THERMODYNAMICS OF HOMOGENEOUS HYDROGENATION PART IV. SYNTHESIS, CHARACTERIZATION AND HYDRIDE FORMATION OF THE Pd(II) COMPLEXES CHLORO-BIS(DIPHENYL-PHOSPHINOETHYL)AMINEPALLADIUM(II) CHLORIDE AND CHLORO-TRIS(DIPHENYLPHOSPHINOETHYL)AMINEPALLADIUM(II) CHLORIDE AND THEIR CATALYSIS IN THE HOMOGENEOUS HYDROGENATION OF CYCLOHEXENE

M. M. TAQUI KHAN*

Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002 (India)

BADAR TAQUI KHAN and SAFIA BEGUM

Department of Chemistry, Osmania University, Hyderabad (A.P.) (India)

(Received June 28, 1987; accepted December 18, 1987)

Summary

The synthesis and characterization of [Pd(DPEA)Cl]Cl 1 and [Pd-(TPEA)Cl]Cl 2, where DPEA and TPEA are bis(2-diphenylphosphinoethyl)amine $NH(CH_2CH_2PPh_2)_2$ and tris(2-diphenylphosphinoethyl)amine N(CH₂CH₂PPh₂)₃ respectively, is reported. The catalytic activity of 1 and 2 in the homogeneous hydrogenation of cyclohexene over the temperature range 10-40 °C and 0.4 to 1 atm of hydrogen partial pressure has been investigated. The rate of hydrogenation of cyclohexene catalyzed by 1 and 2is found to be first order with respect to the catalyst, fractional order with respect to the substrate concentration and independent of H_2 partial pressure. A suitable mechanistic pathway has been proposed in which the catalysts 1 and 2 activate molecular hydrogen by forming hydrido species [Pd(DPEA)(H)]⁺ 1a and [Pd(TPEA)(H)]⁺ 2a, respectively. The formation of an unusual Pd(IV) trihydrido intermediate, $[Pd(DPEA)(H)_3]^+$ 1b and the dihydride $[Pd(TPEA)(H)_2]^{2+}$ 2b by an oxidative addition of H₂ of [Pd(DPEA)(H)]⁺ 1a and 2, respectively, is also reported. The hydrido species 1a and 1b. 2a and 2b were characterized by hydrido proton and ${}^{31}P{}^{1}H{}$ NMR spectra. The activation parameters ΔS^{\ddagger} and ΔH^{\ddagger} for the hydrogenation of cyclohexene catalyzed by 1 and 2, were evaluated.

Introduction

Homogeneous catalytic hydrogenation of olefins catalyzed by platinum group metal complexes has attracted considerable interest in recent years

^{*}Author to whom correspondence should be addressed.

[1-7]. We have recently synthesized platinum group metal complexes of the potential terdentate bis(2-diphenylphosphinoethyl)amine DPEA and potential tetradentate tris(2-diphenylphosphinoethyl)amine TPEA ligands containing mixed donor N, P atoms [8, 9]. The ligands have an amino group for necessary nucleophilicity and P to stabilize low-valent metal complexes through $d_{\pi}-d_{\pi}$ back-bonding factors of direct importance in homogeneous hydrogenation reactions [2].

Though kinetic and mechanistic data are available for the homogeneous hydrogenation catalyzed by Rh(I) and Ir(I) complexes [10-15], data on catalysis by Pd(II) is very scanty. Suzuki *et al.* [16] reported the hydrogenation of acetylene by PdCl₂ solubilized in CH_2Cl_2 and polyethylene glycol. The detailed kinetic parameters of the reaction were not however reported.

In this paper we report the catalytic hydrogenation of cyclohexene by bis(2-diphenylphosphinoethyl)aminepalladium(II) chloride 1 and tris-(2-diphenylphosphinoethyl)aminepalladium(II) chloride 2. In the presence of the Pd(II) complexes 1 and 2 of the terdentate and the tetradentate ligands DPEA and TPEA, respectively, the homogeneous hydrogenation of cyclohexene proceeds through the formation of monohydrido-Pd(II) and -Pd(IV) intermediates by a path independent of molecular hydrogen concentration. The palladium hydrides formed in solution from complexes 1 and 2 were characterized by ¹H and ³¹P{¹H} spectroscopy.

Experimental

Palladium(II) chloride was obtained from Strem Chemical (USA). Cyclohexene was prepared by the published procedure [6] and purified from peroxide by treatment with acidified ferrous sulphate, dried over calcium chloride and distilled under N_2 gas. All the solvents used were of AR grade and were used without further purifications. The ligand DPEA was prepared as reported [6].

Complexes 1 and 2 were characterized by elemental analysis, melting point, IR and ³¹P{¹H} spectra and conductivity measurements. The ³¹P{¹H} NMR spectra were recorded in CDCl₃ on a Jeol FX100 FT-NMR spectrometer, operating at 40.3 MHz, using a deuterium lock. For ³¹P spectra, chemical shifts are reported in δ (ppm) with respect to 85% H₃PO₄. Hydrido proton NMR spectra were recorded in CDCl₃ for 1 and CH₃CH₂OH for 2 on a Jeol FX100 spectrometer, using TMS as an external reference. The IR spectra were taken on a Nicolet Model FT-IR spectrometer.

Preparation of [PdCl(DPEA)Cl] Cl 1

DPEA·HCl 0.2 g (0.42 mmol) was dissolved [8] in benzene (40 ml) under nitrogen atmosphere. $PdCl_2(COD)$ (0.12 g, 0.42 mmol) was added to the above solution in powder form after ~0.5 h when a clear solution was obtained. The refluxing was continued until a greenish-yellow crystalline

compound separated out. The crystalline compound was cooled overnight, filtered and washed thoroughly with benzene. The compound was recrystallized from CH_2Cl_2 -n-hexane mixture. Yield: 0.21 g (72%), m.p. = 248 - 245 °C, Anal. Calcd.: C, 54.3; H, 4.72; N, 2.26; Cl, 11.47%. Found: C, 53.9; H, 4.82; N, 2.4; Cl, 11.1%.

Reaction of [PdCl(DPEA)Cl] with hydrogen

Hydrogen gas was bubbled through a concentrated solution of [PdCl-(DPEA)]Cl in $CDCl_3$ in the NMR tube for 2 h and the hydrido proton and ${}^{31}P{}^{1}H$ NMR spectra recorded.

Preparation of [PdCl(TPEA)Cl]Cl 2

To a methanolic solution (15 ml) of Na_2PdCl_4 (0.11 g, 0.38 mM) was added [9] the ligand TPEA (0.25 g, 0.38 mM) dissolved in 15 ml CH₂Cl₂. The resulting reaction mixture was stirred for 5 h when a yellow precipitate was obtained on the slow addition of diethyl ether. The compound was filtered, washed with water-benzene and finally with petroleum ether. Yield: 0.24 g (75%), m.p. 203 °C, Anal. Calcd.: C, 60.4; H, 5.0; N, 1.70; Cl, 8.5%. Found: C, 60.0; H, 4.9; N, 1.68; Cl, 8.3%.

Kinetic studies

Kinetic studies of the hydrogenation of cyclohexene catalyzed by complexes 1 and 2 were made in the temperature range 10 - 40 °C. The rate of absorption of hydrogen gas was measured using a glass manometric apparatus as described in earlier communications [6, 7]. After the addition of the catalyst, the cell was evacuated and flushed with hydrogen several times to ensure that a complete hydrogen atmosphere prevailed in the reaction cell. Sufficient time was given to the experimental solution to attain equilibrium. A known concentration of cyclohexene was then added rapidly to the cell. A blank experiment under the same conditions of temperature, pressure and volume was also run simultaneously to nullify the effect of solvent vapour pressure. The concentration of substrate was in the range of 0.25 -2.5 M. The reaction was conducted with H₂ partial pressure of 0.4 - 1.0 atm.

The rate of absorption of H_2 ($-d[H_2]/dt$) was obtained from the slope of the plot of the number of moles of hydrogen absorbed versus time, as described in an earlier publication [6].

Results

Reaction of $PdCl_2(COD)$ with the ligand DPEA in CH_3OH resulted in the formation of the complex [PdCl(DPEA)]Cl 1, which is a 1:1 electrolyte in DMF. The $\nu(Pd-Cl)$ of the complex is exhibited at 340 cm⁻¹. The ³¹P{¹H} NMR spectrum of complex 1 in CDCl₃ gives a singlet at δ 37.2, indicating the magnetic equivalence of the two *trans*-coordinated phosphorus donor atoms. Complex 1 can therefore be assigned a square-planar geometry with the donor atoms N and P_2 of the ligand in three coordination positions to the metal ion and the fourth position occupied by Cl.

Complex 2 was obtained [9] by the reaction of TPEA with Na₂PdCl₄ in CH₂Cl₂. The ν (Pd—Cl) of the complex is exhibited at 350 cm⁻¹. The ³¹P{¹H} NMR spectrum of complex 2 in ethanol gives a triplet for P_a at δ 32.3 and a doublet for the equivalent P_b at δ 29.8. Complex 2 can therefore be assigned a square-planar geometry, with *trans* P_b and P_a in three coordination positions and Cl in the fourth. The nitrogen atom of TPEA loosely occupies the apical position.

Catalytic hydrogenation of cyclohexene

The hydrogenation reactions of cyclohexene catalysed by complexes 1 and 2 were carried out in pure ethanol. The overall rate of hydrogenation $-d[H_2]/dt$ was measured manometrically, and the dependence of the rate on substrate, catalyst and H_2 partial pressure investigated.

Dependence of the rate of hydrogenation on cyclohexene concentration In catalytic studies with complexes 1 and 2 the concentration of cyclohexene was varied from 0.5 - 2.5 M. The plot of the rate of hydrogenation of cyclohexene as a function of cyclohexene concentration is linear at low concentration, but becomes non-linear at higher concentrations of cyclohexene. The plot of the reciprocal of the rate versus reciprocal of the cyclohexene concentration is however linear, with a positive intercept (Fig. 1). The rate of hydrogenation of cyclohexene R is related to substrate concentration Sby the relationship:

$$\frac{1}{R} = a\left(\frac{1}{S}\right) + b$$

where a and b are the slope and intercept of the plot of 1/R vs. 1/S.



Fig. 1. Plot of reciprocal of rate vs. reciprocal of cyclohexene concentration for the hydrogenation of cyclohexene catalyzed by complex 1 at 25 $^{\circ}$ C.

Dependence of the rate of hydrogenation on the catalyst concentration

Figure 2 illustrates the dependence of the rate of the hydrogenation of cyclohexene on the catalyst concentration for complex 1. A similar plot was obtained for complex 2. The figure shows a first order dependence of the rate on catalyst concentration. In the absence of the catalyst, no hydrogen uptake was detectable. At higher concentration of catalyst $>10^{-5}$, saturation kinetics was observed.



Fig. 2. Dependence of the rate of hydrogenation of cyclohexene on catalyst concentration at 25 $^\circ\!C.$

The rate of hydrogenation of cyclohexene is independent of the partial pressure of H_2 in the range of 0.4 - 1 atm.

Mechanism

Based on the kinetic data the following mechanism is proposed for the homogeneous hydrogenation of cyclohexene catalyzed by complexes 1 and 2:

$$[PdCl(L)]^{+} + H_2 \xleftarrow{K_1} [Pd(H)L]^{+} + HCl$$
(2)

$$[PdCl(L)]^{+} + S \stackrel{K_{2}}{\longleftrightarrow} [PdCl(L)(S)]^{+}$$
(2)

$$[Pd(H)L]^{+} + S \xrightarrow{R} [Pd(HS)L]^{+}$$
(3)

$$[PdCl(L)(S)]^{+} + H_2 \xrightarrow{k'} [Pd(HS)(L)]^{+} + HCl$$
(4)

$$[Pd(HS)L]^{+} + H_{2} \xrightarrow{\text{fast}} [Pd(H)L]^{+} + SH_{2}$$
(5)

where L = DPEA or TPEA, $SH_2 = alkane$, S = olefin.

 K_1 is the equilibrium constant for the formation of the monohydrido species $[Pd(H)L]^+$, K_2 is the formation constant of the mixed ligand hydrido olefin species, and k is the second order rate constant for the hydrogenation of cyclohexene. The rate law can be written as:

$$-d[H_2]/dt = \frac{K_1 k[C][H_2][S]}{(1 + K_1[H_2])(1 + K_2[S])}$$
(6)

On rearrangement of eqn. (6) we obtain:

$$-\frac{1}{d[H_2]/dt} = \frac{1+K_1[H_2]}{K_1k[H_2][C]} \left(\frac{1}{[S]}\right) + \frac{1+K_1[H_2]}{K_1k[H_2][C]}K_2$$
(7)

A plot of reciprocal of rate versus reciprocal of cyclohexene concentration gives the slope (a) and intercept (b):

$$a = \frac{1 + K_1[H_2]}{K_1 k[H_2][C]}; \qquad b = \frac{1 + K_1[H_2]}{K_1 k[H_2][C]} K_2$$
(8)

Assuming $K_1[H_2] \ge 1$, eqn. (8) reduces to:

$$a = \frac{1}{K[C]}; \qquad b = \frac{1}{K[C]}K_2$$
 (9)

where [C] = catalyst concentration.

The rate constant k at various temperatures calculated from eqn. (9) using the value of the slope (a) are tabulated in Table 1.

TABLE 1

Rate constant and activation parameters obtained for the homogeneous hydrogenation of cyclohexene catalyzed by [Pd(DPEA)Cl]Cl 1

Temperature (℃)	$k \;(\min^{-1} \; \mathrm{M}^{-1})$		Activation parameters for k				
	1	2	$\frac{E_{a}}{(\text{kcal mol}^{-1})}$	$\frac{\Delta H^{\ddagger}}{(\text{kcal mol}^{-1})}$	ΔS‡ (e.u.)	ΔG° (30 °C) (kcal mol ⁻¹)	
10	0.5	0.8	6.44	5.8	-41.0	18.2 for 1	
20	0.9	1.1	4.6	4.0	-41.6	16.6 for 2	
30	1.2	1.4	_				
40	1.5	1.7	-		_		

Under the condition of a large value of K_1 , equilibrium (1) is completely shifted to the hydride side, which will have a larger concentration in solution than the concentration of dissolved hydrogen at a particular partial pressure of H₂. The rate therefore becomes independent of H₂ partial



Fig. 3. Arrhenius plot for the temperature dependence of the rate of hydrogenation of cyclohexene catalyzed by complex 1.

Fig. 4. Arrhenius plot for the temperature dependence of the rate of hydrogenation of cyclohexene catalyzed by complex 2.

pressure. The energy of activation E_a in the temperature range 10 - 40 °C is calculated from the slope of the plot of log k vs. 1/T and is depicted in Figs. 3 and 4 for complexes 1 and 2, respectively, using the Arrhenius equation. The enthalpy of activation ΔH^{\ddagger} and the entropy of activation ΔS^{\ddagger} were calculated from the following equations:

$$\Delta H^{\ddagger} = E_{a} - RT \tag{10}$$

$$2.303 \log k = 2.303 \log \frac{RT}{Nh} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$$
(11)

where N is the Avogadro's number, h is Planck's constant and R is the gas constant. The values of ΔH^{\ddagger} and ΔS^{\ddagger} are given in Table 1. The ratio of intercept to slope of eqn. (8) gives the values of K_2 , the equilibrium constant for olefin complex formation. The thermodynamic parameters involving the formation of the olefin complex, along with the values of K_2 at different temperatures, are presented in Table 2.

Discussion

Hydrogenation of the complex [Pd(DPEA)Cl]Cl

Hydrogenation of complex 1 was conducted in CDCl_3 in situ in a NMR tube. The hydride spectrum taken after 2 h is depicted in Fig. 5 and the

Thermodynamic parameters	for the formation	of cyclohexene	complexes of	[Pd(DPEA)-
(S)Cl]Cl 1 and [Pd(TPEA)(S))C1]Cl 2			

Temperature	$K_2 (M^{-1})$		ΔH^0	Δ <i>S</i> ⁰	ΔG^0
(°C)	1	2	(kcal mol^{-1})	$(kcal mol^{-1})$	(kcal mol^{-1})
10	0.66	0.78	1.5	4.48	0.142 for 1
20	0.72	0.93	5.1	17.3	0.19 for 2
30	0.80	1.36		-	
40	0.89	1.69		-	



Fig. 5. Hydrido proton NMR of hydrido complexes 1a and 1b formed by the hydrogenation of complex 1.

NMR data tabulated in Table 3. The triplet at $\delta = -37.84$ with a J(H-P) of 25 Hz is assigned to the monohydride of Pd(II) 1a (Scheme 1). This hydride is obtained by the nucleophilic displacement of Cl⁻ in 1 by H⁻. Such a Pd(II) hydride was also reported [17] in the hydrogenation of [(PPh₃)₃PdCl]⁺. The ³¹P{¹H} of the hydride 1a gives a singlet at $\delta = -36.87$ for the equivalent *trans* phosphorus atom of 1a.

A novel reaction observed in the hydrogenation of complex 1 is the oxidative addition of H_2 to complex 1a to form trihydridopalladium(IV) complex 1b. To our knowledge this is the first example of a relatively stable Pd(IV) hydrido complex obtained by the oxidative addition of H_2 to a Pd(II) complex (1a). From the relative intensities of the peaks in Fig. 5, the amount of complex 1b formed is estimated to be about 5% with 95% of complex 1a. This is expected because of an enhanced tendency of palladium(IV) hydrido complexes to undergo reductive elimination of H_2 [18 - 20]. The concentration of complex 1b thus does not accumulate to an appreciable extent in solution, and the complex is converted to 1a by reductive elimination of H_2 . The formation of the trihydride 1b in solution

TABLE 3

NMR spectral parameters of the palladium hydride complexes obtained by the hydrogenation of [Pd(DPEA)Cl]Cl^a and [Pd(TPEA)Cl]Cl^b

Complex		¹ H chemical ^c shifts (ppm)	Coupling constants ² J(H-P) (Hz)	³¹ P{ ¹ H} ^d chemical shifts (ppm)	Coupling constants ² J(P-P) (Hz)
1	[Pd ^{II} (DPEA)Cl] ⁺			37.2(s)	
2	[Pd ^{II} (TPEA)Cl] ⁺	_		32.3(t) 29.8(d)	20
1a	[Pd ^{II} (DPEA)(H)] ⁺	-37.84(t)	25	36.87(s)	
1b	[Pd ^{IV} (DPEA)(H) ₃] ⁺	17.37(dd)	trans 54	48.00(d)	25
2a	[Pd ^{II} (TPEA)(H)] ⁺	-33.54(t) -26.44(dt)	cis 20 trans 65 cis 30	 33.7(t) 28.8(d)	20
2b	[Pd ^{IV} (TPEA)(H) ₂] ²⁺	-20.10(q) -24.27(dt)	cis 37 trans 72	42.98(t) 22.9(d)	25

^aMeasured at 25 °C in CH₂Cl₂.

^bMeasured at 25 °C in ethanol.

 c1 H shifts are referred to TMS; d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplets, q = quartet, s = singlet.

 $d^{31}P$ shifts are referred to 85% H₃PO₄.





is supported by both proton and ³¹P{¹H} NMR data. The hydride H_{β} of the Pd(IV) trihydride gave a downfield triplet centered at $\delta = -33.54$ expected for a Pd(IV) complex. The coupling constant $J(H_{\beta}-P)$ is 20 Hz, about 5 Hz less than the coupling constant J(H-P) of the monohydride of Pd(II) 1a.

The axial and equatorial hydrides of complex 1b H_{β} and H_{γ} are non-equivalent. Each hydride therefore gives an overlapping pattern of a doublet of doublets centered at $\delta = -17.37$ with a *trans J*(H-P) of 54 Hz and *cis J*(H-P) of 20 Hz. The *trans J*(H-P) reported [16] in Pd(II) complexes is about 174 Hz. The ³¹P{¹H} spectrum of 1b gives a doublet centered at $\delta = 48.00$, with a value of *cis J*(P-P) of 54 Hz. A large downfield shift of phosphorus resonance to $\delta = 48$ in complex 1b from a value of $\delta = 36.8$ in complex 1a is in accord with the higher oxidation state of palladium in complex 1b.

Hydrogenation of complex 2 was conducted in C_2H_5OH in situ in a NMR tube. The hydrido proton spectrum taken after 2 h is depicted in Fig. 6 and the NMR data tabulated in Table 3. The doublet of triplets centred at $\delta = -26.44$ is assigned to the monohydride 2a (Scheme 2) obtained by the nucleophilic displacement of Cl⁻ in 2 by H⁻ as in 1. The ${}^{31}P{}^{1}H{}$ of the hydride gives the P_a triplet at $\delta = 33.7$ and P_b doublet at $\delta = 28.8$, indicating that there is no change in the geometry of the complex upon substitution of Cl⁻ by H⁻.

Oxidative addition of H_2 to 2 forms the Pd(IV) dihydrido complex 2b (Scheme 2). Unlike complex 1a, the presence of N in the apical position of 2 prevents the formation of a trihydride. The hydride H_{α} of 2b gives a doublet of triplets centered at $\delta = -24.3$ and H_{β} a quartet centered at $\delta = -20.10$ (Table 3). The ³¹P{¹H} of the dihydride gives the triplet for P_a at $\delta = 42.98$ and doublet for P_b at $\delta = 22.9$. The phosphorus resonances in complex 2b



Fig. 6. Hydrido proton NMR of hydrido complexes of 2a and 2b formed by the hydrogenation of complex 2.



Scheme 2.

are shifted considerably downfield as compared to 2a, in accord with the higher oxidation state of the metal ion (+4) in 2b. The ${}^{2}J(P-P)$ coupling constant is slightly higher, 25 Hz, in 2b as compared to 20 Hz in 2a.

Catalysis of the hydrogenation of cyclohexene

The proposed catalytic species in the homogeneous hydrogenation of cyclohexene catalyzed by $[Pd(DPEA)Cl]^+$ and $[Pd(TPEA)Cl]^+$ are the Pd(II) monohydrides 1a and 2a, respectively, as shown in Scheme 2. The rate of the reaction is independent of the H₂ partial pressure, indicating that equilibrium (1) is shifted far to the right. The rate-determining step proposed in the mechanism is the insertion of the olefin in the M—H bond to form an alkyl complex 4 as proposed by Halpern [21, 22] and others [12, 14]. An alternate pathway is the formation of the olefin complex 4 followed by its hydrogenolysis to 3 in a slow step. This is obviously a minor pathway because of the observed independence of the reaction rate from hydrogen partial pressure. The alkyl complex 3 breaks down to the alkane and complex 1a or 2a in a fast step. The participation of the Pd(IV) species 1b or 2b in the catalysis of the hydrogenation reaction is ruled out on the basis of the fast dissociation of these species to 1a or 2a in solution.

The Pd(II) olefin complex 3 is proposed to be a five-coordinate species, as proposed earlier for the Rh(I) and Ir(I) complexes of DPEA [6]. The thermodynamic parameters corresponding to the formation constant K_2 of the olefin complex 2 are presented in Table 2. The enthalpy of formation of 2, ΔH^0 , is slightly more exothermic (~0.2 kcal mol⁻¹) and the entropy of formation ΔS^0 slightly more negative (~0.5 eV) than the [Rh(DPEA)Cl] complex [6]. The stability of the five-coordinate d⁸ metal-olefin complex [6] thus seems to decrease in the order Pd(II) > Rh(I) > Ir(I). The fivecoordinate Pd(II) complexes are the most stable. The activation parameters ΔH^{\ddagger} and ΔS^{\ddagger} corresponding to the rate constant k are presented in Table 1. The enthalpy of activation for the reaction, 5.83 kcal mol⁻¹ is slightly more exothermic (~0.4 kcal mol⁻¹) than that reported [6] for [Rh(DPEA)Cl] catalyzed hydrogenation of cyclohexene, viz. 6.2 kcal mol⁻¹. The entropy of activation -40 e.u. for the Pd(II)-catalyzed reaction is however about 8 e.u. more positive than the Rh(I)-catalyzed reaction. The complex [Pd(DPEA)Cl] is thus more reactive than [Rh(DPEA)Cl] by an order of magnitude of 2.

The difference in the catalytic activity of the Pd(II) complex 1 as compared to its Rh(I) analogue may be partly due to the dissociative heterolytic cleavage of H₂ involved in the catalysis by Pd(II) vs. an oxidative addition in Rh(I) complexes. The entropies of activation for Ru(II)-catalyzed hydrogenation of maleic and fumaric acids, where a heterolytic cleavage of the H₂ bond was proposed [21], are fairly positive and are on the order of magnitude of -8 to -17 e.u. The higher value of the negative entropy of activation in chelated phosphines as observed in complex 1 may be due to the steric constraints involved in the rate-determining migratory insertion of the olefin [22, 23] in the metal-hydride bond.

It is of interest to compare the activation parameters for the hydrogenation of cyclohexene catalyzed by the DPEA complex 1 and the TPEA complex 2. The enthalpy of activation for the reaction by complex 2 is more exothermic by about 2 kcal mol⁻¹ than by complex 1; the entropy of activation is about the same, within experimental error. The phosphorus atoms in complex 1 are more rigidly coordinated than in complex 2, which has a large chelate ring and a loosely bonded N atom. Thus complex 2 behaves as a loosely chelated monodentate phosphine [9], where the rearrangement in the ring to form the hydrido or the olefin complex is much smaller than stable chelate rings. Thus complex 2 is a more reactive catalyst than complex 1.

The thermodynamic stability of the olefin complexes formed by the interaction of 1 or 2 with cyclohexene are presented in Table 2. The olefin complex of 2 is slightly more stable than that of 1, as indicated by the free energy of formation ΔG° (Table 2). The entropy and enthalpy of the formation of 1 and 2 mutually compensate to make ΔG° for 2 slightly more exothermic than 1. This is reflected in the catalytic activity of 2, which is more than that of 1 for the homogeneous hydrogenation of cyclohexene.

References

- 1 M. M. Taqui Khan and A. E. Martell, Homogeneous Catalysis by Metal Complexes, Vol. 1, Academic Press, New York, 1974, Chapt. 3.
- 2 B. R. James, Homogeneous Hydrogenation, Wiley, New York, 1969; B. R. James, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), Comprehensive Organometallic Chemistry, Pergamon Press, New York, 1982, Vol. 8, Chapt. 51.
- 3 J. Halpern, T. Okamoto and A. Zakchariev, J. Mol. Catal., 2 (1976) 65.
- 4 J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, J. Chem. Soc. (A), (1966) 1711.

- 5 F. H. Jardine, J. A. Osborn and G. Wilkinson, J. Chem. Soc., (A), (1967) 1574.
- 6 M. M. Taqui Khan, B. Taqui Khan and S. Begum, J. Mol. Catal., 34 (1986) 9.
- 7 M. M. Taqui Khan, B. Taqui Khan, S. Begum and M. Ali, J. Mol. Catal., 34 (1986) 283.
- 8 M. M. Taqui Khan and E. Rama Rao, Polyhedron, 6 (1987) 1727.
- 9 M. M. Taqui Khan and E. Rama Rao, Polyhedron, 7 (1988) 29.
- 10 A. S. C. Chan, J. J. Pluth and J. Halpern, J. Am. Chem. Soc., 102 (1980) 5952.
- 11 A. S. C. Chan and J. Halpern, J. Am. Chem. Soc., 102 (1980) 838.
- 12 D. C. Roe, J. Am. Chem. Soc., 105 (1983) 7770.
- 13 D. Milstein, Acc. Chem. Res., 17 (1984) 221. and references therein.
- 14 R. H. Crabtree and R. J. Uriarte, Inorg. Chem., 22 (1983) 4152.
- 15 B. J. Fisher and R. Eisenberg, Inorg. Chem., 23 (1984) 3216.
- 16 N. Suzuki, Y. Ayaguchi and Y. Izawa, Chem. Ind., (1983) 166.
- 17 V. N. Zudin, V. D. Chinakov, V. M. Nekipelov and Yu. I. Yermakov, J. Organometall. Chem., 289 (1985) 425.
- 18 U. B. Brandemark, M. R. A. Blomber, L. G. M. Pettersson and P. E. M. Siegbahn, J. Phys. Chem., 88 (1984) 4617.
- 19 J. J. Low and W. A. Goddard, III, Organometallics, 5 (1986) 609.
- 20 H. Nakatsuji and M. Hada, J. Am. Chem. Soc., 107 (1985) 8264.
- 21 J. Halpern and B. R. James, Can. J. Chem., 44 (1966) 671.
- 22 J. Halpern, D. P. Riley, A. S. C. Chan and J. J. Pluth, J. Am. Chem. Soc., 99 (1977) 8055.
- 23 J. Halpern and T. Okamoto, Inorg. Chim. Acta, 89 (1984) L53.