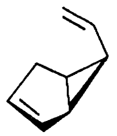
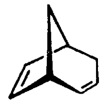
Redirection of the Course of a Cope Rearrangement by Co-ordination; the Thermolysis of *endo*-6-Vinylbicyclo[3,1,0]hex-2-enerhodium(I) Acetylacetonate

By Vanessa Aris, J. M. Brown,* and B. T. Golding
(*School of Molecular Sciences, University of Warwick, Coventry* CV4 7AL)

Summary Co-ordination of a *cis*-divinylcyclopropane to rhodium(I) inhibits Cope rearrangement; at elevated temperatures a vinylcyclopropane–cyclopentene isomerisation is the dominant reaction course.

Thermolysis of *endo*-6-vinylbicyclo[3,1,0]hex-2-ene (**1**) occurs readily ($\Delta G^{\ddagger}$ 24 kcal mol^{-1}) at room temperature and results in quantitative Cope rearrangement to bicyclo[3,2,1]octa-2,6-diene (**2**),[1] in line with the behaviour of other simple derivatives of *cis*-divinylcyclopropane.[2] Having observed a high degree of thermal stability for rhodium(I) derivatives of unstrained hexa-1,5-dienes,[3] we examined complexes derived from (**1**).


(1)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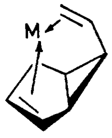

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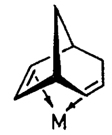

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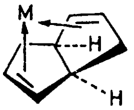
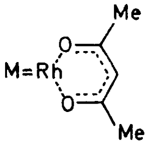
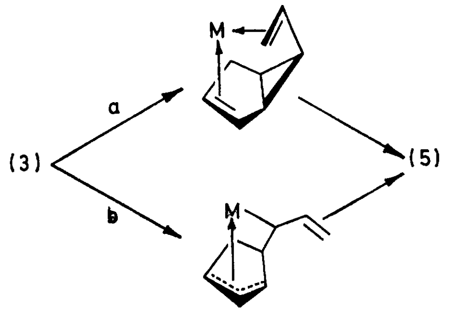


(5)



Addition of a catalytic quantity of bisethylenerhodium(I) acetylacetonate to a solution of (**1**) in $CDCL_3$, with monitoring by n.m.r. spectroscopy, showed that the rate of Cope rearrangement was unaffected. With stoicheiometric quantities in Et_2O at 0°, the new complex (**3**) was formed and purified† by crystallisation from pentane at low temperatures; τ (C_6D_6): 4·92 (s, acac C–H), 4·97 (m, 3-H), 5·18 (t of m, 7-H), J 5·38 (m, 2-H), 6·49 (d, J 8 Hz, with further splitting, *cis*-8-H), 7·38 (d, J 12 Hz, with further splitting *trans*-8-H), 7·9—8·1 (m, 1-, 4-, and 6-H), 8·26 (s, acac Me), and 8·76 (m, 5-H). Reaction of (**3**) with aqueous sodium cyanide gave (**1**) as the sole hydrocarbon product. The new complex was thermally stable under conditions where the hydrocarbon was completely rearranged, and changes in the n.m.r. spectrum (C_6D_6) were noted only after prolonged heating at 80°. At 120°, signals due to (**3**) disappeared with a half-life of *ca.* 2 h ($\Delta G^{\ddagger}$ 30·5 kcal mol^{-1}), concomitant with the appearance of two new sets of resonances. The minor component (*ca.* 20%) was shown to be bicyclo[3,2,1]octa-2,6-dienerhodium(I) acetylacetonate (**4**) by spectral comparison with an authentic sample.[4] It was noted that (**4**) was produced largely in the early part of the reaction, and may very well arise by partial (wall?) decomposition of the complex, followed by Cope rearrangement of (**1**) and recombination. The major product (**5**) was purified by fractional crystallisation, from acetone–isopentane; τ 4·86 (s, acac-C–H), 5·20 [m, 2- and 6-H (or 3- and 7-H?)], 6·28 [m, 3- and 7-H (or 2- and 6-H?)], 7·64 (d, $J_{4,4}$ 13 Hz *syn*-4-H), 8·25 (s, acac-Me), and *ca.* 8·3 br (m, 1-, 5-, and *anti*-4-H). Reaction of (**5**) with 10% aqueous NaCN followed by extraction into Freon and preparative g.l.c. gave bicyclo[3,3,0]octa-2,6-diene,[5] whose structure was proved by n.m.r. comparison with the published spectrum of the dideuterio-derivative. Thermolysis of the hexafluoroacetylacetonate corresponding to (**3**) occurred about ten times more rapidly, and with greater selectivity. In separate control experiments it was shown that the rate of thermolysis was concentration independent over a threefold range, that the course of reaction was unaffected by addition of a catalytic amount of tricyclohexylphosphine, and that benzene was unnecessary for the reaction, since a neat liquid sample of (**3**) followed the same reaction course at 120°, albeit less cleanly. A benzene solution of (**4**) was unaffected by heating to 120° for 9 h.



Scheme

The preferred configuration of (**3**) about the hexa-1,5-diene fragment is likely to be boat-like rather than chair-like by analogy with the structure of the d^8 hexa-1,5-diene complex of palladium dichloride.[7,8] From this geometry, direct rearrangement to (**5**) is stereoelectronically impossible. There are two possible interpretations which avoid this dilemma. One is reversible isomerisation to a chair-configuration (Scheme)[9] and a subsequent $[_{2}\sigma_{s} + {}_{2}\pi_{s}]$ sigmatropic shift. Alternatively, antarafacial opening of the cyclopropane ring[10] in (**3**) could give rise to a σ,π-bis

† Satisfactory analytical data were obtained for new complexes.

allyl rhodium intermediate, with the proper geometry for reclosure to (**5**).

We shall defer a more detailed discussion of the implications of this reaction for the full paper, but note its relevance to the continuing discussion[11] on the rôle of orbital symmetry constraints in organometallic reactions.

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[3] Unpublished observations of the present authors.

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[8] The 5 Hz. coupling between 6- and 7-H in the iridium analogue of (**3**) is consistent with a boat configuration (vicinal dihedral angle *ca.* 30°) but not with chair-configuration (vicinal dihedral angle *ca.* 90°); unpublished 220 MHz spectrum of Dr. D. H. Williamson.

[9] The relative disposition of the two π-bonds towards the metal in the chair configuration is similar to that in the presumed transition state for ethylene rotation in bisethylenerhodium(I) acetylacetonate which is *ca.* 12 kcal mol^{-1} above the ground state; R. D. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.

[10] *Cf.* the conversion of *cis*-divinylcyclobutanenickel(0) into 1 : 6–8-η-octa-*cis*-2,*trans*-6-dienediyl(tricyclohexylphosphine)nickel(0), which must involve an antarafacial opening of the cyclobutane if a concerted pathway is followed; P. W. Jolly, I. Tkatchenko, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1971, **10**, 329.

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