STEREOCHEMICAL CRITERIA FOR THE MECHANISMS OF CATALYTIC HYDROGENATION.[1]
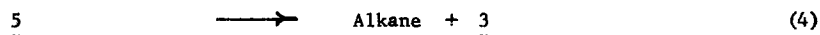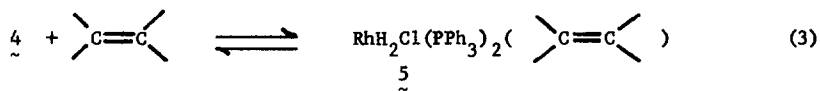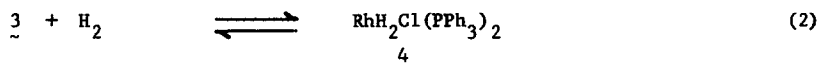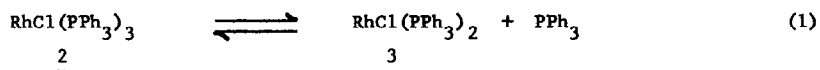
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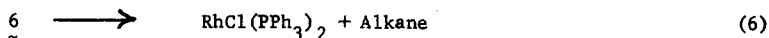
The ratio of the cis and trans isomers obtained upon hydrogenating an alkene such as 4-t-butylmethylenecyclohexane (1), is a function of the pressure of hydrogen; the nature of this function is a characteristic of the catalyst.[2,4] The knowledge of these relationships, therefore, can aid in distinguishing between various proposed reaction schemes and in the identification of the product controlling step. In general, the kinetics of surface catalyzed reactions are not so easily determined or so unambiguously interpreted in terms of mechanism as are reactions occurring in a single phase. Accordingly, it is important to test our general approach for relating stereochemistry to mechanism using homogeneous catalysts whose rate law is known in some detail. The following illustrates our method and first results.

The mechanism of catalysis by chlorotris(triphenylphosphine)rhodium(I) (2) in benzene can be represented approximately by Scheme I.[5,6] Relative to the rate limiting step,
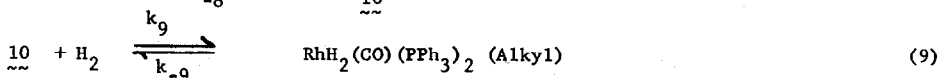
$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3 \qquad (1)$$
$$\underset{\sim}{2} \qquad\qquad\qquad \underset{\sim}{3}$$

$$\underset{\sim}{3} + H_2 \rightleftharpoons RhH_2Cl(PPh_3)_2 \qquad (2)$$
$$\underset{\sim}{4}$$

$$\underset{\sim}{4} + \ce{>C=C<} \rightleftharpoons RhH_2Cl(PPh_3)_2(\ce{>C=C<}) \qquad (3)$$
$$\underset{\sim}{5}$$

$$\underset{\sim}{5} \longrightarrow Alkane + \underset{\sim}{3} \qquad (4)$$

Scheme I

reactions 1 and 2 are rapid and reversible as is, apparently, the formation of the complex 5 (5 may exist in isomeric forms).[6] The observed rate law shows that the transition state of the rate controlling step also has this composition but it offers no help in deciding whether the formation of a π-complex (isomeric with the most stable form of 5), the isomerization of 5 to 6, or the further transformation of 6 to alkane and 3, is rate limiting

$$RhH_2Cl(PPh_3)_2 \quad (\ce{>C=C<}) \quad \rightleftharpoons \quad RhHCl(PPh_3)_2(Alkyl-) \qquad (5)$$

5   6

$$6 \quad \longrightarrow \quad RhCl(PPh_3)_2 + Alkane \qquad (6)$$

Increasing the pressure of hydrogen will not affect the relative rate of reactions 3, 4, 5, or 6 and, if one of these is the rate controlling step at low hydrogen pressures, it will continue to be at high pressure. Accordingly, if the alkene under study is 1, the ratio of saturated stereoisomers (cis/trans) which is produced should be and is independent of pressure (Fig. 1, curve II). However the actual ratio depends upon which elementary reaction is rate controlling. Guided by our analysis of the stereochemistry of hydrogenation of 1 over PtO_2,[2] we propose that the observed ratio of about two is characteristic of the association of 1 with the catalyst i.e. the rate controlling step is the formation of an isomer of 5 which is rapidly transformed to the products.[2] This conclusion is consistent with the small, possible inverse, kinetic hydrogen isotope effect which has been reported for catalysis by 2.[5a,7,8]

The hydrogenation of 1 catalyzed by hydridocarbonyltris(triphenylphosphine)rhodium(I) (7) proceeds by a different mechanism.[9] Scheme II is consistent with the observed rate law

$$RhH(CO)(PPh_3)_2 + \ce{>C=C<} \quad \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \quad RhH(CO)(PPh_3)_2 \quad (\ce{>C=C<}) \qquad (7)$$

8   9

$$9 \quad \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \quad Rh(CO)(PPh_3)_2 (Alkyl) \qquad (8)$$

                                         10

$$10 + H_2 \quad \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \quad RhH_2(CO)(PPh_3)_2 (Alkyl) \qquad (9)$$

$$11 \quad \overset{fast}{\longrightarrow} \quad 8 + Alkane \qquad (10)$$
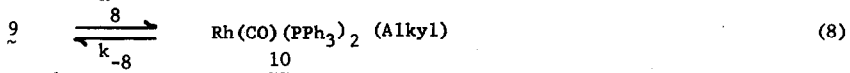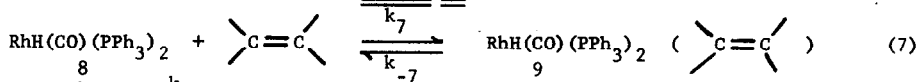
Scheme II

(first order in alkene and in hydrogen). In this scheme, hydridocarbonylbis(triphenylphosphine)rhodium(I) (8) which is formed reversibly from 7, can be considered to be the catalyst. Reaction 9, the oxidative addition of hydrogen to the square planar complex 10, is apparently the rate limiting step at ordinary pressures of hydrogen; the preceding reactions are comparatively fast and reversible.

If this mechanism is correct then 1 should yield mainly the trans isomer.[2,3] Furthermore, increasing the pressure sufficiently will alter the rate of 9 so that either reaction

7 or 8 becomes rate controlling and accordingly the cis/trans ratio should change to a limit-

ing value, (cis/trans)$_\infty$, characteristic either of the formation of the π-complex, 9, or of

the alkyl rhodium complex 10. The ratios of saturated products obtained over a wide range of

pressure (0.5-40 atm) are shown in Fig. 1.[10] Curves III and IV are computed from the re-

lationship (cis/trans) = (cis/trans)$_\infty$ · ([H$_2$] + α) / ([H$_2$]+ β) which is easily derived
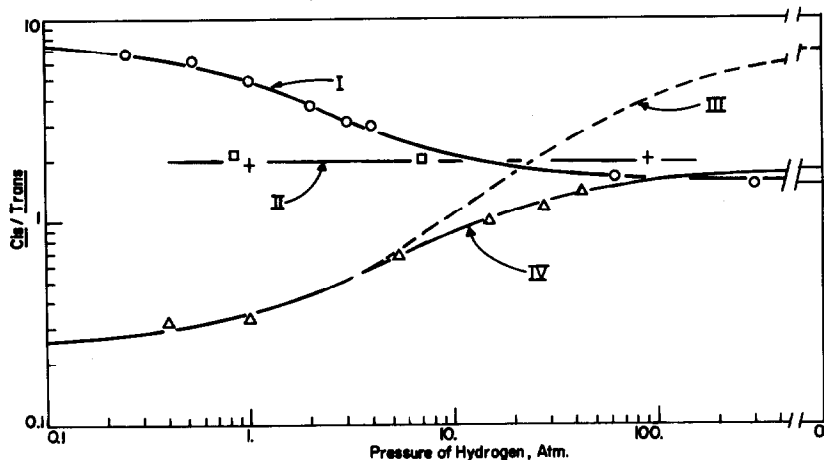

Figure 1. Observed and/or postulated relationships between the pressure of hydrogen and the
ratio of cis to trans isomers formed from 1 due to the action of different cat-
alysts: I, PtO$_2$, (ref. 2); II, Cl(PPh$_3$)$_3$Rh(I); III, Scheme IIA; IV, Scheme IIB.
Data points are represented by O (ref.2), + (ref. 11a), $\triangle$ and □ this report.

from the mechanistic Scheme II.[11] The constants α and β are ratios of rate constants, either

(k$_{-8}$/k$_9$)$_{cis}$ and (k$_{-8}$/k$_9$)$_{trans}$ or (k$_{-7}$/K$_8$k$_9$)$_{cis}$ and (k$_{-7}$/K$_8$k$_9$)$_{trans}$ depending upon whether the

rate controlling step changes from (9) to (8) (Scheme IIA) or from (9) to (7) (Scheme IIB)

respectively. If the first condition applies, the limiting high pressure value of the ratio,

(cis/trans)$_\infty$, should be about seven; if the latter, about two, these assignments being based

upon arguments we have presented before.[2-4] In this instance, the ratio is clearly close to

two (1.8) rather than seven, and accordingly the rate controlling step at high pressure is

the association of the alkene with the catalyst.[12]

One can conceive of a variety of mechanisms which will yield distinctively different re-

lationships between the cis/trans ratio and the pressure of hydrogen. In general, a change

in the ratio will occur whenever the rates of formation of the π-olefin complex, the formation

of the metal-alkyl (σ-complex), and the reaction of the latter with hydrogen, exhibit differ-

ent orders with respect to hydrogen. The observed ratio will depend upon which step is

product controlling, however measurements over a wide range of pressure are required to de-
termine that a particular stereochemical result corresponds to a limiting rather than an
intermediate value of the ratio.

We believe stereochemical studies such as these will prove to be potent adjuncts to
kinetic and other techniques for investigating the mechanism of hydrogenations catalyzed by
transition metal complexes.

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