(η-Allyl)tris(trifluorophosphine)cobalt(I) Complexes

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A series of complexes $[\mathrm{CoL(PF_3)_3}]$ [I; L = 1—3-η-allyl, -(1-methylallyl), -(1,1-dimethylallyl), -(1,2-dimethylallyl), -(1,3-dimethylallyl), -cyclo-octenyl, and -cycloheptadienyl] has been prepared by low-pressure ligand-displacement reactions. ^{1}H and ^{19}F N.m.r. studies indicate the absence of intermolecular phosphine exchange. The reactions of these complexes with hydrogen chloride and dihydrogen are discussed. The 1—3-η-(1,1-dimethylallyl) complex undergoes a novel thermal isomerisation to the *anti*-1,2-complex. The complex $[\mathrm{Co(\eta\text{-}C_7H_9)(PF_3)_2}]$ contains a 1—5-η-cycloheptadienyl group.

(η-ALLYL)TRICARBONYLCOBALT(I) complexes, $[\mathrm{CoL(CO)_3}]$, have been prepared by two general methods; (*a*) insertion of a conjugated diene into the cobalt–hydride bond of $[\mathrm{HCo(CO)_4}]$;[1] or (*b*) treatment of tetracarbonylcobaltate(−I) salts $\mathrm{M[Co(CO)_4]}$ (M = Na, K, or Tl) with allyl halides.[2] We have previously used both these methods to obtain several (η-allyl)tris(trifluorophosphine)rhodium(I) complexes, $[\mathrm{RhL(PF_3)_3}]$, from $[\mathrm{RhH(PF_3)_4}]$ or $\mathrm{K[Rh(PF_3)_4]}$.[3,4] The latter complexes are readily available organometallic precursors.[5-7] Similar preparations of related cobalt complexes from the analogous hydride or metallate would necessitate the use of specialised high-pressure and high-temperature techniques and alternative synthetic routes were sought.

Since displacement of two allyl groups from tris(1—3-η-allyl)cobalt(III) by carbon monoxide is known to produce the simple (1—3-η-allyl)tricarbonylcobalt(I), $[\mathrm{Co(\eta\text{-}C_3H_5)(CO)_3}]$,[8] and the only previously reported organocobalt(I) complex containing trifluorophosphine $[\mathrm{Co(cp)(PF_3)_2}]$ (cp = η-cyclopentadienyl) was obtained by treating bis(η-cyclopentadienyl)cobalt(II) with $\mathrm{PF_3}$,[9] organic-ligand displacement appeared to offer a possible route to the required complexes. While this work was in progress it was reported that treatment of tetrakis(1—3-η-allyl)tantalum(IV), $[\mathrm{Ta(\eta\text{-}C_3H_5)_4}]$, with an excess of $\mathrm{PF_3}$ gives the unstable (1—3-η-allyl)pentakis(trifluorophosphine)tantalum(I), $[\mathrm{Ta(\eta\text{-}C_3H_5)(PF_3)_5}]$.[10] Tris(1—3-η-allyl)chromium(III), $[\mathrm{Cr(\eta\text{-}C_3H_5)_3}]$, on the other hand, reacts differently with $\mathrm{PF_3}$ to form an unstable 1 : 1 adduct which slowly decomposes to the known zerovalent chromium complex $[\mathrm{Cr(PF_3)_6}]$.[11]

RESULTS AND DISCUSSION

Tris(1—3-η-allyl)cobalt(III), $[\mathrm{Co(\eta\text{-}C_3H_5)_3}]$, reacted rapidly with an excess of $\mathrm{PF_3}$ in pentane solution, on warming the mixture from −196 °C to room temperature, to give (1—3-η-allyl)tris(trifluorophosphine)cobalt(I), $[\mathrm{Co(\eta\text{-}C_3H_5)(PF_3)_3}]$, (I). The product is a volatile orange liquid which is very air sensitive, but is thermally stable for several days when stored *in vacuo*. Elemental analysis and mass-spectroscopic studies indicated the presence of three $\mathrm{PF_3}$ ligands, as found for the analogous rhodium complex,[3,4] and the formulation was confirmed by ^{1}H and ^{19}F n.m.r. spectroscopic studies (see below).

Extension of this route to substituted η-allyl complexes should be possible and some tris(η-allyl)cobalt(III) complexes have been reported very recently by Bönnemann.[12] We developed an attractive alternative route, however, which involves displacement of buta-1,3-diene and triphenylphosphine from the complex

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[1] J. A. Bertrand, H. B. Jonassen, and D. W. Moore, *Inorg. Chem.*, 1963, **2**, 601.

[2] R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 655.

[3] D. A. Clement, J. F. Nixon, and B. Wilkins, *J. Organometallic Chem.*, 1972, **37**, C43.

[4] J. F. Nixon, B. Wilkins, and D. A. Clement, preceding paper.

[5] J. F. Nixon and J. R. Swain, *J.C.S. Dalton*, 1972, 1044.

[6] D. A. Clement and J. F. Nixon, *J.C.S. Dalton*, 1972, 1553.

[7] M. A. Bennett and D. J. Patmore, *Inorg. Chem.*, 1971, **10**, 2387.

[8] G. Wilke, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

[9] Th. Kruck, W. Hieber, and W. Lang, *Angew. Chem. Internat. Edn.*, 1966, **5**, 247.

[10] Th. Kruck and H. U. Henzel, *Angew. Chem. Internat. Edn.*, 1971, **10**, 408.

[11] Th. Kruck, H. L. Diedershagen, and A. Engelmann, *Z. anorg. Chem.*, 1973, **397**, 31.

[12] H. Bönnemann, personal communication; *Angew. Chem. Internat. Edn.*, 1973, **12**, 964.

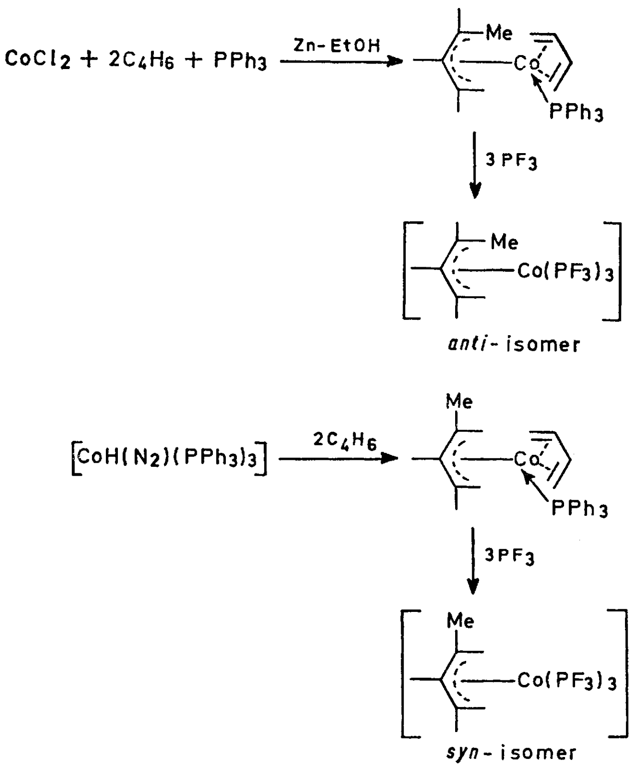
$[\mathrm{Co}(\eta\text{-}\mathrm{C_4H_7})(\eta\text{-}\mathrm{C_4H_6})(\mathrm{PPh_3})]$ by treatment with an excess of $\mathrm{PF_3}$ at room temperature to afford *syn*- and *anti*-isomers of 1—3-η-(1-methylallyl) complexes $[\mathrm{Co}(\eta\text{-}\mathrm{C_4H_7})(\mathrm{PF_3})_3]$ (see Table 1). This method is particularly useful since isomerically pure products are obtained by using either the *syn*-[13] or *anti*-isomers[14] as starting materials (see Scheme 1). The *anti*-isomer is a volatile orange solid while the *syn*-isomer is an orange-red liquid. The former does not undergo isomerisation to the thermodynamically favoured *syn*-isomer, even after heating at 60 °C for several hours, and this contrasts with the known behaviour of the *anti*-isomers of $[\mathrm{Rh}(\eta\text{-}\mathrm{C_4H_7})(\mathrm{PF_3})_3]$ [4] and $[\mathrm{Co}(\eta\text{-}\mathrm{C_4H_7})(\mathrm{CO})_3]$.[1]

TABLE 1

^{19}F N.m.r. data for the complexes $[\mathrm{CoL}(\mathrm{PF_3})_3]$, (I)

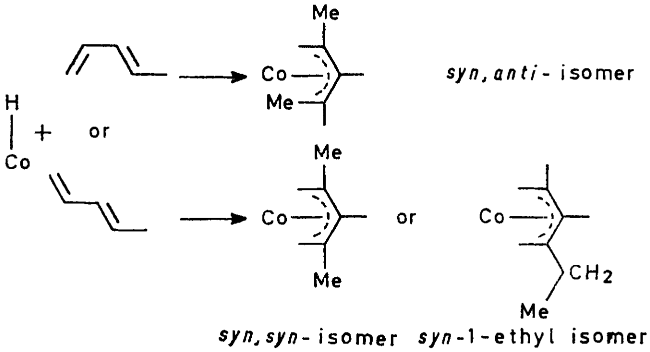
L	$\nu\,[= {}^1J(\mathrm{PF}) + 2\,{}^3J(\mathrm{PF'})]$/Hz	δ/p.p.m.
1—3-η-Allyl	1 268	+10·7
1—3-η-(1-Methylallyl) (*anti*-)	1 268	+11·3
(*syn*-)	1 265	+10·6
1—3-η-(1,1-Dimethylallyl)	1 265	+12·5
1—3-η-*anti*-(1,2-Dimethylallyl)	1 268	+11·8
1—3-η-*syn,syn*-(1,3-Dimethylallyl)	1 260	+11·4
1—3-η-(2-Ethylallyl)	1 268	+11·3
1—3-η-Cyclo-octenyl	1 265	+11·6
1—3-η-Cycloheptadienyl	1 273	+14·3

Chemical shifts were recorded relative to $\mathrm{C_6F_6}$ and values of δ relative to $\mathrm{CFCl_3}$ were calculated assuming $\delta(\mathrm{C_6F_6}) = -162{\cdot}8$ p.p.m.



SCHEME 1 Syntheses of *syn*- and *anti*-[1—3-η-(1-methylallyl)]-tris(trifluorophosphine)cobalt(I)

Several other complexes (I) are readily available by this route; for example, the η-isoprene and η-penta-1,3-diene complexes $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_9})(\eta\text{-}\mathrm{C_5H_8})(\mathrm{PPh_3})]$ (which are prepared in a similar manner as the buta-1,3-diene complex) readily afforded 1—3-η-(1,1-, 1—3-η-(1,2-, and 1—3-η-(1,3-dimethylallyl) derivatives of (I). The major product from the isoprene complex was the corresponding volatile orange solid 1,1-derivative. Smaller, varying amounts of other isomers were usually also present in the reaction products and, as discussed later, they were readily identified by their distinctive ^{19}F n.m.r. spectra. Traces of [1—3-η-(2-ethylallyl)]tris(trifluorophosphine)cobalt(II), [1—3-η-(1,2-dimethylallyl)]tris(trifluorophosphine)cobalt(I) (*anti*-isomer), and a third complex which may be the *syn*-1—3-η-(1,2-dimethylallyl) isomer were formed in the synthesis of the 1,1-derivative. With the exception of the *anti*-isomer of the 1,2-derivative which, as discussed later, results from a novel thermal isomerisation of the 1,1-derivative, these minor products probably arise from small amounts of isomeric impurities present in the starting material.



SCHEME 2

The penta-1,3-diene complex $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_9})(\eta\text{-}\mathrm{C_5H_8})(\mathrm{PPh_3})]$ gave the red liquid *syn,syn*-1—3-η-(1,3-dimethylallyl) derivative of (I) as the main product of the reaction with $\mathrm{PF_3}$, but traces of the *syn,anti*-isomer were also present. In one experiment a considerable amount of another isomer, thought to be the *syn*-1—3-η-(1-ethylallyl) derivative, was detected by n.m.r. spectroscopy. A similar isomer has been reported previously[1] in the products of reaction between $[\mathrm{HCo}(\mathrm{CO})_4]$ and penta-1,4-diene, where the diene undergoes rearrangement prior to insertion into the cobalt–hydrogen bond. The formation of the various isomers reflects the different mechanisms available for diene insertion into the cobalt–hydrogen bond (Scheme 2). None of the complexes obtained from $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_9})(\eta\text{-}\mathrm{C_5H_8})(\mathrm{PPh_3})]$ isomerised over a period of 24 h at 60 °C.

The (1—3-η-cyclo-octenyl)tris(trifluorophosphine)-cobalt(I) complex was obtained as a volatile orange crystalline solid by treating (η-cyclo-octenyl)(η-cyclo-

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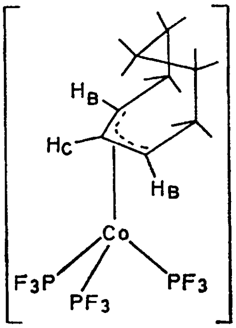
[13] P. V. Rinze and H. Nöth, *J. Organometallic Chem.*, 1971, **30**, 115.

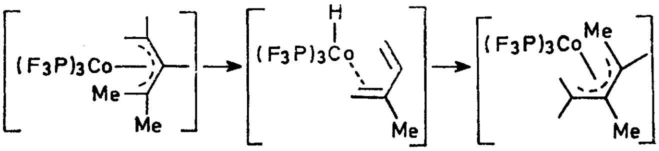
[14] G. Vitulli, L. Porri, and A. L. Segre, *J. Chem. Soc.* (*A*), 1971, 3246.

octa-1,5-diene)cobalt(I),[15] [Co(η-C_8H_{13})(η-C_8H_{12})], with an excess of PF$_3$ at room temperature. The analogous tricarbonylcobalt complex has been reported by Otsuka and Rossi, but was not fully characterised.[16] When the complex [Co(η-C_8H_{13})(η-C_8H_{12})] was heated under reflux in hexane with cyclohepta-1,3,5-triene, a ligand-transfer reaction occurred with hydrogen migration and (η-cycloheptadienyl)(η-cyclo-octadiene)cobalt(I), [Co(η-C_7H_9)(η-C_8H_{12})], was formed in good yield.[17] The latter is reported to react with carbon monoxide to give the dicarbonyl complex [Co(η-C_7H_9)(CO)$_2$], and similarly treatment of excess of the complex with PF$_3$ gave a volatile red oil formulated as (1—5-η-cycloheptadienyl)bis(trifluorophosphine)cobalt(I), [Co(η-C_7H_9)(PF$_3$)$_2$], on the basis of mass, i.r., ^{1}H, and ^{19}F n.m.r. spectroscopic evidence. In this complex the cycloheptadienyl group acts as a five-electron ligand and is analogous to the cp group of [Co(cp)(PF$_3$)$_2$].[9] The complex [Co(η-C_7H_9)(η-C_8H_{12})] reacted with an excess of trifluorophosphine to afford a mixture of the 1—3-η-cycloheptadienyl derivative and [Co(η-C_7H_9)(PF$_3$)$_3$]. The latter, which is a red volatile liquid, was obtained pure by adding triphenylphosphine to [(Co(η-C_7H_9)(PF$_3$)$_2$] to yield [Co(η-C_7H_9)(PF$_3$)$_2$(PPh$_3$)] and then treating this complex with an excess of PF$_3$. The complex [Co(η-C_7H_9)(PF$_3$)$_3$] slowly lost one PF$_3$ molecule when heated *in vacuo*, but the reaction did not go to completion in a closed system.



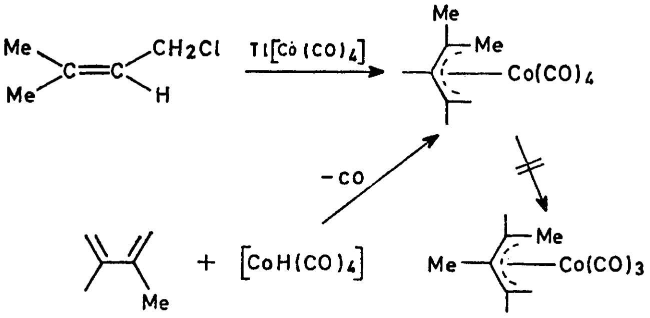
As mentioned earlier, heating a solution of [1—3-η-(1,1-dimethylallyl)]tris(trifluorophosphine)cobalt(I) in either pentane or benzene at 60 °C leads to slow isomerisation to the *anti*-1,2-dimethyl isomer in almost quantitative yield.[18] The progress of the reaction can be conveniently monitored by periodic observation of the ^{1}H and ^{19}F n.m.r. spectra of the solution in a heated n.m.r. tube. As discussed more fully elsewhere,[4] the most likely mechanism for the isomerisation involves a 1,4-hydrogen shift, resulting from formation of an intermediate hydrido–metal–diene species which then undergoes insertion of isoprene to give the favoured *anti*-1,2-dimethyl isomer (Scheme 3).* The analogue [1—3-η-(1,1-dimethylallyl)]tris(trifluorophosphine)-rhodium(I) has been found to undergo a similar rearrangement, but at a much faster rate than the cobalt complex and the final product is the *syn*-1,2-dimethylallyl isomer.[4,18] This is entirely consistent with the proposed mechanism since, as discussed in more detail elsewhere,[4] insertion of isoprene into the rhodium–hydride bond of [RhH(PF$_3$)$_4$] gives initially a mixture of *syn*- and *anti*-1,2-dimethyl isomers and the *anti*-isomer readily rearranges to the *syn*-form on heating.

Recently Kruck *et al.*[19] reported that isoprene reacts with the complex [CoH(PF$_3$)$_4$] to afford the 1,1-dimethylallyl derivative of (I), but on the basis of their reported m.p. and ^{1}H n.m.r. spectra it seems certain that their product is in fact the *anti*-isomer of the 1,2-derivative. Their η-allyl products were usually formed in poor yield and contained organic impurities. No ^{19}F n.m.r. spectra were reported and the poor quality of their ^{1}H n.m.r. spectra did not allow assignment of structures.



SCHEME 3

It is noteworthy that we find that the tricarbonyl-[1—3-η-(1,1-dimethylallyl)]cobalt(I) complex {made from Tl[Co(CO)$_4$] [20] and 1-chloro-3-methylbut-2-ene in diethyl ether solution} shows no evidence of thermal isomerisation. This difference is not unexpected since the 1,1- rather than the 1,2-dimethyl isomer is known to be formed by insertion of isoprene into the metal–hydride bond of [CoH(CO)$_4$] [1] (Scheme 4). It is not clear, however, why the complexes [CoH(CO)$_4$] and [CoH(PF$_3$)$_4$] {or [RhH(PF$_3$)$_4$]} should give different insertion products with dienes, but clearly a previous



SCHEME 4

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* *Added at Proof:* This type of metal diene hydride has now been isolated, *viz.* 2,3-dimethylbuta-1,3-dienehydridobis(triphenylphosphine)cobalt(I), P. V. Rinze, *Angew. Chem. Internat. Edn.*, 1974, **13**, 336.

[15] S. Otsuka and M. Rossi, *J. Chem. Soc.* (*A*), 1968, 2630.

[16] S. Otsuka and M. Rossi, *J. Chem. Soc.* (*A*), 1969, 497.

[17] S. Otsuka and T. Taketomi, *J. Chem. Soc.* (*A*), 1971, 579.

[18] M. A. Cairns, J. F. Nixon, and B. Wilkins, *J.C.S. Chem. Comm.*, 1973, 86.

[19] Th. Kruck, G. Sylvester, and I.-P. Kunau, *Z. Naturforsch.*, 1973, **B28**, 28.

[20] S. E. Pedersen, W. R. Robinson, and D. P. Schussler, *J. Organometallic Chem.*, 1972, **43**, C44.

proposal[21] that the acidity of the hydrogen atom in the metal hydride determines the direction of addition across an olefinic bond does not seem plausible since both carbonyl and trifluorophosphine metal hydrides are known to be strong acids.[22,23]

N.M.R. Spectra.—(a) ^{19}F. All complexes (I) exhibited a similar mirror-image pattern to that shown for $[\mathrm{Co}(\eta\text{-}\mathrm{C_4H_7})(\mathrm{PF_3})_3]$ in Figure 1, as expected for the X part of an $[\mathrm{AX_3}]_3$ spin system [24,25] (where A = P and X = F). This implies that all three $\mathrm{PF_3}$ groups are magnetically equivalent on the n.m.r. time scale. Each spectrum consisted of a doublet of sharp lines with separation $|^1J(\mathrm{PF}) + 2^3J(\mathrm{PF'})|$ and two broad complex multiplets lying outside these lines in a mirror-image pattern. A detailed study of these spectra was not attempted but the ^{19}F n.m.r. spectrum of the analogous (η-allyl)tris(trifluorophosphine)rhodium(I) complex has been fully analysed.[25] The chemical-shift, δ_F, and $|^1J(\mathrm{PF}) + 2^3J(\mathrm{PF'})|$ data for the complexes are listed in Table 1, and the fluorine chemical shifts were found to be significantly downfield of the free-ligand value as is the case in other fluorophosphine transition-metal complexes.[23] Since fluorine chemical shift differences between isomeric complexes were quite large (usually > 0·5 p.p.m.), the purity of a complex is readily ascertained using ^{19}F n.m.r. spectroscopy. Unlike the analogous rhodium complexes,[3,4] there was no ready intermolecular phosphine exchange in the cobalt complexes.

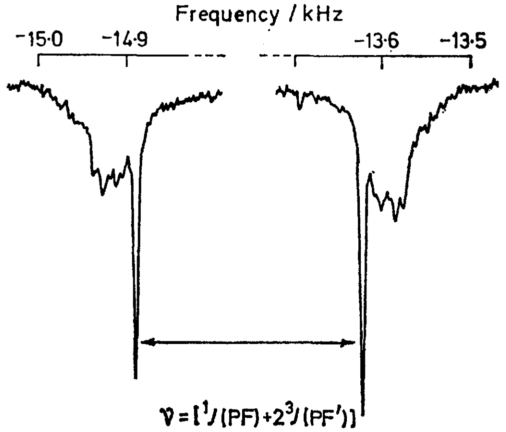

FIGURE 1 ^{19}F N.m.r. spectrum of the *anti*-1-methylallyl derivative of (I)

The ^{19}F n.m.r. spectrum of $[\mathrm{Co}(\eta\text{-}\mathrm{C_7H_9})(\mathrm{PF_3})_2]$ (Figure 2) was unusual and entirely different from those of complexes in Table 1, showing two pairs of mirror-image signals both of about equal intensities and exhibiting second-order splitting. This suggests that the two $\mathrm{PF_3}$ groups may be in different environments, but detailed analysis of the spectra was not undertaken.

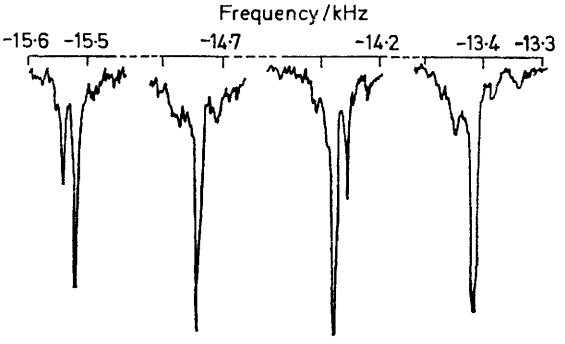

FIGURE 2 ^{19}F N.m.r. spectrum of (1—5-η-cycloheptadienyl)-bis(trifluorophosphine)cobalt

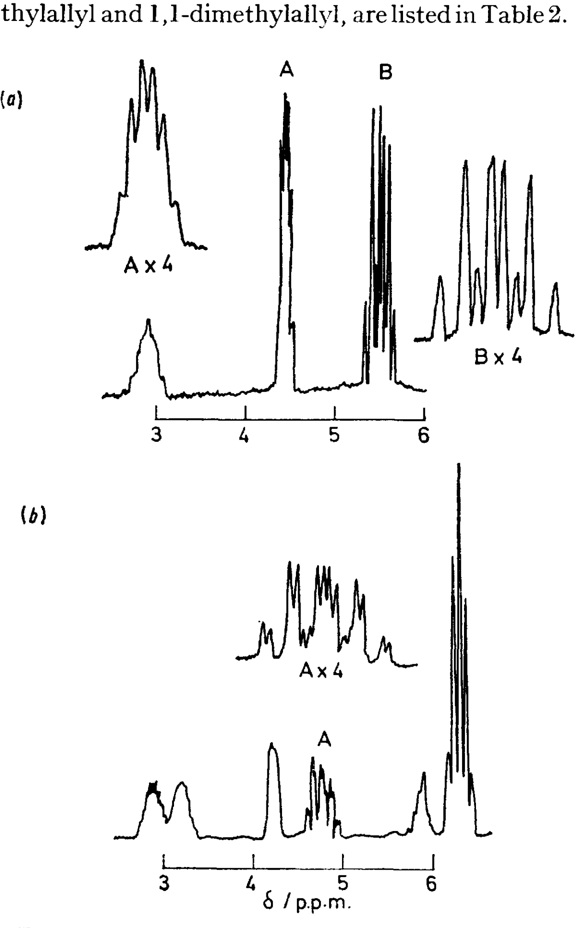

FIGURE 3 ^{1}H N.m.r. spectra of (I) (*a*) and the *anti*-1-methylallyl (*b*) derivative of (1)

(b) ^{1}H. ^{1}H N.m.r. spectra of the 1—3-η-allyl and -(1-methylallyl) (*anti*-) derivatives are shown in Figure 3 and assignments, and chemical-shift and coupling-constant data for these derivatives and those of the *syn*-1-methylallyl and 1,1-dimethylallyl, are listed in Table 2. A feature of the spectra is the appearance of 1 : 3 : 3 : 1 quartet patterns in all of the proton resonances, due to

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[21] C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 850.

[22] Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.

[23] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363.

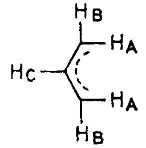
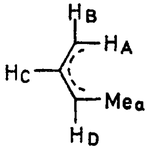
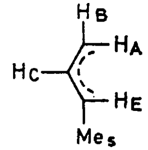
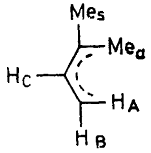
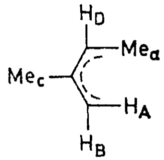
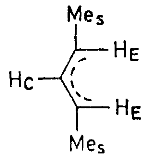
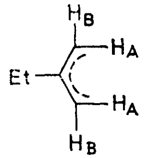
[24] E. G. Finer and R. K. Harris, *J. Chem. Soc.* (*A*), 1969, 1972.

[25] J. F. Nixon, *J. Fluorine Chem.*, 1973, **4**, 179.

TABLE 2

^{1}H N.m.r. data for the complexes [CoL(PF$_3$)$_3$]

Chemical shifts (p.p.m.) are relative to the internal benzene standard; coupling constants, J, are in Hz

	L	H$_A$	H$_B$	H$_C$	H$_D$	H$_E$	Me$_a$	Me$_s$	Me$_c$
	1—3-η-Allyl	5·52 d of qt J(H$_A$H$_C$) 10·5 J(H$_A$P) 7·3	4·46 sxt J(H$_B$H$_C$) 6·0 J(H$_B$P) 3·0	2·92 mult					
	1—3-η-(1-Methylallyl) (*anti-*)	4·78 qt of d * J(H$_A$H$_C$) 11·0 J(H$_A$P) 7·5 J(H$_A$H$_B$) 1·7	4·22 mult	2·88 mult	3·20 mult		6·30 qnt J(Me$_a$H$_D$) 6·4 J(Me$_a$P) 6·4		
	(*syn-*)	*ca.* 5·70 mult	*ca.* 4·42 mult	2·85 mult		4·45 d of spt J(H$_E$H$_C$) 10·0 J(H$_E$Me$_s$) 6·0 J(H$_E$P) 6·0		5·72 qnt J(Me$_s$E) 6·0 J(Me$_s$P) 5·5	
	1—3-η-(1,1-Dimethylallyl)	5·14qt of d * J(H$_A$H$_C$) 10·5 J(H$_A$P) 7·7 J(H$_A$H$_B$) 2·0	4·38 mult	2·94 mult			6·16 qt J(Me$_a$P) 7·0	5·67 qt J(Me$_s$P) 5·3	
	1—3-η-*anti*-(1,2-Dimethylallyl)	4·65 qt of d J(H$_A$P) 8·8 J(H$_A$H$_B$) 1·7	4·10 mult		3·24 mult		6·25 d of qt J(Me$_a$H$_D$) 6·7 J(Me$_a$P) 6·0		5·61 qt J(Me$_c$P) 3·5
	1—3-η-*syn,syn*-(1,3-Dimethylallyl)			2·96 mult		4·76d of spt J(H$_E$H$_C$) 10·0 J(H$_E$Me$_s$) 6·0 J(H$_E$P) 6·0		5·74 qnt J(Me$_s$E) 6·0 J(Me$_s$P) 6·0	
	1—3-η-(2-Ethylallyl)	5·36 qt J(H$_A$P) 8·7	4·31 qt J(H$_B$P) 4·0			CH$_2$ 5·33 qt J(CH$_2$ – Me$_{Et}$) 7·5	Me of Et 6·27 t J(CH$_2$ – Me$_{Et}$) 7·5		

d = Doublet, t = triplet, qt = quartet, qnt = quintet, sxt = sextet, spt = septet, and mult = multiplet. * Each line is further split into a doublet.

coupling with the three equivalent phosphorus nuclei of the PF_3 groups. In the analogous rhodium complexes ready *inter*molecular phosphine exchange at room temperature occurs, and such coupling was only observed at *ca.* −30 °C.[3,4]

The ^1H n.m.r. spectrum of the complex $[Co(\eta\text{-}C_8H_{13})(PF_3)_3]$ is shown in Figure 4. The H_C signal occurred at lowest field as a sextet (two overlapping 1 : 3 : 3 : 1 quartets) due to coupling to the two *syn*-protons [$J(H_CH_B)$ 6·4 Hz] and to the phosphorus nuclei [$J(H_CP)$ 6·4 Hz]. No change was observed in the ^1H n.m.r. spectra on cooling the sample and there was no evidence for either a diene hydride (A) or a σ,η-bonded (B) form.[12,26]

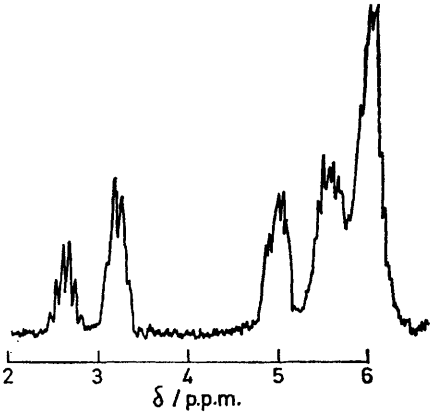
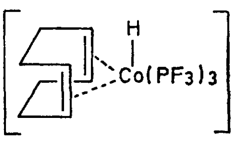
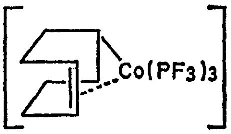


FIGURE 4 ^1H N.m.r. spectrum of the cyclo-octenyl derivative of (I)



(A)



(B)

The ^1H n.m.r. spectrum of the complex $[Co(\eta\text{-}C_7H_9)(PF_3)_3]$ was consistent with its formulation as an 1—3-η complex rather than the usual 1—5-η form of the organic group. Multiplets at 1·28 and 2·02 p.p.m. were assigned to protons of an unco-ordinated [27] double bond. The resonance of the central and *syn*-protons H_A and H_B overlapped to give a multiplet at 2·55 p.p.m., while the broad multiplets between 5·0 and 6·0 p.p.m. were assigned to the remaining methylene protons. The ^1H n.m.r. spectrum of the complex $[Co(\eta\text{-}C_7H_9)(PF_3)_2]$ was significantly different. No signals assignable to protons attached to a double bond were observed and spectra consisted of overlapping multiplets at 1·90—2·50 p.p.m. with a strong line at 1·90 p.p.m. together with methylene resonances at 5·2 and 6·0 p.p.m. and signals due to organic impurities. These assignments are consistent with the published spectra of $[Co(\eta\text{-}C_7H_9)(\eta\text{-}C_7H_{10})]$,[28] but, unlike the related $[Co(\eta\text{-}C_7H_9)(\eta\text{-}C_8H_{12})]$ complex,[29] the spectra of $[Co(\eta\text{-}C_7H_9)(PF_3)_2]$ over the range −30 to +60 °C showed no evidence of fluxional behaviour.

Reactions of Complexes.—(a) *With hydrogen chloride*. A slow reaction occurred when benzene solutions of complexes were treated with an excess of dry hydrogen chloride in a sealed glass tube. The reaction products after several weeks at room temperature were cobalt(II) chloride, free trifluorophosphine, and a chloroalkane. A small amount of SiF_4 was also formed. The chloroalkanes, which are formed *via* addition of HCl to the liberated olefin, are listed in Table 3. The analogous rhodium complexes rapidly react to afford olefins and the stable complex $[(F_3P)_2Rh(\mu\text{-}Cl)_2Rh(PF_3)_2]$ *via* an (η-allyl)hydridorhodium intermediate which has been identified by low-temperature ^{19}F n.m.r. spectroscopy.[30] There is no known cobalt analogue of $[(F_3P)_2Rh(\mu\text{-}Cl)_2Rh(PF_3)_2]$. The observation of Me_2EtCCl rather than $Me_2CHCH(Me)Cl$ as the chloroalkane product from the reaction between the 1,1-dimethyl derivative and hydrogen chloride implies that the intermediate olefin formed is 2-methylbut-2-ene rather than 3-methylbut-1-ene. This indicates that there is specific hydrogen migration from the metal to the least-hindered carbon atom. A similar preference was observed in the analogous rhodium systems.[30]

TABLE 3

	Chloroalkane
1—3-η-Allyl	$Me_2C(H)Cl$
1—3-η-(1-Methylallyl) (*syn*-)	$EtMeC(H)Cl$
(*anti*-)	$EtMeC(H)Cl$
1—3-η-(1,1-Dimethylallyl)	$EtMe_2CCl$
anti-1—3-η-(1,2-Dimethylallyl)	$EtMe_2CCl$
syn,syn-1—3-η-(1,3-Dimethylallyl)	$Et_2C(H)Cl + Pr^nMeC(H)Cl$

(b) *With dihydrogen*. Treatment of the 1,1-dimethylallyl derivative with dihydrogen and excess of PF_3 at room temperature did not lead to any detectable amounts of the complex $[CoH(PF_3)_4]$ even though the *anti*-1-methyl derivative is active for catalysis of isomerisation of oct-1-ene to oct-2-ene under hydrogenation conditions.[31] This behaviour again contrasts with that known for the related rhodium systems; for example, the complex $[Rh(\eta\text{-}C_3H_5)(PF_3)_3]$ readily affords propylene and $[RhH(PF_3)_4]$ when treated with 1 atm dihydrogen at room temperature even in the absence of excess of trifluorophosphine.[32]

EXPERIMENTAL

Reactions were carried out and complexes handled either *in vacuo* or under an atmosphere of dry dinitrogen. Solvents were dried and freshly distilled under dinitrogen

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[32] J. F. Nixon and B. Wilkins, *J. Organometallic Chem.*, in the press.

before use. N.m.r. spectra were recorded in benzene solutions on a Varian HA 100 spectrometer operating at 100 MHz using benzene as internal standard. ^{19}F N.m.r. spectra were recorded at 94·1 MHz with C_6F_6 as internal standard [$\delta(C_6F_6)$ +162·8 p.p.m. relative to CCl_3F]. I.r. spectra in the 4 000—400 cm^{-1} range were recorded on a Perkin-Elmer 457 spectrometer; volatile complexes were studied in the vapour phase, involatile complexes in Nujol mulls between KBr plates. Elemental analyses (Table 4) were carried out by A. Bernhardt, Elbach über Engelskirchen, W. Germany. Mass spectra were recorded on an A.E.I. MS9 spectrometer.

Preparations.— (1—3-η-*Allyl*)*tris*(*trifluorophosphine*)*cobalt*(I). A solution of tris(1—3-η-allyl)cobalt(III) was prepared as outlined in the literature,[8] by treating [Co(acac)$_3$] [33] (0·400 g, 1·2 mmol) (acac = pentane-2,4-dionato) with allylmagnesium bromide (15 cm^3 of a 0·2 mol dm^{-3} solution in diethyl ether, 3·0 mmol) at −60 °C. The mixture was evaporated to dryness at −40 °C, extracted with cold n-pentane (10 cm^3), and filtered. The resulting orange solution of the complex [Co(η-C_3H_5)$_3$] was transferred under a dinitrogen atmosphere to a cooled ampoule and degassed on the vacuum line; PF_3 (0·220 g, 2·5 mmol) was then condensed in and the tube sealed. The mixture was warmed to room temperature and left for 18 h to give a yellow solution. The ampoule was then opened and volatile components were fractionated in the vacuum line. The product, 1—3-η-*allyltris*(*trifluorophosphine*)*cobalt*(I), collected as a yellow solid at −78 °C {0·112 g, 0·32 mmol; 27% yield based on [Co(acac)$_3$]; m.p. 22 °C}. I.r. spectrum: 3 000—2 850vw, br; 997vw; 962vw; 944m; 920s; 882vs; 851vs; and 798w cm^{-1} (vapour phase). Mass spectrum (*m/e*, ion, relative abundance): 412, $[CoH(PF_3)_4]^+ = X^+$, <1; 404, $[Co(C_6H_9)(PF_3)_3]^+ = Y^+$, <1; 364, $[Co(C_3H_5)(PF_3)_3]^+ = M^+$, 4; 345, $(M - F)^+$, <1; 324, $(X - PF_3)^+$, <1; 316, $(Y - PF_3)^+$, <1; 305, $(X - PF_3 - F)^+$, <1; 276, $(M - PF_3)^+$, 31; 257, $(M - PF_3 - F)^+$, 10; 235, $(M - PF_3 - C_3H_5)^+$, 7; 228, $(Y - 2PF_3)^+$, 2; 209, $(Y - 2PF_3 - F)^+$, <1; 188, $(M - 2PF_3)^+$, 29; 169, $(M - 2PF_3 - F)^+$, 9; 147, $(M - 2PF_3 - C_3H_5)^+$, 34; 100, $(M - 3PF_3)^+$, 62; 98, unknown, 10; 91, unknown, 6; 88, $(PF_3)^+$, 56; 69, $(PF_2)^+$, 100; 67, unknown, 24; and 59, Co$^+$, 49.

[1—3-η-anti-(1-*Methylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I). The *anti*-isomer of the complex [Co(η-C_4H_7)(η-C_4H_6)(PPh_3)] was prepared by the literature method [14] from $CoCl_2$ (1·866 g, 14 mmol), triphenylphosphine (3·318 g, 13 mmol), buta-1,3-diene (40 cm^3), and zinc powder (10·356 g, 160 mmol). The product was obtained as a red crystalline solid (1·070 g, 2·5 mmol; 18% yield based on $CoCl_2$), m.p. 105 °C (decomp.) [lit. 110 °C (decomp.)] (Found: C, 72·9; H, 6·8. Calc. for $C_{26}H_{28}CoP$: C, 72·6; H, 6·5%). This complex (0·157 g, 0·37 mmol), n-pentane (5 cm^3), and an excess of PF_3 (0·380 g, 4·3 mmol) were then sealed in an ampoule and warmed to room temperature to give a yellow solution. The tube was opened after 18 h and the volatile compounds were fractionated in the vacuum line. The product, [1—3-η-anti-(1-*methylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I) collected as a yellow solid at −78 °C {0·092 g, 0·24 mmol; 65% yield based on [Co(η-C_4H_7)(C_4H_6)(PPh_3)]; m.p. 45 °C}. The yellow involatile residue in the ampoule was found to be a mixture of [1—3-η-*anti*-(1-methylallyl)]-bis(trifluorophosphine)(triphenylphosphine)cobalt [31] and free PPh_3 by i.r. spectroscopy. I.r. spectrum: 3 000—2 850w,br; 1 040vw; 972w; 927s; 908m; 880vs; 854s(sh); and 846vs cm^{-1} (vapour phase). The mass spectrum showed a molecular ion, $[Co(C_4H_7)(PF_3)_3]^+$, at *m/e* 378 and the usual fragmentation pattern.

TABLE 4

Some physical properties * of the complexes [CoL(PF_3)$_3$], (I)

L	M.p. † (θ_c/°C)	*M* ‡	Analyses (%) C	H	P
1—3-η-Allyl	22	364 (364)	10·1 (9·9)	1·5 (1·4)	25·4 (23·55)
1—3-η-(1-Methylallyl) (*anti-*)	45	378 (378)	12·7 (12·7)	2·0 (1·85)	24·85 (24·6)
(*syn-*)	0	378 (378)	12·8 (12·7)	1·9 (1·85)	24·7 (24·6)
1—3-η-(1,1-Dimethylallyl)	56	392 (392)	15·3 (15·3)	2·4 (2·3)	23·6 (23·7)
1—3-η-*anti*-(1,2-Dimethylallyl)	98	392 (392)	15·5 (15·3)	2·5 (2·3)	23·5 (23·7)
1—3-η-*syn,syn*-(1,3-Dimethylallyl)	−12	392 (392)	15·5 (15·3)	2·4 (2·3)	23·6 (23·7)
1—3-η-Cyclo-octenyl	35	432 (432)	22·1 (22·2)	3·1 (3·0)	§
1—3-η-Cycloheptadienyl	−15	328 (416 − PF_3)	20·0 (20·2)	2·0 (2·2)	§

* Calculated values are given in parentheses. † *In vacuo*. ‡ From mass spectroscopy. § Not obtained.

[1—3-η-syn-(1-*Methylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I). The analogous complex [Co(η-C_4H_7)(PF_3)$_2$(PPh_3)] [31] {0·136 g, 0·25 mmol; made from excess of [Co(η-C_4H_7)(η-C_4H_6)(PPh_3)] [13] and PF_3}, n-pentane (5 cm^3), and excess of PF_3 (0·240 g, 2·7 mmol) were sealed in an ampoule and left at ambient temperature for 3 d. The tube was opened to the vacuum line and volatile compounds were fractionated, the product, [1—3-η-syn-(1-*methylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I), collecting at −78 °C as a yellow solid (0·040 g, 0·11 mmol; 44% yield based on the initial cobalt complex; m.p. 0 °C). The involatile residue in the ampoule was identified as PPh_3 by i.r. spectroscopy. I.r. spectrum: 3 000—2 840w,br; 1 032vw; 978vw; 940w(sh); 922s; 881vs; 870m(sh); and 845vs cm^{-1} (vapour phase). The mass spectrum showed the molecular ion $[Co(C_4H_7)(PF_3)_3]^+$ at *m/e* 378 and the usual fragmentation pattern.

[1—3-η-(1,1-*Dimethylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I). The η-isoprene complex [Co(η-C_5H_9)(η-C_5H_8)(PPh_3)] was prepared by the literature method,[13] using $CoCl_2$ (1·877 g, 14 mmol), triphenylphosphine (3·305 g, 13 mmol), isoprene (40 cm^3), and zinc powder (17·867 g, 275 mmol). The product was a yellow-brown solid (1·187 g, 2·6 mmol; 18% yield based on $CoCl_2$), m.p. 120 °C (decomp.) (Found: C, 73·6; H, 7·5. Calc. for $C_{28}H_{32}CoP$: C, 73·7; H, 7·0%). On occasions the product was not crystallised, but used in the crude form as a thick red-brown oil. This complex (0·507 g, 1·1 mmol) and n-pentane (5 cm^3) were then sealed in an ampoule with PF_3 (0·165 g, 1·9 mmol) and warmed to room temperature. After 18 h the tube

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[33] B. E. Bryant and W. C. Fernelius, *Inorg. Synth.*, 1957, **5**, 188.

was opened *in vacuo* and volatile components were fractionated to afford the product, [1—3-η-(1,1-*dimethylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I), which collected as an orange solid at −78 °C {0·151 g, 0·39 mmol; 35% yield based on [Co(η-C_5H_9)(η-C_5H_8)(PPh_3)]; m.p. 56 °C}. The orange residue in the ampoule was identified as a mixture of [1—3-η-(1,1-dimethylallyl)]bis(trifluorophosphine)(triphenylphosphine)cobalt[31] and PPh_3, by i.r. spectroscopy. I.r. spectrum: 3 000—2 850w,br; 1 072vw; 1 034vw; 970vw; 923vs; 878vs; and 847vs cm^{-1} (vapour phase). The mass spectrum showed the molecular ion $[Co(C_5H_9)(PF_3)_3]^+$ at *m/e* 392 and the normal fragmentation pattern.

[1—3-η-anti-(1,2-*Dimethylallyl*)]*tris*(*trifluorophosphine*)-*cobalt*(I). (a) The 1,1-dimethylallyl derivative (0·160 g, 0·41 mmol) in n-pentane (5 cm^3) was sealed in an ampoule and heated at 60 °C for 24 h. The tube was opened on the vacuum line, volatile components were fractionated, and the product, [1—3-η-anti-(1,2-*dimethylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I), collected as an orange solid at −78 °C (0·150 g, 0·38 mmol; 93% yield; m.p. 98 °C). Only a trace of an involatile solid was left in the ampoule. I.r. spectrum: 3 000—2 850w,br; 1 040vw; 967vw; 922vs; 877vs; 846vs; and 787vw cm^{-1} (vapour phase). The mass spectrum showed the molecular ion $[Co(C_5H_9)(PF_3)_3]^+$ at *m/e* 392 and the usual fragmentation pattern.

(b) The experiment was repeated in a sealed n.m.r. tube with the 1,1-dimethylallyl derivative (0·050 g, 0·13 mmol) in benzene solution and hexafluorobenzene present as an n.m.r. standard. The tube was heated at 60 °C for 24 h and the ^1H and ^{19}F n.m.r. spectra were recorded at intervals. The spectra showed that conversion to the *anti*-1,2-dimethylallyl isomer was complete in *ca.* 8 h and that no further change occurred on prolonged heating.

[1—3-η-syn,syn-(1,3-*Dimethylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I). The new penta-1,3-diene complex [Co(η-C_5H_9)(η-C_5H_8)(PPh_3)] was prepared by the same method as the analogous isoprene complex,[14] using $CoCl_2$ (1·823 g, 14 mmol), triphenylphosphine (3·322 g, 13 mmol), penta-1,3-diene (40 cm^3), and zinc powder (16·129 g, 250 mmol). The product was obtained as orange-brown crystals [m.p. 120 °C (decomp.)], but was usually used in a crude form as a thick red-brown oil (Found: C, 72·8; H, 7·4. Calc. for $C_{28}H_{32}CoP$: C, 73·3; H, 7·0%). Mass spectrum: highest mass peak at *m/e* 458, $[Co(C_5H_9)(C_5H_8)(PPh_3)]^+ \equiv M^+$. A crude sample of this complex was then dissolved in n-pentane (5 cm^3) and sealed in an ampoule with PF_3 (0·476 g, 5·4 mmol). After 1 week at room temperature the tube was opened on the vacuum line and volatile components were separated by fractionation. The product, [1—3-η-syn,syn-(1,3-*dimethylallyl*)]*tris*(*trifluorophosphine*)-*cobalt*(I), was collected as an orange solid at −78 °C (0·220 g, 0·56 mmol; 4% yield based on $CoCl_2$; m.p. −12 °C). The remaining sticky orange solid in the ampoule was found to be a mixture of [1—3-η-*syn,syn*-(1,3-dimethylallyl)]bis(trifluorophosphine)(triphenylphosphine)cobalt[31] and free triphenylphosphine by i.r. spectroscopy. I.r. spectrum of the $(PF_3)_3$ complex: 3 020—2 820w,br; 924vs; 898m; 876vs; and 840vs cm^{-1} (vapour phase). The mass spectrum showed the molecular ion $[Co(C_5H_9)(PF_3)_3]^+$ at *m/e* 392 and the usual fragmentation pattern.

(1—3-η-*Cyclo-octenyl*)*tris*(*trifluorophosphine*)*cobalt*(I). The complex [Co(η-C_8H_{13})(η-C_8H_{12})] was prepared by a modified version of the literature method.[15] A mixture of $CoCl_2$ (2·432 g, 19 mmol), cyclo-octa-1,5-diene (8 cm^3), and tetrahydrofuran (80 cm^3) were stirred at room temperature for 60 h to give a royal blue suspension. Dry pyridine was added until the mixture turned purple (*ca.* 15 cm^3) and the resultant thick suspension was stirred for 1 h. The tube was cooled to 0 °C, sodium chips (1·075 g, 47 mmol) added, and the mixture stirred at 0 °C for 8 h to give a brown-black suspension. The mixture was filtered and the filtrate evaporated to dryness, giving a thick black oil which was used without further purification. This impure complex was dissolved in n-pentane (20 cm^3), sealed in two ampoules with PF_3 (1·026 g, 12 mmol), and left at room temperature for 3 d to give red-brown solutions. The ampoules were then opened and volatile components were fractionated. The product collected as an oily orange solid at −78 °C. This was purified by pumping at room temperature to remove organic impurities, leaving (1—3-η-*cyclo-octenyl*)*tris*(*trifluorophosphine*)*cobalt*(I) as an orange crystalline solid (0·525 g, 1·2 mmol; 7% yield based on $CoCl_2$; m.p. 35°). A black involatile residue remained in the tube. I.r. spectrum: 922w; 892vw; 872w; 848w,br; (vapour phase); 916vs; 886m; 860s; 834s(sh); 824s (benzene solution); 920vs, 890—820vs,br; 540s; 520vs,br; 456m; and 400m cm^{-1} (Nujol mull). Mass spectrum: *m/e* 432 $[Co(C_8H_{13})(PF_3)_3]^+ \equiv M^+$; 344, $(M - PF_3)^+$; 325, $(M - PF_3 - F)^+$; 256, $(M - 2PF_3)^+$; 254, $[Co(C_8H_{11})(PF_3)]^+$; 237, $(M - 2PF_3 - F)^+$; 235, $(M - PF_3 - C_8H_{13})^+$ or $[Co(C_8H_{11})(PF_2)]^+$; 216, $(M - PF_3 - F - C_8H_{13})^+$; 168, $[Co(C_8H_{13})]^+$; 166, $[Co(C_8H_{11})]^+$; 147, $[Co(PF_3)]^+$; 138, $[Co(C_6H_7)]^+$; 137, $[Co(C_6H_6)]^+$; 126, $[Co(C_5H_7)]^+$; 125, $[Co(C_5H_5)]^+$; 109, $C_8H_{13}^+$; 108, $C_8H_{12}^+$; 88, PF_3^+; 79, $C_6H_7^+$; 69, PF_2^+; and 67, $C_5H_7^+$.

(1—3-η-*Cycloheptadienyl*)*tris*(*trifluorophosphine*)*cobalt*(I). The impure complex [Co(η-C_7H_9)$(PF_3)_2$(PPh_3)] (0·506 g, 0·86 mmol), n-pentane (5 cm^3), and PF_3 (0·599 g, 6·8 mmol) were sealed in an ampoule and left at room temperature for 8 d. The tube was then opened on the vacuum line and volatile components were fractionated. The product, (1—3-η-*cycloheptadienyl*)*tris*(*trifluorophosphine*)*cobalt*(I), collected as an orange solid at −78 °C (0·062 g, 0·15 mmol; 17% yield based on cobalt complex; m.p. −15 °C). A red solid remaining in the ampoule was identified as unreacted [Co(η-C_7H_9)$(PF_3)_2$(PPh_3)] by i.r. spectroscopy. I.r. spectrum [decomposition in the vapour phase gave rise to free PF_3 which obscured the ν(P–F) region]: 910vs; 892s; 862s; 840s(sh); and 830vs cm^{-1} (benzene solution). Mass spectrum: *m/e* 412, $[CoH(PF_3)_4]^+ \equiv X^+$; 393, $(X - F)^+$; 379, unknown; 328, $[Co(C_7H_9)(PF_3)_2]^+ \equiv (M - PF_3)^+$; 324, $(X - PF_3)^+$; 304, $(X - PF_3 - F - H)^+$; 290, unknown; 240, $(M - 2PF_3)^+$; 221, $(M - 2PF_3 - F)^+$; 216, unknown; 202, unknown; 186, unknown; 152 $(M - 3PF_3)^+$; 150, $(C_7H_7)^+$; 92, $C_7H_8^+$; 91, $C_7H_7^+$; and 88, PF_3^+.

(1—3-η-*Cycloheptadienyl*)*bis*(*trifluorophosphine*)(*triphenylphosphine*)*cobalt*(I). The impure complex [Co(η-C_7H_9)$(PF_3)_2$] (0·693 g, 2·1 mmol), triphenylphosphine (0·510 g, 2·0 mmol), and n-pentane (3 cm^3) were shaken for 3 d at room temperature in a sealed tube to give a red crystalline solid and solution. The tube was then opened and volatile components were removed *in vacuo*. The solid residue was washed with hexane and dried under high vacuum to give impure [Co(η-C_7H_9)$(PF_3)_2$(PPh_3)] (0·548 g, 0·93 mmol; 48% yield based on the crude cobalt complex). The impure product was further purified by dissolving in hexane (10 cm^3) and treating with a saturated solution of $CoCl_2$ in ethanol (1 cm^3). The resulting precipitate was filtered off and the filtrate evaporated to dryness. The solid residue was extracted with hexane (10 cm^3) and the solution was slowly concentrated to give red crystals of (1—3-η-*cycloheptadienyl*)*bis*(*trifluorophosphine*)(*triphenylphosphine*)*cobalt*(I), m.p. 116—118 °C. I.r. spectrum: 3 060w; 3 020w; 1 479m; 1 435s; 1 180w; 1 090m,s; 1 030w; 1 000w; 873vs; 854s; 840vs; 825s(sh); 819vs; 800vs; 750s; 744m(sh); 720mw; 697s; 688w(sh); 613w; 539s; 525s; 512vs; 545w; and 431w cm^{-1} (Nujol mull).

Reaction of the Complex $[Co(\eta\text{-}C_7H_9)(\eta\text{-}C_8H_{12})]$ *with Trifluorophosphine*.—(a) The complex was prepared by the literature method,[29] heating a mixture of crude $[Co(\eta\text{-}C_8H_{13})(C_8H_{12})]$ and cyclohepta-1,3,5-triene (5 cm^3) in hexane (40 cm^3) under reflux for 3 h. The resulting solution was filtered and evaporated to dryness to give a brown-black oil which was dissolved in n-pentane (10 cm^3), sealed in an ampoule with PF_3 (0·457 g, 5·2 mmol), and left at room temperature for 1 week. The ampoule was then opened and volatile components were fractionated on the vacuum line. (1—5-η-*Cycloheptadienyl*)*bis*(*trifluorophosphine*)*cobalt*(I) collected as a red oil at −78 °C, from which it was not possible to remove all organic impurities. Because of this contamination, a satisfactory elemental analysis was not obtained. An unidentified black residue was left in the ampoule. I.r. spectrum: 908m(sh); 890vs; 855m(sh); 830s(sh); and 818vs cm^{-1} (benzene solution). Mass spectrum : organic impurities prevented accurate identification, but peaks were observed at *m/e* 328, $[Co(C_7H_9)(PF_3)_2]^+$, and 240, $[Co(C_7H_9)(PF_3)]^+$.

(b) In a second experiment, impure $[Co(\eta\text{-}C_7H_9)(C_8H_{12})]$ was treated with an excess of PF_3 (0·931 g, 11 mmol) to give a mixture of the complexes $[Co(\eta\text{-}C_7H_9)(PF_3)_2]$ and $[Co(\eta\text{-}C_7H_9)(PF_3)_3]$, identified by ^1H and ^{19}F n.m.r. spectroscopy.

Effect of Heat on Complexes (I).—Benzene solutions of the complexes in sealed n.m.r. tubes were heated at 60 °C for at least 8 h and the ^1H n.m.r. spectra monitored. No isomerisation was noted, except for the 1,1-dimethylallyl isomer already mentioned. After heating for 1 d, there were signs of slow decomposition with loss of signal strength and line broadening.

Effect of Heat on Tricarbonyl[1—3-η-(1,1-*dimethylallyl*)]-*cobalt*.—The salt $Tl[Co(CO)_4]$ [20] (0·683 g, 1·8 mmol), diethyl ether (2 cm^3), and 1-chloro-3-methylbut-2-ene (0·114 g, 1·1 mmol) were stirred together in a Schlenk tube for 15 min at room temperature to give a brown solution. The volatile components were fractionated on the vacuum line and the product, $[Co(\eta\text{-}C_5H_9)(CO)_3]$, collected as an orange oil at −78 °C (0·051 g, 0·24 mmol; 22% yield based on olefin used). The i.r. and ^1H n.m.r. spectra were identical to those reported in the literature.[1] A benzene solution of the complex in a sealed n.m.r. tube was heated for 1 d at 60 °C, but only slow decomposition was detectable by ^1H n.m.r. spectroscopy.

Reaction of Complexes (I) *with Hydrogen Chloride*.—N.m.r. samples of complexes (I) (*ca.* 0·05 g, 0·13 mmol) in benzene solution were sealed in glass tubes of *ca.* 5 cm^3 capacity with an excess of dry hydrogen chloride (*ca.* 0·10 g, 2·8 mmol) and left at room temperature for *ca.* 1 month. In this time the yellow solutions slowly lost their colour and deposited pale blue precipitates. Each tube was opened separately on the vacuum line and volatile components were fractionated and identified by i.r. spectroscopy. Excess of hydrogen chloride, displaced PF_3, and silicon tetrafluoride (SiF_4) were collected at −196 °C. Unreacted complex, benzene, and the corresponding chloroalkane collected at −78 °C for the methylallyl and dimethylallyl complexes, while the product from reaction with the simple η-allyl complex was collected only at −126 °C.

The chloroalkanes formed were readily identified from the ^1H n.m.r. spectra obtained. The η-allyl complex gave Me_2HCCl [3·42 (1H ≡ H); spt (*J* 6·3); 6·01 p.p.m. (6H ≡ 2Me), d (*J* 6·3 Hz)]; the *anti*- and *syn*-isomers of the 1-methylallyl complex both gave EtMeHCCl [3·53 (1H ≡ H), sxt (*J* 6·3); 5·68 (2H ≡ CH_2), complex qnt (*J ca.* 6·5); 5·93 (3H ≡ Me), d (*J* 6·5); and 6·30 p.p.m. (3H ≡ Me of Et), complex (*J* 7·3 Hz)]; the 1,1-dimethyl-, *anti*-1,2-dimethyl-, and 2-ethyl-allyl complexes all gave $EtMe_2CCl$ [5·59 (2H ≡ CH_2), qt (*J* 7·1); 5·80 (6H ≡ 2Me), s; and 6·24 p.p.m. (3H ≡ Me of Et), t (*J* 7·1 Hz)]; and the *syn,syn*-1,3-dimethylallyl complex gave a mixture of Et_2HCCl and $Pr^nMeHCCl$ in a ratio of 55 : 45, as determined by integration of the ^1H n.m.r. spectrum [Et_2HCCl 3·63 (1H ≡ H), qnt (*J* 6·2); 5·6 (2CH_2), complex multiplet; and 6·22 (2Me of Et_2), t (*J* 7·1); $Pr^nMeHCCl$ 3·38 (1H ≡ H), complex sxt (*J ca.* 6·2); 5·6 (2CH_2), complex multiplet; 5·84 (3H ≡ Me), d (*J* 6·5); and 6·22 p.p.m. (Me of Pr^n), t (*J* 7·1 Hz)].

The pale blue involatile residues in the tubes were found by elemental analysis to be practically free of organic material and were extremely hygroscopic. They were probably mixtures of cobalt(II) chloride and unidentified by-products from the reactions. In all cases SiF_4 was formed, indicating involvement of the glass of the ampoule in the decomposition. Experiments over shorter periods (*e.g.*, 1 week) or with hydrogen chloride not in excess gave incomplete reaction with recovery of starting materials; no eliminated olefin was ever detected, only the chloroalkane.

Reaction of [1—3-η-(1,1-*Dimethylallyl*)]*tris*(*trifluorophosphine*)*cobalt*(I) *with* PF_3 *and Dihydrogen*.—The complex (0·215 g, 0·55 mmol) and PF_3 (0·312 g, 3·5 mmol) were condensed into a Schlenk tube of 150 cm^3 capacity at −196 °C and dihydrogen (10 mmHg) was added. The tube was then closed and left at room temperature for 3 d, with occasional shaking. Fractionation of the contents on the vacuum line gave only unreacted starting materials. A small amount of solid residue indicated some decomposition had taken place.

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