Cleavage of Carbon–Carbon Sigma Bonds by $Ru_3(CO)_{12}$

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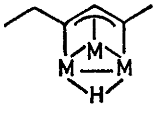
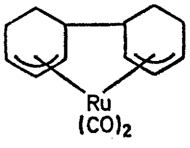
Summary $Ru_3(CO)_{12}$ has been found to catalyse the cleavage and hydrogenation of cyclohexadiene to give the μ-allylruthenium hydride (I).

Recently, Evans, *et al.*[1] reported the formation of the μ-allyl compound (I) from hexadiene in the presence of $Ru_3(CO)_{12}$. We report that the same compound can be formed (30%) from cyclohexa-1,3-diene (4 mol) and $Ru_3(CO)_{12}$ (1 mol) in refluxing heptane. This process must involve the catalytic cleavage of an unstrained carbon carbon bond in addition to concomitant hydrogenation.



M = Ru(CO)3
(I)



(III)

The use of a large excess of cyclohexadiene, or use of benzene as a solvent, leads to the formation of tricarbonyl-(1–4-η-cyclohexa-1,3-diene)ruthenium (II) in high yield. Treatment of (I) with excess C_6H_8 at reflux also leads to (II). $C_6H_8Ru(CO)_3$ (II) is an active catalyst for inter- and intramolecular hydrogen transfer reactions; thus, treatment of (II) with 1,3-C_6H_8 at reflux leads to the formation of 1,4-C_6H_8, benzene, and cyclohexene. Under these conditions, a new ruthenium complex, $(C_6H_8)_2Ru(CO)_2$ (III) is also formed (13%). Decomposition of (II), either in the presence or in the absence of $Ru_3(CO)_{12}$, gives no detectable quantity of (I). Treatment of *cis*-hexa-1,3,5-triene, in heptane at reflux, with $Ru_3(CO)_{12}$ gives benzene (42%), while the *trans*-isomer gives only 1·2% under identical conditions. The rate of formation of benzene from *cis*-triene is comparable to the known[2] rate of thermal cyclization. In no case were any non-cyclic C_6 hydrocarbons detected when cyclohexadiene was the starting material.

Since the ring opening of cyclohexadiene must be several orders of magnitude slower than the cyclization of *cis*-hexatriene (cyclohexadiene is much more stable than the triene), the above results indicate that the ring cleavage is catalysed by co-ordination to some uncharacterized metallic species. Mononuclear species seem to be ruled out by our experiments. In view of the product structure, a trinuclear complex seems most reasonable as the catalyst for the cleavage.

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[1] M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J.C.S. Chem. Comm.*, 1972, 545.
[2] K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 1964, 3080.