Reactions of Co-ordinated Ligands. Part 22.[1] The Reactivity of Bis(ethylene)(η^5-indenyl)rhodium in Displacement Reactions with Olefins, Dienes, and Acetylenes; Crystal Structure of η^5-Indenyl{1—2:3—4-η^4-[6-*endo*-propen-2-yl-1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3-diene]}rhodium formed in a Cyclo-cotrimerisation Reaction

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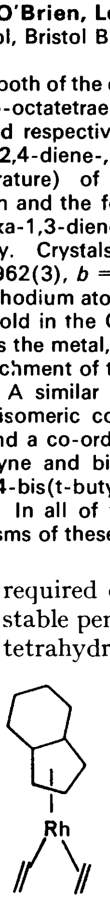
In contrast to the η^5-cyclopentadienyl analogue, both of the ethylenes in the compound bis(ethylene)(η^5-indenyl)rhodium are readily displaced by isoprene, cyclo-octatetraene, *trans*-penta-1,3-diene, *trans,trans*-hexa-2,4-diene, methylenecyclopropane, or acrylonitrile to afford respectively η^4-isoprene-, 1—2 : 5—6-η^4-cyclo-octatetraene-, η^4-*trans*-penta-1,3-diene-, η^4-*trans,trans*-hexa-2,4-diene-, bis(methylenecyclopropane)-, or bis(acrylonitrile)-(η^5-indenyl)rhodium. Reaction (room temperature) of hexafluorobut-2-yne with η^5-indenyl(η^4-isoprene)-rhodium leads to a cyclo-cotrimerisation reaction and the formation of η^5-indenyl{1—2: 3—4-η^4-[6-*endo*-propen-2-yl-1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3-diene]}rhodium, the structure in the solid state being established by a single-crystal *X*-ray diffraction study. Crystals are orthorhombic, space group *Pbca* (no. 61), with eight molecules in a cell of dimensions a = 16.962(3), b = 29.618(5), and c = 8.596(4) Å. The 1,3-diene part of the C_6 ring is planar, and is η^4-bonded to the rhodium atom, but the two carbon atoms originating from the isoprene bend away from the metal to produce a fold in the C_6 ring at a dihedral angle of *ca.* 132°. The propenyl substituent lies on the same side of the C_6 ring as the metal, *i.e.* is in an *endo* configuration. An 18-electron configuration for the rhodium is achieved by η^5-attachment of the indenyl group, but two of these five carbon atoms are less strongly bonded than the other three. A similar reaction of hexafluorobut-2-yne with η^5-indenyl(η^4-*trans*-penta-1,3-diene)rhodium affords related isomeric complexes. A cyclo-cotrimerisation reaction has also been observed between hexafluorobut-2-yne and a co-ordinated ethylene of bis(ethylene)(η^5-indenyl)rhodium. Related reactions between 3,3-dimethylbut-1-yne and bis(ethylene)(η^5-indenyl)rhodium or bis(acrylonitrile)-(η^5-indenyl)rhodium afford respectively [η^4-1,4-bis(t-butyl)cyclohexa-1,3-diene]- and [η^4-5-cyano-1,4-bis(t-butyl)cyclohexa-1,3-diene]-η^5-indenylrhodium. In all of these reactions competitive cyclotrimerisation of the acetylenes occurs to give arenes. The mechanisms of these reactions are discussed.

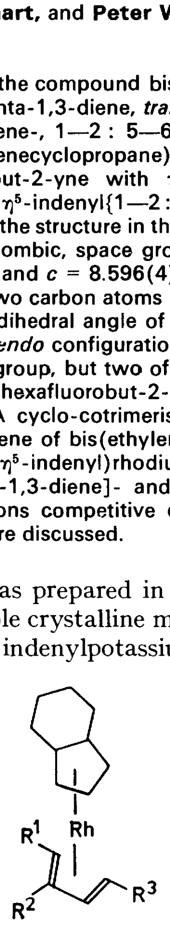
In establishing the stepwise nature of the six-membered carbon ring-forming reaction between co-ordinated acetylenes and 1,3-dienes we observed that u.v. irradiation of tricarbonyl(cyclohexa-1,3-diene)ruthenium in the presence of hexafluorobut-2-yne afforded a ruthenacyclohepta-2,6-diene, in which the seven-membered ring is formed from two $CF_3C_2CF_3$ molecules and one olefinic bond of the cyclohexa-1,3-diene.[2] In principle such a metallacycloheptadiene could undergo a reductive carbon–carbon bond-forming reaction thus formally achieving a cyclo-cotrimerisation reaction of two acetylenes and one olefin. Whilst this reaction was of interest from a mechanistic standpoint, the need to generate the required co-ordination sites for the acetylene molecules by u.v. irradiation clearly limited the synthetic potential, particularly from the organic standpoint. With a view to developing these ideas further, the related chemistry of the isoelectronic η^5-indenylrhodium complexes has been studied. We have previously [3] noted that unlike the corresponding η^5-cyclopentadienyl system the η^5-indenylrhodium(I) complexes show high reactivity in ligand-substitution reactions. This increase in reactivity can be interpreted in terms of a slippage (η^5 to η^3) of the indenyl system, thus making available without u.v. irradiation a site for co-ordination of a reacting unsaturated species such as an olefin or an acetylene.

RESULTS AND DISCUSSION

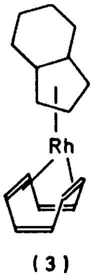
Our initial aim was to establish that both of the co-ordinated ethylene molecules present in the molecule (1) [$Rh(C_2H_4)_2(\eta^5-C_9H_7)$] could be readily displaced. The required complex was prepared in high yield as an air-stable pentane-soluble crystalline material by reaction in tetrahydrofuran of indenylpotassium with di-μ-chloro-tetrakis(ethylene)dirhodium. The structure of (1) was confirmed by elemental analysis, mass spectroscopy (m.s.), and n.m.r. (^1H, ^{13}C) spectroscopy. Treatment (room temperature) of (1) with an excess of isoprene led



(1)



(2) $R^1 = R^3 = H, R^2 = Me$
(4) $R^2 = R^3 = H, R^1 = Me$
(5) $R^2 = H, R^1 = R^3 = Me$



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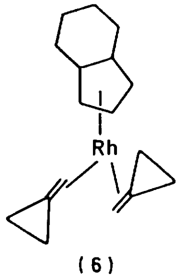

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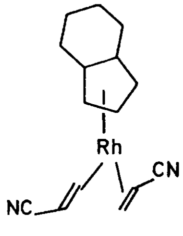
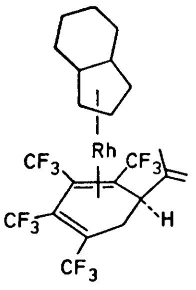


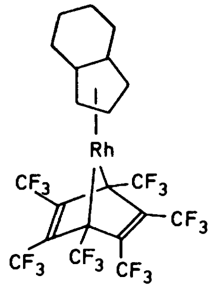
(7)

to the displacement of both ethylenes and the formation (93% yield) of a complex (2), identified (analysis, m.s., i.r., and n.m.r.) as η^5-indenyl(η^4-isoprene)rhodium. This same yellow crystalline material was also formed, but in lower yield (52%), by reaction of indenylpotassium with di-μ-chloro-bis(isoprene)dirhodium. The generality of the ethylene-displacement route was demonstrated by the ready conversion of (1) into (3) 1—2 : 5—6-η^4-cyclooctatetraene(η^5-indenyl)rhodium, (4) η^5-indenyl(η^4-*trans*-penta-1,3-diene)rhodium, and (5) η^4-*trans,trans*-hexa-2,4-diene(η^5-indenyl)rhodium on treatment with an excess of the respective 1,3-diene. Reaction of (1) with the strained olefin methylenecyclopropane or the electronegatively substituted olefin acrylonitrile also led to displacement of both co-ordinated ethylenes and gave respectively (6) η^5-indenylbis(methylenecyclopropane)-rhodium and (7) bis(acrylonitrile)η^5-indenylrhodium. In the former reaction there was no evidence for products arising from opening of the three-membered ring present in methylenecyclopropane and, on heating, (6) was unchanged.[4]

The reactions of the η^4-1,3-diene(η^5-indenyl)rhodium complexes with hexafluorobut-2-yne were next investigated in the belief that the acetylene would be able to enter the co-ordination sphere of the rhodium readily, thus setting up the necessary initial conditions for subsequent carbon–carbon bond formation. Addition of an excess of hexafluorobut-2-yne to a solution of η^5-indenyl(η^4-isoprene)rhodium in hexane led to a rapid reaction at room temperature and the formation of crystalline products. Chromatography of the reaction mixture afforded a moderate yield of the yellow crystalline complex (8) whose elemental analysis and mass spectrum suggested that the compound was a 2 : 1 adduct of hexafluorobut-2-yne and the isoprene complex (2). Since the spectral data for (8) did not establish a definite structure a single-crystal *X*-ray diffraction study was carried out.



(8)



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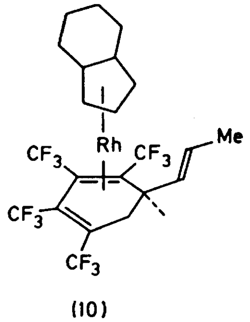

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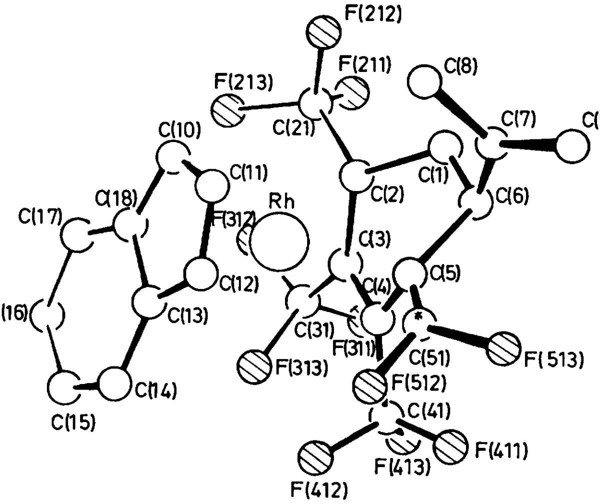


FIGURE 1 Molecular structure of (8) $[Rh(C_9H_7)\{C_6H_3(CF_3)_4C(CH_2)CH_3\}]$ showing the crystallographic numbering system. For clarity in showing the C_6 ring, atom F(511) has been omitted (*)

The molecular structure of (8) is illustrated in Figure 1, which also shows the crystallographic numbering system. It is at once apparent that a cyclo-cotrimerisation reaction has indeed occurred, with the formation of a propenylcyclohexa-1,3-diene ring, which is η^4-attached to the rhodium atom. The cyclohexadiene ring is folded along C(2) $\cdots$ C(5) to give two nearly planar halves (Table 3). The locations of the trifluoromethyl groups show that the four atoms of the C_6 ring which are bonded to the rhodium atom originate from the hexafluorobut-2-yne molecules, while the portion of the ring which is bent away from the metal atom originates from the isoprene moiety. There is extensive delocalisation of the C–C bonding in the 1,3-diene portion of the ring (Table 2), whereas the bonds involving the isoprene portion are single tetrahedral bonds.

The propenyl substituent lies *endo* to the rhodium atom. The remainder of the geometry of the C_6 ring calls for little comment except that the CF_3 groups show the usual feature of F–C–F angles significantly less than the ideal tetrahedral value [mean 106.5(3)°].

An 18-electron configuration for the rhodium atom is achieved by η^5 attachment of the indenyl group. It is interesting that the two bridge atoms of the indenyl group, C(13) and C(18), although well within normal bonding distance of the metal atom, are in fact significantly further away (2.31_5 Å) than the other three [C(10)–C(12) 2.18_2 Å] atoms. The two ring systems of the indenyl group also appear to be not quite coplanar (Table 3). The packing of the molecules within the orthorhombic unit cell is shown in Figure 2; there are no significantly short intermolecular contacts.

Further elution of the reaction mixture, from which

(8) was isolated, afforded an orange crystalline material (9). Elemental analysis and mass spectroscopy suggested that the complex was η^5-indenyl[hexakis(trifluoromethyl)benzene]rhodium, isostructural with the corresponding η-cyclopentadienylrhodium species,[5] which has been shown by single-crystal *X*-ray diffraction studies [6] to adopt a folded structure in the solid state. Comparison of the ^{19}F n.m.r. parameters for (9) with those reported for the cyclopentadienyl compound supports this suggestion.

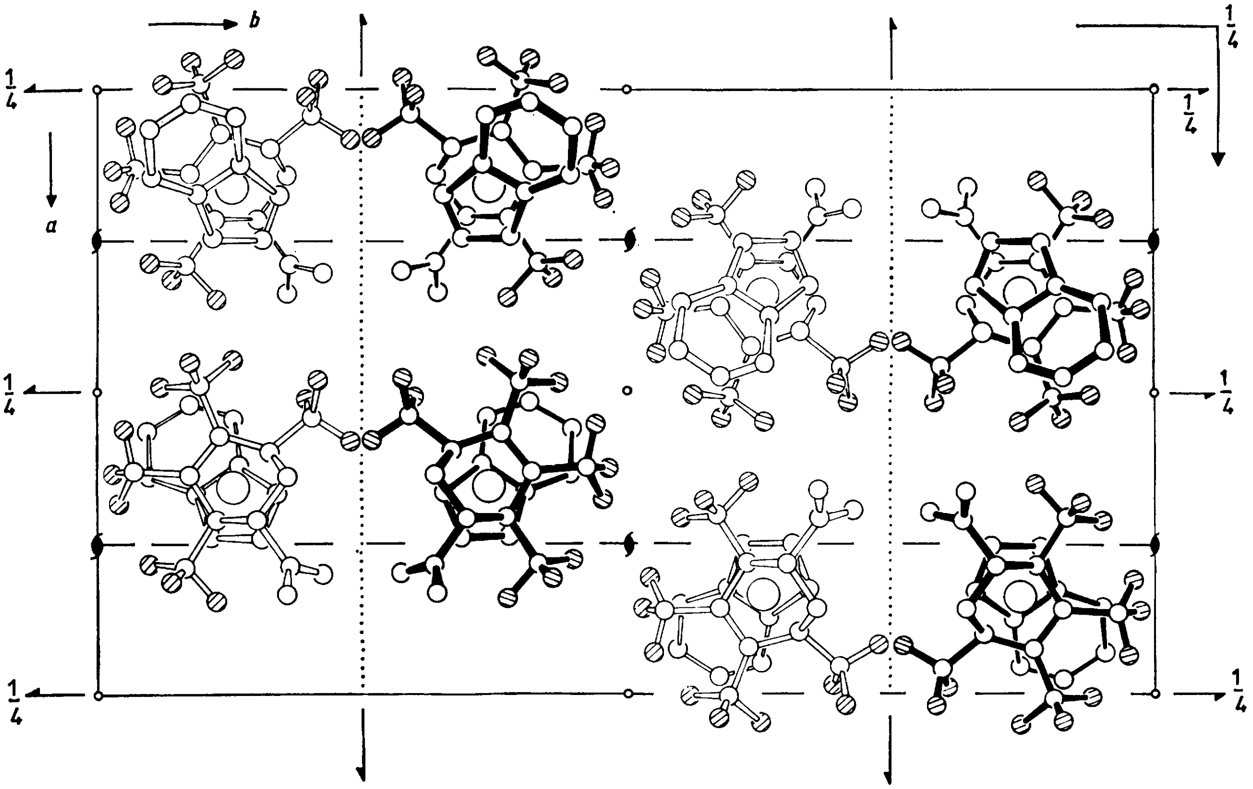


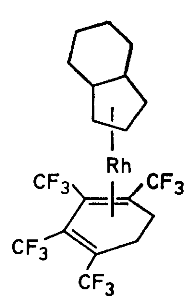
FIGURE 2 Contents of the orthorhombic unit cell seen in projection down *c* looking towards the origin

Reaction of the *trans*-penta-1,3-diene complex (4) with hexafluorobut-2-yne also occurred readily at room temperature to give (9) together with two isomeric complexes (10) and (11), which showed the expected mass-spectral features and chemical analysis for a 2 : 1 adduct of hexafluorobut-2-yne and (4). Comparison of the ^{1}H and ^{19}F n.m.r. spectra parameters of the major isomer (10) with those of (8) suggested the illustrated structure, in which the unsubstituted olefinic bond of *trans*-penta-1,3-diene was incorporated into the C_6 ring of a co-ordinated 1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3-diene.

Due to the small amounts available of the minor isomer (11) it was not possible to obtain n.m.r. spectra of sufficient quality to allow structural identification.

Of further interest was the observation that the cyclo-cotrimerisation reaction was not limited to the use of 1,3-dienes as the olefinic component. Treatment of bis(ethylene)η^5-indenylrhodium with hexafluorobut-2-yne led to the formation in moderate yield (56%) of the yellow crystalline compound (12), which was identified (analysis, m.s., i.r., and n.m.r.) as η^5-indenyl[η^4-1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3-diene]rhodium. The n.m.r. spectra confirmed the presence of a plane of symmetry, the ^{19}F spectrum showing only two resonances of equal intensity.

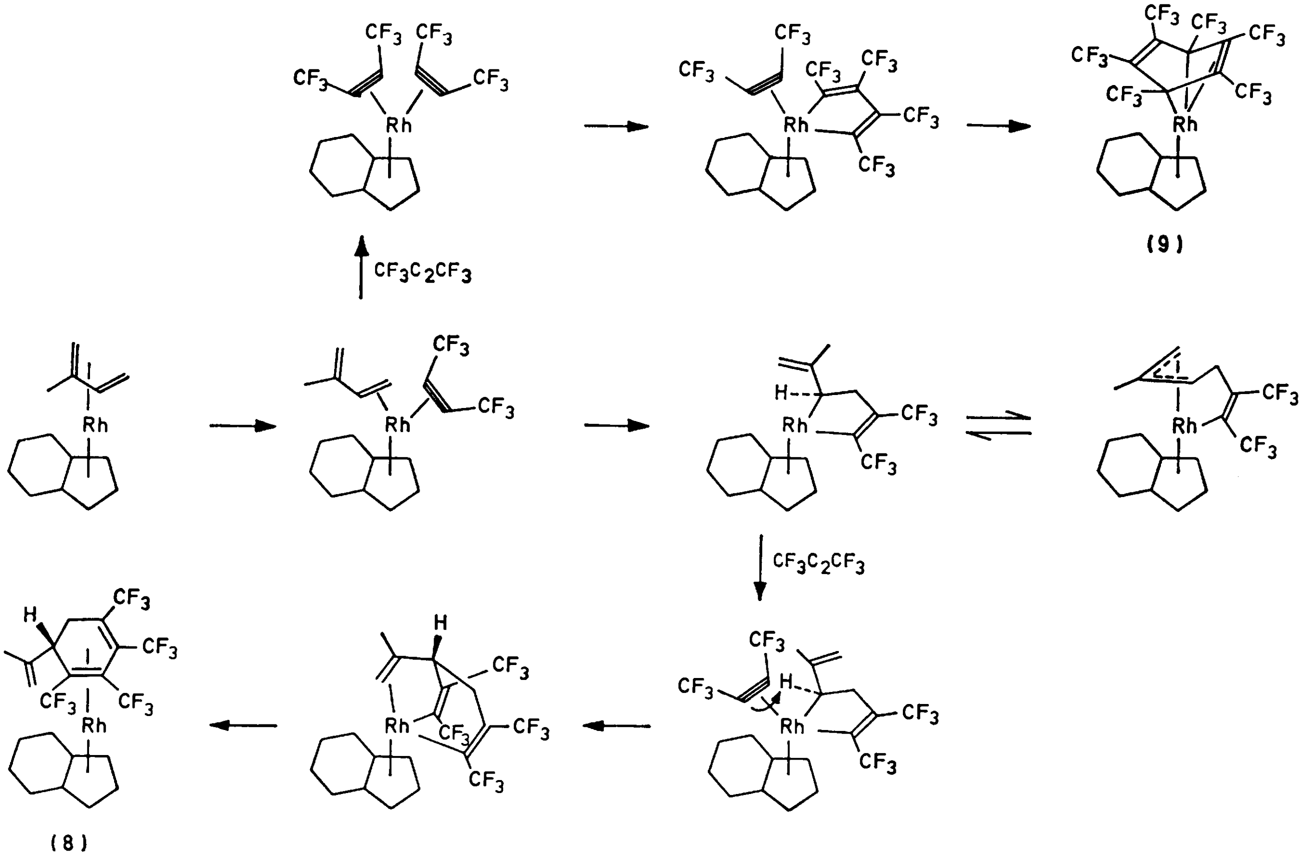
Our previous studies [2] on the reaction of $CF_3C_2CF_3$ with the isoelectronic tricarbonyl(1,3-diene)-iron or -ruthenium compounds suggested that in the formation of the cyclo-cotrimerisation product (8) the initial step involves co-ordination of the acetylene. This step is facilitated by a sideways slippage of the indenyl ligand. In the resulting rhodium(I) species (Scheme 1) the 1,3-



(12)

diene could be bonded in either a η^4 or η^2 mode, the latter seeming more likely. Carbon–carbon bond formation then occurs by electron transfer [7] from the rhodium

(d^8 to d^6) to the η^2-bonded diene and η^2-bonded acetylene resulting in the formation of a rhodacyclopent-2-ene. In the analogous iron system [2] co-ordination of the propenyl group affords a stable η^3-allyl system. However, in the presence of excess of hexafluorobut-2-yne and possibly facilitated by the indenyl-activating effect, co-ordination of a second molecule of acetylene occurs with the rhodium system. The acetylene can then orientate itself *via* rotation such that a *cis*-coplanar insertion reaction can take place to form a 4-propenyl-rhodacyclohepta-2,6-diene. In the ruthenium system mentioned in the introduction the reaction stopped at this stage and the ruthenacyclohepta-2,6-diene could be isolated and was structurally characterised by *X*-ray crystallography. However, the rhodium system proceeds further and undergoes ready reduction (d^6 to d^8) with formation of a carbon–carbon bond, a process which formally corresponds to the coupling of the two σ-bonded vinyl groups. As shown in Scheme 1, such a sequence of steps leaves the appending propenyl group in an *endo* configuration if the insertion step involves retention of the configuration of the propenyl-substituted carbon atom.

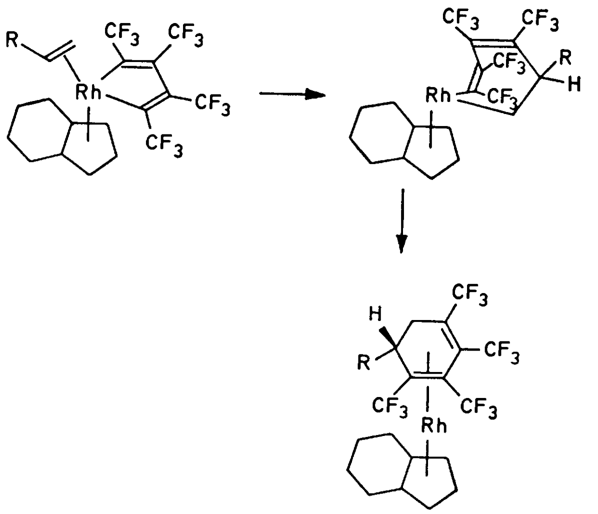


Scheme 1

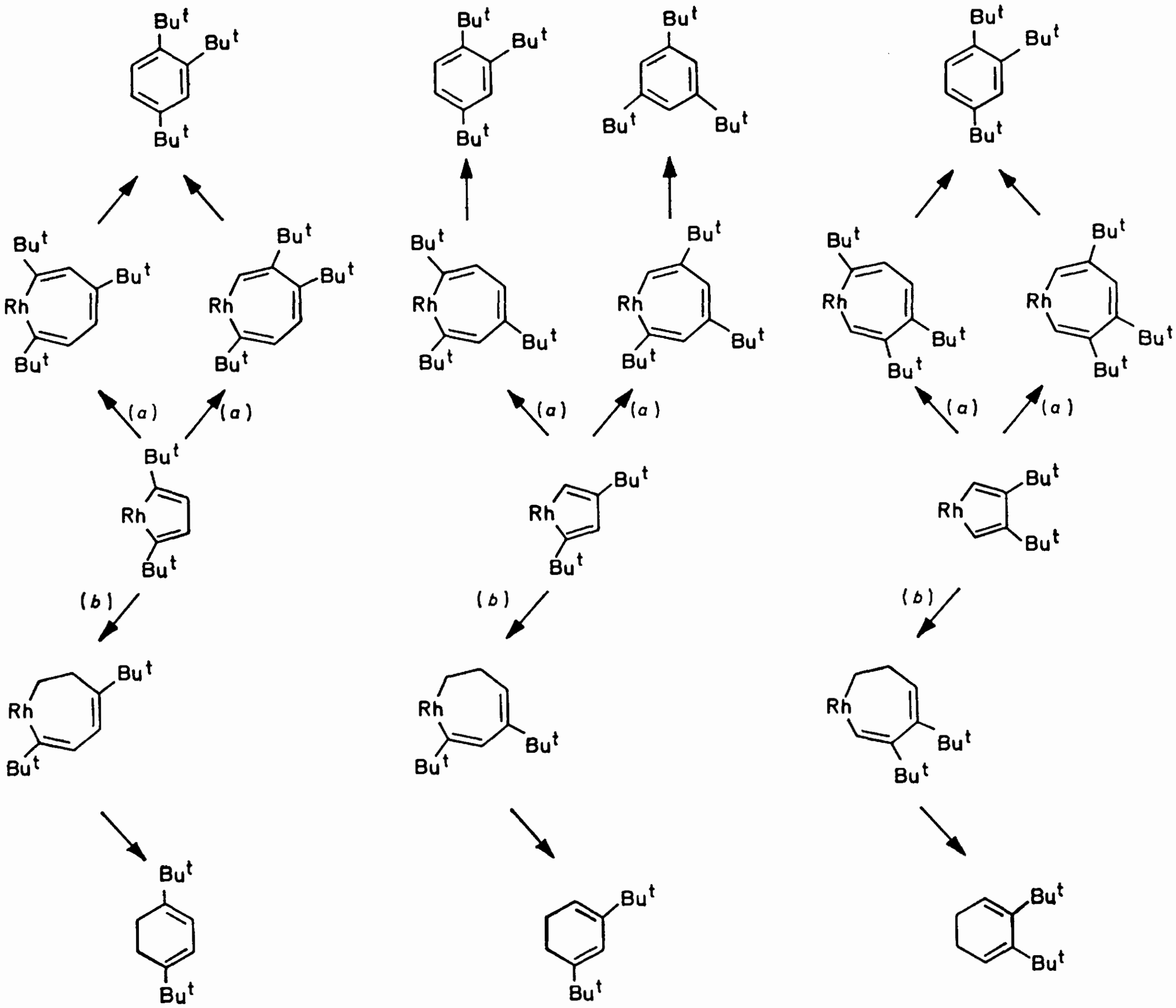
The formation of complex (9) in the reaction of (2) with $CF_3C_2CF_3$ suggests that in the initial stages of the reaction there is a competitive process which results in the complete displacement of the isoprene, thus setting up conditions for the formation of a rhodacyclopentadiene and hence an arene system by cyclotrimerisation of three molecules of hexafluorobut-2-yne.

The reaction paths discussed for the formation of (8) and (9) are clearly applicable to the production of (10) and (11) from (4), and (12) from (1). In the latter case there was no evidence for the arene-forming competitive cyclotrimerisation reaction.

Cyclo-cotrimerisation reactions have been observed [8-11]



Scheme 2



SCHEME 3 Ligands omitted for clarity, (a) Bu^{t}C$_2$H; (b) C$_2$H$_4$

before, although normally only the organic product has been isolated. In a recent [12,13] elegant study of the role of tetrakis(methoxycarbonyl)palladacyclopentadiene in the selective catalysed cyclo-cotrimerisation of dimethylacetylene dicarboxylate with norbornene, cyclopentene, and cyclohexene, the intermediacy of a palladacyclohepta-2,4-diene formed by insertion of the olefin into a Pd–C bond of a palladacyclopentadiene was postulated.

As is shown in Scheme 2, a similar reaction path for the rhodium system *via* a 2,3,4,5-tetrakis(trifluoromethyl)rhodacyclohepta-2,4-diene would also give the observed products (8), (10), (11), and (12). However, as discussed above, we do not favour the intermediacy of a rhodacyclopentadiene in the formation of the tetrakis(trifluoromethyl)cyclohexa-1.3-dienes, because the isolated and structurally defined ruthenacycloheptadiene has a structure incompatible with the pathway shown in Scheme 2, *i.e.* it is a 2,3,6,7-tetrakis(trifluoromethyl)-ruthena-2,6-diene and not a 2,3,4,5-tetrakis(trifluoromethyl)ruthena-2,4-diene, and it is reasonable to expect a close parallel between the isoelectronic η^5-indenylrhodium and tricarbonylruthenium systems. Further support for the suggestion that a metallacyclopent-2-ene is involved derives from an important study [10] of the reaction of (η^2-acetylene)(η-cyclopentadienyl)(triphenylphosphine)cobalt complexes with olefins, where a cobaltacyclopent-2-ene was isolated and structurally characterised by *X*-ray crystallography.

Although a palladacyclopentadiene is used in the catalytic cyclo-cotrimerisation reaction it is possible that this is converted into other species and that the actual immediate precursor of the tetra(methoxycarbonyl)-cyclohexa-1,3-dienes is a 2,3,6,7-tetra(methoxycarbonyl)-palladacyclohepta-2,6-diene and not the suggested 2,3,4,5-tetra(methoxycarbonyl)cyclohepta-2,4-diene. Such a possibility cannot be discounted on the basis of the presently available evidence.

In the light of these observations the reaction of (1) with 3,3-dimethylbut-1-yne was next examined. Reaction at room temperature led to the formation [gas chromatography–mass spectrometry (g.c.–m.s.)] of the volatile organic products 1,2,4- and 1,3,5-tris(t-butyl)-benzene * and 1,4-bis(t-butyl)cyclohexa-1,3-diene. Chromatography of the involatile products afforded the

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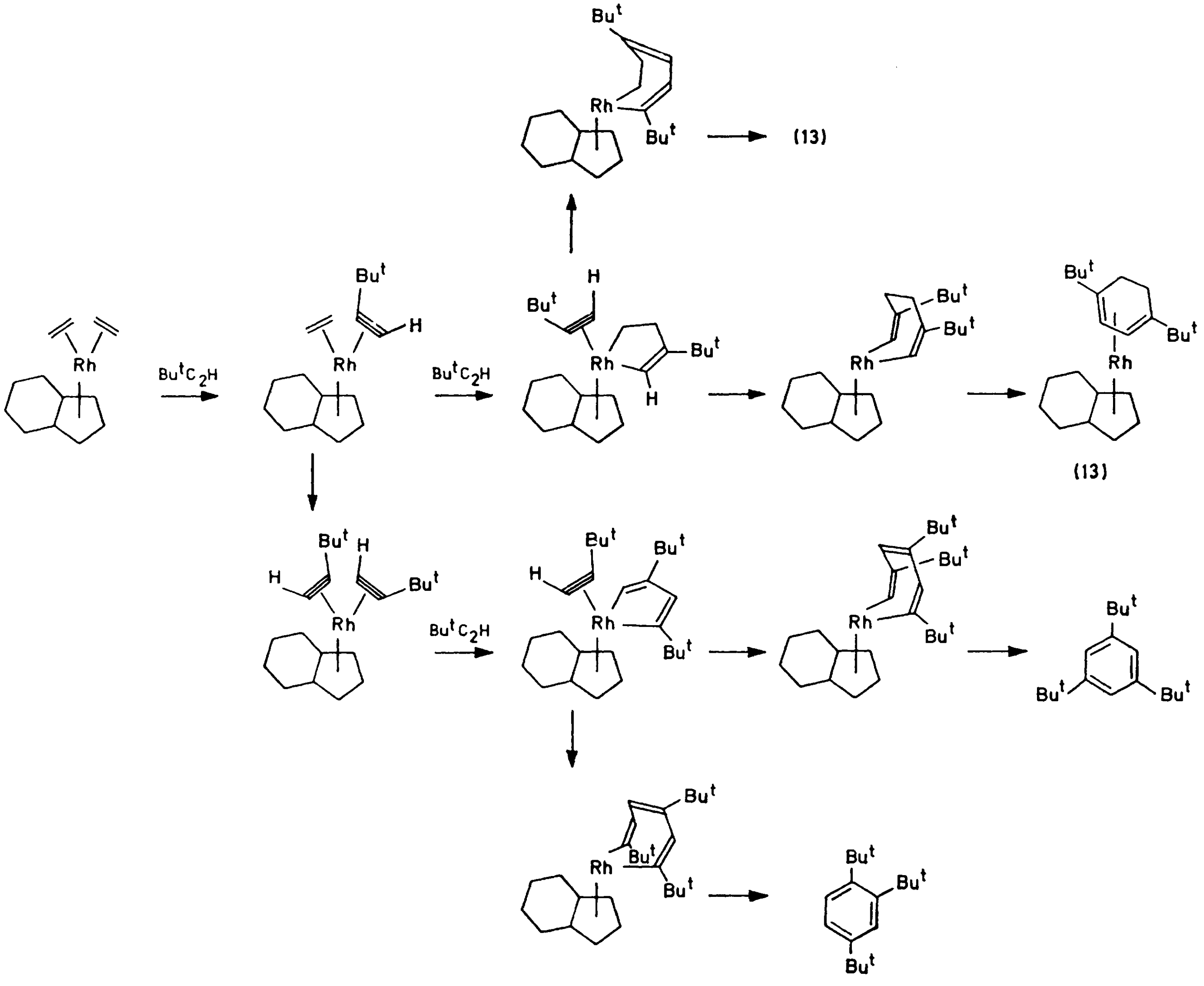
* All of the acetylene was consumed in a catalytic cyclotrimerisation reaction.

yellow crystalline compound (13), which analysed as η^4-1,4-bis(t-butyl)cyclohexa-1,3-diene(η^5-indenyl)-rhodium. This was supported by the ^{1}H n.m.r. spectrum, and also by the ready conversion at room temperature of (13) into dicarbonyl(η^5-indenyl)rhodium and 1,4-bis-(t-butyl)cyclohexa-1,3-diene on treatment with carbon monoxide.



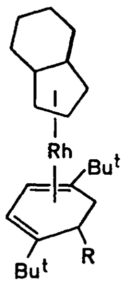
Scheme 4

A similar reaction of 3,3-dimethylbut-1-yne with (7) gave 1,2,4- and 1,3,5-tris(t-butyl)benzene together with the yellow crystalline compound (14). Analysis, i.r. and ^{1}H n.m.r. spectroscopy suggest that (14) is η^4-5-cyano-1,4-bis(t-butyl)cyclohexa-1,3-diene(η^5-indenyl)-rhodium.

The cyclo-cotrimerisation reactions leading to the formation of (13) are interesting in that neither the acetylene nor the olefin component carries an electronegative substituent; moreover, the use of an unsymmetrical acetylene, particularly one carrying a bulky substituent, allows further insight into the reaction paths followed. In the reaction of (1) with 3,3-dimethylbut-1-yne, 1,2,4- and 1,3,5-tris-(t-butyl)benzenes are formed in the ratio of 10 : 1 alongside the cyclo-cotrimerisation product. Since the intermediacy of metallacyclopentadienes[14] is well established in the formation of benzenes from acetylenes, 2,5-, 2,4-, and 3,4-bis(t-butyl)rhodacyclopentadienes could in principle be involved, the predominance of the 1,2,4-substituted product being consistent with either the involvement of all three isomeric rhodacyclopentadienes (Scheme 3) or if only the 2,4- isomer were traversed then the ratio of products requires that insertion to give 2,4,7-tris(t-butyl)rhodacyclohepta-2,4,6-triene is the faster process.

If it is also assumed that these same bis(t-butyl)-rhodacyclopentadienes are the precursors of the cyclo-cotrimerisation product, a cyclohexa-1,3-diene, then there are difficulties. Namely, only the 2,5-bis(t-butyl)-rhodacyclopentadiene, which forms only 1,2,4-tris-(t-butyl)benzene, can serve as a precursor of 1,4-bis-

(t-butyl)cyclohexa-1,3-diene. Moreover, of the three isomeric rhodacyclopentadienes, the greatest steric problems arise in the 2,5 isomer. These problems are avoided if a rhodacyclopent-2-ene is involved as suggested



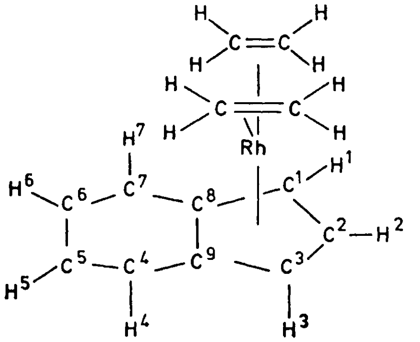
(13) R = H
(14) R = CN

in the formation of (8), (10), (11), and (12). As is illustrated in Scheme 4, one of the ethylenes in (1) is displaced by a molecule of 3,3-dimethylbut-1-yne, which then by electron transfer from the rhodium (d^8 to d^6) to the co-ordinated ethylene and acetylene forms a rhodacyclopent-2-ene. Insertion of a second molecule of 3,3-dimethylbut-1-yne would be expected to form a 3,6-bis(t-butyl)rhodacyclohepta-2,6-diene,* which by reductive (d^6 to d^8) carbon–carbon bond formation gives complex (13). As before, the competitive trimerisation of 3,3-dimethylbut-1-yne is effected by displacement of both ethylenes, this being illustrated only for the 2,4-bis(t-butyl)rhodacyclopentadiene.

EXPERIMENTAL

Hydrogen-1 and ^{19}F n.m.r. spectra were recorded using Varian Associates HA 100 and JEOL PFT-100 spectrometers, respectively. Fluorine chemical shifts were relative to CCl_3F (0.0 p.p.m., external). Carbon-13 spectra were obtained on a JEOL PFT-100 spectrometer at 25.1 MHz, were ^{1}H decoupled, and the shifts are relative to $SiMe_4$. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer, mass spectra on an A.E.I. MS 902 spectrometer operating at 70 eV.† Reactions were carried out in a dry oxygen-free nitrogen atmosphere.

Preparation of Bis(ethylene)(η^5-indenyl)rhodium.—A solution of indenylpotassium (1.7 g, 11.0 mmol) in tetrahydrofuran (thf) (80 cm^3) was added (room temperature) with stirring to a suspension of di-μ-chloro-tetrakis(ethylene)-dirhodium (2.0 g, 5.1 mmol). After 15 min the solvent was removed *in vacuo*, and the residue extracted with hexane (5 × 20 cm^3). Chromatography of this extract on an alumina-packed column (10 × 3 cm) (eluted with hexane) afforded a yellow band. Removal of the solvent followed by recrystallisation (−78 °C) from pentane afforded yellow crystals of (1) *bis(ethylene)(η^5-indenyl)rhodium* (2.4 g, 84%) (Found: C, 57.2; H, 5.8. $C_{13}H_{15}Rh$ requires C, 57.0; H, 5.5%), $\nu_{max.}$ (Nujol) at 3 060m, 1 435m, 1 335 (sh), 1 330m, 1 245m, 1 215m, 1 210m, 1 200s, 1 155w, 1 040m, 1 010w, 975m, 915w, 905w, 880w, 870w, 825m, 805m, 750s, and 740m cm^{-1}. N.m.r. spectra: ^{1}H [$(CD_3)_2CO$, room temperature ‡ (r.t.)], τ 2.6—2.9 (m, 4 H, H^{4-7}), 3.8 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.0 Hz], 4.76 [d, 2 H, $H^{1,3}$, $J(H^1H^2)$ 2.0 Hz], and 7.96 [d, 8 H, C_2H_4, J (RhH) 2.0 Hz]; ^{13}C (C_6D_6, r.t.), −44.1 [d, C_2H_4, $J(RhC)$ 13.5 Hz], −78.6 [d, $C^{1,3}$, $J(RhC^1)$ 4.0 Hz], −91.7 [d, C^2, $J(RhC^2)$ 6.0 Hz], −112.2 (s, $C^{8,9}$), −119.4 (overlapping s, C^{4-7}), and −123.8 p.p.m. The mass spectrum (base peak *m/e* 115) showed peaks at *m/e* 274 (*P*, 9%), 246 (*P* − C_2H_4, 17%), and 218 (*P* − $2C_2H_4$, 70%).



Reaction of Indenylpotassium with Di-μ-chloro-bis(isoprene)dirhodium.—Indenylpotassium (1.1 mmol) in thf (50 cm^3) was added (r.t.) to a stirred suspension of di-μ-chloro-bis(isoprene)dirhodium [15] (0.43 g, 1.0 mmol) in hexane (20 cm^3). After 15 min the solvent was removed *in vacuo*, and the residue extracted with hexane. Column chromatography and elution with hexane afforded after recrystallisation (−78 °C) yellow crystals of (2) *η^5-indenyl(isoprene)rhodium* (0.32 g, 52%) (Found: C, 58.3; H, 5.4. $C_{14}H_{15}Rh$ requires C, 58.8; H, 5.3%), $\nu_{max.}$ (Nujol) at 1 355s, 1 245w, 1 215m, 1 185m, 1 045 (sh), 1 040m, 1 035 (sh), 1 005w, 945m, 915m, 900m, 880m, 865m, 825 (sh), 815s, 810 (sh), 750s, and 745 (sh) cm^{-1}. N.m.r. spectra: ^{1}H ($CDCl_3$, r.t.), τ 2.8—3.2 (m, 4 H, H^{4-7}), 3.84 (2 H), 4.15 (overlapping m, 1 H, H^{1-3}), 5.82 [d of d, 1 H, H^{10}, $J(H^8H^{10})$ 9.0, $J(H^9H^{10})$ 6.0 Hz], 7.34 [d, 1 H, H^9, $J(H^9H^{10})$ 6.0 Hz], 7.44 (s, 1 H, H^{14}), 8.60 (s, 3 H, H^{11-13}), 9.66 (br s, 1 H, H^{15}), and 9.75 [d of m, 1 H, H^8, $J(H^8H^{10})$ 9.0 Hz]; ^{13}C (C_6D_6, r.t.), −20.7 (s, C^{14}), −35.9 [dd, $C^{10,13}$, $J(RhC^{10})$ 18.5 Hz], −36.5, −74.6 [dd, $C^{1,3}$, $J(RhC^1)$ 5.0 Hz], −76.2, −80.8 [d, C^{11}, $J(RhC^{11})$ 7.5 Hz], −88.6 [d, C^2, $J(RhC^2)$ 7.5 Hz], −93.6 [d, C^{12}, $J(RhC^{12})$ 7.5 Hz], −107.1 (s, $C^{8,9}$), −109.5, −119.7 (s, C^{4-7}), −119.8, −122.2, and −122.5 p.p.m.

Reactions of Bis(ethylene)(η^5-indenyl)rhodium.—(*a*) *With isoprene.* An excess of isoprene (3.0 g, 45 mmol) was condensed into a Carius tube (50 cm^3) containing complex (1) (0.4 g, 1.4 mmol) dissolved in hexane (10 cm^3). After 1 week at room temperature the volatile material was removed *in vacuo* and the residue extracted with hexane. Chromatography on alumina followed by recrystallisation from hexane afforded yellow crystals of (2) (0.39 g, 93%), identical with that prepared above.

(*b*) *With cyclo-octatetraene.* Similarly, reaction (r.t., 7 d) of (1) (0.2 g, 0.7 mmol) with cyclo-octatetraene (2.0 g, 20

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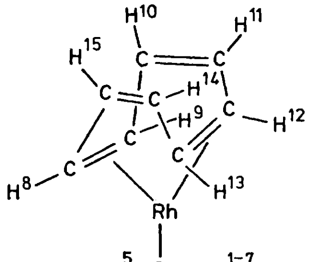
* Unlike the trifluoromethyl-substituted systems where the electronegative substituent strengthens the metal–vinyl σ bond and hence raises the activation energy for 'insertion' into this bond, there is the real possibility that a competitive 'insertion' into the rhodium–vinyl bond [RhCH=C(Bu^t)—] occurs forming a 2,5-bis(t-butyl)rhodacyclohepta-2,4-diene intermediate as a precursor of (13).

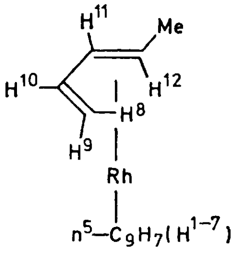
† Throughout this paper: 1eV ≈ 1.60 × 10^{-19} J.

‡ Low-temperature ^{1}H studies show that both ethylene and indenyl rotation occurs, the latter having the lower activation energy. This will be discussed in a subsequent paper.

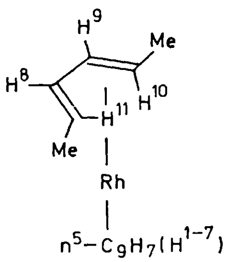
mmol) gave on recrystallisation (−78 °C) from hexane yellow crystals of (3) η^4-cyclo-octatetraene(η^5-indenyl)-rhodium (0.2 g, 85%) (Found: C, 63.6; H, 4.9. $C_{17}H_{15}Rh$ requires C, 63.4; H, 4.7%), $\nu_{max.}$ (Nujol) at 1 625m, 1 350s, 1 330m, 1 325m, 1 240w, 1 215m, 1 130s, 1 040m, 960w, 950w, 915m, 855w, 810s, 805 (sh), 795m, 750s, 745m, 730m, and 725 (sh) cm^{-1}. Proton n.m.r. spectrum (C_6D_6): τ 2.95 (s, 4 H, H^{4-7}), 4.05 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.5 Hz], 4.38 (s, 4 H, $H^{10,11,14,15}$), 5.22 [d, 2 H, $H^{1,3}$, $J(H^1H^2)$ 2.5 Hz], and 5.86 [d, 4 H, $H^{8,9,12,13}$, J(RhH) 3.0 Hz]. The mass spectrum (base peak *m/e* 218) showed peaks at *m/e* 322 (*P*, 63%), 296 ($P - C_2H_2$, 26%), and 218 ($P - C_8H_8$, 100%).



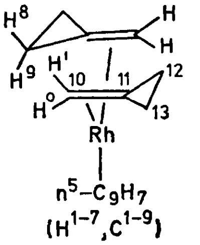
(*c*) *With* trans-*penta*-1,3-*diene*. Reaction (r.t., 2 weeks) of (1) (0.2 g, 0.7 mmol) with *trans*-penta-1,3-diene (3.0 g, 45 mmol) afforded yellow crystals of (4) η^5-*indenyl*(trans-*penta*-1,3-*diene*)*rhodium* (0.17 g, 81%) (Found: C, 59.3; H, 5.5. $C_{14}H_{15}Rh$ requires C, 58.8; H, 5.3%). Proton n.m.r. spectrum (C_6D_6): τ 2.8—3.2 (complex m, 4 H, H^{4-7}), 4.0 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.5 Hz], 4.25 (br s, 1 H, H^1 or H^3), 4.70 (br s, 1 H, H^1 or H^3), 5.7—5.95 (complex m, 2 H, $H^{10,11}$), 7.44 [d, 1 H, H^9, $J(H^9H^{10})$ 6.0 Hz], 8.62 (s, 4 H, $H^{12,Me}$), and 9.6 [dm, 1 H, H^8, $J(H^8H^{10})$ 11.0 Hz]. The mass spectrum (base peak *m/e* 218) showed peaks at *m/e* 286 (*P*, 50%) and 218 ($P - C_5H_8$, 100%).



(*d*) *With* trans,trans-*hexa*-2,4-*diene*. A similar reaction of (1) (0.4 g, 1.4 mmol) with *trans,trans*-hexa-2,4-diene (3.0 g, 38 mmol) afforded after chromatography and crystallisation (hexane, −78 °C) yellow crystals of (5) trans,trans-*hexa*-2,4-*diene*(η^5-*indenyl*)*rhodium* (0.32 g, 73%) (Found: C, 60.0; H, 5.6. $C_{15}H_{17}Rh$ requires C, 60.0; H, 5.7%). Proton n.m.r. spectrum (C_6D_6): τ 2.7—3.1 (complex m, 4 H, H^{4-7}), 4.0 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^3)$ 2.5 Hz], 4.70 [d, 2 H, $H^{1,3}$, $J(H^1H^2)$ 2.5 Hz], 6.0 (m, 2 H, $H^{8,9}$), and 8.64 (m, 8 H, $H^{10,11}$,Me). The mass spectrum (base peak *m/e* 218) showed peaks at *m/e* 300 (*P*, 80%) and 218 ($P - C_6H_{10}$, 100%).



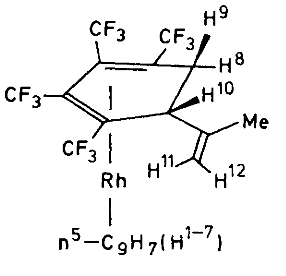
(*e*) *With methylenecyclopropane*. Reaction (r.t., 2 weeks) of (1) (0.25 g, 0.9 mmol) with methylenecyclopropane (2.5 g, 45 mmol) gave, similarly, yellow crystals of (6) η^5-*indenyl-bis*(*methylenecyclopropane*)*rhodium* (0.18 g, 61%) (Found: C, 63.0; H, 5.9. $C_{17}H_{19}Rh$ requires C, 62.6; H, 5.9%), $\nu_{max.}$ (Nujol) at 3 040m, 1 530w, 1 415w, 1 330m, 1 245w, 1 210m, 1 145w, 1 100m, 1 085s, 1 045m, 1 015m, 940m, 920m, 900m, 895m, 865m, 810m, 775m, and 750s cm^{-1}. N.m.r. spectra ($CDCl_3$): ^1H (30 °C), τ 2.9 (s, 4 H, H^{4-7}), 4.2 (m, 1 H, H^2), 4.87 [d, 2 H, $H^{1,3}$, $J(H^1H^2)$ 2.5 Hz], 7.9 (br s, 4 H, $H^{i,o}$), and 9.25 (m, 8 H, $H^{8,9}$); ^1H (−60 °C), τ 2.5—2.95 (m, 4 H, H^{4-7}), 4.1 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.0 Hz], 4.5 (br s, 1 H, H^1 or H^3), 4.94 (br s, 1 H, H^1 or H^3), 6.7 (br s, 2 H, H^o), 8.9 (br s, 2 H, H^i), and 9.5 (m, 8 H, $H^{8,9}$); ^{13}C (−60 °C), −8.5 (s, $C^{12,13}$), −10.3, −36.6 [d, C^{10}, $J(RhC^{10})$ 12 Hz], −56.1 [d, C^{11}, $J(RhC^{11})$ 19.5 Hz], −81.8 [d, $C^{1,3}$, $J(RhC^1)$ 3.5 Hz], −82.8, −94.2 [d, C^2, $J(RhC^2)$ 5.0 Hz], −112.5 (s, $C^{8,9}$), −113.3, −120.1 (s, C^{4-7}), −120.7, −123.4, and −123.8 p.p.m. The mass spectrum (base peak *m/e* 218) showed peaks at *m/e* 326 (*P*, 10%), 272 ($P - C_4H_6$, 50%), and 218 ($P - 2C_4H_6$, 100%).



(*f*) *With acrylonitrile*. After reaction (r.t., 3 d) of (1) (0.2 g, 0.7 mmol) and acrylonitrile (4.0 g, 75 mmol), chromatography (elution with diethyl ether) and recrystallisation (hexane, −30 °C) gave yellow crystals of (7) *bis*(*acrylonitrile*)(η^5-*indenyl*)*rhodium* (0.2 g, 85%) (Found: C, 55.8; H, 4.2; N, 8.2. $C_{15}H_{13}N_2Rh$ requires C, 55.6; H, 4.0; N, 8.6%), $\nu_{max.}$ (Nujol) at 2 220m, 1 365m, 1 335m, 1 330m, 1 245m, 1 195m, 1 160w, 1 045m, 925m, 920 (sh), 870w, 835m, and 775s cm^{-1}. Proton n.m.r. ($CDCl_3$, r.t.): τ 2.48 (s, 4 H, H^{4-7}), 3.8 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.0 Hz], 4.5 [d, 2 H, $H^{1,3}$, $J(H^1H^2)$ 2.0 Hz], 6.5—7.0 (br s, 2 H, C=CHCN), and 7.6—8.3 (br s, 4 H, CH_2=C).

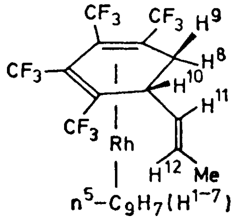
Reactions of Hexafluorobut-2-*yne*.—*With* η^5-*indenyl*(*isoprene*)*rhodium*. An excess of hexafluorobut-2-yne (0.8 g, 5 mmol) was condensed (−196 °C) into a Carius tube fitted with a Westof stopcock containing (2) (0.25 g, 0.9 mmol) in hexane (10 cm^3). After 30 min at room temperature orange crystals were deposited. Volatile material was removed *in vacuo* and the residue chromatographed on an alumina-packed column. Elution with hexane afforded after recrystallisation (−78 °C) from hexane yellow *crystals* of (8) (0.16 g, 30%) (Found: C, 43.3; H, 2.5; F, 37.4. $C_{22}H_{15}F_{12}Rh$ requires C, 43.3; H, 2.5; F, 37.4%). N.m.r. spectra ($CDCl_3$): ^1H, τ 2.6—2.9 (m, 4 H, H^{4-7}), 3.9 (br s, 1 H, H^1 or H^3), 4.0 (br s, 1 H, H^1 or H^3), 4.2 [q, 1 H,

H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.5], 5.3 (br s, H, $H^{11,12}$), 7.5 [dd, 1 H, H^9, $J(H^9H^{10})$ 7.5, $J(H^8H^9)$ 3.0 Hz], 8.1 [dd, 1 H, H^8, $J(H^8H^{10})$ 14.0, $J(H^8H^9)$ 3.0 Hz], 8.3 (s, 3 H, Me), and 8.6 [dd, 1 H, H^{10}, $J(H^8H^{10})$ 14.0, $J(H^9H^{10})$ 7.5 Hz]; ^{19}F, 48.8 [spt, 3 F, $J(FF)$ 14.0 Hz], 54.5 [q, 3 F, $J(FF)$ 14.0 Hz], and 56.4 p.p.m. (m, 6 F). The mass spectrum (base peak m/e 218) showed peaks at m/e 610 (P, 50%), 591 ($P - F$, 15%), 569 ($P - C_3H_5$, 2%), 568 ($P - C_3H_6$, 20%), 541 ($P - CF_3$, 5%), and 539 ($P - CF_3 - 2$ H, 15%).



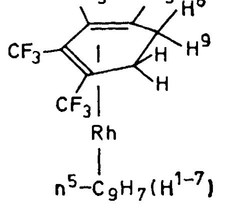
Further elution with hexane gave an orange band, which on recrystallisation (−78 °C) from methylene chloride–hexane gave orange crystals of (9) *η⁵-indenyl[η⁴-hexakis(trifluoromethyl)benzene]rhodium* (0.26 g, 42%) (Found: C, 36.0; H, 1.0; F, 48.0. $C_{21}H_7F_{18}Rh$ requires C, 35.8; H, 1.0; F, 48.6%). N.m.r. spectra [$(CD_3)_2CO$]: ^1H, τ 2.6 (s, 4 H, H^{4-7}) and 3.5 (s, 3 H, H^{1-3}); ^{19}F, 49.7 (m, 6 F), 52.8 (m, 6 F), and 56.7 p.p.m. (m, 6 F). The mass spectrum (base peak m/e 218) showed peaks at m/e 704 (P, 5%), 685 ($P - F$, 7%), and 218 [$P - C_6(CF_3)_6$, 100%].

*With η⁵-indenyl(*trans-*penta-*1,3-*diene)rhodium.* Similarly, treatment of a solution of (4) (0.12 g, 0.4 mmol) in hexane (10 cm³) with hexafluorobut-2-yne (0.5 g, 3 mmol) led to a rapid (15 min) reaction. Volatile material was removed *in vacuo* and the residue chromatographed. Elution with hexane gave first a yellow band which on recrystallisation (−78 °C) from hexane afforded yellow *crystals* of (10) (0.03 g, 12%) (Found: C, 43.2; H, 2.5. $C_{22}H_{15}F_{12}Rh$ requires C, 43.3; H, 2.5%). N.m.r. spectra: ^1H ($CDCl_3$), τ 2.5—2.8 (m, 4 H, H^{4-7}), 3.8 (br s, 1 H, H^1 or H^3), 3.0 (m, 2 H, H^2 and H^1 or H^3), 4.4—4.8 (m, 2 H, $H^{11,12}$), 7.6 (m, 1 H, H^9), 8.32 [d, 3 H, Me, $J(H^{12}Me)$ 6.0 Hz], and 8.4—8.8 (m, 2 H, $H^{8,10}$); ^{19}F [$(CD_3)_2CO$], 49.1 [spt, 3 F, $J(FF)$ 14.0 Hz], 53.6 [q, 3 F, $J(FF)$ 14.0 Hz], 56.5 [q, 3 F, $J(FF)$, 14.0 Hz], and 57.3 p.p.m. [spt, 3 F, $J(FF)$ 14.0 Hz]. The mass spectrum (base peak m/e 218) showed a peak at m/e 610 (P, 50%).

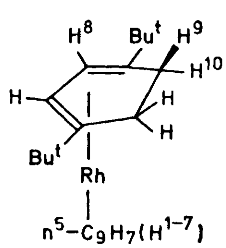


Further elution with hexane gave orange crystals of (9) (0.07 g, 23%). Elution with methylene chloride–hexane gave a red band which on recrystallisation (30 °C) from hexane have orange *crystals* of (11) (0.05 g, 20%) (Found: C, 43.6; H, 2.5. $C_{22}H_{15}F_{12}Rh$ requires C, 43.3; H, 2.5%), $\nu_{max.}$ (Nujol) at 1 570w, 1 325m, 1 300m, 1 265 (sh), 1 260m, 1 230s, 1 215s, 1 200s, 1 175s, 1 165s, 1 130s, 1 050w, 1 000w, 960w, 940w, 880w, 845w, 830w, 775m, 765m, 750m, 735w, and 660w cm⁻¹. The mass spectrum (base peak m/e 218) showed peaks at m/e 610 (P, 50%), 591 ($P - F$, 15%), 569 ($P - C_3H_5$, 2%), 541 ($P - CF_3$, 5%), and 539 ($P - CF_3 - 2$ H, 15%).

With bis(ethylene)(η⁵-indenyl)rhodium. Reaction (room temperature, 48 h) of (1) (0.10 g, 0.4 mmol) in hexane (10 cm³) with hexafluorobut-2-yne (0.16 g, 1 mmol) gave after chromatography and recrystallisation from hexane yellow *crystals* of (12) (0.12 g, 56%) (Found: C, 40.2; H, 2.3; F, 39.3. $C_{19}H_{11}F_{12}Rh$ requires C, 40.0; H, 1.9; F, 40.0%), $\nu_{max.}$ (Nujol) at 1 410w, 1 365m, 1 345w, 1 295s, 1 240s, 1 220s, 1 205s, 1 185s, 1 160vs, 1 145s, 1 120s, 1 085w, 990w, 985m, 865w, 855m, 845m, 760s, 750w, 740w, 700m, and 680m cm⁻¹. N.m.r. spectra ($CDCl_3$): ^1H, τ 2.7—2.9 (m, 4 H, H^{4-7}), 4.0 [d, 2 H, $H^{1,3}$, $J(H^1H^2)$ 2.5 Hz], 4.1 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.5 Hz], 7.9 [d, 2 H, H^8, $J(HH)$ 8.0 Hz], and 8.6 [d, 2 H, H^9, $J(HH)$ 8.0 Hz]; ^{19}F, 54.0 (m, 6 F) and 59.0 p.p.m. (m, 6 F). The mass spectrum (base peak m/e 218) showed peaks at m/e 570 (P, 21%) and 551 ($P - F$, 5%).



Reaction of 3,3-*Dimethylbut-*1-*yne with Bis(ethylene)-(η⁵-indenyl)rhodium.*—Reaction (room temperature, 5 d) of (1) (0.1 g, 0.4 mmol) with 3,3-dimethylbut-1-yne (1.0 g, 6 mmol) in hexane (10 cm³) led to trimerisation and cyclo-co-oligomerisation of the acetylene. Examination of the volatile material by g.c.–m.s. and ^1H n.m.r. spectroscopy showed the presence of 1,2,4- and 1,3,5-tris(t-butyl)benzene (5.0 mmol) and 1,4-bis(t-butyl)cyclohexa-1,3-diene (10 : 1 : 1 respectively). Chromatography of the involatile material and elution with hexane gave on recrystallisation (−78 °C) from hexane yellow crystals of (13) 1,4-*bis(t-butyl)cyclohexa-*1,3-*diene(η⁵-indenyl)rhodium* (0.05 g, 15%) (Found: C, 67.7; H, 8.0. $C_{23}H_{31}Rh$ requires C, 67.3; H, 7.6%), $\nu_{max.}$ (Nujol) at 3 050m, 1 385m, 1 365m, 1 360m, 1 330s, 1 255m, 1 254w, 1 215m, 1 205w, 1 195w, 1 100w, 1 080w, 1 045w, 1 030m, 1 010w, 1 005w, 935w, 895m, 875w, 860m, 835w, 810m, 745s, 740s, and 725m cm⁻¹. Proton n.m.r. spectrum ($CDCl_3$): τ 2.9—3.2 (m, 4 H, H^{4-7}), 3.8 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.5 Hz], 4.1 [d, 2 H, $H^{1,3}$, $J(H^1H^2)$ 2.5 Hz], 5.6 (s, 2 H, H^8), 8.1 (m, 2 H, H^9), 8.3 (m, 2 H, H^{10}), and 8.8 (s, 18 H, Bu^t). The mass spectrum (base peak m/e 410) showed peaks at m/e 410 (P, 100%), 394 (12%), 353 ($P - C_4H_9$, 18%), and 296 ($P - 2C_4H_9$, 18%).



Reaction of (13) *with Carbon Monoxide.*—An excess of carbon monoxide was bubbled through a solution of (13)

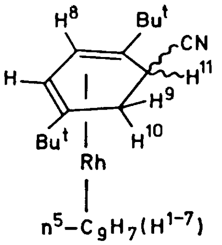
TABLE 1

Atomic positional parameters (fractional co-ordinates) for $[Rh(C_9H_7)\{C_6H_3(CF_3)_4C(CH_2)CH_3\}]$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Rh	0.162 32(4)	0.128 60(2)	0.226 12(7)
C(1)	0.142 1(6)	0.178 8(3)	−0.092 4(11)
H(11)	0.110	0.170	−0.180
H(12)	0.160	0.210	−0.050
C(2)	0.096 1(5)	0.164 8(3)	0.053 1(9)
C(21)	0.043 5(7)	0.202 9(4)	0.111 0(15)
F(211)	−0.017 4(5)	0.210 0(3)	0.012 9(9)
F(212)	0.084 9(5)	0.241 8(2)	0.111 5(11)
F(213)	0.013 9(4)	0.198 9(2)	0.252 3(8)
C(3)	0.074 4(5)	0.117 9(3)	0.063 1(9)
C(31)	−0.007 1(6)	0.099 7(5)	0.097 1(3)
F(311)	−0.045 2(4)	0.090 1(3)	−0.032 0(8)
F(312)	−0.051 9(4)	0.129 9(3)	0.172 4(9)
F(313)	−0.006 5(4)	0.063 0(3)	0.187 3(8)
C(4)	0.140 4(5)	0.088 5(3)	0.030 2(9)
C(41)	0.132 1(8)	0.037 2(4)	0.013 6(3)
F(411)	0.185 9(5)	0.020 7(2)	−0.082 9(9)
F(412)	0.135 4(6)	0.014 7(2)	0.145 5(9)
F(413)	0.062 8(4)	0.026 9(2)	−0.053 5(8)
C(5)	0.213 6(5)	0.112 3(3)	0.010 7(9)
C(51)	0.290 7(6)	0.086 2(4)	0.022 0(11)
F(511)	0.348 6(3)	0.113 0(2)	0.077 4(8)
F(512)	0.287 6(4)	0.050 5(2)	0.115 4(8)
F(513)	0.315 5(4)	0.071 8(3)	−0.117 6(8)
C(6)	0.216 2(5)	0.150 6(3)	−0.110 1(10)
H(61)	0.220	0.130	−0.220
C(7)	0.288 5(6)	0.180 3(4)	−0.111 1(12)
C(8)	0.303 1(8)	0.211 7(4)	0.027 3(18)
H(81)	0.330	0.190	0.060
H(82)	0.260	0.230	0.030
H(83)	0.340	0.250	0.030
C(9)	0.342 0(7)	0.179 2(8)	−0.231 1(14)
H(91)	0.320	0.160	−0.300
H(92)	0.320	0.210	−0.200
C(10)	0.176 0(9)	0.172 0(4)	0.428 9(12)
H(101)	0.140	0.200	0.390
C(11)	0.2472	0.155 9(6)	0.393 6(13)
H(111)	0.290	0.170	0.310
C(12)	0.245 5(7)	0.109 6(5)	0.407 4(13)
H(121)	0.280	0.080	0.400
C(13)	0.171 8(6)	0.095 9(3)	0.470 5(10)
C(14)	0.145 2(9)	0.053 6(4)	0.515 4(14)
H(141)	0.190	0.025	0.510
C(15)	0.069 8(13)	0.052 0(6)	0.578 0(16)
H(151)	0.060	0.015	0.610
C(16)	0.023 1(9)	0.090 6(9)	0.589 4(15)
H(161)	−0.040	0.085	0.650
C(17)	0.047 3(7)	0.130 0(6)	0.542 1(12)
H(171)	0.040	0.160	0.550
C(18)	0.124 3(5)	0.135 5(4)	0.483 3(9)

(0.05 g, 0.1 mmol) in diethyl ether (5 cm³) at room temperature for 10 min. The reaction mixture was chromatographed on alumina. Elution with hexane gave first 1,4-bis(t-butyl)cyclohexa-1,3-diene (0.02 g, 85%) (Found: C, 87.5; H, 12.4. $C_{14}H_{24}$ requires C, 87.5; H, 12.5%). Proton n.m.r. spectrum ($CDCl_3$): τ 4.3 (s, 2 H, C*H*=CH), 7.9 (s, 4 H, CH_2), and 9.0 (s, 18 H, Bu^t). The mass spectrum (base peak *m*/*e* 57) showed peaks at *m*/*e* 192 (*P*, 19%) and 177 (*P* − Me, 54%).

Reaction of 3,3-*Dimethylbut*-1-*yne with Bis*(*acrylonitrile*)-(η^5-*indenyl*)*rhodium*.—A solution of (7) (0.3 g, 0.9 mmol) and 3,3-dimethylbut-1-yne (2.0 g, 40 mmol) in toluene (7 cm³) was allowed to stand at room temperature for 5 d. Chromatography on alumina and elution with hexane afforded 1,2,4- and 1,3,5-tris(t-butyl)benzene. Further elution with hexane–diethyl ether (4 : 1) gave a yellow band which on recrystallisation (−78 °C) from hexane gave yellow *crystals* of (14) (0.13 g, 32%) (Found: C, 66.2; H, 6.7; N, 8.2. $C_{24}H_{30}NRh$ requires C, 66.2; H, 6.9; N, 8.2%), $\nu_{max.}$ (Nujol) at 3 040m, 2 220m, 2 200m, 1 390m, 1 360s, 1 330s, 1 300m, 1 250m, 1 235m, 1 220m, 1 205m, 1 185m, 1 145w, 1 065w, 1 030m, 1 020 (sh), 1 000m, 960w, 885m, 855m, 805s, and 735s cm⁻¹. Proton n.m.r. spectrum



($CDCl_3$): τ 2.8—3.2 (m, 4 H, H^{4-7}), 3.6 [q, 1 H, H^2, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.5 Hz], 3.7 (m, 1 H), 4.1 (m, 2 H, $H^{1,3}$), 5.3 (m, 2 H), 5.72 [d, 2 H, C*H*=CH, *J*(HH) 4.5 Hz], 8.7 (s, 9 H, Bu^t), and 8.8 (s, 9 H, Bu^t).

Structure Determination of Complex (8) (η^5-*Indenyl*)-{1—2:3—4-η^4-[6-endo-*propen*-2-*yl*-1,2,3,4-*tetrakis*(*trifluoro*-

TABLE 2

Bond lengths (Å) and angles (°) of $[Rh(C_9H_7)\{(C_6H_3)(CF_3)_4C(CH_2)CH_3\}]$ with standard deviations in parentheses

(*i*) Distances			
(*a*) Indenyl group			
C(10)–C(11)	1.33(2)	C(14)–C(15)	1.39(3)
C(11)–C(12)	1.38(2)	C(15)–C(16)	1.40(3)
C(12)–C(13)	1.42(2)	C(16)–C(17)	1.30(3)
C(13)–C(18)	1.43(2)	C(17)–C(18)	1.41(2)
C(13)–C(14)	1.38(2)	C(18)–C(10)	1.47(2)
(*b*) Metal–carbon			
Rh–C(10)	2.179(11)	Rh–C(2)	2.151(9)
Rh–C(11)	2.190(14)	Rh–C(3)	2.070(8)
Rh–C(12)	2.176(12)	Rh–C(4)	2.094(8)
Rh–C(13)	2.319(10)	Rh–C(5)	2.102(8)
Rh–C(18)	2.312(9)		
(*c*) C_6 ring			
C(1)–C(2)	1.53(1)	C(41)–F(411)	1.33(1)
C(2)–C(21)	1.52(2)	C(41)–F(412)	1.32(1)
C(21)–F(211)	1.35(2)	C(41)–F(413)	1.34(2)
C(21)–F(212)	1.35(1)	C(4)–C(5)	1.44(1)
C(21)–F(213)	1.32(2)	C(5)–C(51)	1.52(1)
C(2)–C(3)	1.44(1)	C(51)–F(511)	1.35(1)
C(3)–C(31)	1.51(1)	C(51)–F(512)	1.33(1)
C(31)–F(311)	1.32(1)	C(51)–F(513)	1.34(1)
C(31)–F(312)	1.34(2)	C(5)–C(6)	1.54(1)
C(31)–F(313)	1.34(2)	C(6)–C(1)	1.52(1)
C(3)–C(4)	1.45(1)	C(6)–C(7)	1.51(2)
C(4)–C(41)	1.53(1)	C(7)–C(8)	1.53(2)
		C(7)–C(9)	1.37(2)
(*ii*) Angles			
(*a*) Indenyl group			
C(18)–C(10)–C(11)	111(1)	C(14)–C(15)–C(16)	122(2)
C(10)–C(11)–C(12)	109(1)	C(15)–C(16)–C(17)	122(2)
C(11)–C(12)–C(13)	110(1)	C(16)–C(17)–C(18)	121(2)
C(12)–C(13)–C(18)	107(1)	C(17)–C(18)–C(13)	117(1)
C(12)–C(13)–C(14)	131(1)	C(17)–C(18)–C(10)	139(1)
C(13)–C(14)–C(15)	116(1)		
(*b*) C_6 ring			
C(1)–C(2)–C(21)	111.5(8)	C(4)–C(5)–C(51)	119.1(8)
C(1)–C(2)–C(3)	116.0(7)	C(4)–C(5)–C(6)	117.7(7)
C(21)–C(2)–C(3)	123.1(8)	C(51)–C(5)–C(6)	113.1(8)
C(2)–C(3)–C(31)	126.0(9)	C(5)–C(6)–C(1)	108.3(7)
C(2)–C(3)–C(4)	111.8(7)	C(6)–C(1)–C(2)	110.8(8)
C(31)–C(3)–C(4)	122.1(9)	C(5)–C(6)–C(7)	117.3(8)
C(3)–C(4)–C(41)	122.9(8)	C(1)–C(6)–C(7)	110.6(9)
C(3)–C(4)–C(5)	113.4(8)	C(6)–C(7)–C(9)	121.8(11)
C(41)–C(4)–C(5)	123.7(8)	C(6)–C(7)–C(8)	118.8(9)
		C(8)–C(7)–C(9)	119.5(11)
Mean C–C–F	112.3(3)	Mean F–C–F	106.5(3)

TABLE 3

Equations of some least-squares planes. Distances (Å) of relevant atoms from these planes are given in square brackets

(*i*) Cyclohexadienyl group

Plane (1): C(2), C(3), C(4), C(5)

$$3.069x - 0.599y + 0.452z = 0.662$$

[C(2) -0.016, C(3) 0.029, C(4) -0.029, C(5) 0.016, Rh 1.670]

Plane (2): C(1), C(2), C(5), C(6)

$$9.283x + 17.468y + 5.105z = 4.022$$

[C(1) -0.037, C(2) 0.022, C(5) -0.022, C(6) 0.037]

Plane (3): C(2), C(5), C(6)

$$9.349x + 16.596y + 5.134z = 3.919$$

Plane (4): C(1), C(2), C(5)

$$9.670x + 17.708y + 4.843z = 4.108$$

(*ii*) Indenyl group

Plane (5): C(10), C(11), C(12), C(13), C(18)

$$5.551x + 3.579y + 8.056z = 5.068$$

[C(10) -0.020, C(11) 0.033, C(12) -0.031, C(13) 0.019, C(18) 0.000, Rh -1.886]

Plane (6): C(13), C(14), C(15), C(16), C(17), C(18)

$$6.104x + 5.001y + 7.888z = 5.235$$

[C(13) 0.004, C(14) -0.016, C(15) 0.010, C(16) 0.009, C(17) -0.020, C(18) 0.013]

Angles (°) between some of the planes:

(1)–(2)	132.2	(1)–(4)	130.2
(1)–(3)	134.2	(5)–(6)	3.5

methyl)cyclohexa-1,3-*diene*]}*rhodium by Single-crystal* X-*Ray Diffraction Studies*.—Crystals of (8) grow as yellow prisms. Diffracted intensities were measured at room temperature from a crystal of dimensions *ca*. 0.2 × 0.3 × 0.2 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[16] Of the total 3 825 independent intensities recorded to $2\theta = 50°$, 2 879 had $I > 1.0\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, and were used in the solution and refinement of the structure. All computations were carried out with the '*X*-Ray' system of programs [17] on the CDC 7600 at the University of London Computing Centre.

Crystal data. $C_{22}H_{15}F_{12}Rh$, $M = 610.1$, Orthorhombic, $a = 16.962(3)$, $b = 29.618(5)$, $c = 8.596(4)$ Å, $U = 4\,318$ Å^3, $D_m = 1.86$ (flotation), $Z = 8$, $D_c = 1.88$ g cm^{-3}, $F(000) = 2\,400$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 8.9 cm^{-1}, space group *Pbca* (no. 61).

Structure solution and refinement. The rhodium atom was located from a Patterson synthesis, and all the remaining atoms (excluding hydrogen) by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were incorporated at calculated positions (C–H 0.98 Å); positional and thermal parameters for these atoms ($u_H = 1.10\ u_C$) were fixed during refinement. Refinement converged at *R* 0.063 (*R'* 0.082) with a mean shift-to-error ratio in the last cycle of 0.03. A weighting scheme of the form $w = 1/(4.5 - 0.076|F| + 0.000\,84|F|^2)$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >3.0 or <-0.4 e Å^{-3}. Scattering factors were from ref. 18 for carbon and fluorine, ref. 19 for hydrogen, and ref. 20 for rhodium including corrections for the effects of anomalous dispersion ($\Delta f'$ − 1.287, $\Delta f''$ 0.919). No correction for the effects of *X*-ray absorption was made [μ(Mo-K_α) = 8.9 cm^{-1}]. Atomic positional parameters are in Table 1, interatomic distances and angles in Table 2, and relevant least-squares planes and dihedral angles in Table 3. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22700 (18 pp.).*

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

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