Reactions of Co-ordinated Ligands. Part 23.[1] Metalla-ring-forming Reactions between Hexafluoroacetone and η^4-1,3-Diene(η^5-indenyl)-rhodium Complexes; the Crystal and Molecular Structures of $[\overline{Rh\{OC(CF_3)_2CH_2C(Me)\cdots C}H\cdots CH_2\}(\eta^5\text{-}C_9H_7)]$ and $[\overline{Rh\{OC(CF_3)_2C}_3H_3\text{-}C_6H_4\}(\eta^4\text{-}\textit{trans}\text{-}C_4H_4Me_2\text{-}1,4)]$ †

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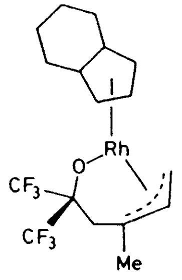
Reaction (room temperature) of hexafluoroacetone with isoprene- or 2,3-dimethylbuta-1,3-diene-(η^5-indenyl)-rhodium affords respectively the η^3-allylic rhodium(III) complexes $[\overline{Rh\{OC(CF_3)_2CH_2C(R^1)\cdots C}(R^2)\cdots CH_2\}(\eta^5\text{-}C_9H_7)]$ (1a; R^1 = Me, R^2 = H), (1b; R^1 = H, R^2 = Me) (ratio 5 : 1), and (2; $R^1 = R^2$ = Me). A single-crystal *X*-ray diffraction study of (1a) showed that the crystals are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions a = 14.020(7), b = 8.690(4), c = 14.669(5) Å, and β = 101.61(3)°. The structure has been solved by heavy-atom methods from automated diffractometer data, and refined to R 0.045 (R' 0.056) for 2 704 reflections. The rhodium adopts an essentially octahedral geometry arising from η^5 bonding of an indenyl ligand, a η^3-allylic group formed from linking of the isoprene to the hexafluoroacetone, and a rhodium–oxygen σ bond. *trans,trans*-Hexa-2,4-diene(η^5-indenyl)rhodium reacts with hexafluoroacetone *via* a different reaction path to form the rhodium(I) complex (3). A single-crystal *X*-ray diffraction study of (3), a tris olefin complex, showed that the crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions a = 8.094(2), b = 16.962(8), c = 12.782(4) Å, and β = 99.81(2)°. The structure has been refined to R 0.021 (R' 0.025) for 2 878 reflections. The rhodium adopts an essentially square-planar configuration the co-ordination sites being occupied by a η^4-bonded *trans,trans*-hexa-2,4-diene, a η^2-bonded indenyl ligand, and an oxygen atom of the hexafluoroacetone molecule σ bonded to rhodium. The hexafluoroacetone is bonded to the C_5 ring of the indenyl ligand. The mechanism of formation of these complexes is discussed. In contrast, hexafluoroacetone reacts with bis(ethylene)(η^5-indenyl)rhodium to form ethyl(hexafluoroacetylacetonato)(η^5-indenyl)rhodium.

It is known that metallacyclopentanes [2–8] and metallacyclopentadienes [9–14] play an important role in the transition-metal catalysed reactions of olefins and acetylenes, and more recently metallacyclopenta-2-enes [1,15,16] formed by a related redox coupling of a co-ordinated acetylene and olefin have been implicated as intermediates in the cyclo-cotrimerisation of acetylenes and olefins. A possible further example of this family of reactions is the head-to-tail coupling of two molecules of hexafluoroacetone with a transition metal to form a five-membered ring.[17] We had previously [18] observed that hexafluoroacetone reacts thermally with 1,3-diene(η-cyclopentadienyl)rhodium complexes to form complexes which can be viewed as 2-rhodiafuran derivatives, and it was of interest to relate these reactions to other metalla-ring forming reactions.

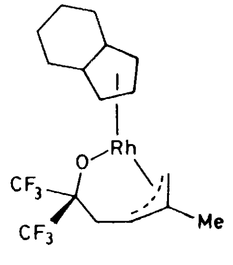
The observation [1,16] that η^5-indenylrhodium complexes are more reactive than the corresponding η-cyclopentadienyl systems provided an opportunity to examine these reactions in more detail, and in particular to structurally define the molecular geometry of the reaction products using single-crystal *X*-ray crystallography.

RESULTS AND DISCUSSION

In contrast with the corresponding η-cyclopentadienyl system, which required elevated temperatures to effect the reaction, treatment of η^5-indenyl(isoprene)rhodium [16] with hexafluoroacetone led, at room temperature, to a rapid reaction and the formation of a mixture of two orange crystalline isomeric complexes (1a) and (1b) (obtained in the ratio 5 : 1 respectively, as determined by n.m.r.). Fractional crystallisation afforded crystals of the two isomers. Elemental analyses and mass spectra confirmed the isomeric nature of the complexes, and examination of the n.m.r. spectra showed that (1a) and (1b) were 1 : 1 adducts of hexafluoroacetone and the isoprene complex. It was not possible to establish unequivocally the structure of the two isomers and therefore a single-crystal *X*-ray diffraction study was undertaken of the major isomer (1a).



(1a)



(1b)

The molecular structure of (1a) is illustrated in Figure 1, which also shows the crystallographic numbering system. An oxidative ($Rh^I \rightarrow Rh^{III}$) coupling reaction has occurred, in which the hexafluoroacetone has linked the rhodium and isoprene fragment. The hexafluoro-

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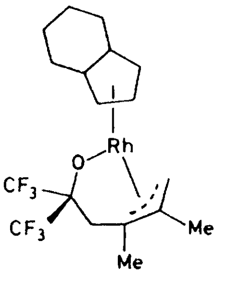
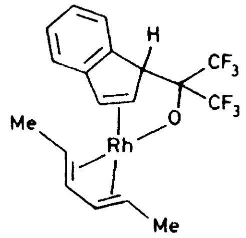
† η^5-Indenyl[1—3-η-6,6,6-trifluoro-3-methyl-5-oxido-5-trifluoromethylhex-2-enyl(2—)-*O*]rhodium and (1—2; 3—4-η^4-*trans*-1,4-dimethylbuta-1,3-diene)[2—3-η-1-(2′,2′,2′-trifluor-o1′-oxido-1′-trifluoromethylethyl)indene-*O*]rhodium.

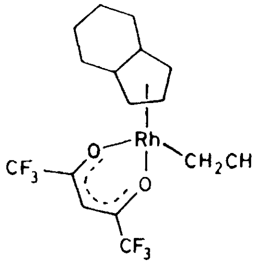
acetone is bonded such that a rhodium–oxygen σ bond has been established, and the carbonyl carbon atom of the $(CF_3)_2CO$ molecule has become attached to the terminal carbon atom of the olefinic bond of the isoprene carrying the methyl substituent. The other three carbon atoms of the isoprene ligand form a η³-allylic system, which is co-ordinated to the rhodium atom [Rh–C(1), 2.12; Rh–C(2), 2.11; Rh–C(3), 2.19 Å]. Thus, the metal is in an octahedral environment if one considers that the η⁵-indenyl ligand occupies three facial sites, and the η³-allylic group two sites. The C–C bond lengths in the C_5 ring of the indenyl ligand show little variation indicating delocalised bonding, and the same is true for the C–C bond lengths in the C_6 ring (Table 1). The Rh–C bond lengths for the C_5 ring show, however, that the indenyl ligand is not symmetrically bonded, C(14) (2.35 Å) and C(10) (2.33 Å) being significantly (>0.1 Å) further from the rhodium atom than C(13), C(12), and C(11) (2.19, 2.22, and 2.21 Å respectively). A similar variation in Rh–C bond lengths has been observed in the complexes duroquinone(η⁵-indenyl)-rhodium [19] and η⁵-indenyl{1—2:3—4-η-[6-*endo*-propen-2-yl-1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3-diene]}-rhodium,[1] although the effect was less marked in the former case.



(2)



(3)



(4)

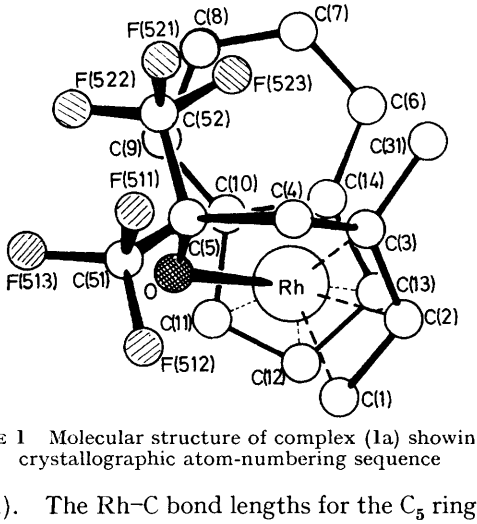


FIGURE 1 Molecular structure of complex (1a) showing the crystallographic atom-numbering sequence

Establishment of the structural identity of (1a) allowed interpretation of the n.m.r. data and assignment of the structure of the minor isomer (1b). A similar reaction between η⁴-2,3-dimethylbuta-1,3-diene(η⁵-indenyl)-rhodium and hexafluoroacetone afforded the orange crystalline complex (2), for which the illustrated structure was established by elemental analysis, a mass spectrum, and comparison of the n.m.r. data with that observed for (1a).

TABLE 1

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses, for compound (1a)

(*a*) Co-ordination around Rh			
Rh–O(1)	2.081(4)	O(1)–Rh–C(1)	87.6(2)
Rh–C(1)	2.124(7)	O(1)–Rh–C(2)	102.5(2)
Rh–C(2)	2.113(6)	O(1)–Rh–C(3)	81.8(2)
Rh–C(3)	2.193(6)	O(1)–Rh–C(11)	97.5(2)
Rh–C(11)	2.211(6)	O(1)–Rh–C(12)	129.6(2)
Rh–C(12)	2.223(8)	O(1)–Rh–C(13)	160.0(2)
Rh–C(13)	2.192(8)	C(1)–Rh–C(11)	124.0(3)
Rh · · · C(10)	2.329(6)	C(1)–Rh–C(12)	100.1(3)
Rh · · · C(14)	2.353(7)	C(1)–Rh–C(13)	109.6(3)
		C(2)–Rh–C(11)	151.7(3)
		C(2)–Rh–C(12)	114.4(3)
		C(2)–Rh–C(13)	97.5(3)
		C(3)–Rh–C(11)	167.7(3)
		C(3)–Rh–C(12)	147.2(3)
		C(3)–Rh–C(13)	113.6(2)
(*b*) Indenyl ligand			
C(11)–C(12)	1.45(1)	C(10)–C(11)–C(12)	108.4(6)
C(12)–C(13)	1.49(1)	C(11)–C(12)–C(13)	106.8(6)
C(13)–C(14)	1.47(1)	C(12)–C(13)–C(14)	107.4(6)
C(14)–C(6)	1.41(1)	C(13)–C(14)–C(6)	131.5(6)
C(6)–C(7)	1.37(1)	C(13)–C(14)–C(10)	108.1(6)
C(7)–C(8)	1.36(1)	C(6)–C(14)–C(10)	120.4(7)
C(8)–C(9)	1.46(1)	C(14)–C(6)–C(7)	117.8(7)
C(9)–C(10)	1.38(1)	C(6)–C(7)–C(8)	123.1(8)
C(10)–C(11)	1.47(1)	C(7)–C(8)–C(9)	121.1(9)
C(10)–C(14)	1.43(1)	C(8)–C(9)–C(10)	115.9(7)
		C(9)–C(10)–C(14)	121.7(6)
		C(9)–C(10)–C(11)	129.7(6)
		C(11)–C(10)–C(14)	108.6(6)
(*c*) Perfluoromethyl ligands and chain atoms			
O(1)–C(5)	1.378(7)	O(1)–C(5)–C(51)	107.4(5)
C(5)–C(51)	1.55(1)	O(1)–C(5)–C(52)	110.7(5)
C(5)–C(52)	1.54(1)	C(51)–C(5)–C(52)	109.4(6)
C(51)–F(511)	1.34(1)	F(511)–C(51)–F(512)	106.2(7)
C(51)–F(512)	1.34(1)	F(511)–C(51)–F(513)	106.3(7)
C(51)–F(513)	1.32(1)	F(512)–C(51)–F(513)	107.4(7)
C(52)–F(521)	1.34(1)	F(521)–C(52)–F(522)	106.8(6)
C(52)–F(522)	1.34(1)	F(521)–C(52)–F(523)	107.1(7)
C(52)–F(523)	1.32(1)	F(522)–C(52)–F(523)	105.4(7)
C(5)–C(4)	1.55(1)	C(4)–C(5)–C(51)	107.3(5)
C(4)–C(3)	1.56(1)	C(4)–C(5)–C(52)	109.8(5)
C(3)–C(31)	1.54(1)	C(4)–C(5)–O(1)	112.0(5)
C(3)–C(2)	1.42(1)	C(5)–C(4)–C(3)	112.5(5)
C(2)–C(1)	1.40(1)	C(4)–C(3)–C(31)	115.0(6)
		C(4)–C(3)–C(2)	119.6(6)
		C(31)–C(3)–C(2)	118.7(6)
		C(3)–C(2)–C(1)	118.6(6)

We had previously [20,21] established that electrophilic unsaturated systems such as tetracyanoethylene, 1,1-

dicyano-2,2-bis(trifluoromethyl)ethylene, and hexafluoroacetone react at room temperature with tricarbonyl(cycloheptatriene)iron to form 1 : 1 adducts, in which the electrophile adds 1,3 to the *exo* face of the co-ordinated triene. Although tricarbonyl(cycloheptatriene)iron contains an additional unco-ordinated olefinic bond it was clearly important to establish which face (*exo* or *endo*) of the co-ordinated η^4-1,3-diene (isoprene or 2,3-dimethylbuta-1,3-diene) was attacked by hexafluoroacetone in the formation of the rhodium complexes (1a), (1b), and (2). Therefore, the reaction of hexafluoroacetone with η^4-*trans,trans*-hexa-2,4-diene(η^5-indenyl)rhodium was examined, in the belief that a detailed examination of the stereochemistry of the product would clarify this question. This information could not be derived from a knowledge of the structure of complex (1a), since if attack occurred by hexafluoroacetone on the face of the 1,3-diene opposite (*exo*) to which the rhodium is co-ordinated then formation of an ionic or biradical intermediate, followed by rotation about a single carbon–carbon bond, could lead to a product in which apparent *endo* attack had occurred.

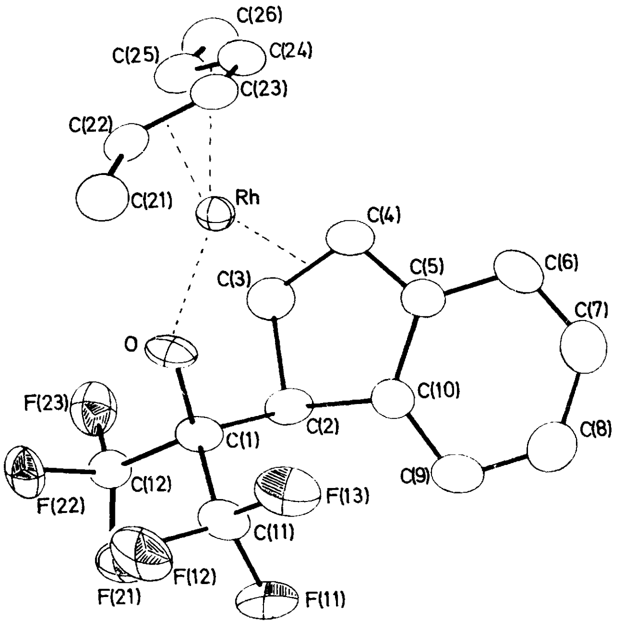


FIGURE 2 Molecular structure of complex (3) showing the crystallographic atom-numbering sequence

At room temperature an orange crystalline product (3) was formed, which from elemental analysis, mass, and n.m.r. spectroscopy was identified as the expected 1 : 1 adduct. However, certain features of the n.m.r. spectra were not consistent with (3) being a simple analogue of the complexes (1) and (2). The mass spectrum supported this idea showing a strong peak attributable to the loss of hexadiene from the parent ion. In view of these findings a single-crystal *X*-ray diffraction study was carried out with a suitable crystal of (3).

The molecular structure is shown in Figure 2, and shows that the hexafluoroacetone has unexpectedly not reacted with the co-ordinated 1,3-diene, but instead has become attached to a carbon atom of the C_5 ring of the indenyl ligand. Thus, the reaction does not involve a change in the oxidation state of the rhodium, but involves the unprecedented formation of a 16-electron tris olefin complex of rhodium(I). The geometry around the metal atom is essentially square planar. The C–C bond lengths in the C_9H_7 ligand are as expected, C(3)–C(4) at 1.39 Å being typical of a co-ordinated olefinic bond, and all the C–C bonds in the C_6 ring are similar (1.39 ± 0.1 Å) indicative of a delocalised bonding system (Table 2). The point of attachment of the $(CF_3)_2CO$ moiety to the C_5 ring, carbon atom C(2), shows typical bond angles for a tetrahedral carbon atom. The asymmetric bonding of the *trans,trans*-hexa-2,4-diene suggested in the ^1H n.m.r. spectrum of (3) is also supported by the rhodium–

TABLE 2

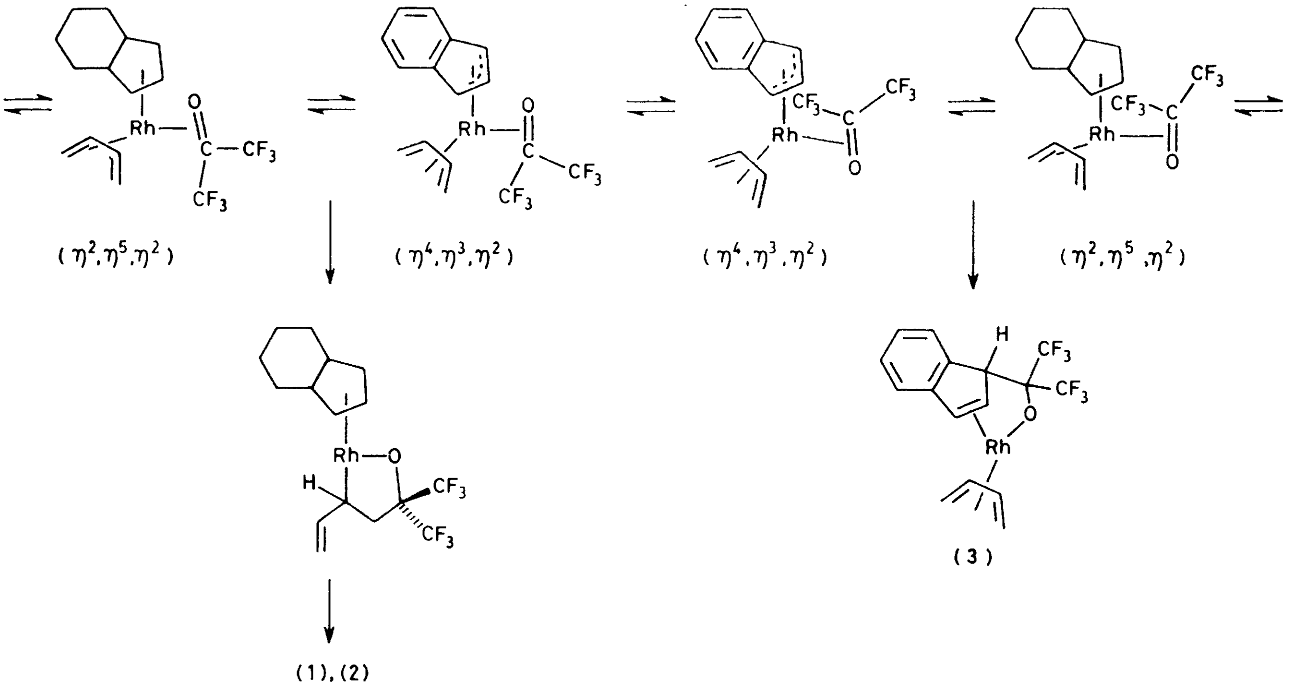
Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses, for compound (3)

(*a*) Distances			
Rh–O(1)	2.013(1)	Rh–C(22)	2.148(2)
Rh–C(3)	2.141(2)	Rh–C(23)	2.113(2)
Rh–C(4)	2.194(2)	Rh–C(24)	2.199(2)
		Rh–C(25)	2.260(2)
Hexadiene			
C(21)–C(22)	1.506(4)	C(24)–C(25)	1.378(3)
C(22)–C(23)	1.396(4)	C(25)–C(26)	1.495(4)
C(23)–C(24)	1.424(4)		
Hexafluoroacetone			
O(1)–C(1)	1.379(2)	C(1)–C(2)	1.568(3)
C(1)–C(11)	1.536(3)	C(1)–C(12)	1.558(4)
C(11)–F(11)	1.352(3)	C(12)–F(21)	1.348(2)
C(11)–F(12)	1.342(3)	C(12)–F(22)	1.332(2)
C(11)–F(13)	1.333(3)	C(12)–F(23)	1.325(3)
Indene			
C(2)–C(3)	1.533(3)	C(7)–C(8)	1.390(4)
C(3)–C(4)	1.390(3)	C(8)–C(9)	1.379(4)
C(4)–C(5)	1.459(4)	C(9)–C(10)	1.385(4)
C(5)–C(6)	1.388(4)	C(10)–C(2)	1.520(3)
C(6)–C(7)	1.376(4)	C(10)–C(5)	1.398(3)
(*b*) Angles			
O(1)–Rh–C(3,4) *	93.5(1)	C(22,23)–Rh–C(24,25)	62.2(1)
O(1)–Rh–C(22,23)	160.3(1)	C(22,23)–Rh–C(3,4)	103.2(1)
O(1)–Rh–C(24,25)	105.1(1)	C(24,25)–Rh–C(3,4)	155.8(1)
Hexadiene			
C(21)–C(22)–C(23)	121.5(2)	C(23)–C(24)–C(25)	121.2(2)
C(22)–C(23)–C(24)	120.7(2)	C(24)–C(25)–C(26)	124.1(2)
Hexafluoroacetone			
Rh–O(1)–C(1)	118.9(1)	F(11)–C(11)–F(12)	105.6(2)
O(1)–C(1)–C(11)	106.8(2)	F(12)–C(11)–F(13)	106.3(2)
O(1)–C(1)–C(12)	109.4(2)	F(11)–C(11)–F(13)	106.6(2)
O(1)–C(1)–C(2)	111.1(2)	F(21)–C(12)–F(22)	106.2(2)
C(11)–C(1)–C(12)	107.3(2)	F(21)–C(12)–F(23)	106.2(2)
		F(22)–C(12)–F(23)	106.3(2)
Indene			
C(1)–C(2)–C(3)	108.0(2)	C(5)–C(6)–C(7)	119.6(2)
C(1)–C(2)–C(10)	116.4(2)	C(6)–C(7)–C(8)	119.7(3)
C(2)–C(3)–C(4)	109.6(2)	C(7)–C(8)–C(9)	121.1(3)
C(3)–C(4)–C(5)	109.3(2)	C(8)–C(9)–C(10)	119.8(2)
C(4)–C(5)–C(6)	130.0(2)	C(9)–C(10)–C(2)	130.8(2)
C(4)–C(5)–C(10)	108.8(2)	C(9)–C(10)–C(5)	119.1(2)
C(10)–C(5)–C(6)	120.8(2)	C(2)–C(10)–C(5)	110.0(2)

* C(*n,m*) represents the midpoint of the line joining atoms C(*n*) and C(*m*).

carbon bond lengths Rh–C(22), 2.15; Rh–C(23), 2.11; Rh–C(24), 2.20; and Rh–C(25), 2.26 Å.

The adduct (3) could only arise if the hexafluoroacetone approached the C_5 ring of the indenyl ligand on the same face as that bonded to the rhodium atom. Since there is a large body of evidence [22, 23] to show that hexafluoroacetone can form η^2-bonded complexes with both d^8 and d^{10} transition-metal species it is likely that the initial interaction of *trans,trans*-hexa-2,4-diene(η^5-indenyl)rhodium with hexafluoroacetone involves formation of such a η^2-bonded complex. In the case of the indenyl system the required co-ordination site for the hexafluoroacetone can be provided by slippage ($\eta^5 \rightarrow \eta^3$) of the indenyl ligand, see Scheme 1, and it is clear that a similar pathway could be followed in the corresponding reactions of isoprene- or 2,3-dimethylbuta-1,3-diene-(η^5-indenyl)rhodium.



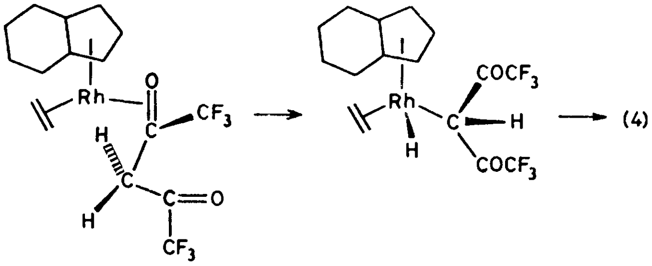
SCHEME 1 Substituents on the 1,3-diene omitted for simplicity

Thus, two different reaction paths are apparently available to the co-ordinated hexafluoroacetone and are illustrated in Scheme 1. One leads to adducts like (1) and (2), and involves a redox reaction ($Rh^I \rightarrow Rh^{III}$) with formation of a five-membered ring incorporating the hexafluoroacetone and one of the olefinic bonds of the 1,3-diene, the rhodium preferentially attaching itself to the 2-position of the co-ordinated diene. The second competing pathway, which leads to complex (3), requires a different initial orientation of the co-ordinated hexafluoroacetone and results in its attachment to the C_5 indenyl ring without a formal change in the oxidation state of the rhodium.

These reactions are selective in that products containing oxygen–rhodium bonds are always formed, there being no evidence for isomeric products incorporating the unit $RhC(CF_3)_2O$. Similarly, no complexes were observed which could have originated from formal attachment of the rhodium to carbon atom 1 of the diene C_4 fragment.

Recently, the reaction of hexafluoroacetone with *trans*-η-cyclopentadienyl(penta-1,3-diene)rhodium was examined [24] in the light of a general analysis of the electronic factors controlling the formation of metallacyclopentanes from bis olefin metal complexes. If it is assumed that the *trans*-penta-1,3-diene is η^2 bonded *via* the unsubstituted olefinic bond then the observed selectivity is as predicted. In the case of the corresponding reaction of η^5-indenyl(isoprene)rhodium the isoprene could, in principle, be bonded in the reaction intermediate either in the η^2 mode *via* the unsubstituted olefinic bond or in the η^4 mode. In both cases if electronic effects were dominant then attack by hexafluoroacetone would be expected [24, 25] to occur preferentially at the unsubstituted olefinic bond of isoprene. Such regioselectivity is not observed experimentally, the isomer (1a) being formed preferentially. This suggests that factors other than those discussed by Hoffmann and Stockis may be important in controlling the regioselectivity of these particular reactions.

Finally, an attempt was made to extend these reactions to hexafluoroacetylacetone and the reaction with bis(ethylene)(η^5-indenyl)rhodium was examined. A rapid reaction occurred at room temperature in hexane as solvent to give the orange crystalline complex (4). Elemental analyses and the mass spectrum indicated that (4) was derived from a molecule of hexafluoroacetylacetone and ethylene(η^5-indenyl)rhodium. The ^{1}H n.m.r. spectrum showed features typical of an η^5-bonded indenyl ligand together with resonances assignable to an ethyl group σ bonded to rhodium and of a hexafluoroacetylacetonate ligand bonded to Rh. The ^{19}F n.m.r. spectrum showed one singlet resonance. These features are consistent with the illustrated structure for (4), and it is suggested that a different reaction path is followed from that hoped for, which involves (Scheme 2) a competitive oxidative reaction followed by ' insertion ' of a co-ordinated ethylene into the rhodium–hydrogen bond.

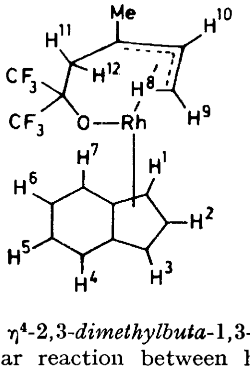


SCHEME 2

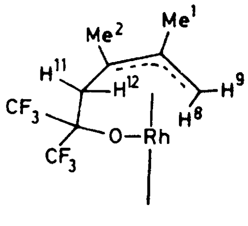
EXPERIMENTAL

Hydrogen-1 and ^{19}F n.m.r. spectra were recorded using Varian Associates HA100 and JEOL PFT-100 spectrometers, respectively. Fluorine chemical shifts are relative to CCl_3F (0.0 p.p.m., external). Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Mass spectra were measured on an A.E.I. MS 902 spectrometer operating at 70 eV.* Reactions were carried out in a dry oxygen-free nitrogen atmosphere.

Reactions of Hexafluoroacetone.—(a) *With η^5-indenyl(η^4-isoprene)rhodium*. An excess of hexafluoroacetone (1.8 g, 5 mmol) was condensed (−196 °C) into a Carius tube containing a solution of η^5-indenyl(η^4-isoprene)rhodium (0.32 g, 1.1 mmol) in hexane (10 cm^3). After 48 h at room temperature the volatile material was removed *in vacuo*. The methylene chloride-soluble material was chromatographed on an alumina packed column. Elution with hexane–diethyl ether (2 : 1) gave an orange band. Recrystallisation (30 °C) gave orange crystals of (1a) and (1b) (5 : 1). Fractional crystallisation afforded orange *crystals* of (1a) (0.3 g, 63%) (Found: C, 44.8; H, 3.4; F, 26.0. $C_{17}H_{15}F_6ORh$ requires C, 45.2; H, 3.3; F, 25.2%), $\nu_{max.}$ (Nujol) 3 080m, 3 060m, 1 345m, 1 320m, 1 310m, 1 280s, 1 245s, 1 220s, 1 205s, 1 190s, 1 170s, 1 150s, 1 140s, 1 060s, 1 040s, 1 030s, 985s, 970m, 880m, 870m, 855m, 755s, 730s, and 685m cm^{-1}. ^{1}H N.m.r. spectrum ($CDCl_3$) τ 2.3—2.9 (m, 4 H, H^{4-7}), 3.44 (bs, 1 H, H^1), 4.32 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.0 Hz], 4.8 [ddd, 1 H, H^{10}, $J(H^8H^{10})$ 11.0, $J(H^9H^{10})$ 6.0, $J(RhH^{10})$ 2.5 Hz], 5.62 [d, 1 H, H^9, $J(H^9H^{10})$ 6.0 Hz], 5.8 (bs, 1 H, H^3), 7.23 [d, 1 H, H^8, $J(H^8H^{10})$, 11.0 Hz], 8.22 [d, 1 H, H^{11}, $J(H^{11}H^{12})$ 14.0 Hz], 8.3 (s, 3 H, Me), and 8.43 [d, 1 H, H^{12}, $J(H^{11}H^{12})$ 14.0 Hz]. ^{19}F N.m.r. spectrum ($CDCl_3$) 76.8 p.p.m. [q, 3 F, J(FF) 9.0 Hz] and 77.1 [q, 3 F, J(FF) 9.0 Hz]. The mass spectrum (base peak *m/e* 218) showed peaks at *m/e* 452 (*P*, 51%), 286 [$P - (CF_3)_2CO$, 74%], and 218 [$P - (CF_3)_2CO - C_5H_8$, 100%]. Fractional crystallisation afforded orange *crystals* of (1b) (0.058 g) (Found: C, 44.7; H, 3.3; F, 26.7. $C_{17}H_{15}F_6ORh$ requires C, 45.2; H, 3.3; F, 25.2%). ^{19}F N.m.r. spectrum ($CDCl_3$) showed resonances at 76.5 p.p.m. [q, 3 F, J(FF) 9.0 Hz] and 77.9 [q, 3 F, J(FF) 9.0 Hz]. The mass spectrum (base peak *m/e* 218) showed peaks at *m/e* 452 (*P*, 45%) and 286 [$P - (CF_3)_2CO$, 70%].



(b) *With η^4-2,3-dimethylbuta-1,3-diene(η^5-indenyl)rhodium*. A similar reaction between hexafluoroacetone (1.6 g, 10 mmol) and η^4-2,3-dimethylbuta-1,3-diene(η^5-indenyl)rhodium (0.1 g, 0.3 mmol) in hexane (10 cm^3) afforded an orange band [hexane–methylene chloride (2 : 1)]. Recrystallisation (−30 °C) from methylene chloride–hexane gave orange *crystals* of (2) (0.06 g, 35%) (Found: C, 46.3; H, 3.6; F, 24.6. $C_{18}H_{17}F_6ORh$ requires C, 46.4; H, 3.7; F, 24.5%), $\nu_{max.}$ (Nujol) 3 070m, 1 645m, 1 385m, 1 340m, 1 320m, 1 300w, 1 275s, 1 240s, 1 235s, 1 215s, 1 210s, 1 190s, 1 165s, 1 150s, 1 130s, 1 115m, 1 040s, 1 020m, 990m, 970s, 915w, 875m, 870m, 855m, 755s, 740w, 730m, 715m, and 680m cm^{-1}. ^{1}H N.m.r. spectrum ($CDCl_3$) τ 2.3—2.9 (m, 4 H, H^{4-7}), 3.57 [d, 1 H, H^1, $J(H^1H^2)$ 2.0 Hz], 4.1 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.0 Hz], 5.6 (s, 1 H, H^9), 6.18 (bs, 1 H, H^3), 7.26 (s, 1 H, H^8), 7.9 [d, 3 H, Me^1, J(RhH) 1.5 Hz], 8.2 [d, 1 H, H^{10}, $J(H^{10}H^{11})$ 14.0 Hz], 8.4 (s, 3 H, Me^2), and 8.5 [d, 1 H, H^{11}, $J(H^{10}H^{11})$ 14.0 Hz]. ^{19}F N.m.r. spectrum ($CDCl_3$) 76.0 p.p.m. [q, 3 F, J(FF) 8.5 Hz] and 76.8 [q, 3 F, J(FF) 9.5 Hz]. The mass spectrum (base peak *m/e* 218) showed peaks at *m/e* 466 (*P*, 35%), 300 [$P - (CF_3)_2CO$, 75%], and 218 [$P - (CF_3)_2CO - C_6H_{10}$, 100%].



(c) *With η^4-*trans,trans*-Hexa-2,4-diene(η^5-indenyl)rhodium*. Similarly, reaction of hexafluoroacetone (0.8 g, 5 mmol) with η^4-*trans,trans*-hexa-2,4-diene(η^5-indenyl)rhodium (0.3 g, 1.0 mmol) in hexane (10 cm^3) gave orange *crystals* of (3) (0.17 g, 36%) (Found: C, 46.0; H, 3.7; F, 24.5. $C_{18}H_{17}F_6ORh$ requires C, 46.4; H, 3.7; F, 24.5%), $\nu_{max.}$ (Nujol) 1 535w, 1 315w, 1 290m, 1 275m, 1 240s, 1 225s, 1 210s, 1 200s, 1 180s, 1 170(sh), 1 160s, 1 120s, 1 020s, 985m, 960w, 915m, 905m, 880m, 855w, 845m, 790m, 770m, 755m, 745m, 725m, and 715m cm^{-1}. ^{1}H N.m.r. spectrum ($CDCl_3$) τ 2.6—2.9 (m, 4 H, H^{4-7}), 3.9 (m, 1 H, H^{10}), 4.3 (m, 1 H, $H^{1\text{ or }2}$), 4.5 (m, 1 H, H^3), 5.8—6.0 (cm, 2 H, H^{11}, $H^{1\text{ or }2}$), 7.1 [m, 1 H, H^9, $J(H^9H^{10})$ 10.0, $J(H^9Me^1)$

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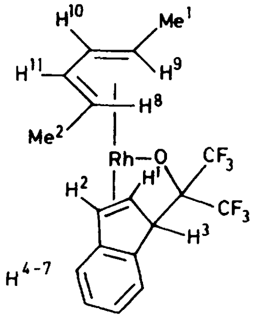
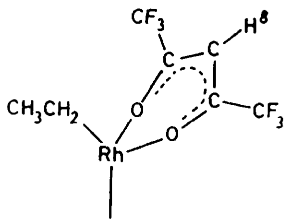
* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

6.0 Hz], 7.5 [m, 1 H, H^8, $J(H^8H^{11})$ 9.0, $J(H^8Me^2)$ 6.0, $J(RhH^8)$ 2.5 Hz], 8.64 [d, 3 H, Me^1, $J(H^9Me^1)$ 6.0 Hz], and 9.2 [d, 3 H, Me^2, $J(H^8Me^2)$ 6.0 Hz]. ^{19}F N.m.r. [$(CD_3)_2CO$] 70.2 p.p.m. [q, 3 F, CF_3, $J(FF)$ 12.0 Hz] and 75.6 [qd, 3 F, CF_3, $J(FF)$ 12.0 $J(FH^3)$ 3.0 Hz]. The mass spectrum (base peak *m/e* 115) showed peaks at *m/e* 466 (*P*, 53%), 384 ($P - C_6H_{10}$, 61%), 300 [$P - (CF_3)_2CO$, 36%], and 218 [$P - C_6H_{10} - (CF_3)_2CO$, 64%].



Reaction of Hexafluoroacetylacetone with Bis(ethylene)(η^5-indenyl)rhodium.—Hexafluoroacetylacetone (0.30 g, 1.4 mmol) was added dropwise (room temperature) to a solution of bis(ethylene)(η^5-indenyl)rhodium (0.135 g, 0.5 mmol) in hexane (10 cm^3). An immediate colour change occurred from yellow to orange. The volatile material was removed *in vacuo* and the residue was recrystallised (−78 °C) from hexane to afford orange *crystals* of compound (4) (0.175 g, 78%) (Found: C, 42.3; H, 2.8. $C_{16}H_{13}F_6O_2Rh$ requires C, 42.3; H, 2.9%), $\nu_{max.}$ (Nujol) 1 625s, 1 570w, 1 545m, 1 510m, 1 485s, 1 370m, 1 315w, 1 265s, 1 225m, 1 210s, 1 170s, 1 160s, 1 150s, 1 140s, 1 105m, 1 055w, 1 020w, 950w, 885w, 875m, 850m, 820w, 790s, 770m, 760s, 755m, and 685s cm^{-1}. ^1H n.m.r. spectrum (C_6D_6) τ 3.0—3.3 (cm, 4 H, H^{4-7}), 4.1 (s, 1 H, H^8), 5.2 (s, 3 H, H^{1-3}), 7.34 [qd, 2 H, Rh$CH_2$$CH_3$, $J(HMe)$ 8 Hz, $J(RhH)$ 3 Hz], and 9.02 [t, 3 H, Rh$CH_2$$CH_3$, $J(HMe)$ 8 Hz]; ^{19}F n.m.r. spectrum (C_6D_6) 91.8 p.p.m. (s, 6 F, CF_3). The mass spectrum (base peak *m/e* 425) showed peaks at *m/e* 454 (*P*, 10%), 425 ($P - C_2H_5$, 100%), and 406 ($P - C_2H_5 - F$, 5%).



Structure Determination of Complexes (1a) *and* (3) *by X-Ray Diffraction.*—Crystals of both (1a) and (3) grow as dark red prisms from methylene chloride and are stable to air and *X*-radiation. Intensity data for both compounds were collected on a Syntex $P2_1$ four-circle diffractometer in the range $2.9 < 2\theta < 50°$ (298 K) according to methods described earlier; 2 704 intensities out of 3 253 (1a) and 2 878 out of 3 649 (3) having $I > 2\sigma(I)$ were used in the solution and refinements for the structures. No corrections were made for the effects of *X*-ray absorption.

Crystal data (1a). $C_{17}H_{15}F_6ORh{\cdot}0.25CH_2Cl_2$, $M = 451.2$, Monoclinic $P2_1/a$, $a = 14.020(7)$, $b = 8.690(4)$, $c = 14.669(5)$ Å, $\beta = 101.61(3)°$, $U = 1\,750.7(13)$ Å^3, $D_m = 1.71$, $Z = 4$, $D_c = 1.72$ g cm^{-3} (including solvent, see below),* $F(000) = 896.0$, $\mu = 10.2$ cm^{-1}, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å.

Crystal data (3). $C_{18}H_{17}F_6ORh$, $M = 466.1$, Monoclinic $P2_1/c$, $a = 8.094(2)$, $b = 16.962(8)$, $c = 12.782(4)$ Å, $\beta = 99.81(2)°$, $U = 1\,729(1)$ Å^3, $D_m = 1.80$, $Z = 4$, $D_c = 1.80$ g cm^{-3}, $F(000) = 928.0$, $\mu = 10.4$ cm^{-1}, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å.

Structure solution and refinement. The rhodium atoms were located from a three-dimensional Patterson synthesis and all the remaining atoms [including hydrogen atoms for (3)] by successive electron-density difference syntheses. The hydrogen atoms for (1a) were incorporated at calculated positions and not refined. Refinement converged at *R* 0.045 (*R′* 0.056) for (1a), and at *R* 0.021 (*R′* 0.025) for (3) with all non-hydrogen atoms given anisotropic thermal parameters. In the case of (3) the hydrogen atoms were refined isotropically and their parameters are deposited together with the structure factor tables and thermal parameters in Supplementary Publication No. SUP 22923 (26 pp.).† Tables 3 and 4 list the final atomic positions for (1a) and (3) respectively. The weighting schemes used were $w^{-1} = |\sigma^2(F) + \alpha|F||$ with $\alpha = 0.017\,5$ for (1a), and $\alpha = 0$ for (3), where $\sigma|F|$ is the estimated error based on counting statistics. These schemes gave a satisfactory weight analysis with a mean shift-to-error ratio of 0.4 for (1a) and 0.35 for (3) in the final cycles of refinement. Computational work was carried out using the ' *X*-Ray ' system of programs for CDC 7 600 at the London Computing Centre for complex (1a), and ' XTL ' (Syntex) programs on a NOVA 1200 computer for complex (3).

TABLE 3

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for compound (1a)

Atom	*x*	*y*	*z*
Rh	0.047 69(3)	0.043 49(5)	0.263 07(3)
O(1)	0.136 6(3)	0.228 2(5)	0.245 1(5)
C(5)	0.102 4(5)	0.322 8(8)	0.170 3(4)
C(51)	0.192 3(6)	0.387 6(10)	0.136 1(5)
F(511)	0.167 7(4)	0.472 8(7)	0.058 5(4)
F(512)	0.248 2(3)	0.273 2(7)	0.115 3(4)
F(513)	0.247 9(4)	0.476 4(8)	0.198 5(4)
C(52)	0.043 0(6)	0.456 8(8)	0.199 1(5)
F(521)	0.017 3(5)	0.563 1(5)	0.132 3(4)
F(522)	0.092 4(4)	0.530 6(6)	0.274 3(4)
F(523)	−0.037 8(3)	0.408 0(6)	0.222 6(3)
C(1)	0.108 3(6)	−0.076 8(8)	0.162 2(4)
C(2)	0.009 5(5)	−0.048 2(8)	0.127 2(4)
C(3)	−0.023 6(4)	0.106 3(8)	0.120 9(4)
C(31)	−0.134 3(5)	0.137 7(11)	0.099 2(5)
C(4)	0.039 9(5)	0.233 9(8)	0.088 0(4)
C(6)	−0.163 3(5)	0.105 6(11)	0.339 3(5)
C(7)	−0.170 0(6)	0.253 9(12)	0.369 1(6)
C(8)	−0.092 0(7)	0.335 6(12)	0.414 1(6)
C(9)	0.005 5(6)	0.267 6(9)	0.434 5(5)
C(10)	0.012 3(4)	0.118 2(8)	0.405 2(4)
C(11)	0.098 2(5)	0.016 9(9)	0.415 0(4)
C(12)	0.066 6(5)	−0.131 7(9)	0.375 7(5)
C(13)	−0.037 8(6)	−0.115 7(8)	0.330 5(4)
C(14)	−0.070 6(4)	0.036 4(8)	0.356 3(4)
Cl	0.271 6(5)	0.307 9(9)	0.405 3(4)

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* Compound (1a) crystallises together with one molecule of solvent per unit cell, lying astride the two-fold axis of rotation. Only the disordered chlorine atom was located with certainty.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

Atomic scattering factors used for (1a) were those of ref. 26 for Rh, ref. 27 for C and F, ref. 28 for H, and ref. 29 for all atoms in (3), with corrections applied to those of Rh for the effects of anomalous dispersion.

TABLE 4

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for compound (3)

Atom	*x*	*y*	*z*
Rh	0.333 94(2)	0.093 44(1)	0.087 35(1)
O(1)	0.318 2(2)	−0.006 4(1)	0.170 2(1)
C(1)	0.364 1(3)	−0.004 6(1)	0.279 1(2)
C(11)	0.239 1(3)	−0.057 2(1)	0.324 7(2)
C(12)	0.541 0(3)	−0.042 4(1)	0.311 0(2)
F(11)	0.253 7(2)	−0.052 7(1)	0.431 4(1)
F(12)	0.259 7(2)	−0.133 7(1)	0.303 2(1)
F(13)	0.080 3(2)	−0.039 8(1)	0.284 8(1)
F(21)	0.575 4(2)	−0.060 3(1)	0.415 2(1)
F(22)	0.662 9(2)	0.005 6(1)	0.292 4(1)
F(23)	0.559 4(2)	−0.108 7(1)	0.259 3(1)
C(2)	0.372 3(3)	0.082 1(1)	0.321 9(2)
C(3)	0.443 2(3)	0.134 3(1)	0.242 2(2)
C(4)	0.324 3(3)	0.190 1(1)	0.200 2(2)
C(5)	0.177 1(3)	0.183 4(1)	0.251 4(2)
C(6)	0.034 2(4)	0.228 8(1)	0.242 0(2)
C(7)	−0.079 6(4)	0.216 1(2)	0.308 9(2)
C(8)	−0.049 7(4)	0.157 2(2)	0.385 4(2)
C(9)	0.091 6(4)	0.110 6(1)	0.394 8(2)
C(10)	0.205 3(3)	0.121 8(1)	0.326 5(2)
C(21)	0.574 7(4)	0.232 6(2)	0.023 9(2)
C(22)	0.456 5(3)	0.162 6(1)	−0.012 8(2)
C(23)	0.292 5(3)	0.170 4(1)	−0.044 5(2)
C(24)	0.190 2(3)	0.103 1(1)	−0.074 4(2)
C(25)	0.257 0(3)	0.028 2(1)	−0.067 4(2)
C(26)	0.151 9(3)	−0.044 8(2)	−0.076 9(2)

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