Reactive Rhodium Complexes Derived from *trans*-6-Vinylbicyclo[3.1.0.]hex-2-ene. Mechanistic Studies and *X*-Ray Structure of η^4-3,1′—3′-(4-Allylcyclopent-1-enyl)hexafluoroacetylacetonatorhodium Tetramer

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Summary The title compound forms rhodium(I) complexes with attendant cyclopropane ring-opening, and the resulting acetylacetonates rearrange cleanly above room temperature.

The *cis*-divinylcyclopropane complex (**1**) rearranges at 393 K to the isomeric complex (**2**) and intervention of a *transoid* bis-π-allyl (**3**) rather than its diastereoisomer (**4**) was suggested in order to rationalise the course of reaction.[1] We now report the formation of 1 : 1 organorhodium complexes from the related *trans*-divinylcyclopropane (**5**)[2] and their thermal behaviour.

Successive reaction of the hydrocarbon (**5**) with bis-ethylenerhodium chloride dimer and thallium cyclopentadienylide gave (**6**) as a distillable oil whose structure and stereochemistry follow from the (fully analysed) ^{1}H and ^{13}C n.m.r. spectra which clearly demonstrate the presence of a Rh–C(3) σ-bond and η^3-bonding to C(1′)—C(3′). Reaction of (**5**) with bis-ethylenerhodium(I) hexafluoroacetylacetonate however gave a crystalline tetrameric 1 : 1 complex (**7**) whose structure has been solved by single crystal *X*-ray analysis. This shows (Figure) that rhodium atoms are disposed 5·10 Å apart, at the corners of a slightly puckered square with acetylacetonate units alternately above and below its plane. Each rhodium is co-ordinated to the cyclopentene double bond of one hydrocarbon ligand and to another by η^4-3,1′—3′ bonding requiring cleavage of the cyclopropane ring.[3] There are two such tetramers in the asymmetric unit and within each one the configuration at C(3) is alternately (*R*) and (*S*). In solution this rigid structure is not maintained [cryoscopic M.w. 1150 (C_6H_6)] and complex changes in the ^{13}C n.m.r. spectrum with variation of temperature indicate equilibration between at least two species. The dominant form at 180 K in $(CD_3)_2CO$ shows Rh–C couplings of 12 and 16 Hz at C(1) and C(2), normal for a π-bonded olefin, but this isomer is not evident above 240 K.

The corresponding acetylacetonate (**8**) is dimeric in benzene solution‡ (cryoscopic M.w. 615) and rearranges readily.

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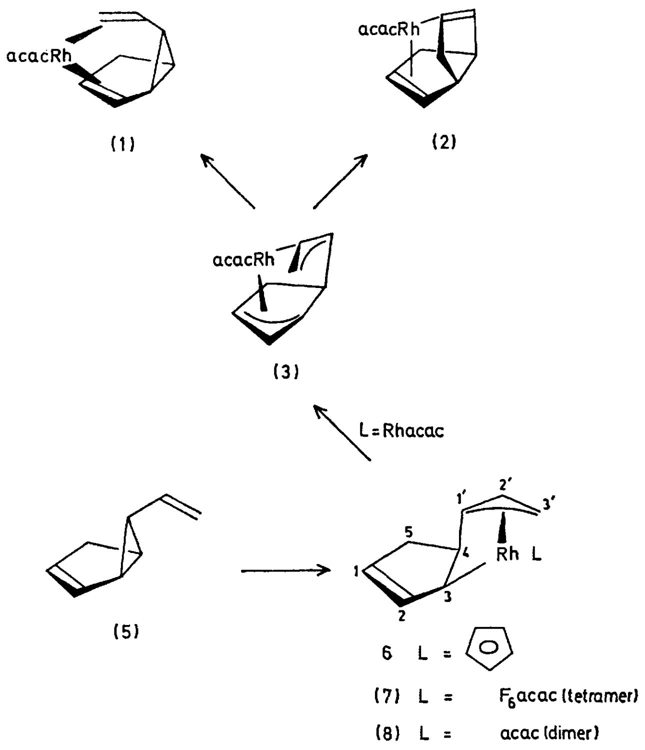
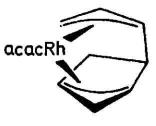
‡ The detailed structure of this dimer is not known at present, but molecular models suggest that a species with double hydrocarbon bridges is sterically possible for the dimer (**8**) but less likely for the fluoro-analogue because of F–H repulsions.





(4)

acac = $CH_3COCHCOCH_3$

F_6acac = $CF_3COCHCF_3$

At 338 K good half-order kinetics are observed over a wide concentration range (monitoring of old and new acac-Me ^{1}H n.m.r. resonances) with some deviation towards first-order response below 0·02 M. For a series of runs in C_6D_6 between 0·036 and 0·205 M, $k_{obs} = 1{\cdot}42 \pm 0{\cdot}12 \times 10^{-4}$ mol$^{-\frac{1}{2}}$ s^{-1}, and quantitative conversion into a mixture of 12% (**1**) and 88% (**2**) occurs in each case. In CD_2Cl_2 at 323 K $k_{obs} = 1{\cdot}1 \pm 0{\cdot}1 \times 10^{-4}$ mol$^{-\frac{1}{2}}$ s^{-1} but now (**1**) predominates over (**2**), in the ratio 67 : 33. The adherence to half-order kinetics indicates that the dimeric acetylacetonate (**8**) undergoes rapid reversible dissociation to an intermediate which subsequently rearranges in the rate-determining step. Precedent[4] suggests the *transoid* bis-π-allyl structure (**3**) for this intermediate, which may subsequently undergo C(3)–C(3′) bond formation, giving (**2**), or epimerisation (*via* η^4-1—3,3′ bis-allyls) and collapse to (**1**) (equation 1).

$$\begin{tikzcd} (8) \arrow[r, shift left, "k_1"] & 2\,(3) \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] \arrow[d, "k_3"] & (1) \\ & (2) & \end{tikzcd} \qquad (1)$$

$$k_{-1} \geqslant 10^2\, k_1$$

The co-ordinatively saturated cyclopentadienyl complex (**6**) which cannot form a bis-π-allyl analogous to (**3**) is much more stable but shows evidence of a similar transformation on protracted maintenance at 393 K; the tetramer (**7**) rearranges to the known hexafluoro-analogue of (**2**) in acetone at 338 K.

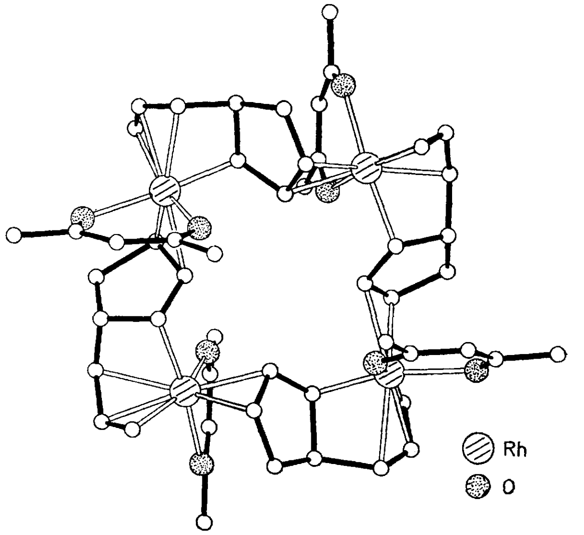


FIGURE. One tetramer of (**7**) with F atoms omitted for clarity. *Crystal data*: monoclinic, space group $P2_1/c$; $a = 19{\cdot}641$, $b = 14{\cdot}353$, $c = 44{\cdot}875$ Å, $\beta = 98{\cdot}03$; $Z = 8$ (tetramer units). 3288 observed reflections [$I/\sigma(I) > 3{\cdot}0$] were collected on a Syntex $P2_1$ four-circle diffractometer with Mo — K_α radiation and graphite monochromator. The structure was solved by direct methods for rhodium followed by numerous cycles of least-squares refinement and Fourier synthesis for the 168 light atoms. The current R-factor is 0·077 (anisotropic temperature factors for Rh and F).

We shall defer a detailed discussion of mechanism for the full paper. For the present, and assuming that the hydrocarbon geometry in (**7**) and (**8**) is similar, we note that little reorganisation is required to promote closure of the C(3)–C(3′) bond.

We thank the S.R.C. for support grants.

(*Received*, *2nd July* 1975; *Com.* 757.)

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[1] V. Aris, J. M. Brown, J. A. Conneely, and D. H. Williamson, *J.C.S. Perkin II*, 1975, 4.

[2] M. Schneider and G. Mössinger, *Tetrahedron Letters*, 1974, 3081; S. Forrester, K. Cann, and J. C. Barborak, *J.C.S. Chem. Comm.*, 1975, 116.

[3] There is an example of a bridging allyl group in platinum chemistry: G. Raper and W. S. McDonald, *J.C.S. Dalton*, 1972, 265.

[4] N. W. Alcock, J. M. Brown, J. A. Conneely, and J. J. Stofko, Jr., *J.C.S. Chem. Comm.*, 1975, 234.