Further Studies on Metal-promoted Vinylcyclopropane to Cyclopentene Rearrangements. Structure and Thermolysis of Rhodium Complexes of *exo*-6-Vinylbicyclo[3.1.0]hex-2-ene and the Crystal Structure of the 1,6—8-η^4-5-Allylcyclopent-2-enyl(hexafluoroacetylacetonato)rhodium(III) Tetramer

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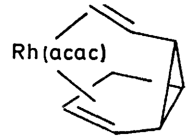
The reactions of *exo*-6-vinylbicyclo[3.1.0]hex-2-ene with bis(ethylene)rhodium(I) complexes lead to displacement of ethylene and formation of ring-opened $\sigma\pi$-bis-allylrhodium derivatives. The hexafluoroacetylacetonate (11) is tetrameric in the solid state and its structure has been determined by *X*-ray methods. Crystals of $[C_{13}H_{11}F_6RhO_2]_4$ are monoclinic, space group $P2_1/c$, a = 19.641(7), b = 14.353(7), c = 44.87(1) Å, β = 98.03(3), Z = 8; 3 266 observed reflections $[I/\sigma(I) > 3.0]$ were collected by diffractometer and refined to R 0.077.

The four rhodium atoms form the corners of a puckered square and are each π-bonded to one hydrocarbon at C(2),C(3) and to another σ at C(1) and π at C(6)—(8). This complex rearranges in acetone solution at 338 K, mainly to the corresponding derivative of bicyclo[3.3.0]octa-2,6-diene; thermolysis of the corresponding dimeric acetylacetonate (12) has been studied in detail by ^{1}H n.m.r. The reaction exhibits half-order kinetics over the concentration range 0.02—0.2M in deuteriobenzene, rearranging rapidly ($t_{\frac{1}{2}}$ [0.205M] 30.30 min) to a mixture of acetylacetonato(bicyclo[3.3.0]octa-2,6-diene)rhodium(I) (2) and acetylacetonato-(*endo*-6-vinylbicyclo[3.1.0]-hex-2-ene)rhodium(I) (1) in 88 : 12 ratio. In deuteriodichloromethane, the ratio is 33 : 67. The cyclopentadienyl complex (14) is monomeric, and thermally stable below 373 K. Reaction of the rhodium chloride complex (13) with bicyclo[2.2.1]hepta-2,5-dienesilver hexafluorophosphate leads directly to a rearranged cation (17) at 273 K.

The mechanisms of these transformations are discussed.

WHILST rhodium acetylacetonate complexes of acyclic 1,5-hexadienes are thermally stable,[1] that derived from *endo*-6-vinylbicyclo[3.1.0]hex-2-ene (1) is sufficiently strained to rearrange at elevated temperatures.[2] The major product is the bicyclo[3.3.0]octa-2,6-diene complex (2) derived by a 1,3-sigmatropic carbon shift, and this contrasts with the 3,3 Cope rearrangement, which is the only reaction pathway for the hydrocarbon at room temperature. The mechanism of complex rearrangement cannot be rationalised simply, for a non-least-motion pathway is required. The *transoid*-bis-η-allyl (3) was suggested to mediate reactant and product;[2]



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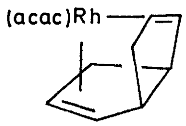

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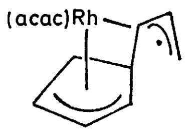
[(2a), f$_6$acac complex]



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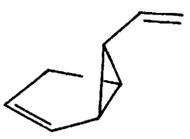

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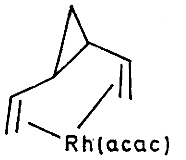

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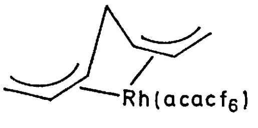

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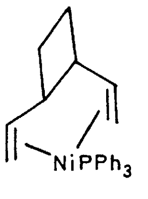

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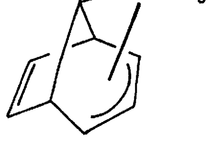

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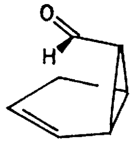

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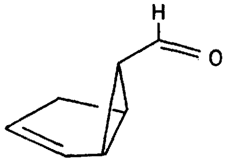
possible mechanisms for its formation were discussed. Since (3) is stereochemically related to the epimeric olefin *exo*-6-vinylbicyclo[3.1.0]hex-2-ene (4) it was of interest to prepare from the latter rhodium complexes, whose structure and thermal behaviour are described here. A preliminary report has been published.[3]

Little is known about complex formation of *trans*-divinylcyclopropanes. Simple metal complexes (5) suffer from the drawback that alignment of the double bonds in parallel planes with maximal metal–ligand orbital overlap enforces severe steric strain. This situation is avoided, in the case of the rhodium hexafluoroacetylacetonate complex (6), by opening of the cyclopropane ring and formation of a bis-η-allyl.[4] Nevertheless, a nickel phosphine complex of *trans*-divinylcyclobutane (7) (where conformational flexibility should be greater) has been reported to have an intact ligand structure.[5] Alternatively (4) could function in the same manner as do vinylcyclopropanes on formation of complexes, and there are now several examples[6] of 1,3—5-η^4-complexes derived from vinylcyclopropanes with attendant ring-cleavage, *e.g.* (8) from semibullvalene and $Fe_2(CO)_9$.

Synthesis of Complexes.—*endo*-Bicyclo[3.1.0]hex-2-ene-6-carbaldehyde (9) may be epimerised in near-quantitative yield by reaction with pyridinium iodide in aqueous dimethyl sulphoxide.[7] The resulting *exo*-aldehyde (10) reacts with methylenetriphenylphosphorane in dimethyl sulphoxide giving the stable, readily isolated (and incredibly odoriferous!) *exo*-6-vinylbicyclo[3.1.0]hex-2-ene (4).

The olefin (4) reacted readily with bis[ethylenerhodium(I)] complexes by ethylene displacement and a crystalline hexafluoroacetylacetonate (11) and acetylacetonate (12) were obtained. The former is tetrameric in the solid state (see later discussion of *X*-ray structure determination) and strongly associated in solution, cryoscopic *M* 1 150. The latter is clearly dimeric in solution in benzene or cyclohexane, *M* 615[$(12)_2$ = 608]. The reaction of (4) with di-μ-chloro-tetrakis(ethylene)dirhodium(I) gave a rather insoluble 1 : 1 chloride complex (13) which further reacted with thallium cyclopentadienide, giving the monomeric cyclopentadienide (14) as a distillable red oil.



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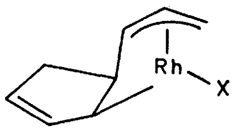
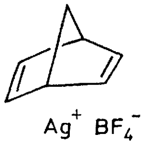


(11) X = hfacac (tetramer)
(12) X = acac (dimer)
(13) X = Cl (*n*–*mer*)
(14) X = cyclopentadienyl

In an attempt to prepare a related cationic complex, the chloride (13) was allowed to react with norbornadienesilver(I) hexafluorophosphate (15) in acetone at 273 K with the expectation that (16) or a related $\sigma\pi$-bisallyl might be formed. A mixture of complexes was obtained because of ready disproportionation,[8] but the bicyclo[3.3.0]octa-2,6-diene derivative (17) was obtained pure, with evidence for the mixed complex (18) derived from the n.m.r. spectrum of later crystallisation fractions. Both these react readily with excess of perdeuteriodimethyl sulphoxide with displacement of one olefin ligand only. Whilst (17) gave (19), only (20) was produced in the corresponding reaction of (18), *i.e.* bicyclo[3.3.0]octa-2,6-diene was selectively removed.



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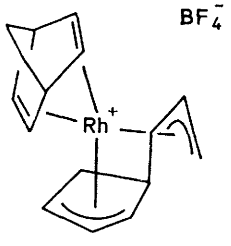

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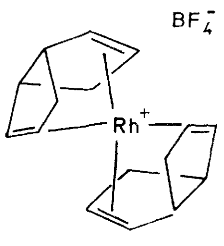

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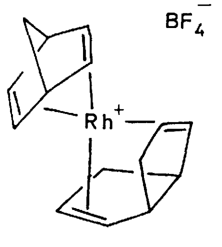

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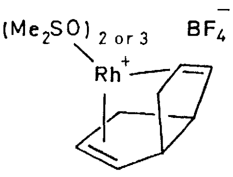

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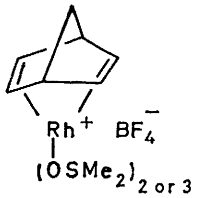

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Structural Identification of the Complexes.—(*a*) *Nuclear magnetic resonance.* The ^1H n.m.r. spectrum of the cyclopentadienide complex (14) proved to be most instructive (Figure 1) and by application of selective decoupling all protons could be assigned unambiguously. It is clear that the cyclopropane ring is strongly perturbed by co-ordination since 1-H shifts upfield by 0.42 p.p.m. whilst 5- and 6-H shift downfield by 1.42 and 2.99 p.p.m. respectively. Additionally H-1 and -6 are no longer coupled, and all available evidence suggests that the hydrocarbon ligand is 1,6—8-η^4-bonded to rhodium.

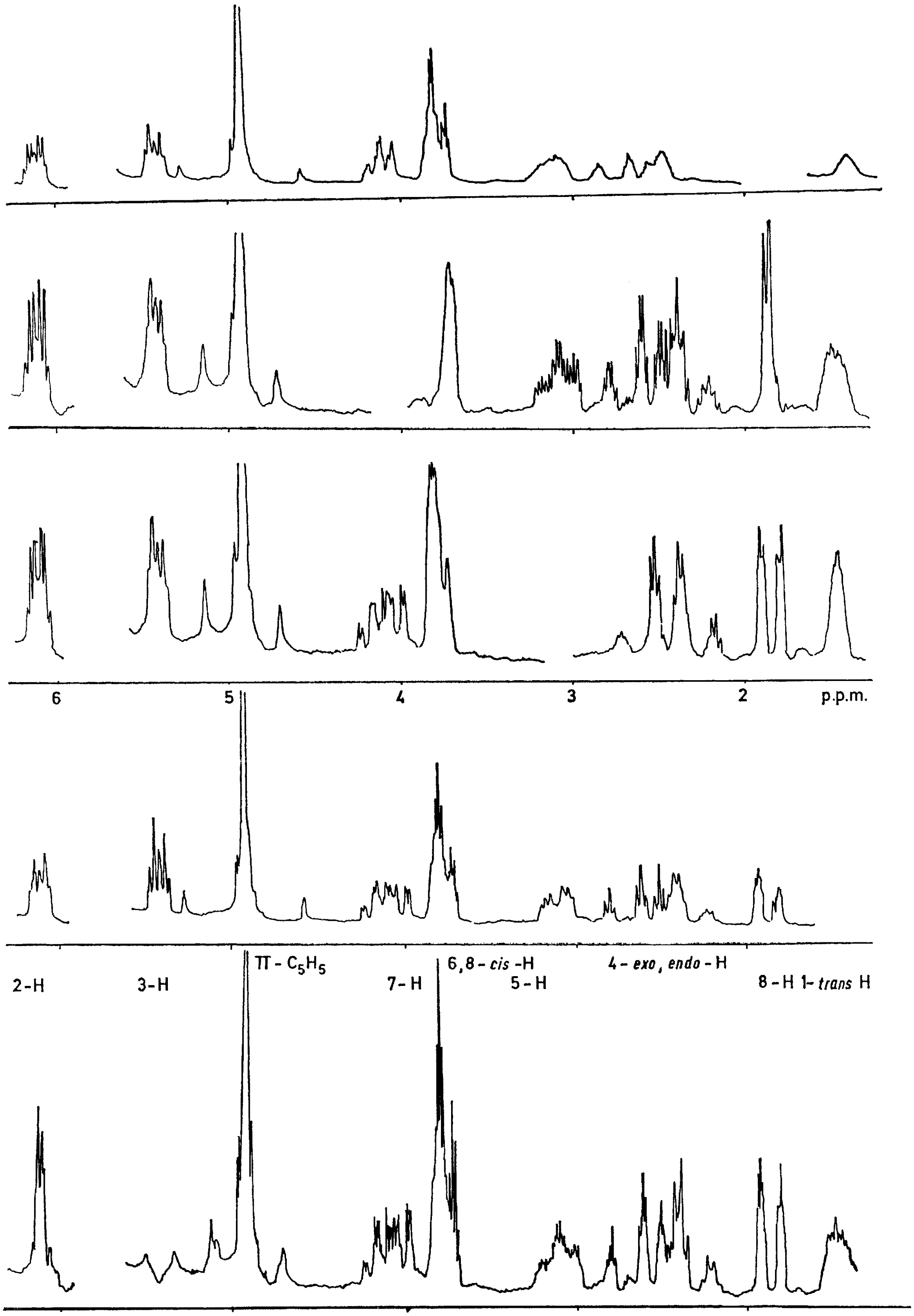
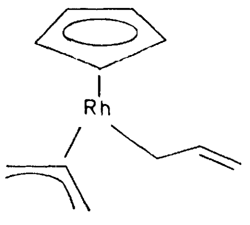


FIGURE 1 ^{1}H n.m.r. spectrum of the cyclopentadienyl complex (14) in deuteriobenzene at 90 MHz, with spin-decoupling at the asterisked frequencies. Assignments (δ in p.p.m.; J in Hz): δ 6.12 (1 H, m, 2-H, $J_{2,3}$ 5, $J_{1,2}$ 5.5, $J_{2,4exo}$ 2, $J_{2,4endo}$ 1.5), 5.42 (1 H, m, 3-H, $J_{1,3}$ 2, $J_{3,4endo}$ 2, $J_{3,4exo}$ 2 Hz), 4.93 (5 H, s π-C_5H_5, J_{RhH} 1), 4.05 (1 H, m, 7-H, $J_{7,8cis}$ 8), 3.75 (2 H, m, 6-H, 8*cis*-H, $J_{6,7}$ 8, $J_{6,8}$ 1.5), 3.09 (1 H, m, 5-H), 2.62 (1 H, m, 4*endo*-H, $J_{4,5}$ 9.5), 2.34 (1 H, m, 4*exo*-H, $J_{4,5}$ 2, $J_{4exo,4endo}$ 17.5), 1.86 (1 H, dm, 8*trans*-H, $J_{8,8'}$ 10.5), and 1.45 (1 H, m, 1-H, $J_{1,3}$, 2, $J_{1,5}$ 6.5)

Inspection of coupling constants reveals that 1- and 5-H are *cis* ($J_{1,5}$ 6.5 Hz), 5- and 6-H *transoid* ($J_{5,6}$ 1.5 Hz), and 6- and 7-H are *cis* ($J_{6,7}$ 8 Hz, and $J_{6,8}$ *cis* 1.4 Hz) defining the stereochemistry as it is illustrated. The cyclopentene region of the spectrum closely resembles that of the parent olefin, suggesting that interaction of the double bond with the metal is unimportant.

The ^{13}C n.m.r. spectrum of (14) (with assignment supported by off-centre double resonance and selective proton decoupling) confirms this structure. The spectrum of η^1-allyl- η^3-allyl-cyclopentadienylrhodium [9] (21) is broadly similar (Figure 2) but one effect of the cyclopentene ring is to displace the chemical shift of C-1 some 15 p.p.m. upfield, implying that there is considerably more negative charge on σ-bonded carbon in (14). It may be pertinent to recognise that (14) can be considered as a homodienyl complex (22) and the effect of this on ligand character is uncertain.



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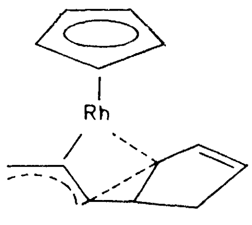

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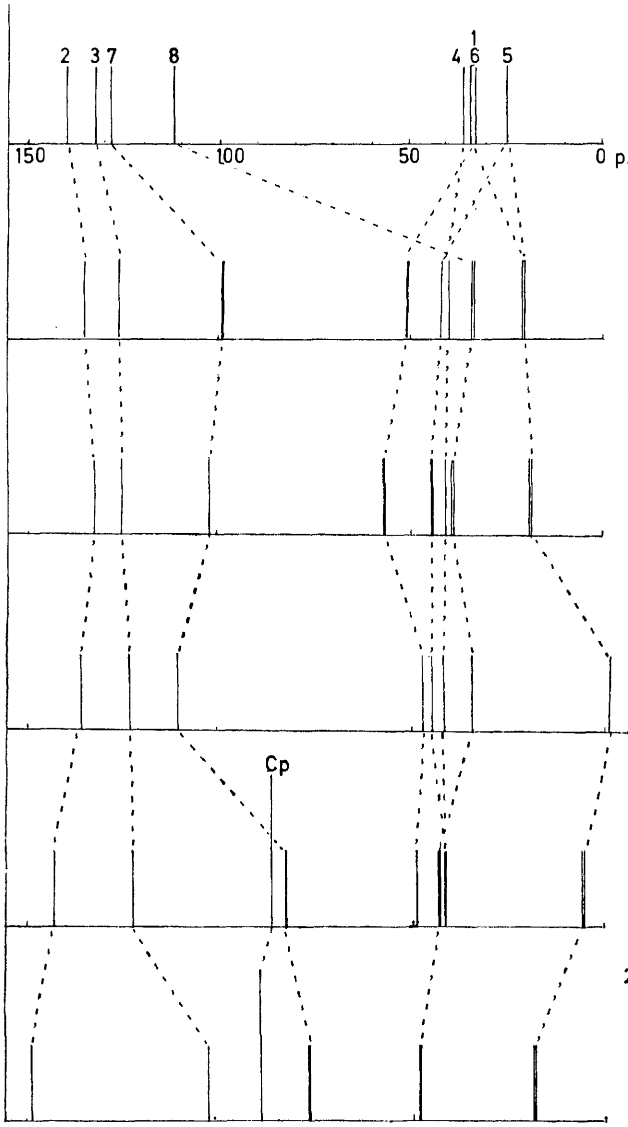


FIGURE 2 ^{13}C N.m.r. spectra of complexes described in the text in deuteriobenzene solution at ambient temperature. The iridium analogue of (12) was prepared *in situ* and proved too unstable for isolation and characterisation. All spectra were recorded at ambient temperature, excepting that of (14) at 323 K

Comparison of the carbon spectra of (14) and the acetylacetonate (12) shows the overall structural similarity of the two compounds. Changes in relative chemical shift at C-1, C-6, C-7, and C-8 are consistent with a lower degree of back-donation to the hydrocarbon ligand in the latter. There is some evidence of broadening of certain resonances in the spectrum of (12) which may reflect the onset of dimer–monomer equilibrium on the n.m.r. time-scale. Interestingly the central carbon of acetylacetonate is the most strongly affected. The n.m.r. spectrum of the hexafluoroacetylacetonate (11) is similar at 323 K but drastic changes occur as the temperature is lowered. In the high-temperature spectrum C-2 and C-3 are not coupled to rhodium, signifying either that the double bond is not co-ordinated to rhodium [which would be consistent with the similarity of the chemical shift with C-2 and C-3 in (4) or (14)] or that interaggregate exchange occurs very rapidly. These two resonances broaden as the sample temperature is lowered, but a new pair of resonances appear at somewhat higher field which show pronounced Rh–C coupling and relate to the dominant isomer at 180 K. This suggests, therefore that a π-bonded cyclopentene aggregate is present at low temperature, but dissociation to simpler aggregates increases in importance with increasing temperature. Similar effects are apparent in the temperature-dependent ^{1}H n.m.r. spectrum of (11) (Figure 3).

(*b*) X-*Ray structure of* (11). There are two independent but identical molecules in the asymmetric unit, each tetrameric (Figure 4; mean distances and angles are in the Table). In each the rhodium atoms are situated 5.10 Å apart at the corners of a slightly puckered square, deviating by $\pm$0.21 Å from the mean plane. Each rhodium atom is co-ordinated to a chelating acetylacetonate, a hydrocarbon unit (Figure 5) (1,6—8-η^4-bonded) and a second hydrocarbon unit which is 2—3-η^2 bonded. The overall geometry about each rhodium atom can be broadly regarded as octahedral with *cis*-pairs of substituents, the two hexafluoroacetylacetonate oxygen atoms, the individual carbon atoms C(1) and C(8), and the pairs of carbon atoms C(2)–C(3) and C(6)–C(7).

The original cyclopropane ring has completely opened [C(1) $\cdots$ C(6) 2.46 Å]. There is some evidence of strain in the $\sigma\pi$-bisallyl entity since both C(1)–C(5) and C(5)–

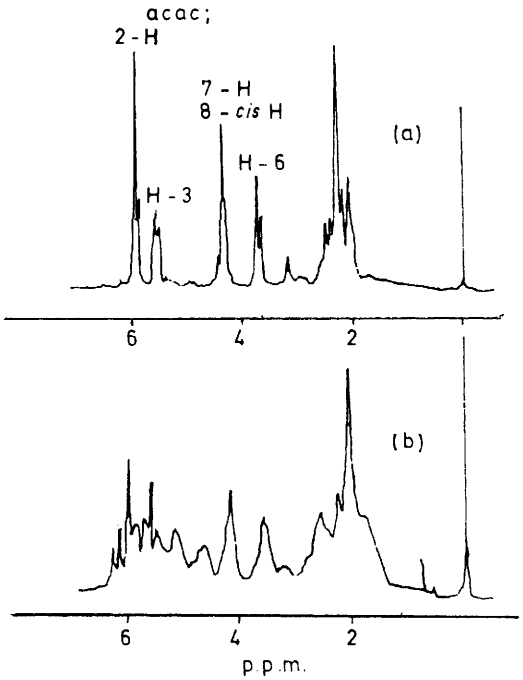


FIGURE 3 Effects of temperature on the ^{1}H n.m.r. spectrum of (11) in deuterioacetone; at a, 300 and b, 240 K

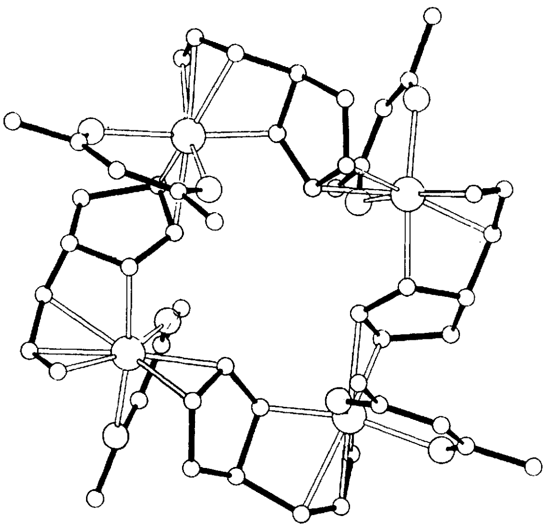


FIGURE 4 View of one tetramer, normal to the $(Rh)_4$ plane, with fluorine atoms omitted for clarity; large circles Rh, intermediate circles O, small circles C

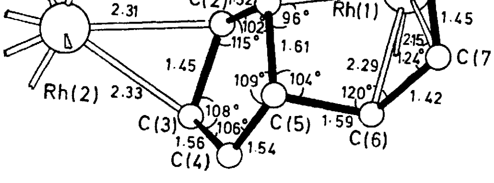


FIGURE 5 One hydrocarbon unit, with mean dimensions

Mean bond lengths (Å) and angles (°), with standard deviations in parentheses

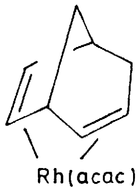
(*a*) Around rhodium			
Rh(1)–O(1)	2.21(1)	Rh(1)–C(7)	2.15(2)
Rh(1)–O(2)	2.14(1)	Rh(1)–C(8)	2.16(2)
Rh(1)–C(1)	2.09(1)	Rh(2)–C(3)	2.33(2)
Rh(1)–C(6)	2.29(3)	Rh(2)–C(2)	2.31(2)
O(1)–Rh(1)–O(2)	88(1)	C(8)–Rh(1)–C(6)	69(1)
O(1)–Rh(1)–C(8)	93(1)	C(8)–Rh(1)–C(1)	82(1)
O(1)–Rh(1)–C(7)	82(1)	C(8)–Rh(1)–C(2) *	115(1)
O(1)–Rh(1)–C(6)	102(1)	C(8)–Rh(1)–C(3) *	81(1)
O(1)–Rh(1)–C(1)	171(1)	C(7)–Rh(1)–C(6)	37(1)
O(1)–Rh(1)–C(2) *	99(1)	C(7)–Rh(1)–C(1)	90(1)
O(1)–Rh(1)–C(3) *	91(1)	C(7)–Rh(1)–C(2) *	153(1)
O(2)–Rh(1)–C(8)	162(1)	C(7)–Rh(1)–C(3) *	118(1)
O(2)–Rh(1)–C(7)	124(1)	C(6)–Rh(1)–C(1)	70(1)
O(2)–Rh(1)–C(6)	93(1)	C(6)–Rh(1)–C(2) *	159(1)
O(2)–Rh(1)–C(1)	95(1)	C(6)–Rh(1)–C(3) *	148(1)
O(2)–Rh(1)–C(2) *	83(1)	C(1)–Rh(1)–C(2) *	90(1)
O(2)–Rh(1)–C(3) *	117(1)	C(1)–Rh(1)–C(3) *	96(1)
C(8)–Rh(1)–C(7)	39(1)	C(2) *–Rh(1)–C(3) *	36(1)
(*b*) Hydrocarbon			
C(1)–C(2)	1.52(2)	C(5)–C(1)	1.61(1)
C(2)–C(3)	1.45(3)	C(6)–C(7)	1.42(2)
C(3)–C(4)	1.56(1)	C(6)–C(5)	1.59(2)
C(4)–C(5)	1.54(3)	C(8)–C(7)	1.45(3)
C(1)–C(2)–C(3)	115(2)	C(4)–C(5)–C(6)	113(2)
C(2)–C(3)–C(4)	108(3)	C(7)–C(8)–Rh(1)	71(3)
C(3)–C(4)–C(5)	106(2)	C(8)–C(7)–C(6)	124(2)
C(4)–C(5)–C(1)	109(1)	C(8)–C(7)–Rh(1)	71(0)
C(5)–C(1)–C(2)	102(1)	C(6)–C(7)–Rh(1)	76(2)
C(2)–C(1)–Rh(1)	108(1)	C(7)–C(6)–C(5)	120(2)
C(5)–C(1)–Rh(1)	96(1)	C(7)–C(6)–Rh(1)	66(1)
C(6)–C(5)–C(1)	104(1)	C(5)–C(6)–Rh(1)	90(1)
(*c*) Hexafluoroacetylacetonate †			
O–C(2)	1.27(2)	C(2)–C(3)	1.40(2)
C(1)–C(2)	1.57(2)	C(1)–F	1.28(2)
O–C(2)–C(1)	111(1)	C(2)–C(1)–F	111(2)
O–C(2)–C(3)	135(1)	F–C(1)–F	106(2)
C(1)–C(2)–C(3)	113(1)	C(2)–O–Rh	121(1)
C(2)–C(3)–C(2′)	117(2)		

* In a different hydrocarbon unit. † Atom numbering: F_3–C(1)–C(2)(:O)–C(3)–C(:O)–CF_3.

C(6) are elongated to 1.6 Å; other bond lengths and angles within the cyclopentene fragment are normal, except for a rather small C(2)–C(1)–C(5) angle. Individual ligand molecules are chiral, and within the tetramer the absolute stereochemistry is alternately (*RR*) and (*SS*). The π-allyl portion of the hydrocarbon is bound asymmetrically to the rhodium atom with C(7)–Rh and C(8)–Rh 2.15(2) and 2.16(2) Å, and C(6)–Rh 2.29(3) Å, but these fall within the range of reported values.[10] The mean value (2.32 Å) for the cyclopentene-carbon–rhodium distance is rather long, however, and may reflect weaker co-ordination, consistent with breakdown of the tetramer in solution.

The Rh–O bond distances are significantly different: Rh(1)–O(1) 2.21(1) and Rh(1)–O(2) 2.14(1) Å. This is probably due to a *trans*-effect as C(1) and C(8) of the hydrocarbon occupy the sites opposite O(1) and O(2) respectively. The strong σ-donor and weak π-acceptor character of the C(1) σ-bond must be reflected in the Rh(1)–O(1) bond elongation.[11] The hexafluoroacetylacetonate groups are alternately disposed above and below the approximate plane of the four rhodium atoms.

From the study of models of the complex, it is apparent that the staggering of the hexafluoroacetylacetonate groups in this manner minimises $F \cdots H$ non-bonding interactions and also blocks the apparent ' hole ' in the molecule.

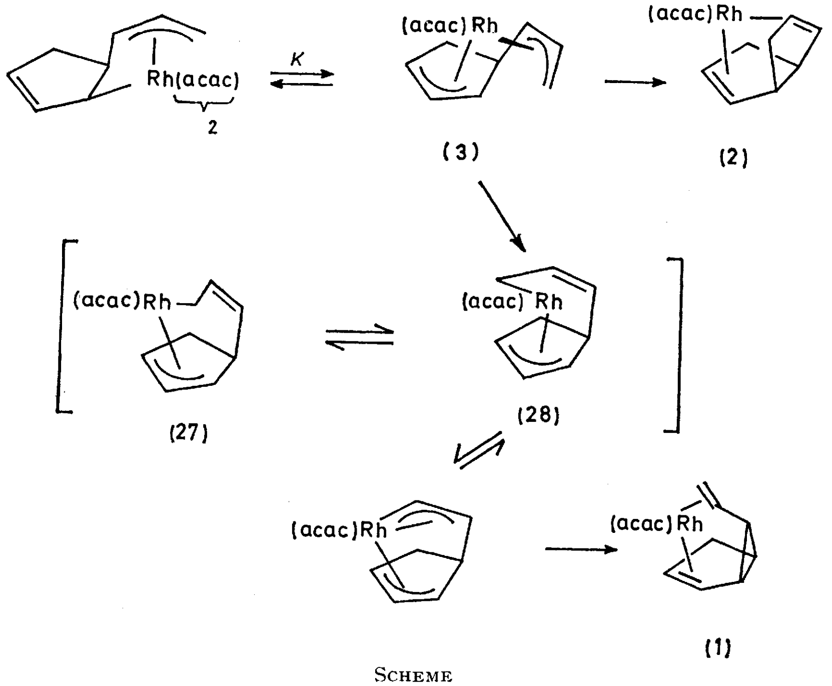


(23)

It remains to consider why (11) is tetrameric, whilst the related compound (6) shows no tendency to aggregation.[12] The corresponding monomer would presumably exist as the bis-π-allyl (3), since this arrangement is greatly preferred to a co-ordinatively unsaturated $\pi\sigma$-form in simple systems (perhaps stabilised by >80 kJ mol^{-1}). In (6) C(1) and C(4) are 3.08 Å apart and insertion of an additional carbon atom bridging these sites [converting it into (3)] cannot be done without considerable strain, giving angle C(1)–C(5)–C(4) 176°, and C–C 1.54 Å. There would also be out-of-plane distortion of the allyl group to accommodate this extra atom. Thus it is clear that (3) is energetically disfavoured, in keeping with its involvement as a reactive intermediate in the thermal rearrangement of (11). Models suggest that the contrast between the dimeric acetylacetonate (12) and the tetrameric fluorinated species (11) is due to non-bonded $F \cdots H$ repulsions in the latter.

There are very few other compounds in which allyl groups form part of polyfunctional bridging hydrocarbons, but the reaction product of nickelocene and hexafluorobut-2-yne is worth noting for the σ- and π-allyl entities in its bridging group.[13]

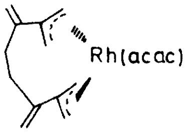
Thermolysis of (12) *and Related Complexes.*—The availability of a cyclopropane ring-opened acetylacetonate (12) complex is very pertinent to the mechanism of thermolysis of (1) where (2) is formed in 85% yield and the rate at 373 K corresponds to a free energy of activation of 127 kJ mol^{-1}, more than 20 kJ mol^{-1} higher than the free energy of Cope rearrangement in the parent hydrocarbon. It was immediately apparent that (12) is very thermolabile and brief heating of its solutions in benzene caused rearrangement to (2) accompanied by a small amount of (1) but no trace of the corresponding bicyclo[3.2.1]octadiene complex (23). Reaction could be followed by n.m.r. at 338 K, the decay of the acetylacetonate methyl signal being monitored *vis-à-vis* the two resolved product methyl resonances. Runs were carried out in deuteriobenzene over a range of concentrations. It was apparent that the half-life is concentration-dependent, and that each individual run shows positive deviation from a first-order response as reaction proceeds. Plotting log (initial rate) *vs.* log (initial concentration) gives a line of slope 0.47 and data were accordingly treated by the standard expressions [14] for half-order kinetics. In all cases correlation coefficients for the half-order line (average 0.9975) were greatly superior to those for a first-order line (average 0.97). No evidence for the existence of monomer could be seen, although the kinetic form implies a reactive monomeric intermediate which rearranges in the rate-determining stage of the reaction. Since (1) and (2) are formed in concentration-independent ratio [although



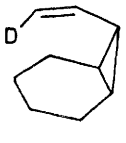
Scheme

there is qualitative evidence that the proportion of (2) increases with increasing temperature] they most likely arise from the same intermediate. If the equilibrium constant K is taken as $0.01\text{M}^{\frac{1}{2}}$ (see Scheme) then the first-order rate constant for rearrangement of intermediate is 1.41×10^{-3} s^{-1}, corresponding to $\Delta G^{\ddagger}_{338}$ 102 kJ mol^{-1}.

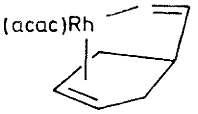
Structure of Reactive Intermediate.—A monomeric bisallylrhodium acetylacetonate complex would be expected to be π-bonded, as (3), based on the precedents of simple systems,[15] the complex (6) derived from *trans*-divinylcyclopropane, and oligomeric allene complexes (24).[16] On the basis of our previous discussions of mechanism [2] there are two possible pathways for further reaction of (3). Thus it may undergo C(1)–C(3) bond formation, giving (2) directly, or alternatively collapse to (1) for which two possible mechanisms have been suggested. Very recently, Salomon [17] has shown by deuterium labelling that an inversion of stereochemistry occurs in the epimerisation which interconverts (25) and (26), catalysed by carbonylrhodium chloride. If the same stereochemical course occurs in the conversion of (3) into (1) then it strongly supports the intervention of the 1—3,8-η^4-bisallyl (27) which can interconvert with its epimer (28) (pseudorotation in a five-co-ordinate intermediate; see Scheme). This process involves an inversion of configuration at C(8). The conversion of (3) into (2) appears from models to involve little atomic reorganisation, but changing the solvent to dichloromethane makes this the less-favoured process, and (1) predominates by 67 : 33 at 323 K.



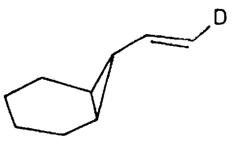
(24)



(25)



(29)



(26)

Reasons why the Postulated Intermediate (3) *is very Thermolabile.*—The parent bis-π-allylrhodium and 1—3, 5—7-η^6-heptadienediylrhodium acetylacetonates are thermally stable, in contrast. Inspection of the structure (6) suggests that some angle strain must be incurred in the course of bridging C(1) and C(4) with a methylene group, thereby raising the energy of (3). Presumably this accounts, at least in part, for the preference of acetylacetonates (11) and (12) for oligomeric structures. Additionally the product (2) has its double bonds correctly aligned for strong ligand–metal overlap, whereas (29) the product of comparable rearrangement of (6), cannot achieve this condition without severe angle strain. Thus the transition state connecting (3) and (2) might be accessible with unusual ease.

No trace of products resulting from hydride-shift processes could be found in the thermolysis of (12). This is owing to the absence of a *cis*-hydrogen β to the carbon–rhodium bond and this rearrangement *via* (3) occurs exclusively.[18–20]

The ease of rearrangement varies very markedly with ligand substitution at rhodium, as expected, the co-ordinatively saturated cyclopentadienyl (14) [where the C(8) ligand cannot rearrange to a bis-π-allyl without violation of the 18-electron rule,[21] or a shift to η^3-cyclopentadienyl bonding] is stable for protracted periods at 393 K although evidence of rearrangement, possibly to the cyclopentadienyl analogue of (2) may be inferred from the n.m.r. spectrum of a sample of (14) in deuteriobenzene maintained for 40 h at that temperature. The hexafluoroacetylacetonate (11) readily rearranges at 338 K in deuterioacetone, mainly to (2).[1] Comparison with (12) is not meaningful because of the differing degrees of aggregation in the two complexes and change of solvent. As a general rule, it might be expected that the equilibrium between a bis-π-allyl and and isomeric σπ-bisallyl would favour the former with increasing π-acceptor quality of counter-ligands, and decreasing electron-density at the metal.[22] Cationic rhodium complexes related to (11)—(14) might therefore provide easy access to the analogue of (3). Thus the chloride (13) was treated with bicyclo[2.2.1]heptadiene-silver hexafluorophosphate at 273 K and a crystalline cationic complex (17) isolated in 29% yield. No evidence for any intermediate allyl complexes was obtained and we infer that (16) is formed and rapidly rearranges, even at 273 K.

EXPERIMENTAL

Microanalyses were carried out by Alfred Bernhardt and by Butterworths Microanalytical Services. N.m.r. spectra were recorded on a Bruker WH 90 pulse Fourier-transform instrument, and i.r. spectra on a Perkin-Elmer 621. All reactions were carried out with distilled and degassed solvents under nitrogen, employing standard Schlenck-tube techniques. Rhodium(I) ethylene complexes were prepared by previously described procedures.

exo-6-*Vinylbicyclo*[3.1.0.]*hex-2-ene* (4).—To a solution of pyridinium iodide (2.9 g, 0.014 mol) in dimethyl sulphoxide (60 ml) and water (20 ml), *endo*-bicyclo[3.1.0]hex-2-ene-6-carbaldehyde (19.8 g, 0.180 mol) was added and the stirred solution monitored at intervals by n.m.r. spectroscopy, changes in the δ 9—10 region being followed. After 90 min no *endo*-aldehyde could be detected, and the reaction was worked up by dilution with water and pentane extraction. After removal of solvent the residue was purified by fractional distillation. There was thus obtained exo-*bicyclo*[3.1.0]*hex-2-ene-6-carbaldehyde* (10), b.p. 79—82 °C at 70 mmHg (17.0 g, 86%); $\nu_{\text{max.}}$ (film): 3 062w, 3 042w, 2 900m, 2 819m, 2 715m, 1 705vs, 1 017s, and 880 m cm^{-1}. N.m.r.: ^{1}H(C$_6$D$_6$) δ 9.34 (1 H, d, 7-H, $J_{6,7}$ 4 Hz), 5.90, 5.52

(2 H, m, m, 2-H, 3-H), 2.5 (4 H, br, 5-H, 1-H, 4,4′-H), and 1.2 (1 H, m, 6 H); ^{13}C($CDCl_3$,{^{1}H}) 200.1 (7-C), 131.87, 130.96 (2-C, 3-C, not individually assigned), 40.49 (4-C), 36.26, 35.35 (1-C, 6-C), and 26.9 (5-C).

A partial solution of methyltriphenylphosphonium iodide (28 g, 0.076 mol) in dimethyl sulphoxide (56 ml) was degassed under nitrogen and sodium dimsyl (20.8 ml, 2.3M in dimethyl sulphoxide) added. The resulting solution was stirred for 15 min at room temperature when isopentane (35 ml) was added and the mixture vigorously stirred and cooled to 7 °C. *exo*-Bicyclo[3.1.0]hex-2-ene-6-carbaldehyde (3.75 g, 0.035 mol) in isopentane (17.5 ml) was added and the mixture stirred for a further 30 min. The isopentane layer was separated, combined with isopentane washings (4 × 5 ml) of the dimethyl sulphoxide layer, and the extracts combined, washed with water (3 × 10 ml), brine (2 × 10 ml), and dried (Na_2SO_4). After removal of isopentane by fractional distillation the residue was purified by spinning-band fractionation, giving exo-6-*vinylbicyclo*[3.1.0]*hex*-2-*ene* (4) (1.8 g, 48%, b.p. 82—85 °C/75 mmHg); $\nu_{max.}$ 3 069s, 3 043m, 3 032s, 3 012vs, 1 641s, 1 465m, 1 437m, 1 419ms, 1 014m, and 862vs cm^{-1}; n.m.r.: ^{1}H(C_2D_6O), δ 5.85 (1 H, m, 2-H, $J_{2,3}$ 5 Hz), 5.30 (2 H, 3-H, $J_{3.4exo}$ 2 Hz, $J_{3,4endo}$ 2 Hz; 7-H, $J_{7,8cis}$ 10 Hz, $J_{7,8trans}$ 16.5 Hz, 4.95 (1 H, dd, 8_{trans}-H), 4.73 (1 H, dd, 8_{cis}-H, $J_{8,8'}$ 2.5 Hz), 2.57 (1 H, m, 4_{endo}-H, $J_{4endo,5}$ 2.5 Hz), 2.31 (1 H, m, 4_{exo}-H, $J_{4exo.5}$ 2 Hz), 1.87 (1 H, m, 1-H; $J_{1,5}$ 7 Hz, $J_{1,6}$ 3 Hz), 1.67 (1 H, m, 5 H), and 0.79 (1 H, m, 6-H, $J_{5,6}$ 3 Hz; $J_{6.7}$ 8.5 Hz), ^{13}C(C_6D_6) 140.2 (2-C), 133.6 (3-C), 128.9 (7-C), 111.8 (8-C), 36.2 (4-C), 34.1, 33.3 (1C,6C, not assigned), and 24.7 (5-C); mass spectrum (8 kV, 70 eV, 120 °C), *m/e* 106 (100%), 105 (75.8%, $M^+ - H$), 91, (73.3%, $M^+ - CH_3$), 79 (75.8%, $M^+ - C_2H_3$).

In a subsequent preparation the yield was improved to 61% by omission of isopentane and direct vacuum distillation of product from the reaction mixture.

1,6—8-η^4-5-*Allylcyclopent*-2-*enylcyclopentadienylrhodium*(III). To a suspension of di-μ-chlorotetrakis(ethylene)-dirhodium (I) (0.750 g, 3.86 mmol) in ether (16 ml) at 10 °C, *exo*-6-vinylbicyclo[3.1.0]hex-2-ene (0.490 g, 4.63 mmol) was added. Immediate ethylene displacement occurred and the brown suspension became yellow. After the mixture had been stirred for 30 min residual ethylene was removed by applying a slight vacuum, and the yellow microcrystalline precipitate was filtered off, washed with dry ether (2 × 8 ml) and isopentane (2 × 5 ml) and dried *in vacuo* to give 1,6—8-η^4-5-*allylcyclopent*-2-*enylrhodium*(III) *chloride* (13) (bridged dimer?), m.p. 147—150 °C (decomp.) (Found: C, 39.05; H, 4.15; Rh, 41.95. $C_{16}H_{20}Cl_2Rh_2$ requires C, 39.30; H, 4.12; Rh, 42.08%); n.m.r.: ^{1}H($CDCl_3$) 6.07 (1 H, m, 2-H, $J_{1.2}$ 5 Hz, $J_{2,4exo}$ 2 Hz, $J_{2.4endo}$ 2 Hz), 5.61 (1 H, m, 3-H, $J_{2.3}$ 6 Hz, $J_{3.4exo}$ 2 Hz, $J_{3,4endo}$ 1.5 Hz), 4.31 (1 H, ddd, 7-H, $J_{7.8trans}$ 13.5 Hz, $J_{7,8cis}$ 8 Hz, $J_{5.7}$ 1.5 Hz, $J_{6,7}$ 5 Hz), 4.03 (1 H, dd, 6-H, $J_{6,8cis}$ 2 Hz), 3.84 (1 H, dd, 8_{cis}-H, $J_{8.8'}$ 8.5 Hz), and 2.16 (5 H, br, m, 1-H, 4,4′-H, 5-H, 8_{trans}-H). The complex was rather insoluble in most solvents but could be dissolved in chloroform to the extent of 11.5 mg/ml.

This chloride complex (0.511 g, 2.28 mmol) was stirred in tetrahydrofuran (15 ml) during addition of freshly sublimed thallium cyclopentadienide (0.546 g, 2.03 mmol). The colour changed from light yellow to deep red during 4 h. After filtration through a bed of alumina, solvent was removed and the resulting red oil dissolved in ether (5 ml) and re-filtered to remove thallium(I) chloride. After removal of ether the residue was distilled at 85 °C/0.001 mmHg to give 1,6—8-η^4-5-*allylcyclopent*-2-*enylrhodium*(III) (14) (0.405 g, 65%), *M* (cryoscopic, C_6H_6) 251; calc. 274; i.r. $\nu_{max.}$ 3 085m, 2 911s, 2 842m, 1 590w, 1 470w, 1 439mw, 1 420ms, 1 350m, 1 029m, 1 013m, and 1 005s cm^{-1}; mass spectrum (2 kV, 70 eV, 70 °C), *m/e* 274 (100%, M^+), 209 (15%, $M^+ - Cp$, 168 (5%, $M^+ - C_8H_{10}$), 103 (71.5%, Rh); n.m.r. ^{1}H, ^{13}C, as Figure.

1,6—8-η^4-5-*Allylcyclopent*-2-*enylrhodium*(III) *Hexafluoroacetylacetonate* (11).—*exo*-6-Vinylbicyclo[3.1.0]hex-2-ene (0.304 g, 2.86 mmol) was added by syringe to a solution of bis(ethylene)rhodium(I) hexafluoroacetylacetonate (0.994 g, 2.72 mmol, freshly recrystallised from pentane) in ether (5 ml). Immediate evolution of ethylene occurred accompanied by considerable lightening of the deep red solution. After 60 min a slight vacuum was applied to displace residual ethylene, after which the ether was removed and replaced by benzene (5 ml). Crystallisation commenced, and the mixture was then cooled to 7 °C prior to filtration. There was thus obtained 1,6—8-η^4-5-*allylcyclopent*-2-*enylrhodium*-(III) *hexafluoroacetylacetonate* (11), (0.837 g, 74%, m.p. 105—107 °C); i.r. ($CHCl_3$) 3 030w, 2 920m, 2 840w, 1 632vs, 1 540m, 1 520br,s, 1 490br,s, 1 350m, 1 110m, 1 050m, 960w, and 735m cm^{-1}; mass spectrum *m/e* 832 (3%) 2M^+ 209 (100%), $M^+ - F_5HF_6O_2$; n.m.r. ^{13}C, as Figure 2; ^{1}H (C_3D_6O) 5.93 (1 H, s, acac), 5.89 (1 H, m, 2-H, $J_{2,3}$ 6 Hz, $J_{2,4endo}$ 3 Hz, $J_{2,4exo}$ 2 Hz), 5.51 (1 H, m, 3-H), 4.34 (2 H, m, 8_{cis}-H, 7-H), 3.64 (1 H, d, 6-H, $J_{6,7}$ 7 Hz), and 2.19 (5 H, br,m, 1-H, 4,4′-H, 5-H, 8_{trans}-H); *M* (cryoscopic, C_6H_6) 1 150.

Crystals suitable for *X*-ray structure analysis were grown by redissolving a portion of the complex in pentane and maintaining it at −20 °C for some time.

1,6—8-η^4-5-*Allylcyclopent*-2-*enylrhodium*(III) *Acetylacetonate* (12).—*exo*-6-Vinylbicyclo[3.1.0]hex-2-ene (0.415 g, 3.92 mmol) was added by syringe to a solution of bis-(ethylene)rhodium(I) acetylacetonate (0.920 g, 3.56 mmol) in pentane (25 ml) and the solution was stirred for 60 min whilst nitrogen was briefly bubbled through it. The volume of pentane was then reduced to 10 ml by evacuation and the solution cooled to −80 °C for 2 h. Filtration gave 1,6—8-η^4-5-*allylcyclopent*-2-*enylrhodium*(III) *acetylacetonate* (12) as a yellow microcrystalline powder, m.p. 120—122 °C (0.695 g, 63%) (Found: C, 50.4; H, 5.5; Rh, 33.8. $C_{13}H_{17}O_2Rh$ requires C, 50.66; H, 5.56; Rh, 33.39%); i.r. ($CHCl_3$) 3 080w, 2 980s, 2 920s, 2 850w, 1 570br,vs, 1 510s, 1 460s, 1 020m, 970m, and 732m cm^{-1}; mass spectrum (2 kV, 70 eV, 70 °C) 308 (91%, M^+), 209 (20.8%, M^+ − acac), 202 (15%, $M^+ - C_8H_{10}$); n.m.r. ^{1}H(C_6D_6) 5.84, (1 H, m, 2-H, $J_{1,2}$ 5 Hz, $J_{2.3}$ 5.5 Hz), 5.69 (1 H, m, 3-H, $J_{3,4exo}$ 2 Hz, $J_{3,4endo}$ 1 Hz), 4.68 (1 H, s, acac), 4.14 (1 H, m, 7-H, $J_{7,8cis}$ 10.5 Hz, $J_{6,7}$ 8 Hz), 3.64 (1 H, br,d, 8_{cis}-H, $J_{8,8}$ 9 Hz), 3.44 (1 H, br,d, 6-H, $J_{6.8cis}$ 1 Hz), 2.05 (5 H, br,m, 1-H,4,4′-H, 5 H, 8_{trans}-H), 1.92 (6 H, s, acac); ^{13}C n.m.r. (see Figure 2); *M* (cryoscopic, C_6H_6, C_6H_{12}) 615.

Bisbicyclo[3.3.0]*octa*-2,6-*dienerhodium*(I) *Hexafluorophosphate* (17).—Freshly distilled norbornadiene (0.092 g, 1 mmol) was added in one portion to silver hexafluorophosphate (0.253 g, 1 mmol) in dry acetone (2 ml) when partial precipitation occurred. 1,6—8-η^4-5-*Allylcyclopent*-2-*enylrhodium*(II) *chloride* (13) (0.244 g, 1 mmol) was added to the stirred suspension held at 0 °C, and the resulting mixture stirred for 45 min at 0 °C. Precipitated silver chloride was filtered off and ether (4 ml) added to the red-orange solution which was then cooled to −80 °C.

The orange crystalline material was filtered off and excess of solvent removed *in vacuo* at 0 °C. There was obtained *bisbicyclo*[3.3.0]*octa*-2,6-*dienerhodium*(I) *hexafluorophosphate* (17), m.p. 102—110 °C (decomp.) (0.065 g, 29%); n.m.r. $^1H(C_3D_6O$, 273 K), 5.72 (2 H, m, 3-H), 5.47 (2 H, m, 2-H), 2.71 (2 H, d, 4 *endo*-H, J_{gem} 12.5 Hz), 2.50 (4 H, br,m, 1-H, 4 *exo*-H); i.r. (C_4Cl_6) 2 922m, 2 844w, 1 660m, 982s, and 853s cm^{-1}. [$^2H_6$]Dimethyl sulphoxide (50 μl) was added to the n.m.r. solution, causing a change in colour from red to yellow. The characteristic vinylic absorbances of bicyclo-[3.3.0]octa-2,6-diene at 5.60 p.p.m. were observed, together with those of a second component showing low-field multiplets at 4.86 and 3.88 p.p.m. The spectrum was unchanged on addition of further [$^2H_6$]dimethyl sulphoxide. This new species was formulated as *tris*- or *bis*-[$^2H_6$]*dimethyl sulphoxide–bicyclo*[3.3.0]*octa*-2,6-*dienerhodium*(I)*hexafluorophosphate* (19). The residues from recrystallisation of this cationic complex were evaporated to dryness and the red residue redissolved in the minimum amount of acetone and then precipitated at −80 °C with diethyl ether. The n.m.r. spectrum of the product suggested that it contained the mixed complex *bicyclo*[2.2.1]*hepta*-2,5-*diene*(*bicyclo*[3.3.0]-*octa*-2,6-*diene*)*rhodium*(I) *hexafluorophosphate* (0.14 g, 31%) but several impurity peaks were apparent.

Thermolysis of Rhodium Complexes.—1,6—8-η^4-5-Allylcyclopent-2-enylrhodium(III) acetylacetonate (12) was weighed into a nitrogen-filled n.m.r. tube and made up to 0.5 ml with [$^2H_6$]benzene. The tube was transferred to the probe of a Bruker WH-90 instrument held at 338 K, and successive spectra accumulated and stored on magnetic disc. Following Fourier-transformation of the time-domain spectra, a portion encompassing the acyl-methyl region (*ca.* 25 Hz) was expanded, traced, and relative peak areas of starting material and product determined by planimetry or triangulation. Between 7 and 10 data points were recorded for each run, and subjected to least-squares analysis, a solution for $k_{obs}/2 = [A_o{}^{\frac{1}{2}} - (A_o - A_x)^{\frac{1}{2}}]/t$ corresponding to half-order decay of starting material being obtained. Each run was also analysed according to the first-order equation $k_{obs} = \ln[H_o/(H_o - H_x)]/t$ when the plots invariably showed pronounced curvature. Runs in dichloromethane were conducted similarly.

Thermolysis of other complexes was studied by n.m.r. but quantative rate measurements were not attempted.

Crystal data for (11). $[C_{13}H_{11}F_6RhO_2]_4$, Monoclinic, $a = 19.641(7)$, $b = 14.353(7)$, $c = 44.87(1)$ Å, $\beta = 98.03(3)°$, $M = 1\,664.74$, $U = 1\,2649$ Å^3, $D_m = 1.77$ (flotation in cadmium borotungstate solution), $Z = 8$, $D_c = 1.75$, Mo-K_α radiation (graphite monochromator), $\lambda = 0.7106\,9$ Å; μ(Mo-K_α) = 11.2.

Needle crystals were obtained from pentane. Data were collected on a Syntex $P2_1$ four-circle diffractometer, using an ω-scan technique to minimise overlap caused by the long c axis, with a scan range of ±0.2°, variable scan-speed between 0.75 and 29.3 ° min^{-1} depending on the intensity of a 2s prescan. Background counts (each 0.25 of scan time) were taken at each end of the scan. The intensities of three standard reflections monitored every 100 reflections showed no variation. Unit-cell constants were obtained by least-squares fit to the reflecting positions of 15 reflections, using the standard Syntex programs. Maximum 2θ was 35°; 3 266 reflections having $I > 3\sigma(I)$ were considered observed and used in the refinement after the initial structure solution. Absorption corrections were not applied. Systematic absences: $h0l, l \neq 2n$ and $0k0$, $k \neq 2n$ indicate space group $P2_1/c$.

The positions of the eight independent rhodium atoms were found by direct methods; they were the highest peaks on the E map calculated from the phase set with highest figure-of-merit, obtained by use of MULTAN.[23] Of the remaining 168 non-hydrogen atoms, 141 were located in 48 cycles of least-squares refinement and Fourier synthesis, possible atoms being selected by peak-searching and bond-length calculation.

Considerable difficulty was encountered in locating the fluorine atoms of the CF_3 groups and they were found by consideration of their idealised geometry. First, ideal acetylacetonate carbon backbones were placed using the RIGBOD [24] program to fit to established atoms, and then the temperature factors of these atoms were refined. The x, y, and z co-ordinates of the carbon skeleton were not refined, as there was previously a tendency for the CF_3 carbon atoms to move out towards the fluorine atoms. Then, using the best-established fluorine positions available on each of the sixteen CF_3 groups, idealised CF_3 group positions were calculated. The 48 fluorine atoms were then refined, first with isotropic and then anisotropic temperature factors. They were then fixed, and four final cycles of refinement were performed on the rhodium, carbon, and oxygen atoms, giving a final R of 0.077 (fluorine and rhodium atoms anisotropic). A difference-Fourier showed only small ripples about the rhodium and CF_3 positions. Computation was with the X-RAY '72 system,[25] on a CDC 7600 computer. Scattering factors were calculated from analytical coefficients,[26] and anomalous dispersion was included.[26]

As the asymmetric unit was found to consist of eight monomer units, it was hoped that corresponding bond lengths and angles in each of the monomers were equivalent. Examination showed this to be correct and it was possible to average the bond lengths and angles to obtain improved estimates and errors, the latter as $\sigma(\bar{l}) = \sqrt{\sum_i (l - \bar{l})^2 / n(n-1)}$ where l is the mean value and n the sample size. None of the individual values differed significantly from the mean values given in the Table. Final structure factors, full bond lengths and angles, and atomic positional and thermal parameters are listed in Supplementary Publication No. SUP 22424 (36 pp.).*

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

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