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Stereochemistry and the Use of H_2/D_2 Mixtures as Probes into the Mechanism of Hydrogenations Catalyzed by Cationic Rhodium(DIPHOS) Complexes[1,2]

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Abstract—The stereochemistry of the hydrogenation of 4-*tert*-butylmethylenecyclohexane (**1**) and the use of D_2 or D_2/H_2 mixtures in place of H_2 furnishes evidence that hydrogenations using the catalyst precursor $[Rh(DIPHOS)(COD)]^+BF_4^-$ proceed via more than one mechanism. This evidence includes the effect of changes in pressure and added triethylamine upon the kinetics and isomerization of **1**, as well as the distribution of the added deuterium in the products of the reaction of **1** or norbornene with either D_2 or H_2/D_2 mixtures. That an alkene necessarily causes the equilibration of H_2/D_2 mixtures, although it need not involve any of the alkene's hydrogen atoms (e.g., norbornene), provides a clue to the process by which the mononuclear mechanism proposed by Halpern, which is dominant near one atmosphere of H_2, merges into another with increasing pressure. It has been proposed that the cationic complex $[Rh(DIPHOS)S_2]^+$ is transformed in the presence of an alkene and hydrogen into a binuclear hydrido complex, such as those described by Sivak and Muetterties (1979) and Fryzuk (1982), which represent a far more active catalyst than its mononuclear precursor. Such an intermediate should readily catalyze the H_2–D_2 equilibration and the isomerization of an alkene in the presence of D_2 without necessarily introducing deuterium into the product.

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In developing stereochemistry as a probe into the mechanisms of catalytic hydrogenation, we have hydrogenated 4-*tert*-butylmethylenecyclohexane (**1**) using several complexes of rhodium as catalysts [1–3]. The complexes $ClRh(PPh_3)_3$ and $HRh(CO)(PPh_3)_3$ or $HRh(PPh_3)_4$, representatives, respectively, of dihydride and monohydride mononuclear alkene hydrogenation catalysts [4], gave results consistent with their generally accepted mechanisms [5–27]; the cationic catalyst derived from $[Rh(DIPHOS)(COD)]^+BF_4^-$, where DIPHOS represents 1,2-bis(diphenylphosphino)ethane and COD refers to 1,5-cyclooctadiene, does not provide such consistent results [19–23]. The effect of increasing the hydrogen pressure upon the rate of hydrogenation and isomerization of **1** together with the results of experiments using D_2 or H_2–D_2 mixtures in place of H_2 indicates that, although the postulated mononuclear reaction path is dominant at relatively low pressures [19–23], another mechanism is important for these unsaturated hydrocarbons under ordinary conditions (30°C, 1 atm) and is dominant at higher pressures.

Effect of pressure on the hydrogenation stereochemistry of 4-*tert*-butylmethylenecyclohexane (1). Our first use of **1** in a stereochemical study of mechanism showed that, over reduced platinum oxide [33, 34], a high ratio of *cis* to *trans* saturated products (~7) is obtained at pressures below one atmosphere, but the ratio falls to a limiting value of about two at 80 atm. This result indicates a change in product and, probably, the rate-limiting process and was interpreted in terms of the Horiuti–Polanyi mechanism [35].

The stereochemistry is more reliably related to this mechanism when soluble catalysts are used because of the greater ease of relating the kinetics to the mechanism in homogeneous compared to heterogeneous systems. If $ClRh(PPh_3)_3$ is the precatalyst, the ratio *cis*/*trans* is independent of the pressure and corresponds to the association of the alkene with a dihydride complex as deduced from the kinetics [2]. When $HRh(PPh_3)_4$ is used, the ratio is a function of pressure (*cis*/*trans* ratio increases with pressure to a limiting value) paralleling its effect upon the reaction rate [3]. In this instance, the product and rate-controlling processes are presumed to be the same and involve the addition of dihydrogen to an alkylrhodium complex in the low-pressure range but changes into an association of the alkene with a monohydride complex at high pressures.

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The cationic rhodium(DIPHOS) complex, $[Rh(DIPHOS)S_2]^+BF_4^-$, is expected to show a different relationship between pressure and the *cis*/*trans* ratio if the reaction proceeds according to the Halpern mechanism, in which the association of the alkene rhodium complex with H_2 is rate-limiting [8a]. Increasing the pressure should shift the rate-limiting reaction to the formation of the alkene complex, a process of lower stereospecificity than the formation of the hydridoalkyl intermediate, and, therefore, lower the *cis*/*trans* ratio [33, 34]. Such an effect of pressure has been observed in the asymmetric catalytic hydrogenation of prochiral eneamides and other negatively substituted alkenes when chiral cationic rhodium complexes containing chelating bis(tertiaryphosphine) ligands have been used as catalysts [30, 36–39]. A detailed study of the asymmetric hydrogenation of methyl-(Z)-α-acetamidocinnamate catalyzed by a cationic rhodium complex containing a chiral chelating diphosphine ligand illustrates how variation in hydrogen pressure can affect the stereoselectivity of the reduction [28]. The results of the present study, however, are not in accord with the Halpern mechanism. The effect of increasing the hydrogen pressure or the introduction of its tertiary alkyl amine, triethylamine, upon the rate of hydrogenation and the isomerization of **1**, together with the results of experiments using D_2 or D_2/H_2 mixtures in place of H_2 with norbornene **5**, as well as alkene **1**, indicate that, although Halpern's mononuclear reaction path is dominant for these unsaturated hydrocarbons in methanol at relatively low pressures, another mechanism is significant under ordinary conditions (15°C, 1 atm) and is dominant at higher pressures.

EXPERIMENTAL

Materials. The unsaturated hydrocarbons 4-*tert*-butylmethylenecyclohexane (**1**), 1-methyl-4-*tert*-butylcyclohexene (**4**), norbornadiene, NOR (Aldrich), and 1,5-cyclooctadiene, COD (Columbia Carbon Co.) were distilled from metallic potassium under nitrogen before use. Methanol (Fisher Scientific Co.) was distilled from Mg under nitrogen. Schlenk tube techniques were used to prepare several rhodium complexes from rhodium chloride trihydrate and corresponding ligands: norbornadienerhodium(I) chloride, [Rh(NOR)Cl] [40], cyclooctadienerhodium(I) chloride, $[Rh(COD)Cl]_2$ [40], 1,2-bis(diphenylphosphinoethane)norbornadienerhodium(I) tetrafluoroborate $[Rh(DIPHOS)(NOR)]^+BF_4^-$ [28], and 1,2-bis(diphenylphosphinoethane)cycloocta-1,5-dienerhodium(I) tetrafluoroborate $[Rh(DIPHOS)(COD)]^+BF_4^-$ [13].

Procedure. 4-*tert*-Butylmethylenecyclohexane was hydrogenated in a stirred, high-pressure autoclave (Autoclave Engineers, Inc., Bench Model ABP-300) at a stirring speed of 500 rpm. The reaction temperature was controlled at 30.0 ± 0.1°C. A weighed portion of the catalyst precursor $[Rh(DIPHOS)(Diene)]^+BF_4^-$ 31.5 ± 0.5 mg was placed in the reaction vessel. The system was evacuated and filled with nitrogen three times, followed by flushing with hydrogen. Freshly distilled methanol (55 mL) and 4-*tert*-butylmethylenecyclohexane (0.25 mL) were introduced via syringe into the vessel through a small temporary opening against a stream of hydrogen. Samples for GLC analysis were removed at intervals through a sampling tube and immediately quenched with an equal volume of 10% DIPHOS in benzene solution. The distribution of reactants and products was determined with a Hewlett-Packard 5720A chromatograph (flame ionization detector) attached to a Varian Aerograph 485 Digital Integrator, using a 0.3 cm × 4.5 m 10% Carbowax 750 on 80/100 mesh Chromosorb W column.

Deuterations and H_2/D_2 addition and exchange reactions, which were conducted at a low pressure (ca. 1 atm), were carried out in an apparatus as described previously [14].

Mass spectra of reactants and products. Quenched samples intended for MS analysis were added to two volumes of water. The resulting mixture was extracted with pentane (3 × 10 ml), and the pentane solution was dried over $MgSO_4$. The extract was concentrated to about 2 ml and then separated on a Varian Aerograph Model 90-P gas chromatograph using an 0.9 cm × 5.4 m column of 30% Carbowax 1000 on 60/80 mesh Chromosorb R. The samples were collected in tubes, which could be attached to the inlet of the mass spectrometer, a Hitachi Perkin-Elmer RMU-6E. The distribution of the various deuteromolecules was determined from the parent ion (P^+) peaks after a correction had been completed for naturally occurring ^{13}C and ^2H (ionization voltage, 8 eV) [20].

RESULTS

Stereochemistry. Using as catalyst precursor $[Rh(DIPHOS)(NOR)]^+BF_4^-$ in methanol, the ratio of *cis*- to *trans*-saturated stereoisomers (**2** and **3**) obtained upon hydrogenating 4-*tert*-butylmethylenecyclohexane (**1**) increases from 0.7 at 1.24 atm to 2.5 at 69 atm, the greatest change occurring below 2 atm (figure). Little, if any, of the *trans*-isomer is formed via the isomerization of **1** to **4**, although the hydrogenation of **4** yields mainly the *trans*-product **3**. The rate of hydrogenating the isomeric alkene **4** is much less than the rate at which **1** forms the *trans*-product (0.9% as fast at 3.0 atm, 3.5% as fast at 69 atm).

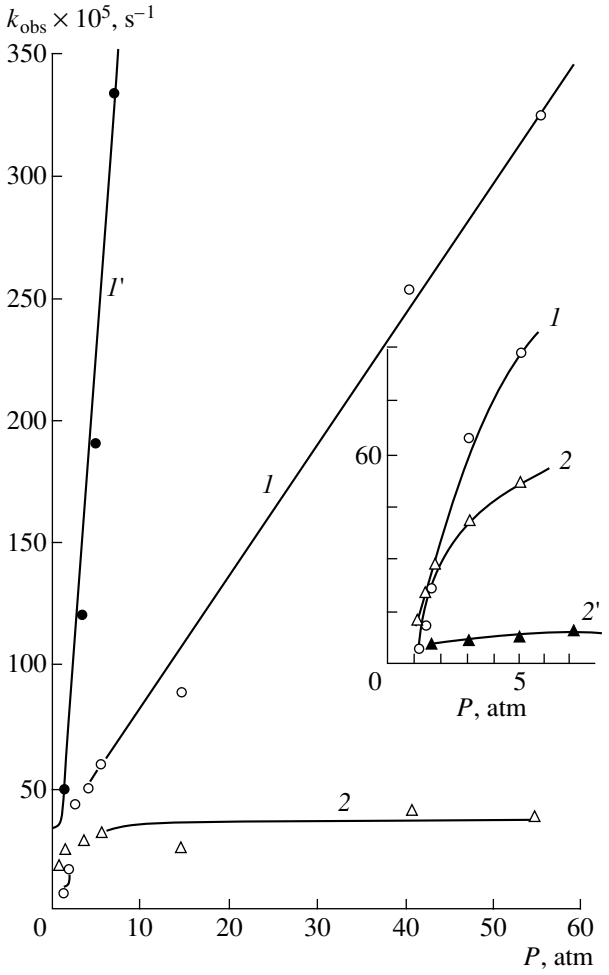
Effect of some acids and bases. As in the reports on the hydrogenation of prochiral eneamino acids (or their derivatives) catalyzed by bidentate phosphine rhodium cationic species, the stereochemistry as well as the rate of hydrogenation of alkene **1** can be altered by various additives (Table 1) [42, 43]. The addition of triethylamine enhances the initial rate of hydrogenation and the stereospecificity and depresses the rate of isomer-

ization; with relatively large amounts of amine, the stereospecificity is somewhat less, and part of the alkene remains unconverted, the amount depending upon the amount of amine added. In contrast, an acid depresses the rate of hydrogenation, increases the rate of isomerization, and lowers the *cis*/*trans* ratio in the product. Small amounts of water do not affect appreciably either the reaction rate or the stereochemistry. In comparison, pyridine and its derivatives depress the rate of addition and isomerization.

Kinetics. The effect of the hydrogen pressure upon the apparent first-order rate constants of hydrogenating **1** in methanol (k_H) exhibits the complex relationship shown in Fig. 1. The rate law appears to have a functional dependence on the pressure of dihydrogen, in which the rate increases linearly with the pressure at both low and at high pressures, with an intermediate region in which the rate is greater than first order in the pressure. The rate constant of isomerization (k_I) is also a function of the hydrogen pressure, accompanying the increase in k_H until isomerization approaches a limiting value at about 3–5 atm.

As noted in Table 1, in experiments conducted under 3 atm of H_2, the addition of triethylamine (Et_3N) to the methanolic solution of the cationic complex affects the initial rates of hydrogenation and isomerization of **1** but not in direct proportion to the amount added; the trend is towards an increase in the rate of hydrogenation and a decrease in the rate of isomerization. At a fixed concentration of triethylamine (3×10^{-3} M), the rate of hydrogenation is proportional to the hydrogen pressure and appears to extrapolate to the origin. Under these conditions, the rate of isomerization is much less affected by the increase in pressure (Fig. 1) and appears to go through a maximum, because little of the isomeric alkene is formed at 18 atm. In the lower pressure range, the rate of isomerization increases with the hydrogen pressure but becomes independent of the pressure above about 3–5 atm.

The distribution of deuterium in the products. The reaction of D_2 (Table 2) or D_2/H_2 mixtures (Table 3) with the alkenes resulted in complicated distribution patterns of D (H) in the products, which indicates the involvement of both addition and exchange processes. With D_2 at 1 atm, the initial product of isomerization, alkene **4**, contains much less than one deuterium atom per molecule. As the reaction proceeds, the distributions of deuterium in the recovered alkene **1** approach the distribution in its isomer, **4**. The addition of acid (70% $HClO_4$) has little effect, but triethylamine appears to enhance the rate of exchange. The distribution of deuterium in the product of addition to 4-*tert*-butylmethylenecyclohexane (**1**) indicates that the addition is in part direct and in part randomized. Similar conclusions are obtained from an inspection of Table 3, in which mixtures of H_2 and D_2 were used at ca. 5 atm and 30°C. Under these conditions, the addition of $H_2(D_2)$ is largely randomized even with norbornene. At a lower temperature (15°C) and pressure, much of the addition product retains the molecular identity of the H_2–D_2 used [4].



Effect of the pressure of hydrogen on the rate constants of hydrogenation (k_H) (*1*, *1'*) and isomerization (k_I) (*2*, *2'*) during the hydrogenation of 4-*tert*-butylmethylenecyclohexane with $[Rh(Diphos)(Nor)]^+BF_4^-$ in methanol. The scale of the axes in the insert has been expanded to show the data at a low pressure of hydrogen. (*1*, *2*) Without and (*1'*, *2'*) upon the addition of Et_3N ($[Et_3N] = 3 \times 10^{-3}$ M).

The equilibration of H_2–D_2 accompanies the addition of $H_2(D_2)$ to either 4-*tert*-butylmethylenecyclohexane or norbornene. The equilibration does not necessarily involve the exchange of deuterium for the hydrogen in the alkene, because no deuterium is found in the recovered norbornene. No HD is formed if a mixture of H_2 and D_2 is allowed contact with a solution (methanol, tetrahydrofuran, or benzene) of the cationic complex for 24 h at room temperature.

Towards an understanding of the deuterium distribution patterns, the method of Smith and Burwell was used to compute the distributions from a relatively simple model of the reaction [44]. The method assumes

Table 1. Effect of additives on the hydrogenation of 4-*tert*-butylmethylenecyclohexane **1**; catalyst precursor $[Rh(DIPHOS)(NOR)]^+BF_4^-$ in methanol[a]

Additive	*cis*, %	Rate × 10^4, s^{-1}	
		k_H	k_I
None	57.6	4.8	1.7
70%$HClO_4$ (4 μl)	43.2	2.3	1.9
H_2O (20 μl)	62.1	2.6	1.2
Qu[b] (20 mg)	74.0	9.7	0.24
Py[c] (20 μl)	76.8	0.56	0.039
2-F-py[d] (20 μl)	73.5	1.7	0.14
Me_3Py[e] (20 μl)	74.4	3.6	0.19
Et_3N (3 μl)	78.6	11.4	2.1
Et_3N (10 μl)	81.0	11.8	0.40
Et_3N (20 μl)[f]	82.3	11.8	0.34
Et_3N (100 μl)	84.1	15.6	0.31
Et_3N (200 μl)	84.7	18.3	0.30
Et_3N (300 μl)[g]	81.1	29	0.20
Et_3N (500 μl)[h]	79.2	62	0.01

[a] $[[Rh(DIPHOS)(NOR)]^+BF_4^-] = 8.0 \times 10^{-4}$ M, [alkene **1**] = 2.50×10^{-2} M in 55 mL MeOH and $T = 30°C$ at 3.04 atm hydrogen pressure.

[b] Quinuclidine.

[c] Pyridine.

[d] 2-Fluoropyridine.

[e] 2,4,6-Trimethylpyridine.

[f] Estimated to be 3×10^{-3} M.

[g] 2.0% alkene **1** remained after reaction virtually ceased.

[h] 8.5% alkene **1** remained when reaction ceased.

that the distribution is a function of the relative probability that D or H will be attached to a particular position (a/b), the mole fraction of the product, which has n positions in the set (N_n), and the distribution function for each set. If the distribution is random, then the fraction of the set that contains m deuterium atoms and s hydrogen atoms ($m + s = n$) is

$$dm(n) = \frac{(a/b)^m n!}{(1 + a/b)^n m! s!}. \quad (1)$$

Other distribution functions may be considered; for example, if the molecular identity of the $H_2(D_2)$ is retained in the product, then the relative concentrations of $H_2(D_2)$ in the gas phase and kinetic isotopic effects determine the distribution function, the ratio of alkane-d_0 to alkane-d_2. In the use of this method of analysis, the parameter a/b and the mole fractions of the sets (less one) are adjusted in order to obtain the best fit of the calculated to the observed distributions (d_0, d_1, d_2) and the average deuterium content. In the analysis of the distributions obtained from 4-*tert*-butylmethylenecyclohexane, the number of sets was deliberately limited to two sets that contain randomized distributions at four and two positions (N_4 and N_2) and one set that corresponds to the addition of $H_2(D_2)$ without isotopic mixing (N_A).

The distributions in the products obtained from norbornene are fitted using a randomized distribution at two positions (N_2) or addition without randomization (N_A). The results of this treatment of data are given in Tables 4–6.

DISCUSSION

Stereochemistry. The effect of pressure on the ratio of *cis*/*trans* saturated isomers, which was obtained from the hydrogenation of 4-*tert*-butylmethylenecyclohexane catalyzed by the diphosrhodium complex, did not meet the expectations that we had formed based upon the mechanism of catalysis proposed by Halpern and coworkers [33, 34]. We expected that the rate-controlling addition of dihydrogen to an alkene complex, at dihydrogen pressures near one atmosphere, would yield a higher proportion of the *cis* isomer than would the addition of dihydrogen to an alkyl intermediate, the apparent rate-controlling step for hydrogenations catalyzed by $HRhL_4$, under these conditions [2, 3]. An increase in the pressure, enough to shift the rate-limiting step to the formation of the alkene–rhodium complex, should lower the *cis*/*trans* ratio for the diphosrhodium catalyzed reaction rather than raise it as occurs using $HRhL_4$. Indeed, the effect upon the stereochemistry, as well as the observed isomerization of the alkene, suggested the action of a monohydride complex. However, experiments with D_2 and the observed kinetics point to a more likely catalytic species, as well as to its mode of formation.

H_2/D_2 exchange. The reaction $H_2 + D_2 \longrightarrow 2HD$ is catalyzed by $[(DIPHOS)RhS_2]^+$ in methanol when an alkene is present; however, the exchange does not necessarily involve any of the latter's hydrogen atoms. This is shown by the lack of deuterium in the recovered norbornene and the presence of no more than two deuterium atoms per molecule in the addition product, norbornane, when D_2 or H_2–D_2 mixtures are used [8]. The use of norbornene in this experiment was dictated by the known mechanism for the *syn* addition of Rh–H to a double bond or its reverse, the *syn* elimination of Rh–H [2, 4]. The result demonstrates that an alkene might involve the formation of the complex species, which, in turn, is the catalyst for the H_2–D_2–HD equilibration.

Isomerization. The isomerization of 4-*tert*-butylmethylenecyclohexane in the presence of D_2 to a product that contains much less than one atom of deuterium per molecule cannot be due to the decomposition of an alkyl intermediate of the Halpern mechanism. This argument has been made by Detellier *et al*. [45] and also by Koenig and Knowles [46] to account for a sim-

Table 2. Deuterium distributions in reactants (R) and products (P) of the addition of D_2 to 4-*tert*-butylmethylenecyclohexane **1**[a]

Additive	HD (%)	R, P (%)	d_0	d_1	d_2	d_3	d_4	$d_{average}$
None	0.9	Sat[b] (5.4)	–	11.8	76.3	11.3	0.6	2.01
		Sub (90.9)	95.9	2.4	1.7	–	–	0.06
		Iso (3.7)	88.3	7.0	3.5	1.4	–	0.17
None	4.1	Sat (27.9)	–	14.2	70.0	14.4	1.4	2.03
		Sub (54.2)	76.7	18.3	4.6	0.4	–	0.29
		Iso (17.9)	74.5	18.9	5.7	0.8	–	0.32
$HClO_4$[c]	6.1	Sat (24.0)	–	22.2	60.8	14.7	2.3	1.93
		Sub (40.3)	85.7	11.8	2.5	–	–	0.17
		Iso (35.7)	87.2	8.7	3.8	0.3	–	0.17
Et_3N[d]	10.4	Sat (69.2)	–	8.2	55.0	26.6	8.9[e]	2.40
		Sub (19.3)	39.0	27.1	21.8	6.5	4.5[e]	1.14
		Iso (11.5)	47.1	24.1	15.6	8.9	2.8[e]	0.98

[a] $[Rh(DIPHOS)(NBD)]^+BF_4^-$ = 8.0×10^{-4} M, [**1**] = 2.5×10^{-2} M.

[b] Saturated product (Sat), unsaturated substrate (Sub), and 4-*tert*-butyl-1-methylcyclohexene (Iso).

[c] 6 μl of 70% $HClO_4$ added to reaction mixture.

[d] 5 μl of Et_3N added.

[e] Significant amounts of d_5 were observed in this exp.: Sat (1.3), Sub (1.1), Iso (0.9).

ilar deficiency of deuterium in the product of the *E–Z* isomerization of an α-acylaminocinnamic acid that is formed in the presence of D_2 and a cationic rhodium complex. As alternatives, they proposed the insertion of rhodium into a C–H or N–H bond of the unsaturated reactant–rhodium complex, but these mechanisms involve functional or phenyl groups, which are absent in the unsaturated hydrocarbons used in this study. The dissociative mechanism of Koenig and Knowles does not adequately explain why H_2 or D_2 is required for the isomerization, which occurs in ethanol or THF but not in benzene. However, a complex hydride that is able to catalyze the exchange between D_2 and H_2 should also catalyze the isomerization of an alkene. The deficiency of deuterium in the isomer formed from **1** and D_2 would result if the rate of isomerization were faster than the rate of exchange with D_2.

The isomerization of allylamines to enamines is catalyzed by Rh(I)DIPHOS complexes in the absence of hydrogen and involves a 1,3-hydrogen migration, as demonstrated by deuterium labeling experiments [47]. If this mechanism occurs in the presence of D_2, it could account for the small amount of deuterium in the product of isomerization. However, the rate of isomerization of **1** is affected by hydrogen, which indicates that catalysis by a rhodium hydride species is a faster process.

Kinetics. The effect of an increase of the hydrogen pressure (from 1 to 55 atm) upon the rate of hydrogenation of 4-*tert*-butylmethylenecyclohexane was not as expected. From 1 to 3 atm, the apparent first-order rate constant, k_H, increases more rapidly than is predicted by the first-order dependence on the hydrogen pressure of the Halpern mechanism [28–32]. Above 3–4 atm, k_H does increase linearly with pressure. A change in the dominant mechanism is indicated, presumably from the Halpern mechanism in the low-pressure range to some other at higher pressures. The change in the apparent first-order rate of isomerization, k_I, parallels that of k_H up to about 3–4 atm, where its constancy suggests that, above this pressure, both hydrogenation and isomerization involve a common intermediate, but hydrogenation requires an additional molecule of hydrogen.

Others have noted that the addition of a tertiary amine to solutions of rhodium complexes in polar solvents causes an acceleration in the rate of hydrogenation and have usually attributed the effect to the abstraction of a proton from a dihydride–rhodium complex to form a monohydride, which is a more reactive catalyst, as occurs, for example, in Eq. (2):

$$[H_2Rh(PPh_3)_2]^+ + NR_3 \rightleftharpoons HRh(PPh_3)_2 + HNR_3^+. \quad (2)$$

This example has been discussed in detail by Schrock and Osborn [48]. However, the corresponding dihydride of the cationic rhodium diphos complex is too unstable to support such a change. It catalyzes the interconversion of *ortho* and *para* hydrogen, which indicates the reversible formation of the dihydride [49–51]. More recently, the PHIP–NMR technique (PHIP, parahydrogen-induced polarization) allowed the identification of such species in the asymmetric hydrogenation [50, 51]. The possibility that more basic chelating diphosphine ligands stabilize cationic rhodium dihydrides has been

Table 3. The deuterium distribution in reactant (R) and products (P) of the addition of H_2–D_2 mixtures to 4-*tert*-butylmethylenecyclohexane **1** and norbornene

Conditions	HD(%)	R, P[a]	d_0	d_1	d_2	d_3	d_4	$d_{average}$
4-*tert*-butylmethylenecyclohexane **1**[b,c]								
1.0 atm	34.5	Sat (8.7)	34.1	44.5	19.1	2.3	–	0.90
15°C		Sub (83.5)	96.5	3.5	–	–	–	0.04
		Iso (7.8)	95.1	4.9	–	–	–	0.05
5.1 atm		Sat (9.5)	26.1	37.0	32.6	3.9	0.4	1.16
30°C	12.3	Sub (87.7)	98.1	1.9	–	–	–	0.02
		Iso (2.8)	87.9	9.9	1.7	0.5	–	0.15
5.1 atm		Sat (11.5)	28.9	36.6	26.6	6.5	1.4	1.15
30°C		Sub (76.7)	92.4	6.0	1.6	–	–	0.09
70%$HClO_4$[d,e]		Iso (11.8)	81.8	12.5	4.9	0.8	–	0.25
5.1 atm		Sat (19.6)	21.0	44.1	31.3	3.3	0.3	1.18
30°C	6.6	Sub (80.0)	89.8	7.1	3.1	–	–	0.13
Et_3N[d,e]		Iso (0.4)	80.8	11.3	5.2	2.7	–	0.30
Norbornene[f]								
1.0 atm	7.7	Sat (26.0)	43.7	13.4	42.9	–	–	0.99
15°C		Sub (74.0)	100	–	–	–	–	0.00
5.1 atm	6.5	Sat (34.3)	23.5	45.4	31.1	–	–	1.08
		Sub (65.7)	100	–	–	–	–	0.00

[a] Sat, addition product; Sub, recovered alkene; Iso, isomerized product.

[b] $[Rh(DIPHOS)(NBD)^+BF_4^-] = 8.0 \times 10^{-4}$ in 50 mL methanol.

[c] [Alkene **1**] $= 2.5 \times 10^{-2}$ M.

[d] H_2/D_2 (1.0/1.5).

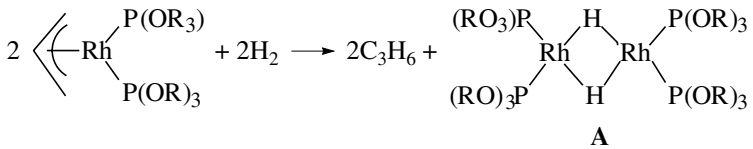
[e] 20 μl.

[f] [Norbornene] $= 5.2 \times 10^{-2}$ M, $[Rh(DIPHOS)(COD)]^+BF_4^- = 8.0 \times 10^{-4}$ M.

suggested by the isolation of complexes that appear to be derived from them [52, 54, 55]. In the presence of a large excess of triethylamine, $[Rh(DIPHOS)S_2]^+$ in methanol is converted to $Rh_2(DIPHOS)_2(OMe)_2$ [28]. At a pressure of 3 atm of H_2, small amounts of triethylamine, 0.5 to 4 mol per mole of the cationic complex, more than doubles the apparent first-order rate constant, which increases further at higher concentrations of the amine.

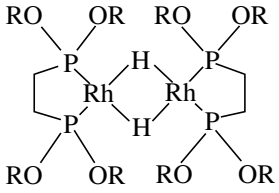
Distribution of deuterium in the addition product. The alkane that is formed initially in the presence of deuterium (1 atm) contains a mixture of molecules containing 1–4 deuterium atoms in a proportion that suggests that the addition of deuterium is in part random among four hydrogen positions but mainly constitutes the simple addition of two deuterium atoms. With increasing conversion, a fifth hydrogen position becomes involved. The randomization must occur during the period in which the alkyl moiety remains bound in the complex, because so little deuterium is found in the recovered alkene, while the alkane averages two deuterium atoms per molecule [44]. A detailed interpretation of these results follows a presentation of the mechanism that we believe best accounts for our observations.

Proposed mechanisms. We suggest that the effect of the base and hydrogen pressure in the presence of an alkene is to transform the diphosrhodium cation into a dimeric rhodium hydride of the type first described and fully characterized by Sivak and Muetterties [52]. They prepared the complexes from the reaction of allyl–rhodium–diphosphites with hydrogen at one atmosphere and showed them to be exceptionally active catalysts for the hydrogenation of simple alkenes.



A (3)

These dinuclear rhodium hydrides "…reacted, reversibly and virtually instantaneously with hydrogen…" to form tetrahydrides whose reaction with alkenes was "…virtually instantaneous at 20°C…," yielding alkanes and the dirhodium dihydride complex **A** [52]. Later, Fryzuk [29] prepared bridged dihydrides containing DIPHOS analogs via the reaction of 1,2-bis(diisoproxyphosphino)ethane(2-methylallyl)rhodium(I), $[\eta^3\text{-}(2MeC_3H_4)Rh(Dipope)]$, with dihydrogen to form $[(Dipope)RhH]_2$ (**B**) and reported on the latter's high catalytic activity for the addition of dihydrogen to 1-hexene and the competitive isomerization to internal double-bonded hexenes [29].



B

The Halpern mechanism serves as a starting point for a sequence of reactions, leading to a dinuclear rhodium(DIPHOS) hydride analog of the above complexes. The key step is the removal of a proton from the hydrido–alkyl intermediate by a base. The resulting alkyl intermediate can add dihydrogen or undergo beta elimination to proceed along a path to the rhodium(DIPHOS) hydride complex that dimerizes. The observed effect of hydrogen pressure on the rates of hydrogen addition and the isomerization of the methylenecyclohexane (**1**) in methanol without added triethylamine indicates that the hydrogenation of the alkyl intermediate is the faster of these processes. The effect of added triethylamine indicates that the abstraction of a proton is an important step in forming the catalytically active complex.

We are not able to offer a direct comparison of the catalytic activity of the $[Rh(DIPHOS)S_2]^+$ based solutions we have described with Fryzuk's dinuclear complex. He reported that the latter complex catalyzed the hydrogenation of 1-hexene at 22°C and 1 atm of hydrogen with a turnover frequency of about 700 h^{-1}; isomerization was faster, to *trans*-2-hexene (about 1000 h^{-1}) and *cis*-2-hexene (about 300 h^{-1}) [57]. In the absence of hydrogen, isomerization was slow (about 5 h^{-1}). His experiments were conducted in neat 1-hexene (ratio of substrate to dimer, 1500–2000 : 1); ours were done with dilute solutions of both the DIPHOS complex and the alkene **1**, a 1,1-disubstituted alkene. The apparent first-order rate constants k_H can be converted to initial turnover numbers by multiplying the rate constant by the initial concentration of alkene **1**. The turnover frequency can be corrected for hydrogen pressure, but the temperature effect was not determined. Thus, at 30°C and 3 atm, the addition of small amounts of triethylamine increased k_H from 11.4×10^{-4} to 62×10^{-4} s^{-1}, which corresponds to a turnover frequency of 128 and 698 h^{-1}, respectively.

Table 4. Computed distribution patterns for the addition of D_2 to 4-*tert*-butylmethylenecyclohexane

Conditions[a], conversion, %	A		B	
	5.4		24.0	
	Obsd.	Calcd.	Obsd.	Calcd.
d_0%	0	2.88	0	1.2
d_1	11.8	11.5	22.2	22.2
d_2	76.3	17.3 (54.0)[b]	60.8	26.6 (34.0)[b]
d_3	11.3	11.5	14.7	14.2
d_4	0.6	2.88	2.3	1.8
d_{ave}	2.01	200	1.96	1.93
N_4 [a/b][c]	–	0.46 [1.00]	–	0.66 [0.80]
N_A [a/b]	–	0.54 [∞]	–	0.34 [∞][d]

[a] Catalyst = $[Rh(DIPHOS)S_2]^+$ in methanol, D_2 (1 atm), 15°C; A, no additives; B, 6 μl 70% $HClO_4$.

[b] Parenthesis indicates fraction of direct addition of D_2.

[c] Brackets indicate the computed ratio, D/H for N_A and the assumed ratio if only D_2 is present.

[d] The direct addition of HD, which has been formed at this stage of the reaction, would tend to increase the fraction N_A relative to N_4.

A detailed kinetic study was not attempted; however, the effect of pressure upon the rate of the hydrogenation and isomerization of alkene **1** in methanol and the effect of triethylamine upon these rates are consistent with the proposal. The Halpern mechanism requires that the rate of hydrogenation be first order in the hydrogen pressure, which appears to be the case at pressures below about 1 atm. The formation of the proposed mononuclear hydride, which dimerizes, requires a second mole of hydrogen, the latter, in methanol, accounting for the increase in rate between 1–3 atm. The rate of isomerization also increases rapidly in the same range of pressure but approaches a limiting value at a somewhat higher pressure (ca. 8 atm). With increasing pressure, the rate of hydrogenation increases in proportion to the increase in pressure corresponding to the reaction of H_2 with the alkene dinuclear dihydride complex. Triethylamine, a stronger base than methanol, increases the rate of forming the hydrido intermediate and results in a rate of hydrogenation that is first order in hydrogen and extrapolates close to the origin of the rate vs. pressure plot. Simultaneously, the rate of isomerization is lowered, which reflects the competition between the addition of hydrogen versus the dissociation of alkene from the intermediate.

The dinuclear complex mechanism of hydrogenation: interpretation of results using deuterium or hydrogen–deuterium mixtures. The mechanism that explains the H_2–D_2 equilibration occuring in solutions

Table 5. Computed distribution patterns for the addition of H_2/D_2 mixtures to 4-*tert*-butylmethylcyclohexane

Conditions[a]	A		B		C	
Conversion, %	9.5		11.5		19.6	
	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.
d_0%	26.1	17.0 (7.8)[b]	28.9	24.1 (4.8)[b]	21.0	20.4
d_1	37.0	37.0	36.6	36.6	44.1	44.7
d_2	32.6	24.6 (9.3)[b]	26.6	20.8 (5.8)[b]	31.3	30.4
d_3	3.9	3.3	6.5	5.3	3.3	4.1
d_{ave}	1.16	1.14	1.15	1.13	1.18	1.19
N_2 [a/b][c]	–	0.49 [1.09]	–	0.0	–	0.50 [1.35]
N_4 [a/b]	–	0.35 [0.49]	–	0.89 [0.43]	–	0.50 [0.45]
N_A [a/b]	–	0.16 [1.19]	–	0.11 [1.21]	–	0.0

[a] Catalyst = $[Rh(DIPHOS)S_2]^+$ (30°C, $H_2 : D_2 = 1 : 1.5$, $P = 5.08$ atm). A, no additive; B, 20 μl 70% $HClO_4$; C, 20 μl Et_3N.
[b] Parenthesis indicates contribution of direct addition of H_2 (D_2).
[c] Brackets are computed ratios D/H for the particular fraction of addition product.

of the rhodium–diphos cationic complex and an alkene also explains why, in the presence of deuterium, the product of the isomerization of the alkene contains so little deuterium. According to this mechanism, the D_2 must compete with alkene for a coordination site on the dinuclear hydride. The amount of deuterium in the formed isomeric alkene should depend upon the relative rates of these competing processes.

The addition appears to be in part direct (alkane-d_2) and in part an exchange-addition, in which some of the hydrogens in the alkene have been exchanged with deuterium. It is not simply the result of the addition of D_2 to alkene, which has undergone exchange, because, at low conversions, the recovered alkene **1** contains so little deuterium (Table 2). Although the addition of small amounts of perchloric acid to the reaction medium somewhat reduces the extent of exchange, the addition of triethylamine markedly increases the rate of exchange with alkene **1** and its isomer **4** and also increases the rate at which the latter is hydrogenated. Apparently, at low conversions, the randomized distribution is limited to four positions in alkene **1**; and it is noteworthy that the relative probability of finding D or H at these positions when D_2 is used is close to unity (Table 4), which indicates that, on the average, about two hydrogen atoms of the alkene and two deuterium atoms from the deuterium gas are distributed among four positions in the saturated product. This would suggest that the hydrogen–deuterium exchange reaction within the complex (**A** or **B**) is faster than the rate at which it proceeds to alkane and the dihydrido intermediate.

Table 6. Computed distribution patterns for the addition of H_2/D_2 mixtures to norbornene

Conditions[a]	D		E	
Conversion, %	26		34	
HD, %	7.7		6.5	
	Obsd.	Calcd.	Obsd.	Calcd.
d_0	43.7	6.8 (36.9)[b]	23.5	19.4 (4.1)[b]
d_1	13.4	13.4	45.4	45.4
d_2	42.9	6.6 (36.3)[b]	31.3	26.6 (4.7)[b]
d_{ave}	0.99	0.99	1.08	1.08
N_2 [a/b][c]	–	0.27 [0.98]	–	0.9 [1.07]
N_A [a/b][c]	–	0.73 [0.98]	–	0.09 [1.15]

[a] Catalyst = $[Rh(DIPHOS)S_2]^+$. D, 15°C, $H_2 : D_2 = 1 : 1$, P = 1.0 atm; E, 30°C, $H_2 : D_2 = 1 : 1.5$, $P = 5.08$ atm.
[b] Parenthesis indicates contribution of direct addition of H_2 (D_2).
[c] Brackets indicate computed ratios D/H for the particular fraction of addition N_2 or N_A.

Similar conclusions may be obtained from an inspection of Table 5, which compares results of experiments in which H_2–D_2 mixtures were used. The results indicate that, in the methanol solvent at 5 atm, some direct addition without a scrambling of the isotopes (N_A) persists, although triethylamine appears to eliminate this fraction. To obtain a satisfactory fit with the observed distributions requires a combination of two randomized distributions, which involve two (N_2) and four (N_4) sites in the product molecule. Curiously, these two sets of sites are associated with different probabilities of gaining a deuterium rather than a hydrogen atom (a/b), the value for the N_4 set (0.43–0.45) being appreciably less than for the N_2 set (1.30–1.35). Again, the set of four (N_4) has a lower probability of gaining D, perhaps because, on the average, two hydrogen atoms from the alkene are mixed with the one molecule of H_2 and 1.5 molecules of D_2. The resulting formal ratio of D/H—that of 3.0/4.0—would be lowered further by a kinetic isotope effect in favor of the addition of hydrogen.

The set of two (N_2) is associated with a higher probability of introducing deuterium in the product (*a*/*b* 1.30–1.35) and corresponds to an addition that does not involve any of the alkene hydrogens. This is consistent with the results with norbornene, in which only addition to two positions occurs (Table 6). Interestingly, with norbornene, both direct (N_A) and randomized (N_2) addition is observed at a higher pressure and temperature, over 90% of the addition being random.

An obvious explanation for the two randomized distributions of D/H in the saturated product of **1** is that they correspond to alternative orientations in the addition of Rh–D to the double bond [23]. The attachment of the metal to the methylene group in the alkyl intermediate can lead only to addition at two positions with no exchange; the alternative orientation in the intermediate leads to exchanged alkene **1**, isomerization to **4**, and exchange-addition involving hydrogen atoms in the ring.

CONCLUSIONS

The proposed mechanism accounts well for the results of this study and explains other reported observations relevant to the mechanism of the isomerization of alkenes and electronegative group substituted ethylenes. Apparently, the transformation of $[Rh(DIPHOS)S_2]^+$ to a dimeric hydride occurs more readily when unsaturated hydrocarbons are hydrogenated than when alpha amido cinnamates are the substrates. Unsaturated hydrocarbons are much more weakly bound to rhodium in the cationic complexes than are the more negatively substituted olefinic compounds, and, undoubtedly, other important elementary processes, which determine the major reaction paths traversed, must differ in relative rates. The objective of this study was to observe phenomena of a mechanistically well-defined catalytic process, which can be used to better interpret the mechanisms of supported metal catalysis, but our search led to an unsuspected mechanism—one that is likely to be more relevant for this purpose [56–59].

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