(1—3-η-Allyl)tris(trifluorophosphine)rhodium(I) Complexes: Syntheses, Phosphine-ligand Exchange, and an Unusual η-Allyl Isomerisation Process

By **John F. Nixon,* Brian Wilkins,** and (in part) **D. Alun Clement,** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Different synthetic routes to a series of volatile (1—3-η-allyl)tris(trifluorophosphine)rhodium(I) complexes [RhL(PF_3)$_3$] are described [I; L = 1—3-η-allyl, -(2-methylallyl), -(1-methylallyl) (*syn*- and *anti*-), -(1,2-dimethylallyl) (*syn*- and *anti*-), -(1,1-dimethylallyl), -(1,3-dimethylallyl) (*syn*- and *anti*-), -(1-ethyl-3-methylallyl) (*syn*- and *anti*-), and cyclohexenyl]. A novel thermal isomerisation of the 1—3-η-(1,1-dimethylallyl) complex to the 1,2-form is reported and a possible mechanism discussed. Variable-temperature ^{19}F and ^{1}H n.m.r. spectra are presented and establish that ready *inter*- and *intra*-molecular phosphine-exchange processes are both occurring in all these complexes.

RELATIVELY few η-allyl complexes of rhodium(I) have been reported; [RhL(PPh_3)$_2$] (L = 1-3-η-allyl) has been prepared by reacting allylmagnesium chloride with [RhCl(PPh_3)$_3$],[1] while substituted allyl analogues have been obtained from the reaction between [RhH(PPh_3)$_4$] and conjugated dienes.[1] More recently complexes of the type [RhL(CO)(PPh_3)$_2$] [L = 1—3-η-allyl or 1—3-η-(2-methylallyl)] have been described using either [RhH(CO)(PPh_3)$_3$] or *trans*-[RhCl(CO)(PPh_3)$_2$] as precursors,[2] while the lack of an analogous series of η-allyl carbonyl rhodium(I) complexes reflects the extreme instability of [RhH(CO)$_4$]. There is disagreement regarding the formulation of the air-sensitive complex [RhL(CO)$_x$] (L = 1—3-η-allyl) which has been made by different routes and is variously reported to be a dicarbonyl [3,4] or a tricarbonyl [5] complex.

We now describe a series of η-allyl rhodium complexes containing trifluorophosphine which are thermally stable, and present n.m.r. spectroscopic evidence which establishes that these complexes undergo a ready *inter*- and *intra*-molecular phosphine ligand-exchange process.†

RESULTS AND DISCUSSION

Tris(1—3-η-allyl)rhodium(III) reacts at room temperature with a large excess of trifluorophosphine to afford the volatile yellow liquid complex (1—3-η-allyl)tris(trifluorophosphine)rhodium(I), (I). Complex (I) was also obtained from the reaction between [RhH(PF_3)$_4$] and allene or from K[Rh(PF_3)$_4$] and allyl bromide. A series of substituted 1—3-η-allyltris(trifluorophosphine)rhodium(I) complexes, [RhL(PF_3)$_3$], was obtained similar routes. Addition of [RhH(PF_3)$_4$] to buta-1,3-diene, or of K[Rh(PF_3)$_4$] to but-2-enyl bromide, gave the 1—3-η-methylallyl complex in both *syn*- and *anti*-forms, the former being the major product. In a similar fashion were prepared the 1—3-η-cyclohexenyl, -(2-methylallyl), -(1,2-dimethylallyl) (*syn*- and *anti*-forms), -(1,1-dimethylallyl), -(1,3-dimethylallyl) (*syn,syn*- and *anti,syn*-forms), and -(1-ethyl-3-methylallyl) complexes in (*syn,syn*- and *syn,anti*-forms). The presence of isomeric forms of the complexes in the reaction products was unambiguously established by both their ^{19}F and ^{1}H n.m.r. spectra (see later).

All the complexes are volatile yellow liquids at room temperature except the L = 1—3-η-(1,2-dimethylallyl) derivative which is a low-melting crystalline solid. The complexes were conveniently handled in a high-vacuum system, but the 1—3-η-cyclohexenyl and -(1-ethyl-3-methylallyl) derivatives are only slightly volatile. In solution the complexes are stable in the absence of air for several days, but may be stored for longer periods in the presence of a slight pressure of trifluorophosphine. Microanalytical data obtained for all the complexes were in good agreement with the presence of three trifluorophosphine ligands, and this was confirmed by a careful study of the reaction stoicheiometries. The low-temperature ^{19}F n.m.r. spectra were interpreted as $[AX_3]_3$ spin systems (A = P, X = F) [6] and are discussed elsewhere.

Interestingly, ambient-temperature mass spectra of the complexes in all cases showed molecular ions corresponding to [RhL(PF_3)$_2$]$^+$ rather than the parent ion. The spectra can be interpreted in terms of stepwise loss of ligands from the complexes [RhL(PF_3)$_2$]. It would seem, therefore, that under electron impact one trifluorophosphine ligand is much more easily lost than in the recently reported [7,8] analogous cobalt complexes, which show a parent ion corresponding to [CoL(PF_3)$_3$]$^+$. These observations are compatible with the ease with which the rhodium complexes undergo intermolecular exchange compared with their cobalt analogues (see below), and suggest that the complex [RhL(CO)$_2$] (L = 1—3-η-allyl), which was partly characterised by its mass spectrum,[3] may in fact be a tricarbonyl species.

The initial products of the reactions were modified in several cases by subsequent thermal *anti–syn*-isomerisation processes. *anti*- and *syn*-Forms of the 1—3-η-(1,2-dimethylallyl) derivative were formed in a 3 : 2 ratio on addition of [RhH(PF_3)$_4$] to 2-methylbuta-1,3-diene. When heated to 60 °C in solution, the *anti*-form totally

† A preliminary report of part of this work has appeared (D. A. Clement, J. F. Nixon, and B. Wilkins, *J. Organometallic Chem.*, 1972, **37**, C43).

[1] C. A. Reilley and H. Thyret, *J. Amer. Chem. Soc.*, 1967, **89**, 5144.

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

[3] S. O'Brien, *Chem. Comm.*, 1968, 751.

[4] E. W. Abel and S. Moorhouse, *Angew. Chem. Internat. Edn.*, 1971, **10**, 339.

[5] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 583.

[6] J. F. Nixon, *J. Fluorine Chem.*, 1973, **3**, 179.

[7] M. A. Cairns and J. F. Nixon, *J. Organometallic Chem.*, 1973, **51**, C27.

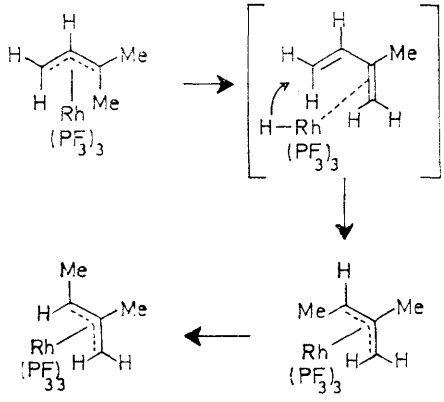
[8] M. A. Cairns and J. F. Nixon, following paper.

isomerised to the *syn*-form, after 1 h. A similar isomerisation of the *anti,syn*- and *syn,syn*-forms of the 1—3-η-(1,3-dimethylallyl) derivative was observed when roughly equimolar amounts of the two forms were heated. This isomerisation also took place at 0 °C over a period of weeks. Similar isomerisations have been shown *not* to occur for the analogous cobalt complexes,[8] but are well known for η-allyl derivatives of tricarbonylcobalt(I) [9] and tris(trimethyl phosphite)nickel(I) complexes.[10] It is interesting to note that complexes which undergo this type of isomerisation also readily undergo ligand exchange. It has been suggested [11] that isomerisation involving rotation about carbon–carbon bonds in the allyl ligand is unlikely if these carbon atoms carry alkyl substituents. A more probable alternative is a process involving a σ-intermediate.

Isomers of the 1—3-η-(1,2-dimethylallyl) complex were prepared by addition of $[RhH(PF_3)_4]$ to 2-methylbuta-1,3-diene. There are, however, two directions in which a metal hydride may add to 2-methylbuta-1,3-diene. Addition to C(3),C(4) would result in a 1—3-η-(1,2-dimethylallyl) complex, whereas a 1—3-η-(1,1-dimethylallyl) complex would be formed by addition to C(1),C(2). It has been suggested [2] that the acidity of a transition-metal hydride determines its direction of addition to an asymmetrical conjugated diene. It has been shown previously that $[CoH(CO)_4]$ adds to the more basic double bond at C(1),C(2),[9] whereas the weakly acidic hydride $[IrH(CO)_2(PPh_3)_2]$ adds at C(3),C(4).[2] The different behaviour of the strongly acidic hydrides $[RhH(PF_3)_4]$ and $[CoH(CO)_4]$ towards 2-methylbuta-1,3-diene, affording 1—3-η-(1,2-dimethylallyl) and -(1,1-dimethylallyl) complexes respectively, is not compatible with this proposal. It is noteworthy that the complex $[RhH(PF_3)_4]$ adds to the *least*-substituted double bonds in all 1,3-dienes studied in this work. The reaction between $[NiH\{P(OMe)_3\}_4]^+$ and 2-methylbuta-1,3-diene has been reported to give 1—3-η-(1,2-dimethylallyl) and -(1,1-dimethylallyl) complexes in a 5 : 1 ratio.[10]

The complex $[RhH(PF_3)_4]$ reacts with penta-1,4-diene affording only the 1—3-η-(1,3-dimethylallyl) derivative, whereas $[CoH(CO)_4]$ is known to give a mixture of 1—3-η-(1,3-dimethylallyl) and -(1-ethylallyl) complexes.[12] Formation of the 1—3-η-(1-ethylallyl) complex has been rationalised in terms of hydrogen transfer to the diene followed by 1,2-hydrogen shift. Since in general 1—3-η-(1,3-dimethylallyl) complexes are produced by addition of a metal hydride to penta-1,3-diene, formation of such a derivative from penta-1,4-diene and $[RhH(PF_3)_4]$ probably involves isomerisation of the diene to the 1,3-form prior to metal-hydride addition. Further supporting evidence comes from the observation that $[NiH\{P(OMe)_3\}_3]^+$ is known to add to an excess of penta-1,4-diene to form a 1,3-dimethylallyl complex and penta-1,3-diene.[10]

The 1—3-η-(1,1-dimethylallyl) complex is *not* a product of the reaction between $[RhH(PF_3)_4]$ and 2-methylbuta-1,3-diene, but is afforded by the reaction between $K[Rh(PF_3)_4]$ and 1,1-dimethylallyl chloride. A careful study of this latter reaction led to the discovery of a novel type of η-allyl isomerisation.[13] The first product isolated the 1,1-dimethylallyl complex, but on prolonged heating a mixture of *syn*- and *anti*-isomers of the 1,2-methylallyl complex was formed. Furthermore, on heating a sample of the 1,1-complex at 60 °C in an n.m.r. tube and following the reaction by ^1H n.m.r. spectroscopy, the *anti*-isomer of the 1,2-complex was the initial product observed and subsequently isomerised to the *syn*-isomer. Since the *syn*- and *anti*-isomers are the *sole* products of the reaction between 2-methylbuta-1,3-diene and $[RhH(PF_3)_4]$, the mechanism of the isomerisation process most likely involves a 1,4-hydrogen shift, with intermediate formation of a diene metal hydride



SCHEME

as shown in the Scheme.* The initial preferential formation of the *anti*-isomer suggests the diene is co-ordinated in the *cisoid* form in the intermediate. It has recently been shown that the analogous cobalt complex [1—3-η-(1,1-dimethylallyl)]tris(trifluorophosphine)cobalt(I) isomerises to [*anti*-1—3-η-(1,2-dimethylallyl)]tris(trifluorophosphine)cobalt(I) on heating.[13] Furthermore, on the basis of published n.m.r. data, it seems likely that the complex $[CoH(PF_3)_4]$, on addition to 2-methylbuta-1,3-diene, affords [*anti*-1—3-η-(1,2-dimethylallyl)]tris(trifluorophosphine)cobalt(I).[14] As already mentioned, tricarbonyl[1—3-η-(1,1-dimethylallyl)]cobalt(I) is the *sole* product of addition of $[CoH(CO)_4]$ to 2-methylbuta-1,3-diene and as expected shows no tendency to isomerise to the 1,2-dimethylallyl complex.[13] These results support a previous suggestion [15] that tetracarbonyl[1—3

* *Added at Proof:* Such a type of intermediate has recently been isolated, *viz.* (2,3-dimethylbuta-1,3-diene)hydridobis(triphenylphosphine)cobalt(I), P. V. Rinze, *Angew. Chem. Internat. Edn.*, 1974, **13**, 336.

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

[10] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6777.

[11] P. W. N. M. Van Leeuwen and A. P. Praot, *Chem. Comm.*, 1970, 365.

[12] S. Husebye, H. B. Jonassen, and D. W. Moore, *Acta Chem. Scand.*, 1964, **18**, 1581.

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

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

[15] M. Green and R. I. Hancock, *J. Chem. Soc.* (*A*), 1968, 109.

η-(1-phenacylallyl)]manganese(I) (not isolated) is the first product of reaction between buta-1,3-diene and pentacarbonylphenylmanganese(I) and subsequently isomerises to [1—3-η-(3-benzoyl-1-methylallyl)]tetracarbonylmanganese(I) by a similar mechanism which involves a 1,4-hydrogen shift.

The stabilities of the (η-allyl)tris(trifluorophosphine)rhodium(I) complexes contrasts with the much lower stabilities of the related (η-allyl)carbonylbis(triphenylphosphine)rhodium(I) complexes reported by Wilkinson and his co-workers.[2] In particular the 1—3-η-cyclohexenyl complex is sufficiently stable to allow complete characterisation, whereas no such complex could be isolated by Wilkinson from the reaction between cyclohexa-1,3-diene and [RhH(CO)(PPh_3)$_3$]. The ^{1}H n.m.r. spectra of the trifluorophosphine complexes are also much better resolved and greatly assist their characterisation.

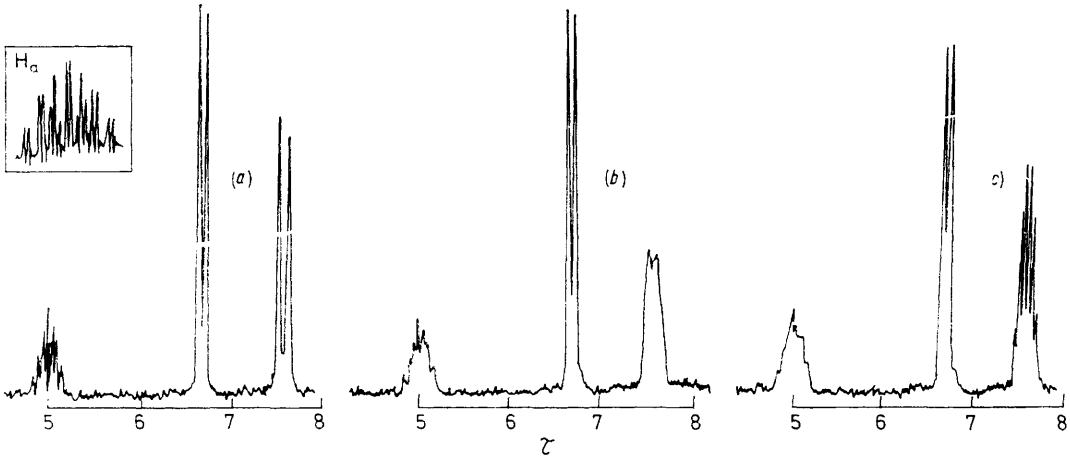
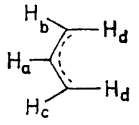


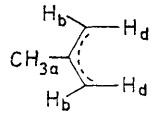
FIGURE 1 ^{1}H N.m.r. spectra of (1—3-η-allyl)tris(trifluorophosphine)rhodium(I) at (*a*) room temperature, (*b*) −20, and (*c*) −50 °C in CCl_3F solution

^{1}H *N.m.r. Spectra.*—*(1—3-η-Allyl)tris(trifluorophosphine)rhodium*(I). The room-temperature spectrum shown in Figure 1 is easily interpreted on the basis of a η-allyl ligand symmetrically bonded to rhodium. The doublet at highest field was assigned to the pair of *anti*-protons, H_d, coupled to the central proton H_a. Similarly



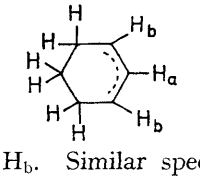
the pair of *syn*-protons, H_b, gave rise to a doublet at lower field. The signal assigned to H_a was split into a symmetrical 16-line pattern of relative intensities 1 : 1 : 2 : 2 : 2 : 3 : 1 : 4 : 4 : 1 : 3 : 2 : 2 : 2 : 1 : 1, arising from coupling to the *syn*- and *anti*-protons and to ^{103}Rh ($I = \frac{1}{2}$, 100% natural abundance). The spectrum above room temperature sharpened slightly, but was basically unchanged even at 100 °C. Chemical-shift and coupling-constant data are listed in Tables 1—3. On cooling the sample to −50 °C, the ^{1}H n.m.r. spectrum changed significantly. The doublet resonance of the *anti*-protons changed into a six-line pattern of relative intensity 1 : 3 : 4 : 4 : 3 : 1, arising from coupling to three equivalent phosphorus nuclei. The resonance of the *syn*-protons broadened slightly, and the fine structure of the H_a resonance disappeared.

The 1—3-η-(2-*methylallyl*) *derivative.* The room-temperature ^{1}H n.m.r. spectrum * consisted of three lines



of relative intensity 3 : 2 : 2 assigned to the unique methyl group CH_{3a}, the pair of *anti*-protons H_d, and the pair of *syn*-protons H_b, respectively. At −50 °C, the CH_{3a} resonance and the H_d and H_e resonance both became 1 : 3 : 3 : 1 quartets, due to coupling to three magnetically equivalent phosphorus nuclei, while the other resonance was unchanged.

The 1—3-η-*cyclohexenyl derivative.* The room-temperature spectrum consisted of four groups of resonances of relative intensity 2 : 4 : 2 : 1. The two high-field resonances were assigned to the methylene protons of the cyclohexenyl ring and were rather poorly resolved. The resonance assigned to the pair of allylic protons H_b was also a poorly resolved multiplet, while the low-field resonance assigned to H_a occurred as a triplet arising



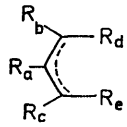
from coupling to H_b. Similar spectra have been reported for di-μ-chloro-bis[(1—3-η-cyclohexenyl)palladium(II)] [16] and [Rh(η-C_6H_9)(PPh_3)$_2$].[1] On cooling the sample to −50 °C, all the resonances broadened.

* ^{1}H N.m.r. spectra of the substituted η-allyl derivatives are to be found in Supplementary Publication No. SUP 21064 (7 pp.). For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

[16] B. L. Shaw and N. Sheppard, *Chem. and Ind.*, 1961, 517.

TABLE 1

^{1}H N.m.r. chemical shifts and coupling constants (J/Hz) of some η-allyl complexes [RhL$(PF_3)_3$] *



L	$\tau(R_a)$	$\tau(R_b)$	$\tau(R_c)$	$\tau(R_d)$	$\tau(R_e)$	$J(R_aR_b)$	$J(R_aR_c)$	$J(R_aR_d)$	$J(R_aR_e)$	$J(R_bR_d)$	$J(R_cR_e)$	$J(RhR_a)$
1—3-η-Allyl: R = H	5·0	6·7		7·6		6·1		10·2				1·8
1—3-η-(2-Methylallyl): R_a = Me, R_{b-e} = H	7·9	6·5		7·5								
1—3-η-(1-Methylallyl) (*syn*-): $R_{a,c-e}$ = H, R_b = Me	5·1	8·1	6·9	6·4	7·9		6·0	10·0	9·5	6·5	1·5	
(*anti*-): $R_{a,c-e}$ = H, R_d = Me	5·1	5·4	6·4	8·6	6·9		6·5		10·0	6·5		
1—3-η-(1,1-Dimethylallyl): $R_{a,c,e}$ = H, $R_{b,d}$ = Me	5·1	7·9	6·8	8·3	7·3		6·4		10·5		2·0	1·0
1—3-η-(1,2-Dimethylallyl) (*syn*-): $R_{a,b}$ = Me, R_{c-e} = H	7·9	8·2	6·8	6·5	7·9					6·0		
(*anti*-): $R_{a,d}$ = Me, $R_{b,c,e}$ = H	8·0	5·4	6·4	8·5	6·9					6·5		
1—3-η-(1,3-Dimethylallyl) (*syn,syn*-): $R_{a,d,e}$ = H, $R_{b,c}$ = Me	5·2	8·2		6·7				9·3		6·0		1·0
(*anti,syn*-): $R_{a,b,e}$ = H, $R_{d,c}$ = Me	5·1	5·6	8·1	8·6	5·8	6·0			10·0	6·8	6·3	1·0

* Chemical shifts are relative to tetramethylsilane; spectra were recorded at room temperature in CCl_3F.

TABLE 2

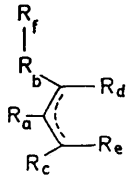
Phosphorus–hydrogen spin coupling constants (Hz) for some η-allyl complexes [RhL$(PF_3)_3$] *

L †	$J(PR_a)$	$J(PR_b)$	$J(PR_d)$	$J(PR_e)$
1—3-η-Allyl			4·6	
1—3-η-(2-Methylallyl)	4·0		5·9	
1—3-η-(1-Methylallyl) (*syn*-)		7·5		5·0
(*anti*-)			9·0	
1—3-η-(1,1-Dimethylallyl)		7·5	9·0	
1—3-η-(1,2-Dimethylallyl) (*syn*-)	4·0	7·5		
(*anti*-)	4·0		8·5	5·0
1—3-η-(1,3-Dimethylallyl) (*syn,syn*-		7·5 ‡		
(*anti,syn*-)			8·0	

* CCl_3F Solutions at −50 °C. † For key see Table 1. ‡ $J(PR_c)$ 7·5 Hz.

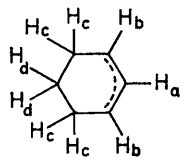
TABLE 3

^{1}H N.m.r. chemical shifts and coupling constants (J/Hz) for complexes [RhL$(PF_3)_3$] *



	$\tau(R_a)$	$\tau(R_b)$	$\tau(R_c)$	$\tau(R_d)$	$\tau(R_e)$	$\tau(R_f)$	Solvent
1—3-η-(1-Ethyl-3-methylallyl) (*syn,syn*-): $R_{a,d,e}$ = H, R_b = CH_2, $R_{c,f}$ = Me	5·2	7·8	8·1	6·6	6·6	8·7	C_6H_5F
(*syn,anti*-): $R_{a,c,d}$ = H, R_b = CH_2, $R_{e,}$ = Me	5·0		5·5	5·7	8·5	8·7	C_6H_5F

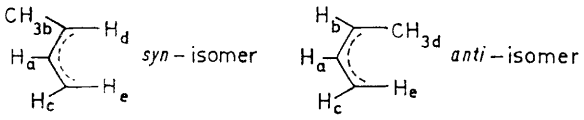
	$J(R_aR_d)$	$J(R_aR_e)$	$J(R_cR_e)$	$J(R_bR_f)$	$J(PR_c)$	$J(PR_e)$	
(*syn,syn*-)	9·0	9·0	6·0	7·5	7·5		C_6H_5F
(*syn,anti*-)			6·5	7·5		8·0	C_6H_5F



	$\tau(H_a)$	$\tau(H_b)$	$\tau(H_c)$	$\tau(H_d)$	$J(H_aH_b)$	
1—3-η-Cyclohexenyl	5·1	5·4	8·4	8·8	6·0	C_6H_5F

* Chemical shifts relative to tetramethylsilane. All measurements were at room temperature except for $J(PR_c)$ and $J(PR_e)$ of the 1-ethyl-3-methylallyl derivative which were at −50 °C.

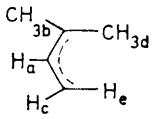
syn- *and* anti-*Isomers of the* 1—3-η-(1-*methylallyl*) *derivative*. At room temperature the spectrum of the *syn*-isomer exhibited five resonances of relative intensities 3 : 1 : 1 : 1 : 1. The doublet at highest field (intensity 3) was unambiguously assigned to CH_{3b} coupled to the



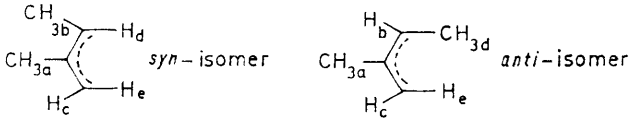
anti-proton H_d. The H_e resonance consisted of a doublet arising from coupling to H_a and was further broadened by interaction with H_c. Expansion showed the H_c resonance to be a doublet of doublets arising from coupling to the protons H_a and H_e. The eight-line pattern of relative intensity 1 : 3 : 1 : 3 : 3 : 1 : 3 : 1 was assigned to H_d, and arises from coupling to H_a and CH_{3b}. The six-line pattern at lowest field was assigned to H_a, and arises from coupling to H_c, and almost equal coupling to both H_d and H_e. On cooling the sample to −50 °C, the H_e and CH_{3b} resonances clearly showed further 1 : 3 : 3 : 1 quartet patterns due to coupling with three magnetically equivalent phosphorus nuclei. All the other resonances broadened.

The room-temperature spectrum of the *anti*-isomer was poorly resolved and could not be fully assigned. The CH_{3d} group occurred as a doublet, arising from coupling to H_b, and at −50 °C this resonance showed coupling to three equivalent phosphorus nuclei. The other resonances were rather weak and partially obscured by the spectrum of the *syn*-isomer.

The 1—3-η-(1,1-*dimethylallyl*) *derivative*. The room-temperature ^1H n.m.r. spectrum consisted of five resonances. The CH_{3d} and CH_{3b} groups occurred as sharp singlets at high field. A broad doublet resonance was assigned



to H_c. On expanding this resonance geminal coupling to H_c and coupling to the rhodium nucleus was resolved. The H_c resonance occurred as a sharp doublet of doublets arising from coupling to H_a and geminal coupling to H_c. On expansion, the resonance assigned to H_a was found to be a pattern of eight lines of equal intensity arising from coupling to H_c, H_e, and the rhodium nucleus. On cooling the sample to −50 °C, the CH_{3d} and CH_{3b} resonances both became well resolved 1 : 3 : 3 : 1 quartets arising from coupling to three magnetically equivalent phosphorus nuclei. The other resonances showed broadening.

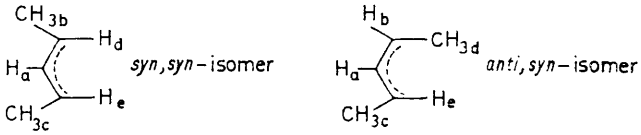


syn- *and* anti-*Isomers of the* 1—3-η-(1,2-*dimethylallyl*) *derivative*. The room-temperature spectrum of the *syn*-isomer consisted of five resonances. The CH_{3b} resonance occurred as a sharp doublet arising from coupling to H_d, and the CH_{3a} resonance was a sharp singlet. The resonance assigned to H_e was totally obscured by the CH_{3a} resonance and was a singlet. The H_c resonance occurred as a sharp singlet, and the resonance assigned to H_d was partially overlapped by the H_c resonance of the *anti*-isomer and occurred as a 1 : 3 : 3 : 1 quartet. On cooling the sample to −50 °C, the CH_{3b} and CH_{3a} resonances both showed further coupling to three magnetically equivalent phosphorus nuclei.

The room-temperature spectrum of the *anti*-isomer consisted of five resonances. The CH_{3d} group occurred as a doublet arising from coupling to H_b, and the CH_{3a} resonance was a sharp singlet. Resonances assigned to H_e and H_c were both singlets, and the H_b resonance was a quartet of doublets due to coupling to CH_{3d} and further coupling to the rhodium nucleus. On cooling to −50 °C, the CH_{3d}, CH_{3a}, and H_e resonances all showed further coupling to three magnetically equivalent phosphorus nuclei.

syn,syn- *and* anti,syn-*Isomers of the* 1—3-η-(1,3-*dimethylallyl*) *derivative*. The room-temperature spectrum of the *syn,syn*-isomer consisted of three resonances of relative intensity 6 : 2 : 1. The pair of methyl groups, CH_{3b} and CH_{3c}, occurred as a sharp doublet arising from coupling to the pair of *anti*-protons H_d and H_e. A resonance of eight lines of relative intensity 1 : 3 : 1 : 3 : 3 : 1 : 3 : 1 was assigned to these *anti*-protons, which are coupled to the methyl groups and to the central proton H_a. The H_a resonance occurred as a triplet arising from coupling to the *anti*-protons H_d and H_e. On cooling the sample to −50 °C, the resonance assigned to the methyl groups showed further coupling to three equivalent phosphorus nuclei, and the other resonances broadened.

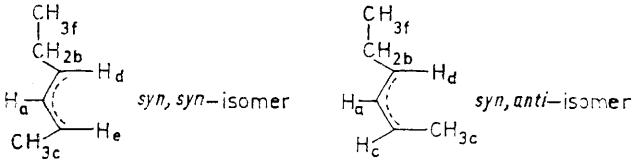
The room-temperature spectrum of the *anti,syn*-isomer consisted of five resonances of relative intensities 3 : 3 : 1 : 1 : 1. The methyl groups CH_{3d} and CH_{3c} both occurred as doublets arising from coupling to H_b and H_e respectively. The protons H_e and H_b showed



coupling to the methyl groups CH_{3c} and CH_{3d} respectively, and to H_a. On cooling the sample to −50 °C, both the methyl groups CH_{3d} and CH_{3c} showed coupling to three magnetically equivalent phosphorus nuclei, and the other resonances were all broadened.

syn,syn- *and* syn,anti-*Isomers of the* 1—3-η-(1-*ethyl*-3-*methylallyl*) *derivative*. The room-temperature spectrum of the *syn,syn*-isomer consisted, as expected, of six resonances. The CH_{3f} group occurred as a triplet arising from coupling to the methylene group CH_{2b}. The resonance assigned to CH_{3c} was a doublet due to coupling with H_e. The methylene group CH_{2b} occurred as a poorly resolved multiplet. The resonance assigned

to the protons H_d and H_e was also a poorly resolved multiplet. The H_a resonance occurred as a triplet arising from almost equal coupling to H_d and H_e. On



cooling to −50 °C, the CH_{3c} resonance showed coupling to three magnetically equivalent phosphorus nuclei. No change was observed in CH_{3f}, but the remaining resonances all broadened.

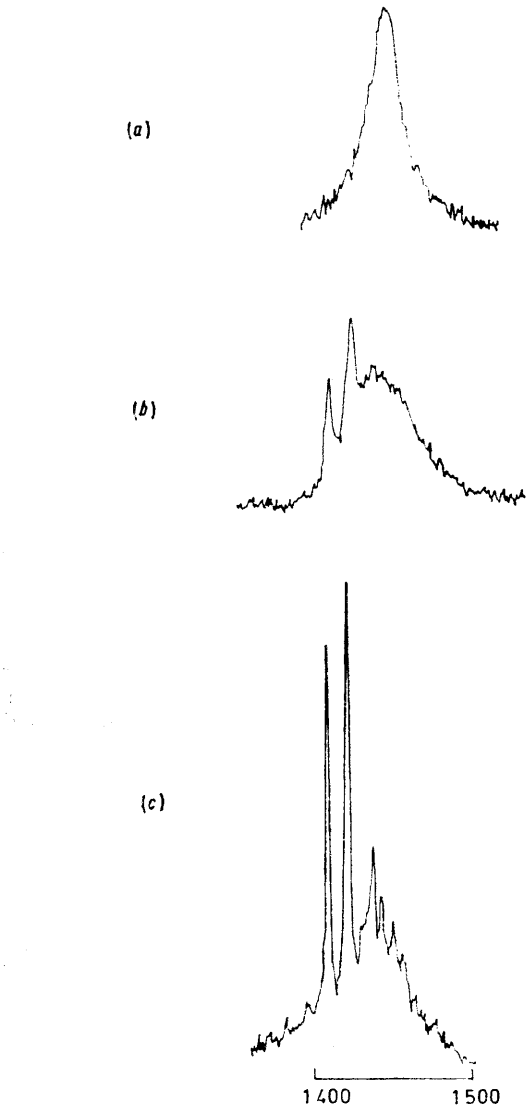


FIGURE 2 High-field half of ^{19}F n.m.r. spectra of the complex $[Rh(\eta\text{-allyl})(PF_3)_3]$ at (*a*) room temperature, (*b*) −20, and (*c*) −50 °C in toluene solution. The scale is in Hz relative to CCl_3F

The spectrum of the *syn,anti*-isomer was weak and poorly resolved.

^{19}F *N.m.r. Spectra.*—The room-temperature ^{19}F n.m.r. spectrum of (1—3-η-allyl)tris(trifluorophosphine)rhodium-(I) consisted of two widely spaced broad resonances arising from spin coupling to phosphorus (Figure 2). On cooling the sample little change was observed in the spectrum until at −20 °C each half of the spectrum started to exhibit fine structure. The well resolved limiting spectrum was reached at −40 °C and was analysed as an $[AX_3]_3$ spin system (A = P, X = F).[6] Each line in the spectrum was further split into doublets by coupling to ^{103}Rh. The chemical shifts and coupling constants are listed in Table 4. The 1—3-η-(2-methylallyl), -cyclohexenyl, and -(1,1-dimethylallyl) derivatives showed similar temperature-dependent ^{19}F n.m.r. spectra.

TABLE 4

^{19}F N.m.r. chemical shifts (p.p.m.) and coupling constants (J/Hz) of some η-allyl $[RhL(PF_3)_3]$ complexes in fluorobenzene at −50 °C *

L	δ_F †	δ_F	$^1J(PF) + {}^2J(PF')$ ‡	
1—3-η-Allyl	8·1	8·4	1 342	§
1—3-η-(2-Methylallyl)	8·3	8·5	1 340	
1—3-η-Cyclohexenyl	8·4	8·1	1 346	
1—3-η-(1-Methylallyl) (*syn*-)	8·2	9·4	1 340	
(*anti*-)	8·2	8·7	1 341	
1—3-η-(1,1-Dimethylallyl)	9·6	9·7	1 340	
1—3-η-(1,2-Dimethylallyl) (*syn*-)	8·7	8·5	1 347	
(*anti*-)	8·7	9·4	1 342	
1—3-η-(1,3-Dimethylallyl) (*syn,syn*-)	9·3	8·6	1 342	
(*anti,syn*-)	9·3	9·7	1 340	
1—3-η-(1-Ethyl-3-methylallyl) (*syn,syn*-)	9·2	9·4	1 333	
(*syn,anti*-)	9·2	8·1	1 334	

* Chemical shifts relative to CCl_3F; $^2J(RhF)$ 18 Hz. † At room temperature. ‡ $^1J(PF)$ and $^3J(PF')$ are of opposite sign. § $^3J(PF')$ 40 and $^2J(PP')$ 19 Hz.

As discussed above, isomers of the 1—3-η-(1-methylallyl), -(1,2-dimethylallyl), -(1,3-dimethylallyl), and -(1-ethyl-3-methylallyl) derivatives were identified by ^1H n.m.r. spectroscopy, and the assignments were verified by the low-temperature ^{19}F n.m.r. spectra. Each isomer gave rise to a separate $[AX_3]_3$ spectrum, and the differences in fluorine chemical shifts were sufficient for the spectrum of each isomer to be clearly seen. There was little difference in the coupling constants $^2J(RhF)$ and $^1J(PF)$ between the isomers. Figure 3 shows the spectrum at low temperature of a mixture of the *syn*- and *anti*-isomers of the 1—3-η-(1-methylallyl) derivative. Similar spectra were obtained for mixtures of isomers of the other three derivatives and the ^{19}F n.m.r. parameters are listed in Table 4.

A feature of the ^{19}F and ^1H n.m.r. spectra is loss of rhodium–fluorine and phosphorus–hydrogen couplings respectively as the temperature is raised from −50 °C to room temperature. This suggests that there is *intermolecular* exchange of the trifluorophosphine ligands at the higher temperatures. At lower temperatures the three trifluorophosphine ligands are magnetically equivalent since the ^{19}F n.m.r. spectra can be analysed as a $[AX_3]_3$ spin system and lines in the ^1H n.m.r. spectra

occur as 1 : 3 : 3 : 1 quartet patterns. The phosphine ligands would become equivalent if the complexes were regarded as containing four-co-ordinate rhodium (A) and the allyl ligand was free to rotate about the three-fold axis through the rhodium atom. This type of structure has been found recently for the related complex (1—3-η-allyl)tricarbonylcobalt where the plane of the allyl ligand is inclined at an angle of 36° to the plane containing the carbonyl ligands.[17] An alternative explanation is that there is a Berry or pseudo-rotation process [18] occurring within a formally trigonal-bipyramidal structure (B) which interchanges axial (a) and equatorial sites (e). This type of *intra*molecular rearrangement in five-co-ordinate transition-metal complexes is well known and has recently been reviewed.[19]

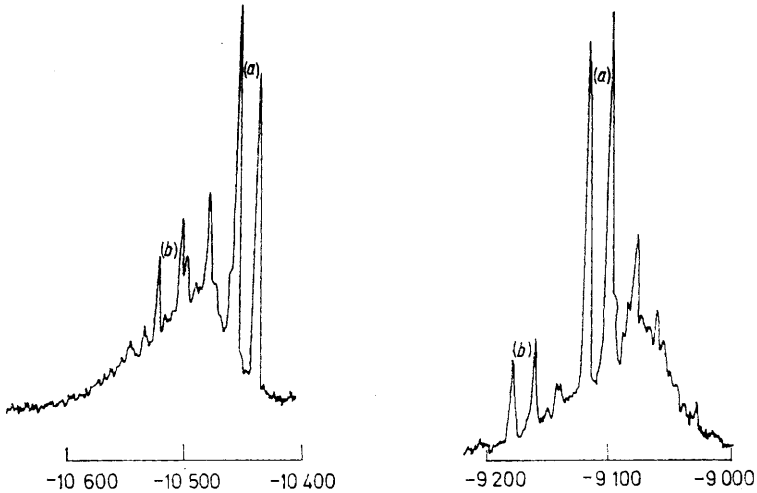
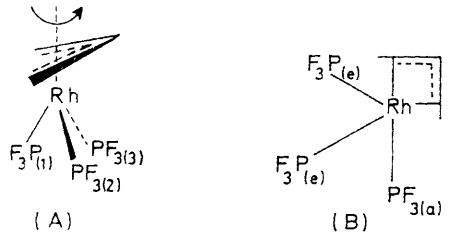


FIGURE 3 ^{19}F N.m.r. spectra of a mixture of (*a*) the *syn*- and (*b*) the *anti*-isomer of the 1—3-η-(1-methylallyl) derivative at −50 °C in fluorobenzene solution. The scale is in Hz relative to fluorobenzene



It is interesting to note that in the present complexes the *inter*- and *intra*-molecular exchange processes are independent of each other.

EXPERIMENTAL

All the new complexes are moderately volatile and air sensitive and, by analogy with volatile carbonyl complexes, are probably toxic and best handled *only* in a high-vacuum line. Elemental analyses on samples sealed in capillaries were carried out by A. Bernhardt, Elbach über Engelskirchen, W. Germany. ^{19}F and ^{1}H N.m.r. spectra were recorded as described previously.[20] Tris(1—3-η-allyl)rhodium(III) was prepared by the literature method [5] and freshly sublimed before use.

Preparations.—Potassium tetrakis(trifluorophosphine)rhodate(−1). In a typical experiment the complex $[(F_3P)_2Rh(\mu\text{-}Cl)_2Rh(PF_3)_2]$ [20,21] (0·615 g, 0·978 mmol), PF_3 (0·820 g, 9·32 mmol), and 1% potassium amalgam (50 g) were sealed with diethyl ether (30 cm^3) *in vacuo* and the mixture shaken at room temperature for 1 day to afford a colourless solution over a black-grey solid. The solution was filtered, and diethyl ether removed under reduced pressure to give a light brown crystalline solid which on washing with n-pentane afforded colourless crystals of $K[Rh(PF_3)_4]$ {0·793 g, 1·61 mmol; 83·8% based on $[(F_3P)_2Rh(\mu\text{-}Cl)_2Rh(PF_3)_2]$}, m.p. 140—145 °C, whose i.r. spectrum was identical with that in the literature.[22]

Hydridotetrakis(trifluorophosphine)rhodium(I). The complex $[(F_3P)_2Rh(\mu\text{-}Cl)_2Rh(PF_3)_2]$ (1·600 g, 2·55 mmol), PF_3 (1·790 g, 20·3 mmol), and 1% potassium amalgam (80 g) gave a light brown solid in a similar manner to the above. Dropwise addition of 50% H_3PO_4 at liquid-nitrogen temperature followed by slow warming to room temperature yielded the volatile liquid $[RhH(PF_3)_4]$ which was dried over P_2O_5 *in vacuo* (1·620 g, 3·55 mmol; 69·6%), m.p. −40 °C, identified by its characteristic i.r., ^{1}H, and ^{19}F n.m.r. spectra.[22–24]

(1—3-η-*Allyl*)*tris(trifluorophosphine)rhodium*(I). (i) *From tris*(1—3-η-*allyl*)*rhodium*(III). The complex $[Rh(\eta\text{-}C_3H_5)_3]$ (0·397 g, 1·63 mmol) and PF_3 (0·899 g, 10·2 mmol) were sealed *in vacuo* and shaken at room temperature for 5 h. Fractionation of the volatile products produced PF_3, hexa-1,5-diene (i.r. and ^{1}H n.m.r. spectra), and the pale yellow, volatile, liquid *complex* (0·565 g, 1·38 mmol; 84·7%) (Found: C, 9·0; H, 1·3; P, 22·9. Calc. for $C_3H_5F_9P_3Rh$: C, 8·80; H, 1·20; P, 22·8%). I.r. spectrum: (vapour phase) 3 080w; 3 017w; 2 930vw; 1 468w; 969w; 941m; 917vs;

[17] R. Seip, *Acta Chem. Scand.*, 1972, **26**, 1966.
[18] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.
[19] J. R. Shapley and J. A. Osborn, *Accounts Chem. Res.*, 1973, **6**, 305.
[20] J. F. Nixon and J. R. Swain, *J.C.S. Dalton*, 1972, 1044.
[21] D. A. Clement and J. F. Nixon, *J.C.S. Dalton*, 1972, 2553.
[22] W. Lang, Dr. rer Nat. Thesis, Technischen Hochschule München, 1966.
[23] J. P. Jesson, P. Meakin, E. L. Muetterties, and F. N. Tebbe, *J. Amer. Chem. Soc.*, 1971, **93**, 1797.
[24] Th. Kruck and W. Lang, *Angew. Chem. Internat. Edn.*, 1965, **4**, 870.

895(sh); 884vs; 860vs; 849vs; 535m; 520s; 509s; and 490w cm^{-1}. The highest mass peak in the mass spectrum occurred at *m/e* 320 corresponding to $C_3H_5F_6P_2Rh^+$.

(ii) *From hydridotetrakis(trifluorophosphine)rhodium*(I). The complex $[RhH(PF_3)_4]$ (0·275 g, 0·603 mmol) and allene (0·024 g, 0·599 mmol) were sealed with n-pentane (1 cm^3) *in vacuo* and kept at 0 °C for 4 days. Fractionation afforded PF_3 (0·042 g, 0·477 mmol), n-pentane, and the *complex* {0·171 g, 0·419 mmol; 69·5% based on $[RhH(PF_3)_4]$}. The product was identical with a sample prepared by method (i).

(iii) *From potassium tetrakis(trifluorophosphine)rhodate* (−1). The complex $K[Rh(PF_3)_4]$ (0·100 g, 0·202 mmol) and allyl bromide (0·023 g, 0·190 mmol) were sealed with diethyl ether (2 cm^3) *in vacuo*. Shaking at room temperature afforded a yellow solution over a white precipitate (potassium bromide). Fractionation gave PF_3 (0·016 g, 0·180 mmol), diethyl ether, and the *complex* (0·059 g, 0·145 mmol; 76·3% based on allyl bromide). The product was identical with a sample prepared by method (i).

[1—3-η-(2-*Methylallyl*)]*tris(trifluorophosphine)rhodium*(I). The complex $K[Rh(PF_3)_4]$ (0·200 g, 0·405 mmol) and 2-methylallyl chloride (0·035 g, 0·386 mmol) were sealed with diethyl ether (2 cm^3) *in vacuo*, and heated at 60 °C for 15 h to afford a yellow solution over a white precipitate (potassium chloride). Fractionation gave PF_3 (0·036 g, 0·409 mmol), diethyl ether, and the yellow, volatile, liquid *complex* (0·158 g, 0·374 mmol; 92·3% based on 2-methylallyl chloride), m.p. −20 °C (Found: C, 11·5; H, 1·5; P, 20·8. Calc. for $C_4H_7F_9P_3Rh$: C, 11·4; H, 1·65; P, 22·0%). I.r. spectrum (in P–F stretching and bending regions): 970w; 920vs; 890(sh); 858vs; 848vs; 810w; 795vw; 538m; 522s; 508s; and 490w cm^{-1} (vapour phase). The mass spectrum showed a highest mass peak at *m/e* 334 corresponding to $[Rh(\eta\text{-}C_4H_7)(PF_3)_2]^+$.

(η-*Cyclohexenyl*)*tris(trifluorophosphine)rhodium*(I). The complex $[RhH(PF_3)_4]$ (0·144 g, 0·316 mmol) and cyclohexa-1,3-diene (0·020 g, 0·250 mmol) were sealed with n-pentane (2 cm^3) *in vacuo* and kept at 0 °C for 4 days to afford a bright yellow solution. Fractionation gave PF_3 (0·022 g, 0·250 mmol), n-pentane, and the yellow, volatile, liquid *complex* (0·097 g, 0·216 mmol; 68·4% based on cyclohexa-1,3-diene), m.p. 0 °C (Found: C, 15·9; H, 2·1. Calc. for $C_6H_9F_9P_3Rh$: C, 16·1; H, 2·00%). I.r. spectrum: 918s; 895(sh); 870vs; 855vs; 530m; 518m; and 490w cm^{-1} (vapour phase). The mass spectrum showed a highest mass peak at *m/e* 360 corresponding to $[Rh(\eta\text{-}C_6H_9)(PF_3)_2]^+$.

[1—3-η-(1-*Methylallyl*)]*tris(trifluorophosphine)rhodium*(I). (i) *From hydridotetrakis(trifluorophosphine)rhodium*(I). The complex $[RhH(PF_3)_4]$ (0·148 g, 0·325 mmol) and buta-1,3-diene (0·017 g, 0·314 mmol) were sealed with n-pentane (2 cm^3) *in vacuo* and kept at 0 °C for 5 days to give a yellow solution. Fractionation afforded PF_3 (0·024 g, 0·273 mmol), n-pentane, and the volatile, yellow, liquid *complex* (0·100 g, 0·237 mmol; 72·9% based on buta-1,3-diene), m.p. −20 °C (Found: C, 11·1; H, 1·70; P, 22·2. Calc. for $C_4H_7F_9P_3Rh$: C, 11·4; H, 1·65; P, 22·0%). I.r. spectrum: 940m; 919vs; 890(sh); 880vs; 855vs; 845vs; 535m; 520s; 510s; and 485(sh) cm^{-1} (vapour phase). The ^{19}F and ^1H n.m.r. spectra of the product established the presence of *syn*- and *anti*-isomers. The *anti*-isomer was present only in a trace amount. The mass spectrum showed a highest mass peak at *m/e* 334 corresponding to $[Rh(\eta\text{-}C_4H_7)(PF_3)_2]^+$.

(ii) *From potassium tetrakis(trifluorophosphine)rhodate*(−1). The complex $K[Rh(PF_3)_4]$ (0·158 g, 0·320 mmol) and but-2-enyl bromide (0·036 g, 0·266 mmol) were sealed with diethyl ether (2 cm^3) *in vacuo* and shaken at room temperature for 2 h to afford a yellow solution over a white precipitate (potassium bromide). Fractionation gave PF_3 (0·024 g, 0·273 mmol), diethyl ether, and the *complex* (0·098 g, 0·232 mmol; 72·5% based on but-2-enyl bromide) which was identical with a sample prepared by route (i).

[1—3-η-(1,2-*Dimethylallyl*)]*tris(trifluorophosphine)rhodium*(I).—The complex $[RhH(PF_3)_4]$ (0·175 g, 0·384 mmol) and 2-methylbuta-1,3-diene (0·025 g, 0·367 mmol) were sealed *in vacuo* in n-pentane (3 cm^3) and kept at 0 °C for 4 days to afford a bright yellow solution. Fractionation gave PF_3 (0·032 g, 0·363 mmol), n-pentane, and yellow volatile crystals of the *complex* (0·135 g, 0·310 mmol; 80·7% based on 2-methylbuta-1,3-diene), m.p. 35 °C (Found: C, 14·1; H, 2·2; P, 20·9. Calc. for $C_5H_9F_9P_3Rh$: C, 13·9; H, 2·10; P, 21·3%). I.r. spectrum: 955w; 918vs; 895(sh); 877vs; 855vs; 845vs; 805vw; 770w; 535m; 520s; 510s; and 490w cm^{-1} (vapour phase). The ^{19}F and ^1H n.m.r. spectra of the product established the presence of *syn*- and *anti*-isomers in a 2 : 3 ratio. The mass spectrum showed a highest mass peak at *m/e* 348 corresponding to $[Rh(\eta\text{-}C_5H_9)(PF_3)_2]^+$.

[1—3-η-(1,3-*Dimethylallyl*)]*tris(trifluorophosphine)rhodium*(I). (i) The complex $[RhH(PF_3)_4]$ (0·152 g, 0·333 mmol) and penta-1,3-diene (0·026 g, 0·381 mmol) were sealed with n-pentane (2 cm^3) *in vacuo* and kept at 0 °C for 7 days to afford a bright yellow solution. Fractionation yielded PF_3 (0·029 g, 0·330 mmol), n-pentane, and the volatile, yellow, liquid *complex* {0·128 g, 0·294 mmol; 88·3% based on $[RhH(PF_3)_4]$}, m.p. −15 °C (Found: C, 13·9; H, 2·1; P, 21·2. Calc. for $C_5H_9F_9P_3Rh$: C, 13·9; H, 2·10; P, 21·3%). I.r. spectrum: 921vs; 895(sh); 878vs; 855s; 842vs; 535m; 520(sh); 510s; and 485s cm^{-1} (vapour phase). The ^{19}F and ^1H n.m.r. spectra of the product established the presence of the *syn,syn*- and *anti,syn*-isomers in roughly equimolar amounts. The mass spectrum showed a highest mass peak at *m/e* 348 corresponding to $[Rh(\eta\text{-}C_5H_9)(PF_3)_2]^+$.

(ii) In a similar reaction using the complex $[RhH(PF_3)_4]$ (0·242 g, 0·531 mmol) and penta-1,4-diene (0·035 g, 0·514 mmol), fractionation after 3 days at 0 °C afforded the *complex* (0·139 g, 0·317 mmol; 61·7% based on penta-1,4-diene). The ^{19}F and ^1H n.m.r. spectra of the product again established the presence of roughly equimolar amounts of the *syn,syn*- and *anti,syn*-isomers.

[1—3-η-(1-*Ethyl*-3-*methylallyl*)]*tris(trifluorophosphine)rhodium*(I). The complex $[RhH(PF_3)_4]$ (0·140 g, 0·307 mmol) and hexa-1,3-diene (0·023 g, 0·280 mmol) were sealed with n-pentane (2 cm^3) *in vacuo* and kept at 0 °C for 5 days, affording a yellow solution. Fractionation yielded PF_3 (0·023 g, 0·261 mmol), n-pentane, and the volatile, yellow, liquid *complex* (0·108 g, 0·240 mmol; 85·7% based on hexa-1,3-diene), m.p. 0 °C (Found: C, 15·9; H, 2·3; P, 20·5. Calc. for $C_6H_{11}F_9P_3Rh$: C, 16·0; H, 2·45; P, 20·65%). I.r. spectrum: 952w; 918vs; 892(sh); 875vs; 850vs; 840vs; 530m; 520(sh); and 510m cm^{-1} (vapour phase). The ^{19}F and ^1H n.m.r. spectra of the product established the presence of *syn,syn*- and *syn,anti*-isomers. The *syn,anti*-isomer was present only in a trace amount. The mass spectrum of the product showed a highest mass peak at *m/e* 362 corresponding to $[Rh(\eta\text{-}C_6H_{11})(PF_3)_2]^+$.

Reaction between Potassium Tetrakis(trifluorophosphine)-rhodate(−1) *and* 1,1-*Dimethylallyl Chloride*.—(i) The complex $K[Rh(PF_3)_4]$ (0·142 g, 0·287 mmol) and 1,1-dimethylallyl chloride (0·026 g, 0·249 mmol) were sealed with diethyl ether (2 cm^3) *in vacuo* and heated at 60 °C for 5 h to give a

yellow solution over a white precipitate. Fractionation yielded PF_3 (0·018 g, 0·205 mmol), diethyl ether, and the yellow, volatile, liquid complex [1—3-η-(1,1-*dimethylallyl*)]-*tris*(*trifluorophosphine*)*rhodium*(I) (0·079 g, 0·181 mmol; 72·6% based on 1,1-dimethylallyl chloride) m.p. 0 °C (Found: C, 14·0; H, 2·1; P, 21·6. Calc. for $C_5H_9F_9P_3Rh$: C, 13·9; H, 2·10; P, 21·3%). I.r. spectrum: 923s; 913(sh); 890(sh); 880vs; 858vs; 846vs; 530m; 513s; and 490m cm^{-1} (vapour phase). The mass spectrum showed a highest mass peak at *m/e* 348 corresponding to $[Rh(\eta\text{-}C_5H_9)(PF_3)_2]^+$.

(ii) In a similar experiment using the complex $K[Rh(PF_3)_4]$ (0·109 g, 0·221 mmol) and 1,1-dimethylallyl chloride (0·020 g, 0·197 mmol), heating at 60 °C for 14 h afforded the 1,2-derivative (0·071 g, 0·162 mmol; 84·8% based on 1,1-dimethylallyl chloride), m.p. 35 °C. The ^1H n.m.r. spectrum of the product established the presence of roughly equimolar amounts of the *syn*- and *anti*-isomers.

We thank the S.R.C. for the award of studentships (to B. W. and D. A. C.).

[4/180 *Received*, 30*th January*, 1974]