Organorhodium Complexes of *cis*- and *trans*-Divinylcyclopropane; The Crystal Structure of (±)-*ZZ*-1,2,3-η-5,6,7-η-Heptadienediylrhodium(I) Hexafluoroacetylacetonate

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Summary Both *cis*- and *trans*-divinylcyclopropane form 1:1 hexafluoroacetylacetonatorhodium(I) complexes; in the former, the integrity of the cyclopropane ring is maintained whilst in the latter it is essentially opened, as shown by a crystal structure determination.

Cis-DIVINYLCYCLOPROPANE, prepared as previously described,[1] reacts at −20° in iso-pentane solution with bis-ethylenehexafluoroacetylacetonatorhodium(I) (**1**) to give a yellow crystalline 1:1 complex by ethylene displacement, m.p. 79—80°, ^{1}H n.m.r. (C_6D_6), δ 5·95 (acac C–H) 4·34 [H(2)] 3·33 [H(1)$_{cis}$, J_{cis} 8 Hz] 2·16 [H(1)$_{trans}$, J_{trans} 13 Hz] 1·02 [H(4)$_{syn}$] and 0·62 [H(2) H(4)$_{anti}$]. The vanishingly small coupling between H(2) and H(3) indicates a transoid configuration (**2**). ^{13}C n.m.r. chemical shifts and ^{103}R–^{13}C couplings are typical of vinyl-olefin-rhodium complexes, and the high-field uncoupled C(3) and C(4) resonances demonstrate the integrity of the cyclopropane ring; δ (C_6D_6) 90·2 (acac-C) 81·8 [C(1)], 63·1 [C(2)], 22·7 [C(3)], and 11·4 [C(4)]. As anticipated,[2] (**2**) is stable in solution at room temperature. At 65° in C_6D_6, conversion into a new complex occurs with < 10% side-products at completion ($t_{\frac{1}{2}}$ = 10 h). Structure (**3**) is indicated for the rearrangement product, as treatment of

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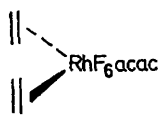
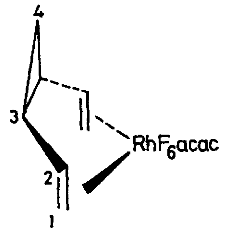
the resulting solution with [$^2H_6$]-dimethyl sulphoxide, causes quantitative degradation to cyclohepta-1,4-diene. Reaction probably proceeds by trace dissociation of (**2**) to *cis*-divinylcyclopropane‡ followed by rearrangement and recombination, since it is suppressed by addition of 20 mole % of (**1**).



(1)



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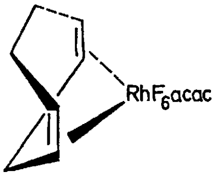

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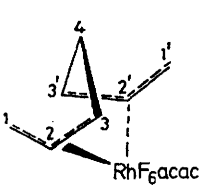

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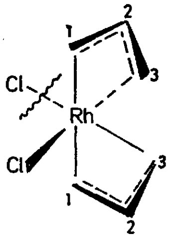

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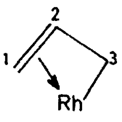

(6)

Trans-divinylcyclopropane, prepared by reacting methylenetriphenylphosphorane with *trans*-1-formyl-2-vinylcyclopropane,[3] displaces ethylene from (**1**) at room temperature, again giving a monomeric 1:1 complex, m.p. 68—69°, ^1H n.m.r. (C_6D_6), δ 5·97(acac C-H) 4·50 [$H(1)_{cis}$, H(2)] 4·08 [$H(1)_{trans}$, J_{trans} 11·4 Hz) 1·93 [H(3), $J_{2,3}$ 6·1 Hz] and 0·80 [H(4), $J_{3,4}$ 5·7 Hz]. Whilst the equivalence of the H(4) protons suggests C_2 symmetry there are several compatible alternative structures. ^{13}C n.m.r. chemical shifts and ^{103}Rh–^{13}C couplings accord better with a bis-allylic form (**4**) in solution, δ (C_6D_6) 115·3 [C(2), J_{Rh-C} 6 Hz] 89·5 (acac–C) 56·4 [C(1), J_{Rh-C} 9 Hz] 30·9 [C(3), J_{Rh-C} 7 Hz] and 24·4 [C(4)] with assignments confirmed by off-centre double resonance. The crystal structure of (**4**) confirms the bis-π-allyl configuration[4] in the solid state, and also shows it to be the *ZZ*-configurational isomer. The complex (**4**) is thermally stable (20 h, 100°). In the presence of a catalytic quantity of (**1**), however, *trans*-divinylcyclopropane is slowly converted at 95° in C_6D_6 into cyclohepta-1,4-diene.

Crystal data: $RhC_{12}H_{11}F_6O_2$, orthorhombic, a = 8·599(1), b = 14·684(3), c = 11·264(2) Å, Z = 4, space group C222$_1$, 521 observed reflections collected on a Syntex P2$_1$ diffractometer. The structure was solved by the heavy-atom method and refined to a current R value of 0·069 (all atoms with anisotropic temperature factors); data quality is limited by crystal decomposition, and the accuracy of the refined structure by high correlations due to pseudo-symmetry and by disorder in the CF_3 groups; the molecule is shown in the Figure.

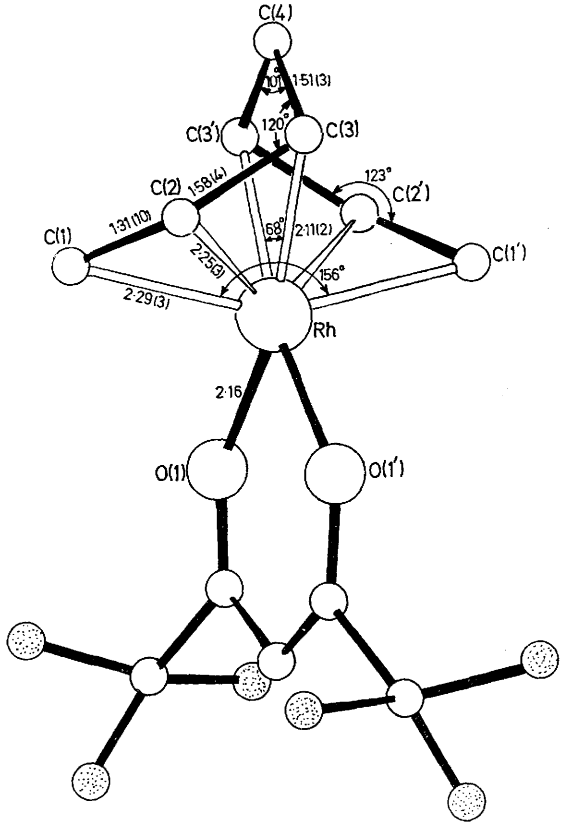

FIGURE. *trans*-Divinylcyclopropanerhodium(I) hexafluoroacetylacetone complex. Only one set of disordered fluorine atoms is shown. Dihedral angle C(1)C(2)C(3)/C(2)C(3)C(4) = 38°.

The cyclopropane ring has opened and the overall structure resembles that of bis-η-allylrhodium chloride dimer, (**5**).[5] However, the bis-η-allyl unit in (**4**) is distorted from octahedral geometry (Figure) and the effect of the bridging atom C(**4**) is to increase the extent of η-allyl localisation, as in (**6**), with partial rehybridisation of C(**3**).

We thank the S.R.C. for support (J.J.S.) and for a grant for the diffractometer (N.W.A.). Co-operation with I.C.I. Corporate laboratories under the CASE scheme is also acknowledged.

(*Received*, 17*th January* 1975; *Com.* 054.)

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‡ The half-life for rearrangement of *cis*-divinylcyclopropane at 65° is approximately 5 s.

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