Hz, $J(\mathrm{Me_aP'})$ = 4.0 Hz].

The spectrum is distorted by the presence of a small amount of the *anti*-1,2-dimethyl-π-allylic isomer.

Co(anti-1,2-diMe-π-all)(PF$_3$)$_2$(PPh$_3$) (V). Substitution in the 2-position of the allylic group is indicated by the lack of an H$_C$ signal at about 3.00. A broad multiplet is assigned to H$_D$, coupling to Me$_a$ and the phosphine ligands. The geminal protons, H$_A$ and H$_B$, give a complex overlapping multiplet which is very similar to that observed for the *anti*-1-methyl-π-allylic isomer (II). The 2-methyl group, Me$_c$, appears as a doublet of doublets from coupling to the phosphorus nuclei [$J(\mathrm{Me_cP})$ = 7.0 Hz, $J(\mathrm{Me_cP'})$ = 3.8 Hz]. The *anti*-methyl group, Me$_a$, gives a signal which is a doublet of triplets from coupling to H$_D$ [$J(\mathrm{Me_aH_D})$ = 7.0 Hz] and two phosphorus nuclei [$J(\mathrm{Me_aP})$ = 7.0 Hz, $J(\mathrm{Me_aP'})$ = 4.3 Hz]. Weak signals due to the 2-ethyl-π-allylic isomer are also present in the spectrum.

Co(syn,syn-1,3-diMe-π-all)(PF$_3$)$_2$(PPh$_3$) (VI). The spectrum of the *syn,syn*-1,3-dimethyl-π-allylic isomer shows broad signals due to the presence of paramagnetic impurities which could not be eliminated.

The central proton, H$_C$, gives a multiplet at lowest field while the resonanc of the *anti*-protons, H$_E$, appears at 5.00. The methyl groups, Me$_s$, give a strong, narrow multiplet at 5.82.

Co(2-Et-π-all)(PF$_3$)$_2$(PPh$_3$) (VII). The *syn*-protons, H$_B$, give a quartet coupling equally to all three phosphorus nuclei [$J(\mathrm{H_BP})$ = 3.6 Hz], while the *anti*-protons, H$_A$, couple to different extents to give a doublet [$J(\mathrm{H_AP'})$ = 6.0 Hz] of triplets [$J(\mathrm{H_AP})$ = 8.2 Hz]. The ethyl group gives rise to the expected two resonances, the methylene group appearing as a quartet [$J(\mathrm{CH_2{-}Me_{Et}})$ = 7.4 Hz] and the methyl group, Me$_{Et}$, as a triplet. No phosphorus coupling to the ethyl group is observed.

A trace of Co(*anti*-1,2-diMe-π-all)(PF$_3$)$_2$(PPh$_3$) (V) was present as impurity

Co(2-Et-π-all)(PF$_3$)(PPh$_3$)$_2$ (VIIa). The spectrum of the mono(trifluorophosphine) complex is similar to VII, but is rather simpler in appearance. The *syn*-protons, H$_B$, give rise to a doublet [$J(\mathrm{H_BP})$ = 3.6 Hz] while the *anti*-protons, H$_A$, give a broad singlet. The ethyl resonances show the usual quartet and triplet patterns [$J(\mathrm{CH_2{-}Me_{Et}})$ = 7.4 Hz].

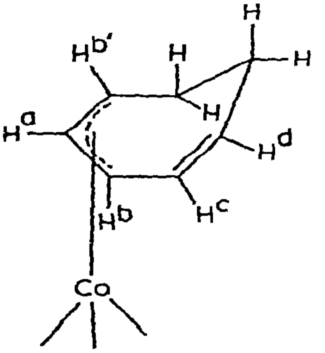


Fig. 1. Numbering of protons in the C$_7$H$_9$ ring of IX.

$Co(\pi$-$C_8H_{13})(PF_3)_2(PPh_3)$ (VIII). The multiplet at 2.64 (1H) is assigned to the central proton of the π-allylic section of the cyclooctenyl ring, and the multiplet at 3.48 (2H) to the *syn*-protons. Overlapping multiplets at 4.70 (2H), 5.20 (2H) and 5.85 (6H) are assigned to the remaining ring protons.

$Co(\pi$-$C_7H_9)(PF_3)_2(PPh_3)$ (IX). The spectrum of the cycloheptadienyl complex shows the expected resonances for the C_7H_9 moiety behaving as a *trihapto* ligand. The broad resonances of protons adjacent to an uncoordinated double bond, H^c and H^d, occur at 1.00 [(1H) and 1.83 (1H)]. The allylic protons H^a and $H^{b,b'}$ give overlapping multiplets at 2.6 and 2.9 while broad multiplets between 4.6 and 6.0 are assigned to the aliphatic ring protons (see Fig. 1). A very similar spectrum has been reported very recently by Rinze for the related $Co(C_7H_9)(CO)_2(PPh_3)$ complex [6].

^{19}F *NMR spectra of* $Co(\pi$-$all)(PF_3)_2(PPh_3)$ *complexes*

The ^{19}F NMR spectra of the mixed phosphine π-allylic complexes fall into two distinct classes: (a) those containing an unsubstituted or symmetrically substituted allylic group, and (b) those containing an asymmetric allylic group. For convenience the two types will be discussed separately. Chemical shift values and coupling constants are listed in Table 3.

(a) Symmetric type. This group includes the simple π-allyl complex, $Co(\pi$-$C_3H_5)(PF_3)_2(PPh_3)$ (I), the *syn,syn*-1,3-dimethyl-π-allyl-(VI), 2-ethyl-π-allyl-(VII) and π-cyclooctenyl-bis(trifluorophosphine)mono(triphenylphosphine)-cobalt(I) complexes. All give similar ^{19}F NMR spectra to that shown below for I (Fig. 2). These are typical in appearance for $[AX_3]_2$ spin systems [13] (X = F; A = P) the basic spectrum being further complicated by the presence of the triphenylphosphine ligand.

The basic pattern is a strong doublet of separation $\nu = |^1J(PF) + {}^3J(PF')|$ exhibiting weak fine-structure around each of the main lines. The lines in the spectra appear as doublets resulting from coupling to the phosphorus of the triphenylphosphine ligand, $^3J(P''F)$ lying between 8.0 and 13.0 Hz, depending on the system. The ^{19}F NMR spectrum shows no evidence for any intermolecular phosphine exchange between −30° and room temperature in agreement with the observations from the ^{1}H NMR spectrum.

The spectrum of the mono(trifluorophosphine) complex, $Co(2$-Et-π-$all)(PF_3)(PPh_3)_2$ (VII), shows two broad singlets at a separation of 1308 Hz equal to $^1J(PF)$, with a chemical shift of $\phi = +7.4$ ppm (relative to $CFCl_3$).

(b) Asymmetric Type. The spectra of the *syn*- and *anti*-1-methyl-π-allyl (II) and (III) 1,1-dimethyl-π-allyl (IV), *anti*-1,2-dimethyl-π-allyl (V) and h^3-π-cycloheptadienyl (IX) mixed phosphine cobalt(I) complexes are very different from those with a symmetric π-allylic group and give rise to much more complex patterns of lines. These spectra will be discussed in more detail in a later publication.

The observation of different ^{19}F NMR spectra for complexes with symmetric and asymmetric π-allylic groups indicates that there is no process occurring which would lead to an averaging of the position of the allylic group with respect to the phosphine ligands. A rigid trigonal-bipyramidal structure cannot rationalise the ^{19}F NMR observations, since there should be no difference between complexes with symmetric or asymmetric π-allylic groups (Fig. 3).

TABLE 8

^{19}F NMR DATA FOR Co(π-all)(PF$_3$)$_2$(PPh$_3$) COMPLEXES. COUPLING CONSTANTS *J* ARE IN Hz

Compound	ν	$\nu = {}^1J(PF) + {}^3J(PF')$	$^4J(FF')$	$^3J(P''F)$	ϕ = ppm (rel. CFCl$_3$)^b
(a) Symmetric type					
Co(π-C_3H_5)(PF$_3$)$_2$(PPh$_3$) (I)		1278d		8.0	+12.0
Co(π-C_5H_9)(PF$_3$)$_2$(PPh$_3$) (*syn,syn*-1,3-diMe) (VI)		1277d		13.0	+11.6
Co(π-C_5H_9)(PF$_3$)$_2$(PPh$_3$) (2-Et) (VII)		1282d		13.0	+11.6
Co(π-C_8H_{13})(PF$_3$)$_2$(PPh$_3$) (VIII)		1281d		12.0	+12.0
(b) Asymmetric type					
Co(π-C_4H_7)(PF$_3$)$_2$(PPh$_3$) (*anti*-1-Me) (II)	1288dq		7.0	9.0	+13.4
	1265dq		7.0	9.0	+11.6
Co(π-C_4H_7)(PF$_3$)$_2$(PPh$_3$) (*syn*-1-Me) (III)	1287qn		8.5	8.5	+13.45
	1268qn		8.5	8.5	+11.0
Co(π-C_5H_9)(PF$_3$)$_2$(PPh$_3$) (1,1-diMe) (IV)	1323m		^{c}	^{c}	+13.9
	1304d (*J* = 47.0)sext		6.0	12.0	+11.8
Co(π-C_5H_9)(PF$_3$)$_2$(PPh$_3$) (*anti*-1,2-diMe) (V)	1290dq		7.0	9.0	+13.3
	1274dq		7.0	10.0	+12.0
Co(π-C_7H_9)(PF$_3$)$_2$(PPh$_3$) (IX)	1297sext		6.0	11.0	+16.3
	1287sext		6.0	12.0	+14.7

[a] Recorded in benzene solution with C_6F_6 as internal standard. [b] Calculated assuming $\phi(C_6F_6)$ = +162.8 ppm. [c] Not measurable.

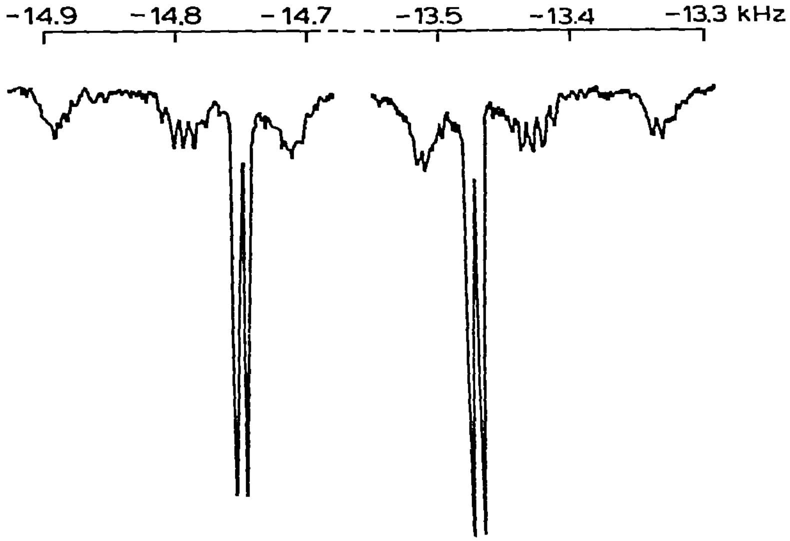


Fig. 2. ^{19}F NMR spectrum of Co(π-C_3H_5)(PF_3)$_2$(PPh_3).

Trifluorophosphine ligands will either be equivalent (if the molecule has a plane of symmetry, not passing through the PF_3 groups) or inequivalent (if there is no such plane of symmetry) for both types of π-allylic group, depending on the orientation of the allylic group.

Pseudo-rotation of phosphine ligands within trigonal bipyramids in Fig. 3 should be much less favoured, since the energy differences between the proposed intermediates would be expected to increase, the structures with adjacent triphenylphosphine and π-allylic substituents being least favoured.

The tetrahedral structures illustrated in Fig. 4 with the trifluorophosphine ligands arranged symmetrically can account for the different ^{19}F NMR spectra of the two types of complex. With a symmetric π-allylic group both PF_3 ligands will be equivalent, giving an $[AX_3]_3$ spectrum. Assymmetric substitution of the π-allylic group makes the PF_3 ligands inequivalent, giving an $[ABX_3Y_3]$ system, where A and B are phosphorus nuclei and X and Y are fluorine nuclei.

It seems likely that the bulky triphenylphosphine ligand would make rotation of a π-allylic group occupying one site of a tetrahedral molecule very difficult.

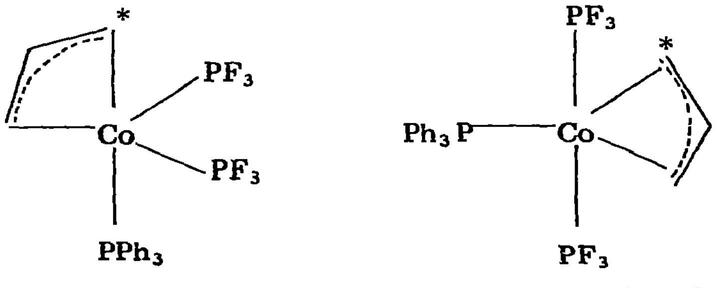


Fig. 3. Possible trigonal-bipyramidal structures of Co(π-all)(PF_3)$_2$(PPh_3).

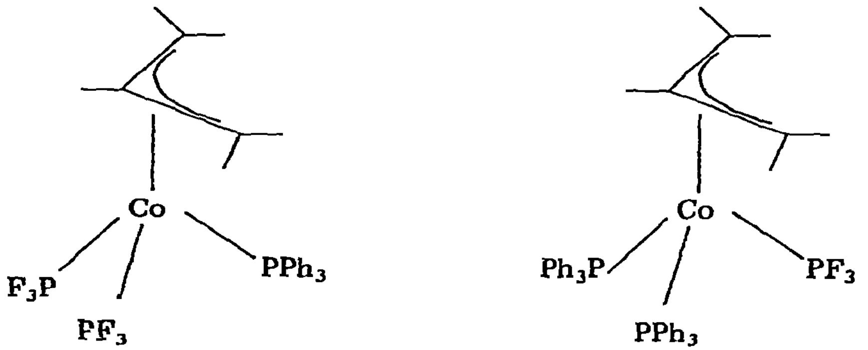


Fig. 4. Possible structures of $Co(\pi\text{-all})(PF_3)_2(PPh_3)$ and $Co(\pi\text{-all})(PF_3)(PPh_3)_2$ complexes.

Catalytic activity of $Co(\pi\text{-all})(PF_3)_2(PPh_3)$

Hexane solutions of the complexes $Co(\pi\text{-all})(PF_3)_2(PPh_3)$ (where π-all is $\pi\text{-}C_3H_5$, *syn*-1-Me-π-all, *anti*-1-Me-π-all, 1,1-diMe-π-all or *syn,syn*-1,3-diMe-π-all) do not catalyse the hydrogenation of 1-octene at 50° and one atmosphere hydrogen pressure, but a slow isomerisation of 1-octene to a 50/50 mixture of *cis*- and *trans*-2-octene is observed, with between 60 and 80% conversion in one day. Under a nitrogen atmosphere the solutions are completely inert, but are rapidly activated by changing to a hydrogen atmosphere. Addition of free triphenylphosphine greatly decreases the rate of isomerisation (Fig. 5).

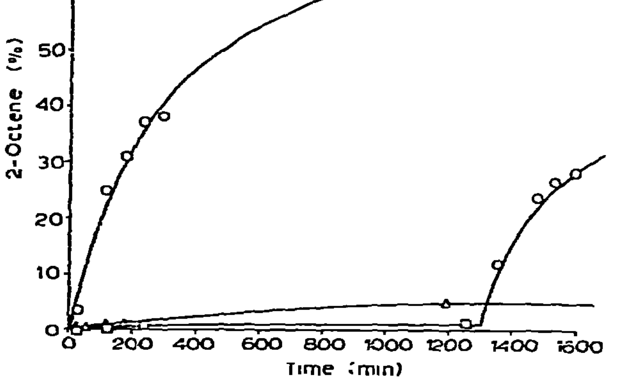


Fig. 5. Isomerisation of 1-octene with *anti*-$Co(\pi\text{-}C_4H_7)(PF_3)_2(PPh_3)$ at 50° in hexane under various conditions.

The similar carbonyl complexes, $Co(\pi-C_4H_7)(CO)_2(PR_3)$ are thought to react to give carbonyl bridged trimers, $[Co(CO)_2(PR_3)]_3$, which yield $CoH(CO)_2(PR_3)$ under hydrogenation conditions [14]. The cluster compounds $[Co(CO)_2PR_3]_3$ (R = Ph, or n-Bu) have been found to be active hydrogenation catalysts at 70°/15 atm hydrogen pressure. Olefin isomerisation is a competing reaction of similar rate [14, 15]. Analogous bridged cluster compounds would not be possible for the trifluorophosphine complexes, and treatment of a solution of *anti*-$Co(\pi-C_4H_7)(PF_3)_2(PPh_3)$ with hydrogen does not give any isolable new product, only a slow decomposition. This reaction is inhibited by free triphenylphosphine and unchanged starting materials are recovered.

On the basis of these observations, it is tentatively proposed that the active catalyst is $CoH(PF_3)_2(PPh_3)$, formed by hydrogenation of the π-allylic complexes. The initial step would be dissociation of a triphenylphosphine ligand, followed by oxidative addition of molecular hydrogen. This process would be inhibited by free triphenylphosphine.

The slight variation in catalytic activity between the different π-allylic isomers (and even different samples of the same isomer) is probably an indication of the presence of varying small amounts of free triphenylphosphine impurity.

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 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 obtained in Nujol mulls between KBr plates using a Perkin Elmer 457 spectrometer. Elemental analyses were carried out by Mrs. A.E. Olney of this department. Mass spectra were recorded on an AEI MS9 spectrometer.

Catalytic studies were carried out as described previously [16], using an Engelhard Hydrogenation Control Unit. Samples of the reaction mixtures were analysed by GLC using an Aerograph Autoprep chromatograph. $Co(\pi-C_7H_9)(PF_3)_2$ and the $Co(\pi\text{-all})(PF_3)_3$ complexes were prepared as described elsewhere [7], while *anti*-$Co(\pi-C_4H_7)(C_4H_6)(PPh_3)$ and *syn*-$Co(\pi-C_4H_7)(C_4H_6)(PPh_3)$ were obtained by literature methods [5 and 17].

Preparation of $Co(\pi-(C_3H_5)(PF_3)_2(PPh_3)$ *(I)*

$Co(\pi-C_3H_5)(PF_3)_3$ (0.111 g, 0.30 mmol), triphenylphosphine (0.079 g, 0.30 mmol) and diethyl ether (2 ml) were heated at 60° in a sealed ampoule for 4 h, the yellow solution slowly becoming orange. The tube was opened on the vacuum line and the volatile components were removed, leaving an involatile yellow crystalline solid. This was extracted with n-hexane (15 ml) and the resulting solution was treated with a saturated solution of cobalt chloride in absolute ethanol (1 ml) to remove excess triphenylphosphine. The blue precipitate was filtered off and the filtrate evaporated to dryness under high vacuum. The greenish solid residue was extracted with n-hexane (10 ml) and filtered to give an orange solution which was slowly concentrated to give the orange crystalline product, π-allylbis(trifluorophosphine)(triphenylphosphine)cobalt(I), $Co(\pi\text{-}C_3H_5)(PF_3)_2(PPh_3)$ (0.086 g, 0.16 mmol; 53% yield based on cobalt complex; m.p. 145-147°). IR spectrum: 3060w, 1480m, 1437s, 1187w, 1093s, 1025w, 1000w, 970w, 921w, 870vs, 846s(sh), 830vs(sh), 818vs, 798vs(sh), 750s, 699vs, 690m(sh), 590w, 540s, 522vs(br), 456w(sh), 446m cm^{-1} (Nujol mull).

A small amount of unreacted $Co(\pi\text{-}C_3H_5)(PF_3)_3$ (identified by IR spectroscopy) was recovered.

Preparation of Co(anti-1-Me-π-all)(PF₃)₂(PPh₃) (II)

anti-$Co(\pi\text{-}C_4H_7)(C_4H_6)(PPh_3)$ (0.887 g, 2.1 mmol), PF_3 (0.318 g, 3.6 mmol) and n-pentane (5 ml) were shaken in a sealed ampoule at room temperature for one week to give an orange solution. The tube was opened on the vacuum line and the volatile components were removed, giving a small amount of Co(*anti*-1-Me-π-all)$(PF_3)_3$ [7] at −78° (0.026 g, 0.07 mmol; 2% yield based on cobalt complex) and a trace of excess PF_3 at −196°.

The orange residue in the ampoule was extracted with hexane (30 ml) and the solution was stirred with a saturated solution of $CoCl_2$ in absolute ethanol (5 ml). The resulting blue precipitate was filtered off and the filtrate evaporated to dryness. The residue was extracted with hexane (20 ml) to yield an orange solution which gave a crystalline precipitate on concentration under high vacuum. The crude product was filtered off and recrystallised from hexane (20 ml) to give orange crystals of *anti*-1-methyl-π-allylbis(trifluorophosphine)-(triphenylphosphine)cobalt(I), $Co(\pi\text{-}C_4H_7)(PF_3)_2(PPh_3)$, [0.797 g, 1.5 mmol; 70% yield based on $Co(\pi\text{-}C_4H_7)(C_4H_6)(PPh_3)$; m.p. 114-115°]. IR spectrum: 3060w, 1480m, 1436s, 1182w, 1091s, 1070vw, 1038w, 1030w, 1000w, 898m, 880m(sh), 870s(sh), 860vs, 850s(sh), 810vs(br), 755m(sh), 748s, 696s, 690m(sh), 539s, 524vs, 514vs, 505s(sh), 454w(sh), 440m cm^{-1} (Nujol mull).

Preparation of Co(syn-1-Me-π-all)(PF₃)₂(PPh₃) (III)

syn-$Co(\pi\text{-}C_4H_7)(C_4H_6)(PPh_3)$ was prepared according to the literature [7], by passing butadiene into a suspension of $CoH(N_2)(PPh_3)_3$ [5.398 g, 6.2 mmol; stirred in diethyl ether (70 ml) at 0°], to give a dark brown-red solution. Most of the displaced triphenylphosphine was removed by repeated recrystallisation from hexane solutions and the supernatant liquid was evaporated to dryness under high vacuum.

The resulting brown oil was dissolved in n-pentane (10 ml) and treated with PF_3 (0.795 g, 9.0 mmol) in two sealed ampoules at room temperature for three days. The tubes were opened on the vacuum line and the volatile components removed and fractionated. A very small amount of Co(*syn*-1-Me-π-all)$(PF_3)_3$ collected at −78° and was identified by its IR spectrum.

The oily, red solid residues in the ampoules were extracted with hexane (40 ml) and the solutions filtered. The combined filtrates were concentrated under vacuum to give a crystalline precipitate. This was filtered off and recrystallised from hexane to give *syn*-1-methyl-π-allylbis(trifluorophosphine)(triphenylphosphine)cobalt(I), $Co(\pi\text{-}C_4H_7)(PF_3)_2(PPh_3)$, as red-orange crystals (1.751 g, 3.2 mmol; 52% yield based on the dinitrogen complex; m.p. 125-126°. IR spectrum: 3060w, 1480m, 1436s, 1182w, 1091s, 1031w, 1000w, 898w, 860vs, 849s, 808vs(br), 791vs(sh), 749s, 745w(sh), 700s, 687w, 580w, 540s, 522vs, 515s(sh), 443m cm^{-1} (Nujol mull).

Preparation of Co(1,1-diMe-π-all)(PF$_3$)$_2$(PPh$_3$) (IV)

The isoprene complex Co(π-C_5H_9)(C_5H_8)(PPh_3) was prepared as outlined in reference 5 from cobalt(II) chloride (2.089 g, 16 mmol), isoprene and triphenylphosphine. The crude product (a red-brown oil) was dissolved in n-pentane (10 ml) and sealed in an ampoule with PF_3 (0.340 g, 3.9 mmol) for three days at room temperature. The tube was opened on the vacuum line and the volatile components were removed. Only a small amount of Co(1,1-diMe-π-all)(PF_3)$_3$ collected in the —78° trap.

The oily, red solid left in the ampoule was extracted with hexane (25 ml) and the resulting solution was treated with a saturated solution of $CoCl_2$ in ethanol. The precipitate formed was filtered off and the filtrate evaporated to dryness under vacuum. The residue was extracted with hexane (25 ml) and the solution concentrated slowly to give a crystalline precipitate which was filtered off and recrystallised from hexane (20 ml) to give the product, 1,1-dimethyl-π-allylbis(trifluorophosphine)(triphenylphosphine)cobalt(I), Co(π-C_5H_9)(PF_3)$_2$-(PPh_3), as red-brown crystals (0.747 g, 1.3 mmol; 8% yield based on $CoCl_2$; m.p. 153-157°). IR spectrum: 3060w, 1481m, 1437s, 1188w. 1091s, 1072s, 1030w, 1002w, 920w, 869s(sh), 860vs, 850s, 840s, 819s(sh), 803vs, 795vs(sh), 750m, 741s, 700s, 687w(sh), 600w, 539s, 526vs(br), 502m, 459w, 446w(sh), 440s, 432w, 398w cm^{-1} (Nujol mull).

Preparation of Co(anti-1,2-diMe-π-all)(PF$_3$)$_2$(PPh$_3$) (V)

Co(*anti*-1,2-diMe-π-all)(PF_3)$_3$ (0.176 g, 0.45 mmol) [7], triphenylphosphine (0.299 g, 1.2 mmol) and diethyl ether (3 ml) were heated at 60° in a sealed ampoule for 25 h. The tube was opened on the vacuum line and the volatile components were removed, unreacted Co(π-C_5H_9)(PF_3)$_3$ collecting in the —78° trap (0.093 g, 0.24 mmol).

The involatile residue was extracted with hexane (10 ml) and the solution was treated with a saturated solution of $CoCl_2$ in ethanol (1 ml). The blue precipitate formed was filtered off and the filtrate evaporated to dryness. The solid residue was extracted with hexane (5 ml) and the resulting solution was slowly concentrated under vacuum to give the product, *anti*-1,2-dimethyl-π-allylbis(trifluorophosphine)(triphenylphosphine)cobalt(I), Co(π-C_5H_9)(PF_3)$_2$-(PPh_3), as orange crystals (0.060 g, 0.11 mmol; 25% yield based on cobalt complex; m.p. 150-152°). IR spectrum: 3060w, 1484m, 1438s, 1187w, 1093s, 1030m, 1001w, 943w, 867vs, 851s(sh), 830s(sh), 810vs(br), 800vs(sh), 753m(sh), 747s, 700s, 695s, 540s, 527vs, 519vs, 507s, 458w, 440m cm^{-1} (Nujol mull).

Preparation of Co(syn,syn-1,3-diMe-π-all)(PF$_3$)$_2$(PPh$_3$) (VI)

The penta-1,3-diene complex Co(π-C_5H_9)(C_5H_8)(PPh_3) was prepared from cobalt(II) chloride (1.689 g, 13 mmol), penta-1,3-diene and triphenylphosphine. The crude product, a red-brown oil, was dissolved in n-pentane (10 ml) and treated in two sealed ampoules with PF_3 (0.639 g, 7.3 mmol) at room temperature for a week. The ampoules were opened on the vacuum line and the volatile components removed and fractionated. Only a trace of Co(*syn,syn*-1,3-diMe-π-all)(PF$_3$)$_3$ was collected at −78°.

The oily, red involatile residues were extracted with hexane (50 ml) and the solutions filtered. The combined filtrates were concentrated under vacuum to form a crystalline precipitate which was filtered off and recrystallised from hexane (20 ml) to yield the product, *syn,syn*-1,3-dimethyl-π-allylbis(trifluorophosphine)(triphenylphosphine)cobalt(I), Co(π-C$_5$H$_9$)(PF$_3$)$_2$(PPh$_3$), as red crystals (0.662 g, 1.2 mmol; 9% yield based on CoCl$_2$; m.p. 114-115°). IR spectrum: 3060w, 1480m, 1434s, 1185w, 1092m, 1088m, 1033m, 1023w(sh), 1000w, 950mw, 891s, 871vs, 861vs, 846vs, 838vs, 820vs, 809vs, 796vs, 756m, 747s, 705m(sh), 697s, 682w, 538s(sh), 523vs, 510ms, 500m, 455w, 445m, 429w(sh), 419w, 391m cm^{-1} (Nujol mull).

Preparation of Co(2-Et-π-all)(PF$_3$)$_2$(PPh$_3$) (VII)

A crude sample of Co(*anti*-1,2-diMe-π-all)(PF$_3$)$_3$ (0.268g, 0.68 mmol) was heated at 60° with triphenylphosphine (0.304 g, 1.2 mmol) and diethyl ether (3 ml) in a sealed ampoule for 6 h. The tube was opened on the vacuum line and the volatile components were removed, unreacted Co(π-C$_5$H$_9$)(PF$_3$)$_3$ collecting at −78° (0.176 g, 0.45 mmol). The involatile residue was extracted with hexane (20 ml) and the solution was treated with a saturated solution of CoCl$_2$ in ethanol (1 ml). The precipitate formed was filtered off and the filtrate evaporated to dryness. The residue was extracted with hexane (5 ml) and the resulting solution was slowly concentrated to give orange crystals (0.055 g, 0.09 mmol; 8% yield based on total cobalt complex; m.p. 96-98°) which were identified by their ^{1}H NMR spectrum as 2-ethyl-π-allylbis(trifluorophosphine)-(triphenylphosphine)cobalt(I), Co(π-C$_5$H$_9$)(PF$_3$)$_2$(PPh$_3$). IR spectrum: 3060w, 1481m, 1436s, 1186w, 1097ms, 1091ms, 1030w, 1001w, 961m, 927w, 867vs(br), 849s(sh), 833vs, 810vs(br), 800vs(sh), 780s, 755m(sh), 747s, 700s, 688w(sh), 540s, 526vs, 520vs, 508m(sh), 460w, 446m cm^{-1} (Nujol mull).

Preparation of Co(2-Et-π-(all)(PF$_3$)(PPh$_3$)$_2$ (VIIa)

The crude product from a preparation of the isoprene complex Co(π-C$_5$H$_9$)(C$_5$H$_8$)(PPh$_3$) (from 1.794 g, 1.4 mmol CoCl$_2$) was treated with PF$_3$ (0.174 g, 2.0 mmol) at room temperature in a sealed ampoule for four months to give an orange solution and a precipitate of large red crystals and free triphenylphosphine. The tube was opened on the vacuum line and the volatile components were removed. The red crystals were picked out from the solid residues and were washed with hexane to remove triphenylphosphine and Co(1,1-diMe-π-all)(PF$_3$)$_2$(PPh$_3$) (IV). The resulting solid (0.055 g, 0.07 mmol; 1% yield based on CoCl$_2$; m.p. 145-152°) was identified as 2-ethyl-π-allyl(trifluorophosphine)bis(triphenylphosphine)cobalt(I), Co(π-C$_5$H$_9$)(PF$_3$)(PPh$_3$)$_2$, by IR, ^{1}H NMR and ^{19}F NMR spectroscopy. IR spectrum: 3059w, 1481m, 1436s, 1188w, 1160w, 1090m, 1027w, 1000w, 915w, 855w, 826vs, 794s, 783s, 755m(sh), 747s, 741m(sh), 700s, 685w(sh), 650w, 540m, 526s(sh), 519vs, 510m(sh), 492w, 450m, 410w cm^{-1} (Nujol mull).

Preparation of Co(π-C$_8$H$_{13}$)(PF$_3$)$_2$(PPh$_3$) (VIII)

Crude Co(π-C$_8$H$_{13}$)(PF$_3$)$_3$ (1.050 g, 2.3 mmol) containing a small amount of organic impurities was stirred in a Schlenk tube with triphenylphosphine (0.412 g, 1.6 mmol) in diethyl ether (5 ml) at room temperature for 18 h, the orange solution slowly becoming red. The volatile components were removed in vacuo and the solid residue was extracted with hexane (20 ml). The resulting solution was treated with a saturated solution of $CoCl_2$ in ethanol (2 ml) and the precipitate formed was filtered off. The filtrate was evaporated to dryness and the solid residue extracted with hexane (20 ml). The solution was slowly concentrated under vacuum to give red crystals which were filtered off and recrystallised from hexane to give the product, π-cyclooctenylbis(trifluorophosphine)(triphenylphosphine)cobalt(I), $Co(\pi\text{-}C_8H_{13})(PF_3)_2(PPh_3)$ (VIII) (0.062 g, 0.10 mmol; 4% yield based on total crude starting material; m.p. 137-139°). IR spectrum: 3058w, 1480m, 1436ms, 1261w, 1186w, 1091ms, 1025w(br), 1000w, 970w, 872vs, 851s, 841s, 827vs, 811s(sh), 798vs, 754s, 746ms, 700s, 690w(sh), 540s, 529vs, 513vs, 461w, 438m cm^{-1} (Nujol mull).

Preparation of $Co(\pi\text{-}C_7H_9)(PF_3)_2(PPh_3)$

$Co(\pi\text{-}C_7H_9)(PF_3)_2$ (0.693 g, 2.1 mmol), triphenylphosphine (0.510 g, 2.0 mmol) and n-pentane (3 ml) were shaken for three days at room temperature in a sealed tube to give a red crystalline solid and solution. The tube was opened and the volatile components were removed in vacuo. The solid residue was washed with hexane and dried under high vacuum to give crude $Co(\pi\text{-}C_7H_9)(PF_3)_2(PPh_3)$ (0.548 g, 0.93 mmol; 48% yield based on the crude cobalt complex).

The crude product was further purified by dissolving in hexane (10 ml) and treating with a saturated solution of $CoCl_2$ in ethanol (1 ml). The resulting precipitate was filtered off and the filtrate evaporated to dryness. The solid residue was extracted with hexane (10 ml) and the solution was slowly concentrated to give red crystals of h^3-π-cycloheptadienylbis(trifluorophosphine)(triphenylphosphine)cobalt(I), $Co(\pi\text{-}C_7H_9)(PF_3)_2(PPh_3)]$ (m.p. 116-118°). IR spectrum: 3060w, 3020w, 1479m, 1435s, 1180w, 1090ms, 1030w, 1000w, 873vs, 854s, 840vs, 825s(sh), 819vs, 800vs, 750s, 744m(sh), 720mw, 697s, 688w(sh), 613w, 539s, 525s, 512vs, 454w, 431w cm^{-1} (Nujol mull).

Thermal isomerisation of $Co(1,1\text{-diMe-}\pi\text{-all})(PF_3)_2(PPh_3)$

A sample of $Co(1,1\text{-diMe-}\pi\text{-all})(PF_3)_2(PPh_3)$ (IV) in benzene solution was heated at 60° in a sealed NMR tube and the ^1H NMR spectrum monitored. Rapid change over 2 h indicated the formation of Co(*anti*-1,2-diMe-π-all)$(PF_3)_2(PPh_3)$ (V) almost quantitatively. Further heating for 8 h caused no other changes. The tube was opened and the solution evaporated to dryness to give an orange crystalline solid whose ^1H NMR, ^{19}F NMR, and IR spectra were identical with those of a known sample of V.

Reaction of $Co(anti\text{-}1\text{-}Me\text{-}\pi\text{-}all)(PF_3)_2(PPh_3)$ with butadiene

Co(*anti*-1-Me-π-all)$(PF_3)_2(PPh_3)$ (III) (0.095 g, 0.17 mmol) and butadiene (5 ml) were shaken for a week at room temperature in a sealed ampoule to give an orange solution. The tube was opened on the vacuum line and the volatile components were fractionated. A trace of yellowish liquid in the −78° trap was identified as 4-vinyl-1-cyclohexene (VCH) by ^1H NMR spectroscopy. The sticky orange residue was found by IR spectroscopy to be unreacted starting material.

Reaction of Co(anti-1-Me-π-all)(PF$_3$)$_2$(PPh$_3$) with molecular hydrogen

Hydrogen gas was bubbled through a solution of Co(*anti*-1-Me-π-all)(PF$_3$)$_2$(PPh$_3$) (II) (0.060 g, 0.11 mmol) in hexane (20 ml) at 50° for 3 h. A small amount of a white precipitate formed was filtered off and dried. The IR spectrum of this solid indicated the presence of triphenylphosphine oxide and an unidentified cobalt complex, formed by decomposition. The filtrate was evaporated to dryness and identified as unreacted starting material.

The experiment was repeated with added triphenylphosphine (0.026 g, 0.10 mmol), but no difference was observed in the reaction.

Activity of Co(anti-1-Me-π-all)(PF$_3$)$_2$(PPh$_3$) (II)

(a) Under hydrogen. Co(*anti*-1-Me-π-all)(PF$_3$)$_2$(PPh$_3$) (0.050 g, 0.09 mmol) was investigated in hexane solution at 50°, but was found to be inactive for hydrogenation, with no hydrogen uptake after 24 h. GLC analysis of the solution showed a slow isomerisation of 1-octene to a 50:50 mixture of *cis*- and *trans*-2-octene. Small amounts of 3-octene were detected when the 2-octene became the major component. The orange solution slowly became pale yellow during the reaction, indicating decomposition. The percentage of 2-octene found at various times was: 30 min, 3%; 120 min, 25%; 240 min, 37%; 300 min, 38%; 1380 min, 66% + 1% 3-octene.

(b) Under nitrogen. The experiment was repeated with Co(*anti*-1-Me-π-all)(PF$_3$)$_2$(PPh$_3$) (0.047 g, 0.09 mmol) under similar conditions, but with a nitrogen atmosphere above the reaction mixture. Isomerisation was negligible, even after a day. Percentage of 2-octene, 30 min, 0%; 120 min, 0%; 240 min, 0%; 1260 min, < 1%.

After 1300 min the atmosphere was changed to hydrogen and an increase in activity occurred immediately. Percentage of 2-octene: 60 min, 12%; 180 min, 24%; 240 min, 26%; 300 min, 28%; 360 min, 30%; 1320 min, 53% + 1% 3-octene.

(c) Under hydrogen with added triphenylphosphine. The experiment was repeated with Co(*anti*-1-Me-π-all)(PF$_3$)$_2$(PPh$_3$) (0.050 g, 0.09 mmol) under hydrogen with triphenylphosphine (0.100 g, 0.38 mmol) in solution. Very slow isomerisation was detected. Percentage of 2-octene: 30 min, 0%; 60 min, > 0%, 120 min, 0.5%; 180 min, 1%; 1200 min, 5%.

The results for (a), (b) and (c) are represented graphically in Fig. 5.

Activity of other Co(π-all)(PF$_3$)$_2$(PPh$_3$) complexes

These complexes were investigated in the same way as the *anti*-1-methyl-π-allylic isomer, at 50° in hexane under hydrogen. All were found to be active for the isomerisation of 1-octene to *cis*- and *trans*-2-octene and the results are listed below:

Co(π-C$_3$H$_5$)(PF$_3$)$_2$(PPh$_3$) (I) (0.031 g, 0.06 mmol). Percentage of 2-octene: 60 min, 17%; 120 min, 27%; 180 min, 34%; 1200 min, 80% + 6% 3-octene.

Co(syn-1-Me-π-all)(PF$_3$)$_2$(PPh$_3$) (III) (0.046 g, 0.08 mmol). Percentage of 2-octene: 60 min, 12%; 120 min, 27%; 180 min, 34%; 280 min, 46%; 340 min, 49% + 1% 3-octene.

Co(1,1-diMe-π-all)$(PF_3)_2(PPh_3)$ *(IV) (0.050 g, 0.09 mmol).* Percentage of 2-octene: 75 min, 17%; 225 min, 24%; 285 min, 29%; 345 min, 33%; 1335 min, 50%.

Co(syn,syn-1,3-diMe-π-all)$(PF_3)_2(PPh_3)$ *(VI) (0.049 g, 0.09 mmol).* Percentage of 2-octene: 45 min, 15%; 75 min, 17%; 120 min, 25%; 165 min, 31%; 285 min, 37%; 330 min, 43%; 1305 min, 57%.

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