

CATALYTIC HYDROGENATION OF CYCLOPROPYL ALKENES. III. ON THE  
MECHANISM OF HOMOGENEOUS HYDROGENATION IN THE PRESENCE OF  
TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM(I).

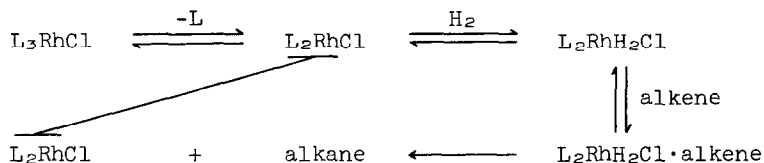
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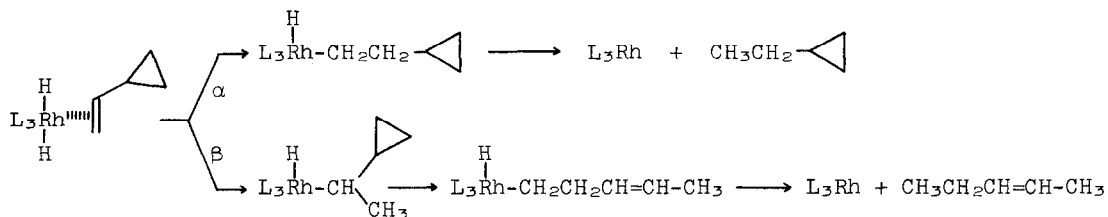
Tris(triphenylphosphine)chlororhodium(I) has been shown to be an efficient catalyst for the low pressure hydrogenation of alkenes and alkynes (3,4). Wilkinson and coworkers have proposed a mechanism (Scheme I) involving: 1) dissociation of one ligand, 2) oxidative insertion of rhodium into the hydrogen bond, 3) coordination of alkene with the resulting cis-dihydridorhodium(III) species, and 4) simultaneous transfer of the bound hydrogens to the alkene (3).



Scheme I (L = triphenylphosphine)

Hussey and Takeuchi have recently presented evidence that the transfer of bound hydrogen from rhodium to the alkene linkage is not concerted (5). In our studies of cyclopropyl alkene reduction (6), we have found additional evidence for such a non-concerted transfer.

Table I summarizes the products obtained when a series of cyclopropyl alkenes were hydrogenated at 1 atm. in the presence of  $(\phi_3\text{P})_3\text{RhCl}$ . We feel that the results require a mechanism involving stepwise addition of the bound hydrogens (Scheme II). If the first hydrogen is added  $\alpha$  to the cyclopropane ring, an




























Scheme II (L = triphenylphosphine or Cl)

alkylrhodium(III) species results, which collapses to cyclopropylalkane and  $(\phi_3P)_2RhCl$ . If the first hydrogen is added  $\beta$  to the cyclopropane ring, the resulting cyclopropylcarbinylrhodium species can undergo rearrangement to a homoallyl rhodium compound prior to final collapse. The possibility of synchronous 1,4-addition of bound hydrogen is eliminated by the observation that trans-2-pentene is observed as an intermediate in the reduction of vinylcyclopropane (1).

The effect of alkyl groups on the degree of hydrogenolysis (Table I, cf. compounds 1, 2 and 3) and the direction of ring cleavage (Table I, compounds 4 and 5) offer further support for the proposal embodied in Scheme II, if one makes the reasonable assumption that a primary alkylrhodium bond is of lower energy than a secondary or tertiary alkylrhodium bond (7,8). In the early stages of the reduction of 1, 2 and 5, the only intermediate olefins detected were 2-pentene, 3-hexene and 4-methyl-2-pentene, respectively. This observation strengthens the assertion that attack occurs initially at the double bond rather than on the cyclopropane ring.

The direction of opening of 5 suggests that the proposed cyclopropylcarbinylrhodium to homoallyl rhodium rearrangement is either concerted or proceeds via a cyclopropyl carbanion, rather than a cyclopropylcarbinyl cation or radical. We prefer a concerted mechanism since olefins may be deuterated in the presence of  $(\phi_3P)_3RhCl$  in ethanol without incorporation of protium from solvent (1,8). Although addition of  $(\phi_3P)_2RhH_2Cl$  to 6 and 7 must occur from both sides of the molecules, ring opening of the exo-cyclopropylcarbinylrhodium does not occur because the conformation necessary for ring opening cannot be achieved.

Table I  
 Hydrogenation of Cyclopropylalkenes  
 in the Presence of  $(\phi_3P)_3RhCl^a$

<u>Substrate</u>			<u>Products, %</u>		
<u>1</u>		 85	 14	 1	
<u>2</u>		 70	 27	 3	
<u>3</u>		 97	 1.5	 1.5	
<u>4</u>		 99	 1		
<u>5</u>		 86	 11		
<u>6</u>		 93	 6.7	 0.3	
<u>7</u>		 82	 17		

<sup>a</sup>Reductions were carried out with 20 mg of catalyst and 20-30  $\mu l$  of alkene in 1.5 ml of benzene at atmospheric pressure and 22-25°C.

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#### References

1. Fellow of the Alfred P. Sloan Foundation.
2. National Science Foundation Summer Fellow, 1965.
3. J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, J. Chem. Soc. A., 1711 (1966).
4. F. H. Jardine, J. A. Osborn and G. Wilkinson, ibid., 1574 (1967).
5. A. S. Hussey and Y. Takeuchi, J. Am. Chem. Soc., 91, 672 (1969).
6. For previous paper see, S. R. Poulter and C. H. Heathcock, Tetrahedron Letters, 5343 (1968).
7. J. Chatt, R. S. Coffey, A. Gough and D. J. Thompson, J. Chem. Soc. A., 190 (1968).
8. C. Djerassi and J. Gutzwiller, J. Am. Chem. Soc., 88, 4537 (1966).