Synthesis and Thermolysis of Rhodium and Iridium Complexes of *endo*-6-Vinylbicyclo[3.1.0]hex-2-ene. A Metal-promoted Vinylcyclopropane to Cyclopentene Rearrangement [1]

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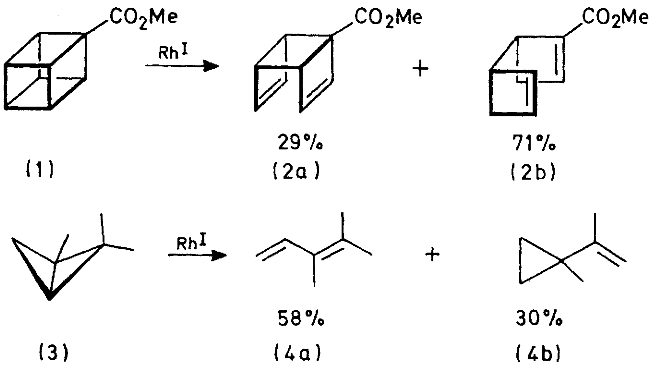
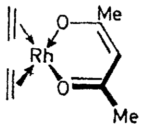
The reaction of *endo*-6-vinylbicyclo[3.1.0]hex-2-ene with bisethylenerhodium(I) acetylacetonate gives rise to a 1 : 1 complex by displacement of ethylene in which the integrity of the divinylcyclopropane is maintained. Unlike the parent hydrocarbon, which rearranges at room temperature to bicyclo[3.2.1]octa-2,6-diene, the derived rhodium complex is stable to 80°, and then the major product of rearrangement is the corresponding complex of bicyclo[3.3.0]octa-2,6-diene, minor amounts of the bicyclo[3.2.1]octa-2,6-diene derivative also being formed. Related studies on the hexafluoroacetylacetonatorhodium(I) and acetylacetonatoiridium(I) derivatives of *endo*-6-vinylbicyclo[3.1.0]hex-2-ene are reported. Possible mechanisms for the thermal transformation are discussed.

THERE now exists a range of skeletal rearrangements of hydrocarbons effected by low-valent transition metals in either catalytic or stoicheiometric reactions. A majority of the catalytic transformations involve strained, saturated hydrocarbons,[2] and the course of reaction *vis-à-vis* the nature of the catalyst and substrate has been extensively studied. It appears that typical reactions [3] (Scheme 1) proceed by co-ordination of a strained bond to a vacant site at the metal and subsequent internal rearrangement to an olefin complex, possibly preceded by intramolecular hydrogen shift. Other reactions studied include catalysed Cope rearrangements [4] and the nickel-catalysed rearrangement of hexa-1,4-dienes to 2-methylpenta-1,3-dienes.[5]



SCHEME 1

Our research has been based on the premise that rearrangements of stoicheiometric complexes, where starting material and product have well-defined structure, are potentially better systems for mechanistic studies than catalytic reactions. Previous investigations of stoicheiometric reactions include metal-promoted Cope rearrangements,[6] other sigmatropic carbon shifts and electrocyclic reactions,[7] and skeletal transformations proceeding by indeterminate pathway.[8] In order to obtain systematic information on the nature of transition-metal induced skeletal rearrangements, we specified the following prerequisites: starting materials should be relatively stable and easily prepared; the metal should be co-ordinatively unsaturated (or able to become so by loss of a labile ligand) to facilitate interaction with carbon–carbon bonds in the hydrocarbon; there should be appreciable electron density at the metal to minimise its role as a Lewis acid; finally, both reactant and product complexes should



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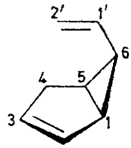
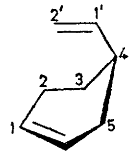


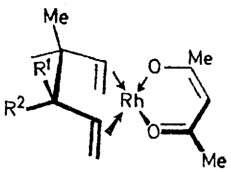
(6a)



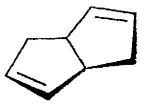
(7)

b; Rh(acac) complex
c; Rh(hexafluoro acac)
d; Ir(acac)

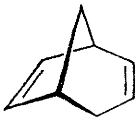
7a; Rh (acac) complex
b; PdCl$_2$



(8)
a; R^1 = H R^2 = Me
b; R^1 = Me, R^2 = H

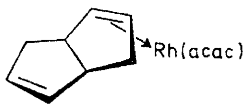


(9a)



(10a)

b - d as (6)



(11)

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[1] V. Aris, J. M. Brown, and B. T. Golding, *J.C.S. Chem. Comm.*, 1972, 1240.

[2] W. G. Dauben, A. J. Kielbania, jun., and K. N. Raymond, *J. Amer. Chem. Soc.*, 1973, **95**, 7166; P. G. Gassmann and R. R. Reitz, *ibid.*, p.3057; H. Hogoreen and H. C. Volger, *ibid.*, 1967, **89**, 2486, and intervening papers.

[3] M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 1043; L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, 1970, **92**, 6366.

[4] W. Brenner, P. Heimbach, H. Hey, E. W. Müller, and G. Wilke, *Annalen*, 1969, **727**, 161; H. Buchholz, P. Heimbach, H. J. Hey, H. Selbeck, and W. Wiese, *Coordination Chem. Rev.*, 1972, **8**, 129.

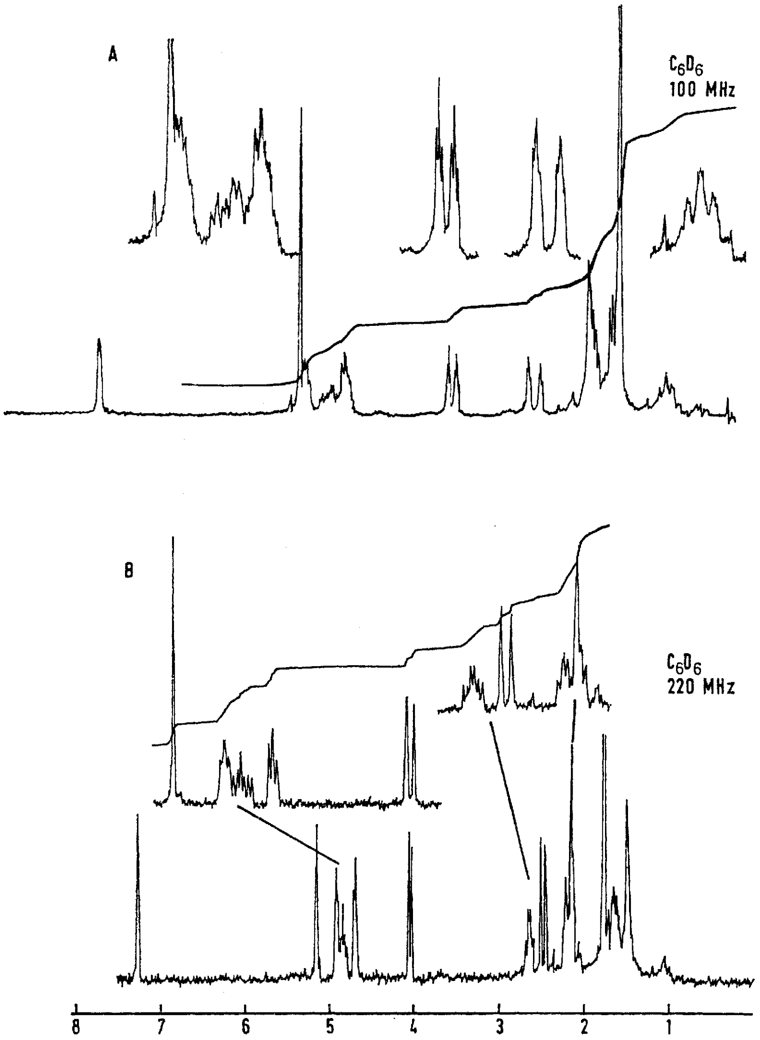
[5] R. G. Miller, P. A. Pinke, and D. J. Baker, *J. Amer. Chem. Soc.*, 1970, **92**, 4490.

[6] P. Heimbach and M. Molin, *J. Organometallic Chem.*, 1973, **49**, 477, 483.

[7] W. Grimme, *Chem. Ber.*, 1967, **101**, 113; R. Aumann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 190; L. A. Paquette, J. M. Photis, J. Fayos, and J. Clardy, *J. Amer. Chem. Soc.*, 1974, **96**, 1217.

[8] E. J. Reardon, jun., and M. Brookhart, *J. Amer. Chem. Soc.*, 1973, **95**, 4311; M. Brookhart, N. M. Lippmann, and E. J. Reardon, jun., *J. Organometallic Chem.*, 1973, **54**, 247; R. Aumann, *Angew. Chem. Internat. Edn.*, 1970, **9**, 800.

readily exchange hydrocarbon ligands so that catalytic reactions might also be achieved. All these criteria are fulfilled by square-planar d^8 rhodium(I) diolefin complexes prepared from bisethylenerhodium(I) acetylacetonate (5). In earlier experiments[9] with complexes of *meso*- and (±)-3,4-dimethylhexa-1,5-diene no rearrangements were observed. To increase the reactivity of the system studies have now been carried out on complexes of the *cis*-divinylcyclopropane (6a), which itself undergoes Cope rearrangement readily at 25°.



N.m.r. spectra: A, of (6b); B, of (6d)

Synthesis and Structure of the Complexes.—Preliminary experiments established that the rate of Cope rearrangement of (6a) in $CDCl_3$ was essentially unaffected by addition of 20 mole % of (5). When stoicheiometric quantities of (5) and (6a) reacted at 0° in ether solution, a new complex (6b) was formed with rapid and complete displacement of ethylene. The structure of this product was established by combustion analysis, by production of pure (6a) on reaction with aqueous sodium cyanide or [$^2H_6$]dimethyl sulphoxide, and particularly from its n.m.r. spectrum. This shows (Figure) the typical resonances of a co-ordinated vinyl group, a co-ordinated disubstituted olefin, and the methyl and methine groups of acetylacetonate. Most of the remaining signals are contained in a featureless envelope, although 5-H is sufficiently upfield at δ 1·25 to be readily assigned.

The hexafluoroacetylacetonate (6c) was similarly prepared from bisethylenerhodium hexafluoroacetylacetonate, likewise the iridium complex (6d) from bisethyleneiridium(I) acetylacetonate.[10] The n.m.r. spectrum of the latter at 220 MHz is particularly useful in structure assignment (Figure 1b) for there the 6-H multiplet is separated from other saturated C–H resonances, and a 4 Hz coupling between 6- and 1′-H can be recognised. Cross-reference to the

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[9] V. Aris, J. M. Brown, and B. T. Golding, *J.C.S. Perkin II*, 1974, 700.

[10] D. H. Williamson, unpublished work, from the reaction of tetrakisethyleneiridium chloride (A. L. Onderdelinden and H. C. van der Ent, *Inorg. Chim. Acta*, 1972, **6**, 420) with sodium acetylacetonate.

spectrum of (6b) then permits a comparable 3 Hz coupling to be allotted to $J_{1',6}$ which may be compared with a 3·5 Hz coupling between 4- and 1′-H in 4-vinylcyclohexenerhodium(I) acetylacetonate [11] (7a). Since a crystal structure determination [12] on the d^8 palladium dichloride complex (7b) demonstrates that the 1,5-diene unit is in a boat configuration, a similar stereochemistry should be adopted by (7a) and thus by (6b—d) (*i.e.* as drawn). Furthermore, the observed coupling constant of 3—4 Hz is more consistent with a boat configuration [HC(6)–C(1′)H dihedral angle *ca.* 60°, from Prentice–Hall models] than with the alternative twist configuration [(17) dihedral angle *ca.* 90°]. In the acyclic complexes (8a and b) the n.m.r. spectra reveal a preference for boat configurations with a considerable energy barrier to boat–twist interconversion.[9] However, the available evidence does not preclude a small amount of twist isomer (17) in equilibrium with (6b), nor is it possible to assess the energy barrier to formation of the twist isomer.

Thermal Behaviour of endo-6-*Vinylbicyclo*[3.1.0]*hex*-2-*ene Complexes*.—Whilst the hydrocarbon (6a) rearranges with a half-life of a day at 25° ($\Delta G^\ddagger$ 24 kcal mol^{-1}), complexes (6b—d) are indefinitely stable at this temperature. Rearrangement of (6b) only occurs readily above 80°, and is accompanied by considerable darkening of the solution. The half-life for disappearance of starting material is 46 h at this temperature and reaction is more conveniently followed at 120°, the half-life then being *ca.* 2 h in C_6D_6 ($\Delta G^\ddagger$ 30·5 kcal mol^{-1}). Two new species are formed during the reaction, and monitoring by n.m.r. suggests good mass balance between starting material and products. The major isomer (85%) gave rise to two new broad singlets at δ 3·7 and 2·4. The most conspicuous signal of the minor product was a doublet at δ 0·88. When starting material was completely consumed, solvent was distilled off *in vacuo* and shown by g.l.c. to contain no volatile hydrocarbon other than C_6D_6. A small portion of the residue was treated with aqueous sodium cyanide and extracted into $CFCl_3$. G.l.c. analysis showed two volatile products, the minor isomer being identified as bicyclo[3.2.1]octa-2,6-diene [13] (10a). The remainder of the product was recrystallised from pentane, which removed some dark insoluble material and subsequently six times from methanol at low temperature, giving a light yellow crystalline complex. A portion was treated with aqueous sodium cyanide, and the resulting hydrocarbon purified by preparative g.l.c. The eluate was identified as bicyclo[3.3.0]octa-2,6-diene by comparison of its n.m.r. spectrum in CCl_4 with that published [14] for the dideuterio-analogue. The analysis and n.m.r. spectrum of the complex itself were entirely consistent with the structure (9b).

In separate control experiments it was shown that benzene was unnecessary to effect rearrangement, and reaction proceeded with similar facility for the neat liquid complex, or for a solution in cyclohexane at 120°. Addition of 10 mole % of tricyclohexylphosphine to a solution of (6b) in benzene was without gross effect on the rate of rearrangement, and changing the concentration of (6b) in benzene threefold did not alter the course or rate of reaction. The results are therefore best explained in terms of a unimolecular reaction of (6b) without participation of external liganding agents. The minor product (10b) was shown to be stable under the reaction conditions, and no bicyclo[3.3.0]octa-2,6-diene was produced when (6a) was thermolysed at 120°. This latter experiment removes the possibility that (9b) is produced by dissociation in (6b), followed by rearrangement and recombination.

The related hexafluoroacetylacetonate (6c) rearranged to (9c) more readily, having a half-life in benzene of *ca.* 6 h at 80°. No (10c) was detected in the reaction product, although some of the starting material was consumed in polymer-forming side reactions, manifested by a broad background absorbance which appeared at δ *ca.* 2·0, and amorphous residues remaining after sublimation of the product. In complete contrast, the iridium(I) acetylacetonate (6d) showed no evidence of thermal rearrangement up to 145° and above this temperature decomposed to intractable products. No trace of either (9d) or (10d) could be detected in the n.m.r. spectrum, when 5% of either might reasonably have been found. Thus co-ordination of a *cis*-divinylcyclopropane to iridium(I) raises the activation energy for carbon–carbon bond cleavage by more than 10 kcal mol^{-1}. The difference between (6b and d) is remarkable, finding some precedent in previously cited examples of low lability in iridium complexes.[15]

Mechanism of Rearrangement.—(a) *Intervention of bisallyl intermediates*. Rearrangement of the hydrocarbon (6a) could proceed in principle to either (9a) or (10a) by a single-step concerted pathway. Preference for the latter is dictated by stereoelectronic factors and orbital symmetry, since a concerted route to (9a) would require antarafacial bond breaking or making. The situation is quite different for (6b) since only (10b) can be produced by a single-stage concerted reaction in which bonding to rhodium is maintained throughout. The requirement of *cis*-stereochemistry in the new double bond of (9b) necessitates that (11) and not (8b) is the product of [1,3] shift, since the migrating 1,6-bond must necessarily remain proximate to the same face of the rhodium atom. This difficulty makes it desirable to consider alternative pathways in which a bisallyl intermediate is formed.

In the case of dimeric bisallylrhodium chloride [16] and of bisallylrhodium acetylacetonate,[17] a co-ordinatively

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[11] V. Aris, unpublished work.

[12] I. A. Zakharova, G. A. Kukina, T. S. Kuli-Zade, I. I. Moiseer, G. Yu-Pek, and M. A. Porai-Koshits, *Zhur. neog. Khim.*, 1966, **11**, 2543.

[13] W. R. Moore, W. R. Moser, and J. E. La Prade, *J. Org. Chem.*, 1963, **28**, 2200.

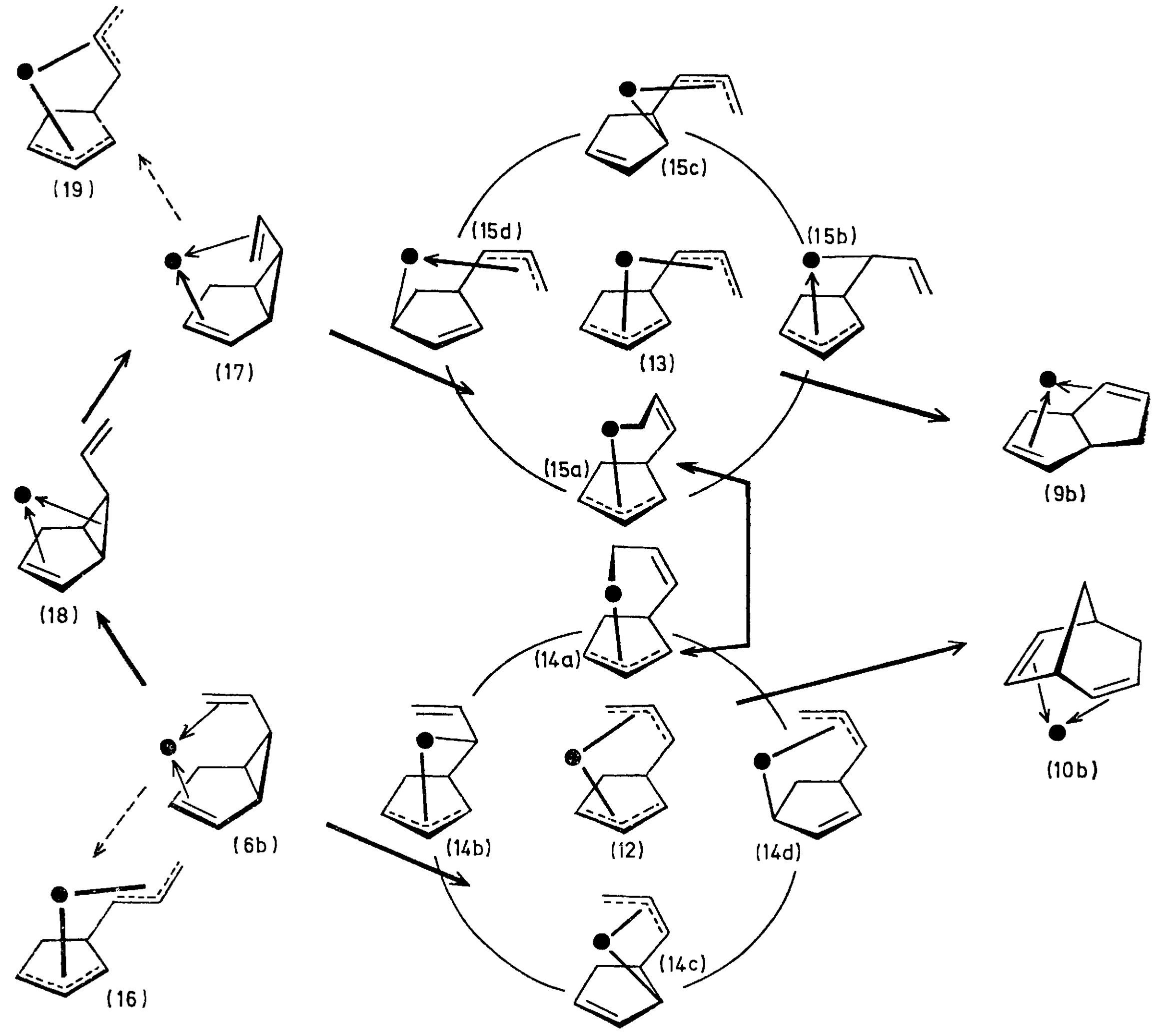
[14] J. E. Baldwin and M. S. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 3969.

[15] J. W. Kang, R. F. Childs, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 720; C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 850.

[16] M. McPartlin, and R. Mason, *Chem. Comm.*, 1967, 16.

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

saturated bis-π-allyl structure is preferred to the alternative unsaturated π-allyl-η-allyl form. N.m.r. experiments suggest that the latter is probably considerably higher in energy. It is also apparent that an octahedral configuration is preferred to the alternative form of C_{2v} symmetry. Now there are two diastereomeric bis-π-(Z)-allyls derived from (6b), namely (12) and (13). Whilst (12) is closer in geometry to the twisted C_{2v} form, (13) has octahedral symmetry, making it likely that the latter is energetically preferred. Since (13) may collapse to (9b), and (12) to (10b) by simple suprafacial bond relocations, any mechanism which accounted for the preferred derivation of (13) might provide an acceptable explanation of experimental observations.



Scheme 2

(b) *Ring-opening routes.* There are a number of possible routes to (13) and whilst these include partial ligand dissociation followed by recombination [*e.g.* the direct conversion of (12) into (13) by rotation about C(5)–C(6) and rebonding], the instability of underco-ordinated low-valent transition metals[18] makes alternatives more attractive. A formal analysis of available pathways is shown (Scheme 2) and two distinct possibilities may be identified. Suprafacial bond-opening in (**6b**) can give rise to (12), either directly or *via* one of the four possible bis-σ,η-allyls (14a—d). The energy difference between (12) and (14) cannot be assessed, and it may well be that the latter are lower in energy because of the unfavourable C_{2v} configuration of the cisoid bis-π-allyl. Whatever the situation, if (14a) is kinetically accessible it may undergo conversion into (15a) by a pseudorotation involving simultaneous translation of the C–Rh bond and co-ordinated acetylacetonate (15a) may in turn interconvert with bis-σ,η-allyls (15b—d), and with (13), which may in turn collapse to (9b).

The above mechanism represents the most reasonable sequence when the intermediacy of boat isomer (6b) and suprafacial opening of the 1,6-bond are the only possibilities considered. The twist isomer (17) is considered to be higher in energy than the boat isomer (6b) but may be formed reversibly [*via* (18)?] under the conditions of thermolysis. Suprafacial cleavage of the 1,6-bond gives

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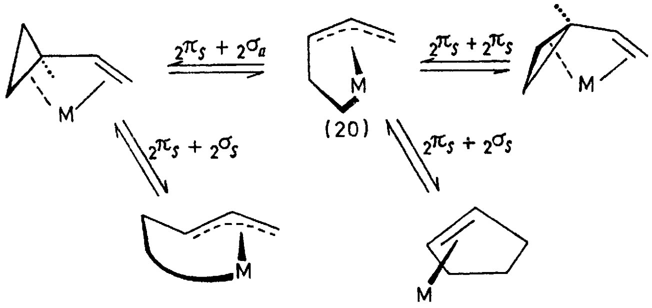
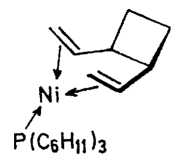
[18] C. A. Tolman, *Chem. Soc. Rev.*, 1972, **1**, 337.

(19), but an antarafacial cleavage produces (13) directly.* Note that antarafacial opening of the 1,6-bond in (6b) would result in formation of the bis-π-(*E*)(*Z*)-allyl (16) where the orientation of the two allyl groups appears from molecular models to be unfavourable for good binding to rhodium. Thus if (14a) and (16) were of inaccessibly high energy, the boat–twist interconversion (6b) $\rightleftharpoons$ (17) might provide a feasible method for generating an intermediate of appropriate stereochemistry. Therefore, two distinct possibilities for derivation of (9b) emerge, namely *via* interconversion of (14a) and (15a), and alternatively *via* antarafacial opening of the cyclopropane ring of (17). There is operational distinction between these, for they make different predictions on the stereochemical outcome of the reaction with regard to the relationship between a substituent at C-2′ in (6b) and at C-4 in (9b). Experimental tests are in progress.

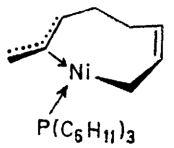
With free organic substrates, antarafacial bond breaking and making components are usually stereoelectronically unfavourable and bonding along the reaction co-ordinate is better maintained in a purely suprafacial process. There are several reasons why the reaction of a co-ordinated ligand is not strictly comparable with that of the free ligand and these may be exemplified by the conversion of a vinylcyclopropane complex into the corresponding cyclopentene complex (Scheme 3). Rearrangement of the parent hydrocarbon may proceed by a non-concerted mechanism in which a diradical intermediate is formed, or by a concerted [$_2\pi_s + {}_2\sigma_a$] pathway; experimental evidence suggests that these are rather similar in energy.[9] Whilst a diradical must be much less stable than either starting material or product here, this is not the case for the metal-promoted reaction. In principle the ring-opened species (20) may be the most stable species of the reaction co-ordinate, for no overall loss of bonds is incurred in its formation and the total pool of electrons in the co-ordination sphere remains constant. One of the major driving forces for concerted reactions in organic chemistry does not apply to organometallic species, therefore. Additionally, even the stepwise process is subject to the tenets of orbital symmetry, since the nodal symmetry of bond making and breaking at the reaction termini remains correlated and a closed bonding loop is maintained throughout. Hence, bond breaking in an organometallic ligand may be forced into one or other mode because of the constraints imposed by co-ordination geometry, and this may easily over-ride symmetry factors. Yet another complication is the extra symmetry elements introduced by the metal. For example, there are two suprafacial processes in which (20) is converted into a vinylcyclopropane complex, and these will clearly be subject to differing symmetry constraints.



SCHEME 3



(21)



(22)

The closest precedent for our results lies in the conversion of *cis*-divinylcyclobutane(tricyclohexylphosphine)-nickel(0) (21) into the bis-π,σ-allyl (22).[20] This is more conducive to explanation by antarafacial opening of the cyclobutane bond than by pseudorotation in an intermediate bisallyl because of the relative stereorigidity of four-co-ordinate nickel. Similarly, the nickel-catalysed cyclodimerisation of penta-1,3-diene [4] requires an antarafacial bond closure, or its equivalent. The steric course of Cope rearrangement of 2,ω-dimethyl-*cis*-divinylcyclobutane [6] to 3,7-dimethylcyclo-octa-1,5-dienepalladium dichloride in the presence of an equivalent of bisbenzonitrilepalladium dichloride is more complex, but again there appears to be preference for a non-least motion pathway.

Finally, we emphasise that the role of orbital symmetry in transition-metal promoted rearrangements is ill-defined and probably complex. Other stereoelectronic factors may be dominant.

EXPERIMENTAL

N.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer R12 instrument and at 100 MHz on a Varian HA-100 machine (through PCMU). In two cases 220 MHz spectra were obtained through the courtesy of I.C.I. Corporate Laboratories, Runcorn Heath. All tubes were filled under nitrogen with clear oxide-free solutions and sealed with air-tight pressure caps (Wilmad Scientific). Microanalyses were carried out by Alfred Bernhardt. G.l.c. was conducted on an F and M Aerograph instrument employing 20 ft × $\frac{1}{4}$ in columns (12% squalane or 12% Carbowax 4000 M on firebrick) for both analytical and preparative purposes. Preparative work was executed on a vacuum-line using standard Schlenck-tube and pressure filtration techniques.

Preparation of endo-6-*Vinylbicyclo*[3.1.0]*hex*-2-*enerhodium*-(I) *Acetylacetonate*.—Bisethylenerhodium(I) acetylacetonate (1·032 g, 4 mmol) was dissolved in ether (20 ml) and the solution filtered under nitrogen to remove traces of insoluble material. 6-Vinylbicyclo[3.1.0]hex-2-ene (440 mg, 510 µl, 4·15 mmol) was added by syringe to the stirred solution held at 0°. Immediate ethylene evolution occurred, and the cooled solution was stirred for a further 2 h. Removal of solvent *in vacuo* and analysis of a portion by n.m.r. in C_6D_6 showed that

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* In principle (17) can be transformed directly to (9b) in a single-step synchronous [$_2\pi_s + {}_2\sigma_a$] reaction but this is perhaps a less likely alternative.

[19] *E.g.* W. R. Roth and A. Friedrich, *Tetrahedron Letters*, 1968, 2607.

[20] P. Heimbach, I. Tkatchenko, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1971, **10**, 328, 329.

a small amount of ethylene complex was still present. Consequently the residues were dissolved in dry ether under nitrogen and a further 150 μl of 6-vinylbicyclo[3.1.0]hex-2-ene added. After further stirring (30 min) the solvent was evaporated off and dry pentane sufficient to dissolve all the complex at room temperature was added. The solution was filtered repeatedly under nitrogen until clear, and cooled to −78° until crystallisation was complete. Three further low temperature recrystallisations from pentane in similar manner gave the *complex* (700 mg), m.p. 59°, δ (C_6D_6; 100 MHz) 5·06 (1H, s, acac H), 5·00 (1H, m, 3-H), 4·72 (1H, dddd, $J_{1',6}$ 4, $J_{1',^{103}Rh}$ 3 Hz, 1′-H), 4·59 (1H, m, 2-H), 3·45 (1H, ddd, $J_{1',cis\text{-}2'}$ 8·5, J_{gem} 1·5 $J_{cis\text{-}2',^{103}Rh}$ 1·5 Hz, *cis*-2′-H), 2·59br (1H, d, $J_{1',trans\text{-}2'}$ 11·5 Hz, *trans*-2′-H), 2·04 (3H, m, 1-, 4-, 6-H), 1·72 (6H, s, acac CH_3), and 1·25 (1H, m, 5-H) (Found: C, 50·8; H, 5·4; Rh, 33·3. $C_{13}H_{17}O_2Rh$ requires C, 50·65; H, 5·65; Rh, 33·4%). A portion of the complex (45 mg) was treated with 10% sodium cyanide (0·5 ml) until degradation was complete and the resulting mixture extracted with $CFCl_3$. The n.m.r. spectrum of the resulting solution was characteristic of *endo*-6-vinylicyclo[3.1.0]hex-2-ene, with no observable resonances due to other products.

Thermolysis of endo-6-*Vinylbicyclo*[3.1.0]*rhodium*(I) *Acetylacetonate*.—Preliminary runs were carried out in C_6D_6 solution in nitrogen-blanketed n.m.r. tubes held in a bath at 80 or 120°, with frequent monitoring.

A solution of the *endo*-6-vinylbicyclo[3.1.0]hex-2-ene complex (700 mg, 227 mmol) in benzene (*ca.* 5 ml) was degassed, sealed under nitrogen, and heated to 120° for 6 h. The dark solution was then evaporated to dryness by trap-to-trap distillation *in vacuo*, and the oily solid recrystallised once from pentane at −78°. Examination by n.m.r. showed the presence of two complexes in 85 : 15 ratio. A small portion was treated with 10% aqueous sodium cyanide and extracted into $CFCl_3$. G.l.c. examination of the resulting solution (Carbowax 4000; 20 ft; 100°) and comparison with authentic samples confirmed that the major component was bicyclo[3.3.0]octa-2,6-diene, and the minor bicyclo[3.2.1]-octa-2,6-diene. Examination of the residue from trap-to-trap distillation failed to reveal the presence of any hydrocarbon other than benzene.

The crystallised material was recrystallised six further times from methanol at −78°, which effectively removed the rhodium complex of bicyclo[3.2.1]octa-2,6-diene. There was thus obtainedyellow *bicyclo*[3.3.0]*octa*-2,6-*dienerhodium*-(I) *acetylacetonate*, δ (C_6D_6; 100 MHz) 5·14 (1H, s, acac C-H), 4·82 (2H, m, 2-H), 3·73 (2H, m, 3-H), 2·40 (2H, d, J_{gem} 12·5 Hz *endo*-4-H), 2·00 (2H, m, 1-H), 1·78 (6H, s, acac CH_3) and 1·60br (2H, d, *exo*-4-H) (Found: C, 50·75; H, 5·25; Rh, 33·3. $C_{13}H_{17}O_2Rh$ requires C, 50·65; H, 5·55; Rh, 33·4%).

A portion of the product (*ca.* 150 mg) was treated with 10% aqueous sodium cyanide as before and extracted into a small volume of $CFCl_3$. The product was purified by preparative g.l.c. (Carbowax 4000; 20 ft; 100°) the effluent being condensed into firebrick. Short-path distillation of the condensate *in vacuo* gave bicyclo[3.3.0]octa-2,6-diene, identified by comparison of the n.m.r. spectrum with the published spectrum of the dideuterio-analogue.

Control Experiments.—(a) *High temperature thermolysis of* endo-6-*vinylbicyclo*[3.1.0]*hex*-2-*ene*. A small Pyrex tube was heated to 120° and olefin (60 μl) added by syringe. After 30 s the tube was rinsed with CCl_4 and the n.m.r. spectrum recorded. Only bicyclo[3.2.1]octa-2,6-diene could be detected.

(b) *Concentration dependence of thermolysis rate*. Samples (15 and 44 mg) of *endo*-6-vinylbicyclo[3.1.0]hex-2-ene-rhodium(I) acetylacetonate were separately dissolved in benzene (0·6 ml) and the solutions heated to 120° under nitrogen. The n.m.r. spectrum was monitored after 30, 75, and 180 min and the extent of conversion into the corresponding bicyclo[3.3.0]octa-2,6-diene complex measured from disappearance of signals at δ 3·45 and 2·59 and appearance of signals at δ 3·73 and 2·40. No difference in rate was detected.

Medium Dependence of Thermolysis.—Three samples (20 mg) of *endo*-6-vinylbicyclo[3.1.0]hex-2-enerhodium acetylacetonate were separately transferred to n.m.r. tubes. To the first was added cyclohexane (0·6 ml) and the solution centrifuged and filtered to remove traces of insoluble material. To the second were added benzene (0·6 ml) and tricyclohexylphosphine (0·002 g). The three tubes were heated separately to 120° for 90 min and monitored by n.m.r., benzene (0·5 ml) being added to the third. In each case the corresponding bicyclo[3.3.0]octa-2,6-diene complex was the major product, and tricyclohexylphosphine had no observable effect on the rate.

Test for Catalysis of Rearrangement.—Samples of *endo*-6-vinylbicyclo[3.1.0]hex-2-ene (0·035 g, 40 μl, 0·33 mmol) were separately dissolved in $CDCl_3$ (0·5 ml) and to one was added bisethylenerhodium(I) acetylacetonate (0·016 g, 0·06 mmol). The solutions were maintained at 35° and monitored by n.m.r. at intervals over 2 days. No difference in the rate of rearrangement to bicyclo[3.2.1]octa-2,6-diene could be detected.

Preparation and Thermolysis of Bicyclo[3.2.1]*octa*-2,6-*dienerhodium*(I) *Acetylacetonate*.—The *complex* was prepared as before from bicyclo[3.2.1]octa-2,6-diene (0·120 g) and bisethylenerhodium(I) acetylacetonate; m.p. 172—173°, δ (C_6D_6, 220 MHz) 5·21 (1H, s, acac H), 5·03 (1H, ddd, $J_{6,(7)}$ 4, $J_{(5),6}$ 7 Hz, 6-H), 4·29br (1H, dd, 7-H), 3·79br [1H, t, $J_{2,3}$ 7; $J_{3,exo\text{-}4}$ 6 Hz, and evidence of long-range coupling (to 1-H?), 3-H], 3·60br (1H, d, 2-H), 2·88 (1H, m, 1-H) overlapping with 2·87 (1H, dm, J_{gem} 16 Hz, *exo*-4-H), 2·18 (1H, d, *endo*-4-H) 2·09br (1H, s, 5-H), 1·84 and 1·81 (6H, 2s, acac CH_3), 1·38 (1H, dt, J_{gem} 11, $J_{1,8;5,8}$ 5 Hz *anti*-8-H), and 0·88 (1H, d, *syn*-8-H) (Found: C, 50·45; H, 5·55. $C_{13}H_{17}O_2Rh$ requires C, 50·65; H, 5·55%). A sample of the complex (0·06 g) was dissolved in benzene (0·5 ml) and heated to 120° in a sealed nitrogen-filled n.m.r. tube. The n.m.r. spectrum was recorded at intervals and after 9 h was superimposable on the initial spectrum.

Preparation and Thermolysis of endo-6-*Vinylbicyclo*[3.1.0]-*hex*-2-*enerhodium*(I) *Hexafluoroacetylacetonate*. To a solution of sodium hexafluoroacetylacetonate (0·880 g, 0·0383 mmol) in dry ether (*ca.* 20 ml) was added tetraethylenedirhodium dichloride (0·490 g, 0·019 mmol). The suspension was stirred under nitrogen at room temperature for 4 h at which time an off-white solid and a red-orange solution had formed. Filtration and removal of solvent *in vacuo* gave *bisethylenerhodium*(I) *hexafluoroacetylacetonate* in near quantitative yield, which was purified by recrystallisation from ether–pentane (1 : 2) at −80°.

The ethylene complex (0·910 g, 2·5 mmol) was dissolved in dry, degassed ether (20 ml) and cooled to 0° during addition of *endo*-6-vinylbicyclo[3.1.0]hex-2-ene (450 μl, 3·3 mmol). Successive crystallisation from pentane and acetone at −80° gave endo-6-*vinylbicyclo*[3.1.0]*hex*-2-*enerhodium*(I) *hexafluoroacetylacetonate* (0·402 g), m.p. 89°, δ (C_6D_6, 90 MHz) 5·96 (1H, acac H), 4·80 (1H, m, 3-H) 4·46 (1H, ddd, 1′-H)

4·31 (1H, m, 4-H), 3·16br (1H, d, $J_{1',6}$ 12·5 Hz, 6-H) 1·76br (4H, m, 1-, 4-, 6-H), and 1·10 (1H, m, 5-H) (Found: C, 37·9; H, 2·7; Rh, 24·1, 22·95. $C_{13}H_{11}F_6O_2Rh$ requires C, 37·5; H, 2·65; Rh, 24·7%).

A sample of the complex was heated in benzene solution to 80° and the n.m.r. spectrum monitored at regular intervals. The only detectable new product was the corresponding bicyclo[3.3.0]octa-2,6-diene complex, identified by characteristic n.m.r. signals in the δ 2—5 region, together with evidence of polymer formation (broad, ill-defined signals at δ *ca.* 2·0). The half-life for thermal rearrangement was estimated to be *ca.* 6 h. After 36 h the solution was evaporated to dryness and the residue sublimed (60° and 10^{-3} mmHg). There was thus obtained *bicyclo*[3.3.0]*octa*-2,6-*dienerhodium*(I) *hexafluoroacetylacetonate*, m.p. 110—111°, δ (90 MHz, C_6D_6) 6·02 (1H, s, acac H), 4·63br (2H, s, 3-H), 3·53br (2H, s, 2-H), 2·10 (2H, d, $J_{4,4'}$ 13 Hz, *exo*-4-H), 1·45 (2H, d, *endo*-4-H), and 1·25br (2H, s, 1-H) (Found: C, 38·75; H, 2·5. $C_{13}H_{11}F_6O_2Rh$ requires C, 37·5; H, 2·65%).

Preparation and Thermolysis of endo-6-*Vinylbicyclo*[3.1.0]-*iridium*(I) *Acetylacetonate*.—The complex was prepared in similar manner to the rhodium analogue, from bisethylene-iridium(I) acetylacetonate, and recrystallised from pentane. There was obtained yellow endo-6-*vinylbicyclo*[3.1.0]*hex*-2-*eneiridium*(I) *acetylacetonate*, m.p. 72—73°, δ (C_6D_6; 220 MHz) 5·03 (1H, s, acac H), 4·78br (1H, t, 3-H), 4·73 (1H, ddd, $J_{1',6}$ 4 Hz, 1′-H), 4·58 (1H, dd, $J_{2,3}$ 4, $J_{1,2}$ 4 Hz, 2-H), 3·92 (1H, d, $J_{1',cis\text{-}2'}$ 8 Hz *cis*-2′-H), 2·51 (1H, dt, $J_{1(5),6}$ 7 Hz, 6-H), 2·36 (1H, d, J 11 Hz, *trans*-2′-H), 2·08 overlapping with 2·02 (3H, m, 1- and 4′-H), 1·74 (6H, s, acac CH_3), and 1·50 (1H, m, 5-H) (Found: C, 39·4; H, 4·35; Ir, 48·2. $C_{13}H_{17}IrO_2$ requires C, 39·3; H, 4·3; Ir, 48·35%).

Samples of the complex (*ca.* 50 mg) were dissolved in C_6D_6 (0·5 ml) and sealed under nitrogen in 5 mm n.m.r. tubes. Thermolysis was carried out at various temperatures. After 46 h at 120° half the complex had decomposed, but the only new absorbances detectable by n.m.r. were broad envelopes between δ 6 and 4·5 and between 3 and 1 p.p.m. At 145° a sharp new singlet appeared at δ 4·93 over 4·5 h, accompanied by considerable darkening of the solution but this was not associated with identifiable features elsewhere in the spectrum. At 165° similar behaviour was observed over 1 h.

Photolysis of endo-6-*Vinylbicyclo*[3.1.0]*rhodium*(I) *Acetylacetonate*.—A solution of the complex (0·04 gm) in C_6D_6 (0·75 ml) was photolysed in an n.m.r. tube exposed to a 125 W Hanovia ' black-light ' lamp and cooled by an intervening water condenser. The n.m.r. spectrum was monitored at frequent intervals. After 135 h a broad complex spectrum was apparent, and the solution was shaken with 10% aqueous sodium cyanide, the resulting mixture being extracted into $CFCl_3$. The aqueous layer was further washed with $CFCl_3$ and the combined organic fractions subjected to trap-to-trap distillation *in vacuo*. No features attributable to any possible C_8H_{10} products were apparent in either the distillate or the residue.

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