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MECHANISTIC ASPECTS OF CATALYTIC HYDROGENATION OF KETONES BY RHODIUM(I)-PERALKYLDIPHOSPHINE COMPLEXES *

KAZUHIDE TANI*, EIJI TANIGAWA, YOSHITAKA TATSUNO, and SEI OTSUKA*

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560 (Japan)

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Summary

Mechanistic aspects of the hydrogenation of ketones employing cationic rhodium(I) complexes $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$ (NBD = norbornadiene) and $[Rh(CyDIOP)(NBD)]ClO_4$ (CyDIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(dicyclohexylphosphino)butane) and a neutral complex, "Rh-(CyDIOP)Cl" were studied. The cationic complex-catalyzed hydrogenation of the poor coordinating simple ketone substrates followed a rate equation $r_0 = k_{obs}[Rh][ketone]_0[H_2]_0$ and showed an unusual negative temperature dependence of the reaction rate. The hydrogenation of the chelating substrate $PhCOCONHCH_2Ph$ followed a rate equation $r_0 = k_{obs}[Rh][H_2]_0$ with the activation parameters E_a 5.51 kcal mol^{-1}, $\Delta H^{\ddagger}_{308}$ 4.90 kcal mol^{-1}, $\Delta S^{\ddagger}_{308}$ −32.0 e.u. ($[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$ catalyst); E_a 5.36 kcal mol^{-1}, $\Delta H^{\ddagger}_{308}$ 4.75 kcal mol^{-1}, $\Delta S^{\ddagger}_{308}$ −30.9 e.u. ($[Rh(CyDIOP)(NBD)]ClO_4$ catalyst). For the neutral complex-catalyzed hydrogenation of $PhCOCONHCH_2Ph$, the rate equation $r_0 = [Rh]^{0.25}[ketone]_0[H_2]_0$ was obtained with the activation parameters (E_a 3.99 kcal mol^{-1}, $\Delta H^{\ddagger}_{308}$ 3.38 kcal mol^{-1}, $\Delta S^{\ddagger}_{308}$ −43.0 e.u.). Several intermediate complexes in the cationic complex-catalyzed hydrogenation were also detected spectroscopically or isolated. On the basis of these observations, a general reaction scheme was proposed.

Introduction

Transition metal complexes, especially rhodium(I) phosphine complexes, which are extremely active for catalytic hydrogenation of olefinic double bonds have been found and extensive mechanistic studies have been made [1]. A few phosphine rhodium complexes have been claimed to be active for ketone hydrogenation under atmospheric pressure of hydrogen [2–5]. According to our experience, however, most

* Dedicated to Prof. J. Halpern on the occasion of his 60th birthday.

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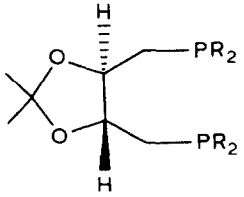
of the rhodium hydrogenation catalysts, which contain monophosphine or diphosphine ligands carrying aryl group(s) on the phosphorous atom, show only moderate to poor activity for hydrogenation of carbonyl groups [6]. Grey et al. have observed high catalytic activity in some anionic ruthenium arylphosphine complexes for hydrogenation of various carbonyl compounds including esters [7]. We have also developed highly active rhodium systems based on fully alkylated diphosphine ligands such as $R_2P(CH_2)_nPR_2$ (**1**) [6] and alkyl analogs of DIOP (2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) (**2**) [8,9]. With a strongly electron-donating diphosphine ligand **1** or **2**, even the cationic form $[Rh(\mathbf{1})(diene)]^+$



R = Et, i-Pr, Cy

(Cy = cyclohexyl)

(−)-**2**

or $[Rh(\mathbf{2})(diene)]^+$ exhibits a high catalytic activity for hydrogenation of carbonyl compounds. In the absence of systematic mechanistic studies in this field it will be of interest to see: (1) What is the rate-determining step in the catalytic cycle for a particular substrate or a catalyst? (2) How does the nature of ligands or the charge of the whole complex affect the rate? And (3) could the nature of substrate or of the catalyst complex alter the entire kinetic aspects?

In order to find answers to these questions we have undertaken kinetic studies employing a variety of carbonyl compounds. The catalyst precursor was mainly cationic complexes $[Rh(diphosphine)(diene)]^+$ but a neutral form "RhCl(diphosphine)" was also tested for some ketones.

Experimental

Although we have not had a hazardous accident with rhodium perchlorate complexes described below, we recommend to avoid high temperature whenever and wherever they are involved.

Preparations of diphosphine ligands and their metal complexes were carried out under a pure nitrogen atmosphere. ^1H NMR (100 MHz), $^{13}C\{^1H\}$ NMR (25 MHz), and $^{31}P\{^1H\}$ NMR (40.5 MHz) spectra were recorded on a JEOL FX-100. Tetramethylsilane (^1H and ^{13}C NMR) and 5% phosphoric acid in methanol-d_4 (^{31}P NMR) were used as standards and downfield shifts from the standards were taken as positve. IR spectra were run with a Hitachi Infrared Spectrophotometer 295.

Materials. Transition metal complexes, $[Rh(NBD)Cl]_2$ (NBD = norbornadiene) [10], $[Rh(C_8H_{14})_2Cl]_2$ [11], $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) [12], and diisopropylphosphine [13] were prepared according to the literature methods. (−)-CyDIOP (**2**, R = cyclohexyl) [8] and $[Rh((-)\text{-CyDIOP})(NBD)]ClO_4$ [8] were also prepared as described previously. Methyl isopropyl ketone, methyl t-butyl ketone, acetophenone, trifluoromethyl phenyl ketone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, and cyclododecanone were of reagent grade and distilled under nitrogen before use. Benzophenone of reagent grade was used without further purification.

Preparation of $(i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2$

To a suspension of lithium diisopropylphosphide in ether and n-hexane mixture prepared from diisopropylphosphine (7.7 g, 65 mmol) and n-butyllithium (1.6 *M*, 67 mmol) was added under ice-cooling 1,3-dichloropropane (3.5 g, 31 mmol) during 10 min. The resulting mixture was stirred for 10 h at ambient temperature and then heated to reflux for 30 min. After addition of deoxygenated water (25 ml), the organic layer was separated and the water layer was extracted with ether. The combined ether extract was dried over magnesium sulfate. After removal of the solvents, the residue was distilled in vacuo to give the diphosphine as a colorless liquid, 7.3 g (84%), b.p. 95–98°C/0.01 mmHg. ^{31}P NMR (THF): δ 1.21 ppm(s).

Preparation of $(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$

The diphosphine was similarly prepared from lithium diisopropylphosphide and 1,4-dichlorobutane as a colorless liquid in 96% yield, b.p. 102–103°C/0.01 mmHg. ^{31}P NMR (THF): δ 2.04 ppm(s).

Preparation of $[Rh((i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2)(NBD)]ClO_4$

To a stirred suspension of $[Rh(NBD)Cl]_2$ (224 mg, 0.49 mmol) in acetone (15 ml) was added silver perchlorate (211 mg, 1.0 mmol). After ca. 30 min the resulting pale yellow solution was filtered from silver chloride. To this solution was added an acetone solution (5 ml) of $(i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2$ (267 mg, 0.97 mmol). The resulting deep-red solution was stirred at ambient temperature for about 3 h. The solvent being removed in vacuo, the resulting orange-red residue was recrystallized from acetone/ether mixture to give deep-red crystals (496 mg, 90% yield), m.p. 153°C(dec., in a nitrogen filled capillary). (Found: C, 46.32; H, 7.34. $C_{22}H_{42}ClO_4P_2Rh$ calcd.: C, 46.29; H, 7.42%). ^{31}P NMR (MeOH): δ21.52 ppm (d, J(P–Rh) 148.4 Hz).

Preparation of $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$

The complex was similarly prepared from $[Rh(NBD)Cl]_2$ and $(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$ as red crystals in 89% yield, m.p. 173°C (dec., in a nitrogen filled capillary). (Found: C, 47.07; H, 7.57. $C_{23}H_{44}ClO_4P_2Rh$ calcd.: C, 47.23; H, 7.58%). ^{31}P NMR (MeOH): δ 33.00 ppm (d, J(P–Rh) 152.3 Hz).

Preparation of $[Ir((i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2)(COD)]PF_6$

To an orange-red suspension of $[Ir(COD)Cl]_2$ (0.12 g, 0.19 mmol) in acetone (5 ml) was added solid ammonium hexafluorophosphate (70 mg, 0.42 mmol) and subsequently an acetone solution (5 ml) of $(i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2$ (0.16 g, 0.46 mmol). The initial orange-red suspension changed immediately into a red solution containing colorless precipitates. The resulting suspension was stirred at ambient temperature further for about 1 h. The red solution was filtered from the colorless precipitates and concentrated to ca. 1–1.5 ml. Ether was slowly added to the red solution until the clear red solution just began to become cloudy and the mixture was allowed to stand at 0°C overnight. The dark brown-red crystals precipitated, were collected, washed with ether, and dried in vacuo to give the pure complex, 0.15 g (56% yield), m.p. 199–201°C(dec., in a nitrogen filled capillary). (Found: C, 38.32; H, 6.40. $C_{23}H_{46}F_6IrP_3$ calcd.: C, 38.28; H, 6.42%). ^{31}P NMR (MeOH): δ – 146.79(heptet, J(P–F) 708.0 Hz, PF_6^-), 6.61 ppm (s, P of the diphosphine ligand).

Preparation of N-benzylphenylglyoxylamide, $PhCOCONHCH_2Ph$

To an ethanol solution (7.5 ml) of ethyl phenylglyoxalate (5.5 g, 30.9 mmol) was added benzylamine (3.6 g, 34 mmol) at ambient temperature. The reaction mixture was stirred for 2 h. On addition of n-hexane, a colorless solid of the amide precipitated and was recrystallized from benzene/n-hexane mixture to give the pure compound, 4.6 g (61% yield), m.p. 101–102°C. (Found: C, 75.20; H, 5.42; N, 5.77. $C_{15}H_{13}NO_2$ calcd.: C, 75.30; H, 5.47; N, 5.86%). IR (Nujol) 3290 (NH), 1690 (C=O), 1647br (C=O), 1575 cm^{-1} (amide). ^1H NMR (acetone-d_6): δ 4.59 (d, J 6 Hz, 2H, CH_2), 7.38 (m, 5H, Ph), 7.60 (m, 3H, arom.), 8.20 (m, 2H, arom.), 8.40 (br, 1H, NH). ^{13}C NMR (acetone-d_6): δ 43.33 (CH_2), 127.93, 128.40, 129.22, 129.34, 131.16, 134.39, 134.97, and 139.44 (arom.), 164.27 (PhC(=O)), 189.75 ppm (C(=O)NH).

Reaction of [Rh(diphosphine)(NBD)]ClO_4 (diphosphine = $(i\text{-}Pr)_2P(CH_2)_nP(i\text{-}Pr)_2$ (n = 3,4) and (−)-CyDIOP) with hydrogen

About 50 mg of the diphosphine complexes were dissolved or suspended in ca. 1 ml of methanol and the nitrogen atmosphere was replaced with dihydrogen. The initial reddish solution (the $(i\text{-}Pr)_2P(CH_2)_nP(i\text{-}Pr)_2$ complex) or the orange suspension (the (−)-CyDIOP complex) changed in a few minutes to an orange-yellow or an orange-red solution, respectively. The resulting solutions were allowed to stand at ambient temperature under an atmospheric pressure of hydrogen for one to two days. The following dihydride complexes were precipitated as yellow crystals. Their physical and spectral data are summarised in Table 4.

"*$[Rh((i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2)(H)_2]ClO_4$*": 31% yield. (Found: C, 37.69; H, 7.55. $C_{15}H_{36}ClO_4P_2Rh$ calcd.: C, 37.48; H, 7.74%).

"*$[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(H)_2]ClO_4$*": 29% yield. (Found: C, 38.51; H, 7.50. $C_{36}H_{38}ClO_4P_2Rh$ calcd.: C, 38.84; H, 7.74%).

"*$[Rh((-)\text{-}CyDIOP)(H)_2]ClO_4$*": 20% yield. (Found: C, 52.41; H, 8.45. $C_{31}H_{58}ClO_6P_2Rh$ calcd.: C, 51.21; H, 8.04%).

Preparation of $[IrH((i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2)(O\text{–}CH(Ph)\text{–}C(=O)NHCH_2Ph)]PF_6$

$[Ir((i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2)(COD)]PF_6$ (0.18 g, 0.25 mmol) and $PhCOCONHCH_2Ph$ (0.06 g, 0.26 mmol) were dissolved in 5 ml of THF. The resulting red solution was cooled to −15°C and the nitrogen atmosphere was replaced with dihydrogen. In a few minutes, the initial red color faded to pale yellow. After about 1 h, the solvent was removed in vacuo below −10°C. The resulting yellow amorphous solid was washed with ether and dried in vacuo. The yellow solid was recrystallized from acetone/ether to give the hydrido-alkoxo complex as yellow crystals, 0.16 g (76% yield), m.p. 163–165°C (dec. with gas evolution in a nitrogen filled capillary). (Found: C, 41.76; H, 5.82; N, 1.65. $C_{30}H_{49}F_6IrNO_2P_3$ calcd.: C, 42.15; H, 5.78; N, 1.65%). IR (Nujol): 3380 (NH), 2300 (IrH), 1600 and 1550 (amide), 1580 cm^{-1} (arom.). ^1H NMR (acetone-d_6): δ − 29.59 (t, J(P–H) 25.7 Hz, 1H, IrH), 1.12 (m, 24H, CH_3), 1.55–2.70 (m, 10H, CH_2 and CH of the diphosphine ligand), 4.50 (br s, 2H, NCH_2), 5.93 (d, J 4 Hz, 1H, CH–O), 6.15–6.35 (m, 10H, Ph), 7.82 ppm (br, 1H, NH). ^{13}C NMR(acetone-d_6): δ 17–31 (complex, C of the diphosphine ligand), 45.23 (CH_2NH), 86.42 (CH–O), 127.67, 128.09, 128.85, 129.08, 129.20, 137.81, and 142.59 (arom.), 190.90 ppm (C(=O)NH). ^{31}P NMR (methanol): δ −152.20 (heptet, J(P–F) 707 Hz, PF_6^-), −1.48 (d, J(P–P) 21.5 Hz), and −0.27 ppm (d, J(P–P) 21.5 Hz).

Kinetic measurements

The reaction kinetics were followed by measuring the initial rate of uptake of hydrogen gas at a constant total pressure. The reaction flask of ca. 20 ml having a side neck covered with a rubber septum is connected to a gas buret via capillary glass tubes of 1 mm ∅. The reaction vessel has a fairly large flat bottom (∅ 40 mm) to facilitate efficient stirring with a teflon coating stirring bar. When combined with the use of small volumes of solution in a relatively large vessel (2 ml in 20 ml), the apparatus prevents a diffusion control due to slow dissolution of dihydrogen. The reaction vessel is immersed in a thermostatted bath up to the neck. The temperature was maintained within $\pm 0.1°C$.

After the whole system was thoroughly replaced with dihydrogen the substrate solution (1.8 ml) was introduced with a syringe (in case of solid carbonyl compounds, the substrate was weighed into the reaction flask). The flask was immersed into the thermostatted bath and allowed to equilibrate by stirring the solution under hydrogen for about 20 min. After adjusting the total pressure at 1 atm, a catalyst solution (0.2 ml), which was pre-equilibrated to a desired temperature, was syringed through the rubber septum and the hydrogen absorption recorded. The reproducibility of the kinetic measurements is over about 95%.

For measurements of hydrogen pressure dependence a desired dihydrogen partial pressure was obtained by mixing hydrogen and helium in a rubber balloon in a required volume ratio. The solubilities of dihydrogen in methanol at various temperatures were taken from the literature [14] and those in THF were estimated according to the method described in the literature [15] and corrected for the vapor pressure of THF [16].

The reaction order was determined by plotting logarithms of the initial rates against logarithms of the initial concentration of each reactant keeping the concentrations of other reactants constant.

Results and Discussion

Rate dependence on substrates

Employing $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$ as the catalyst precursor, we first examined the initial rate varying the substrate. Under the atmospheric pressure

TABLE 1

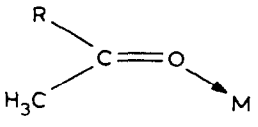
HYDROGENATION OF R^1CR^2 (with O) WITH $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$ [a]

Ketone		r_0
R^1	R^2	(mmol H_2 mmol Rh^{-1} min^{-1})
Me	Me	11.9
Me	i-Pr	4.03
Me	t-Bu	0.353
Me	Ph	9.48
Ph	Ph	10.2
CF_3	Ph	1.02

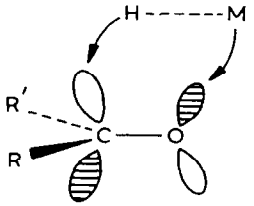
[a] H_2 (1 atm) at 35° in MeOH, $[ketone]_0 = 0.1$ *M*.

of dihydrogen the catalytic reaction of most of the carbonyl compounds we tested proceeds with reasonable rates in MeOH at ambient or slightly higher temperature (Tables 1 and 2).

The rate trend $Me_2CO > MeCO(i\text{-}Pr) > MeCO(t\text{-}Bu)$ presents two facets; (i) the enhanced σ-donating properties of carbonyl oxygen lone pairs cannot be a favorable factor for the catalytic rate as the steric bulk of the R group in MeCOR would not hinder the σ-coordination (**3**) per se and (ii) the apparent steric effect may then be ascribed to the hindrance in the intramolecular nucleophilic hydride migration (**4**) since the LUMO of a ketone molecule slants toward the alkyl substituents [17].

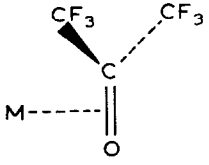


(3)



(4)

The facile reduction of PhCOPh and $PhCOCF_3$ (Table 1) is of interest as it implies dispensability of an enol form for the hydrogenation. Acetophenone was hydrogenated with a rate of about an order of magnitude faster than that observed for $PhCOCF_3$, a strong electron acceptor. A stable η^2-coordination (**5**) of a ketone to



(M = Pt^0, Pd^0, Ir^I)

(5)

a metal center occurs when the ketone has a highly electronegative group like CF_3 and simultaneously the metal center is electron rich as in Pt^0, Pd^0, or Ir^I [18]. It is tempting, therefore, to infer that the η^2-coordination, if it occurs at all, would not be a requisite for the smooth catalytic turnover. Regardless the mode of ligation, the

TABLE 2

HYDROGENATION OF $(CH_2)_{n-1}C{=}O$ WITH $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$ [a]

Ketone n	r_0 (mmol H_2 mmol Rh^{-1} min^{-1})
5	8.97
6	74.5
7	1.90
8	0.345
12	0.683

[a] H_2 (1 atm) at 35 °C in MeOH, $[ketone]_0 = 0.1$ *M*.

strong affinity of a substrate to the catalyst metal does not lead to the fast rate.

The results shown in Table 2 suggest that the overall rate is not simply governed by the π^* level of ketones [19]. The rate trend observed for the hydrogenation of cyclic ketones cyclohexanone ≫ cyclopentanone > cycloheptanone > cyclododecanone > cyclooctanone is very similar to that reported for the sodium borohydride reduction [20] or the addition of cyanide anion [21], a trend which has been explained in terms of a steric strain, so-called *I*-strain.

A neutral Rh^I complex was tested as catalyst for hydrogenation of several ketones. The complex was prepared in situ from $[Rh(C_8H_{14})_2Cl]_2$ and 2 mol of (−)-CyDIOP **2** (R = cyclohexyl) in THF. The neutral complex showed a very low activity for hydrogenation of simple ketones such as cyclohexanone or benzophenone (in THF at ambient conditions). α-Ketoamide, $PhCOCONHCH_2Ph$, was hydrogenated rapidly in THF by the neutral Rh^I complex under the atmospheric pressure of hydrogen at ambient temperature. These results, when combined with those obtained with the cationic complex, suggest that the coordination of the simple ketone to the Rh^I center in a neutral complex is much less favorable compared to the Rh^I center in a cationic form. In addition to the charge effect, the solvent effect may also be operating. The neutral complex-catalyzed reaction was carried out in THF which is a rather strongly coordinating solvent whereas the cationic complex-catalyzed reaction was in the weakly coordinating methanol.

Kinetic aspects

A typical time-conversion curve for the catalytic hydrogenation of cyclohexanone with $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$ as a catalyst is shown in Fig. 1. An induction period is practically absent. The initial rates r_0 were measured for three

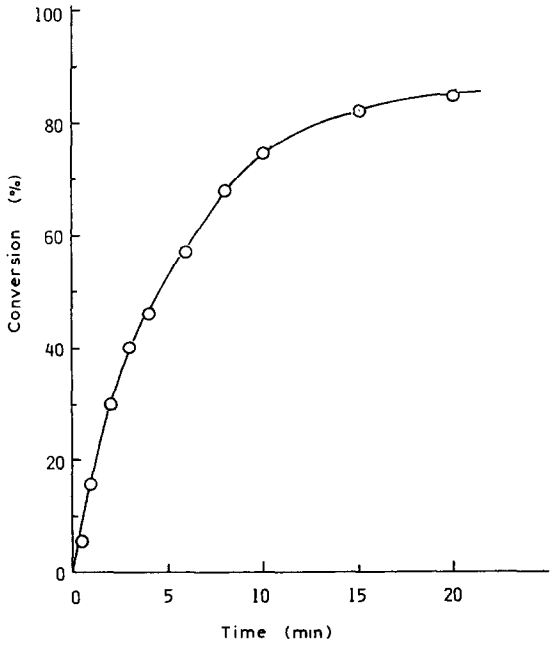


Fig. 1. Typical conversion curve of hydrogenation of cyclohexanone catalyzed by $[Rh((i\text{-}Pr)_2(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$; [Rh] = 0.5 m*M*; $[ketone]_0$ = 0.1 *M*; $[H_2]$ = 1.0 atm; in MeOH at 35°C.

substrates, cyclohexanone, benzophenone, and *N*-benzylphenylglyoxylamide, $PhCOCONHCH_2Ph$. With respect to the three reactants, H_2, ketone, and the catalyst, the concentration effects on the initial rate r_0 were determined independently. In the case of cyclohexanone and benzophenone, the plots of logarithms of r_0 against logarithms of concentration of the rhodium(I) complex [Rh] (0.3–1.0 m*M* for cyclohexanone; 1.0–3.0 m*M* for benzophenone), and the initial concentration of substrate $[H_2]_0$ (0.3–1.0 atm for both ketone substrates) and $[ketone]_0$ (0.03–0.2 *M* for cyclohexanone; 0.1–0.3 *M* for benzophenone) produced a clear first order dependence (within ±8%) for all the three reactants. Thus the rate law, as far as the initial stage is concerned, can be expressed by eq. 1. Unexpectedly the rates for both

$$r_0 = k_{obs}[Rh][H_2]_0[ketone]_0 \quad (1)$$

substrates exhibit unusual thermal behaviors as shown in Fig. 2. We will discuss this problem later.

The initial rate of catalytic hydrogenation of $PhCOCONHCH_2Ph$ with $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]^+$ as catalyst was found to be independent of the substrate concentration following eq. 2. Ligation of this ketoamide to the [Rh(diphosphine)]$^+$ center (eq. 3) is assisted through chelation as will be described. The

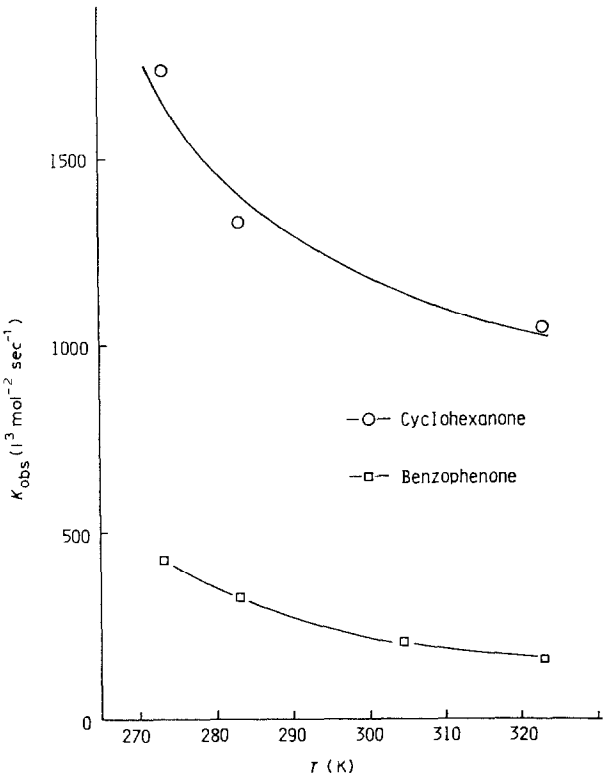


Fig. 2. Temperature dependence of k_{obs} for hydrogenation of cyclohexanone and benzophenone catalyzed by $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$ in MeOH.

$$r_0 = k_{obs}[Rh][H_2]_0 \quad (2)$$

rate of substrate complex formation (in THF at 25 °C) was too fast to measure accurately. In the presence of an excess of the ketoamide the substrate complex formation appears to be virtually complete since the ^{31}P NMR spectrum indicated

$$[Rh(diphosphine)(MeOH)_2]^+ + PhCOCONHCH_2Ph \rightleftharpoons [Rh(diphosphine)(PhCOCONHCH_2Ph)]^+ \quad (3)$$

diphosphine = $(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$

the absence of free $[Rh(diphosphine)(MeOH)_2]^+$ (vide infra). Accordingly the rate law (eq. 2) can be understood in terms of these favorable kinetic as well as thermodynamic aspects of the substrate-Rh^I complex formation. The catalytic hydrogenation of $PhCOCONHCH_2Ph$ by $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]^+$ provided activation parameters given in Table 3.

All the results so far described were obtained with $[Rh((i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2)(NBD)]ClO_4$ as catalyst. An analogous 1,4-diphosphine CyDIOP **2** (R = cyclohexyl) is available. This ligand enables us to achieve a high enantioselectivity (78% e.e.) in the asymmetric catalytic hydrogenation of ketoamides [9,22]. Owing to its constrained carbon frame work bearing two PCy_2 groups, the diphosphine chelation is presumably secured during the catalysis; otherwise the high degree of chiral recognition could not be explained. On the contrary, the diphosphine $(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$ has no such a device, and the 1,4-chelation is not secured. Accordingly it was deemed of interest to compare kinetic details between these two ligands. The rate equation for the hydrogenation of $PhCOCONHCH_2Ph$ with $[Rh(CyDIOP)(NBD)]^+$ was found to be exactly the same (eq. 2). Further, the activation parameters are also comparable as shown in Table 3. It is very likely, as these results suggest, that $(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$ functions as a chelating diphosphine during the catalytic cycles.

The rate equation was also obtained for the neutral complex "Rh(CyDIOP)Cl"-catalyzed hydrogenation of $PhCOCONHCH_2Ph$ in THF. The initial rate showed first-order dependence on the initial concentration of both ketone and H_2, but a fractional order for the Rh^I concentration (eq. 4). This may be derived from some

$$r_0 = k_{obs}[Rh]^{0.25}[H_2]_0[ketone]_0 \quad (4)$$

TABLE 3

THERMODYNAMIC PARAMETERS FOR HYDROGENATION OF $PhCOCONHCH_2Ph$ WITH Rh^I-DIPHOSPHINE COMPLEXES

Catalyst [a]	E_a (kcal mol^{-1})	$\Delta H^{\ddagger}_{308}$ (kcal mol^{-1})	$\Delta S^{\ddagger}_{308}$ (e.u.)
$(i\text{-}Pr)_2(CH_2)_4P(i\text{-}Pr)_2\text{-}Rh^+$ [b]	5.51	4.90	−32.0
(−)-CyDIOR-Rh^+ [b]	5.36	4.75	−30.9
(−)-CyDIOP-Rh^N [c]	3.99	3.38	−43.0

[a] Diphosphine-Rh^+ = $[Rh(diphosphine)(NBD)]ClO_4$; diphosphine-$Rh^N$ = $[Rh(C_8H_{14})_2Cl]_2$ + 2 diphosphine. [b] In MeOH. [c] In THF.

aggregation of rhodium(I) species resulting in a partial formation of an active form. We have not exploited this kinetic aspect further but merely measured the activation parameters (Table 3). They differ significantly from those obtained with discrete cationic complexes.

It is noteworthy that the neutral complex-catalyzed hydrogenation of the chelating substrate $PhCOCONHCH_2Ph$ shows the first order dependence of rates on substrate concentration (eq. 4) whereas the rate is independent on that in the cationic complex-catalyzed reaction (eq. 2). These features again reflect the coordination capability of the Rh^I center toward the substrate. Namely, the substrate coordination to a Rh^I center in the cationic complex is more facile than that in the neutral form. The substrate complex formation should then be one of the most important processes governing the entire kinetic feature.

Substrate complexes and intermediates

The substrates are H_2 and ketones. We were able to isolate or spectroscopically detected both of these substrate complexes.

Although oxidative addition of H_2 to cationic Rh^I diphosphine complexes has been postulated in the hydrogenation catalysis [23], the adduct has never been isolated or observed [24]. In fact, treatment of $[Rh(diphosphine)(diene)]^+$ with H_2 under atmospheric pressure in methanol merely results in $[Rh(diphosphine)(MeOH)_2]^+$ when the diphosphine ligand is bis(diphenylphosphino)ethane [1k], chiraphos (2,3-bis(diphenylphosphino)butane) [1n], or binap (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) [25]. Note that all these ligands carry at least two phenyl groups on each phosphorous atom.

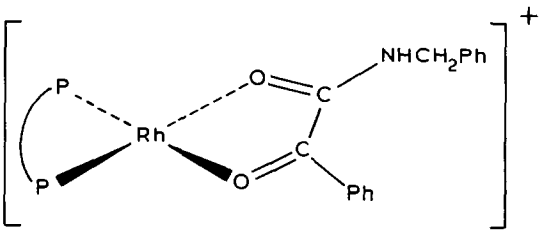
The reaction of H_2 with $[Rh((i\text{-}Pr)_2P(CH_2)_nP(i\text{-}Pr)_2)(NBD)]ClO_4$ ($n = 3,4$) in MeOH (1 atm, 25 °C) was very fast until 2 mol of H_2 were consumed to give $[Rh((i\text{-}Pr)_2P(CH_2)_nP(i\text{-}Pr)_2)(MeOH)_2]^+$ which was detected by the ^{31}P NMR (δ 55.39 ppm, d, J(Rh–P) 196.3 Hz for $n = 3$; δ 62.11 ppm, d, J(Rh–P) 205.1 Hz for $n = 4$). The subsequent absorption of 1 mol of H_2 occurs at a much slower rate (1–2 days at ambient temperature). The hydride product can be isolated as pale yellow or yellowish orange crystals from the methanol solution. Similarly a yellow hydride product was obtained from $[Rh(CyDIOP)(NBD)]ClO_4$. Their relevant IR and ^1H NMR data are summarized in Table 4.

The elemental analysis and the spectral data point to the formation "$[Rh(H)_2(diphosphine)]ClO_4$", which contains no coordinated methanol molecules. However, we found the complex to be polymeric as evidenced by its ^{31}P NMR which shows a complex higher order spectrum [26] and also by its low solubility in organic solvents such as alcohols and ethers. So far we have been unable to obtain single crystals of this polymeric complex suitable for an X-ray analysis. The molecular structure must await further investigations.

Coordination of a ketone to Rh^I was studied mainly by ^{31}P NMR spectroscopy. In the case of simple ketones such as PhCOPh or cyclohexanone, the doublet signal (δ 46.74 ppm, J(Rh–P) 204.1 Hz) of ^{31}P NMR of $[Rh(CyDIOP)(MeOH)_2]^+$ in MeOH did not produce any significant change upon addition of an excess of the ketones. In contrast, when $PhCOCONHCH_2Ph$ was added (Rh/ketoamide = 1/5), the doublet signal disappeared and two sets of double doublet signals appeared at δ 43.87 ppm (J(Rh–P) 193, J(P–P) 58 Hz) and 48.80 ppm (J(Rh–P) 210, J(P–P) 58 Hz) (at +10 °C) indicating the formation of a substrate chelate complex. Con-

sistently, the IR carbonyl stretching band (1630br cm^{-1}) of the free ketoamide shifted to 1590 cm^{-1}.

Although the ketoamide-Rh^I complex may be isolated at low temperature, it is not thermally very stable. Single crystals suitable for an X-ray analysis have not been obtained yet. Tentatively we assume a square planar structure **6**, as similar coordination of an amide carbonyl oxygen to Rh^I is known [11]. Although we could not determine the formation constant exactly, it must be fairly large as the ^{31}P NMR



(6)

spectrum indicated the absence of the doublet signal (δ46.74 ppm) of $[Rh(CyDIOP)(MeOH)_2]^+$ in the presence of an excess (4.7 mol/1 mol Rh) of the ketoamide. These coordination propensities of ketones we have examined reflect the rate law variation (eqs. 1 and 2).

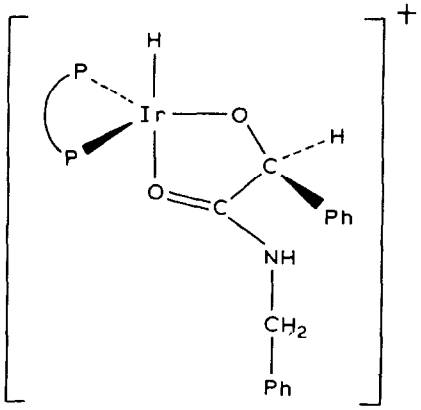
At a later stage of the catalytic sequence a hydrido-alkoxo complex [RhH(diphosphine)(OCH(R)R′)S]$^+$(S = solvent) may be formed. Our searches for such a species have led to the use of an iridium(III) complex. Treating a 1/1 mixture of [Ir((i-Pr)$_2$P(CH$_2$)$_3$P(i-Pr)$_2$)(COD)]PF_6 and PhCOCONHCH$_2$Ph in acetone with H_2 (1 atm, at ambient temperature) yielded a pale yellow crystalline complex. This was well characterized by elemental analysis and spectroscopic methods, but the X-ray diffraction studies have failed due to the disorder in crystals. A triplet signal at δ −29.59 ppm (J(P–H) 25.7 Hz) in ^1H NMR (acetone-d_6) and an IR absorption

TABLE 4

PHYSICAL PROPERTIES OF "[Rh(H)$_2$(diphosphine)]ClO_4"

Diphosphine	M.p. (°C)	Color	IR(ν,cm^{-1})		^1H NMR (δ, ppm)	
			RhH	ClO_4	Rh–H[a]	Rh–H[b]
(i-Pr)$_2$P(CH$_2$)$_3$-P(i-Pr)$_2$	142–146 (dec.)	pale-yellow	2000br	1030 1100 1150	−8.1(septet)	−20.5(complex quartet)
(i-Pr)$_2$P(CH$_2$)$_4$-P(i-Pr)$_2$	149–152 (dec.)	yellowish orange	2000br	1028 1100br 1150	−9.3(septet)	−20.7(complex quartet)
(−)-CyDIOP	148–150 (dec.)	yellow	2070 2100	1045 1100br 1160	−8.2(br)	−19.8(br)

band at 2300 cm^{-1} show the presence of an Ir–H group. This triplet resonance appears to be indicative of two equivalent phosphorous atoms. However, the ^{31}P NMR (MeOH, 27 °C) indicated clearly the presence of two inequivalent phosphorous atoms in very similar environments (δ −1.48 ppm, d and δ −0.27 ppm, d, J(P–P) 21.5 Hz). The ^{31}P NMR was temperature dependent and showed much complicated signals at lower temperature (below −10 °C). The presence of an alcoholato group was shown from its ^{1}H NMR (δ 5.93 ppm, d, C*H*–O) and ^{13}C NMR (δ 86.4 ppm, *C*H–O) and the presence of the coordinated amide carbonyl group was shown in the IR spectrum (1600 and 1550 cm^{-1}). One of the possible structures consistent with the low energy fluxional behavior is depicted as 7; we do not claim 7 to be the most probable structure among the possible geometrical



(7)

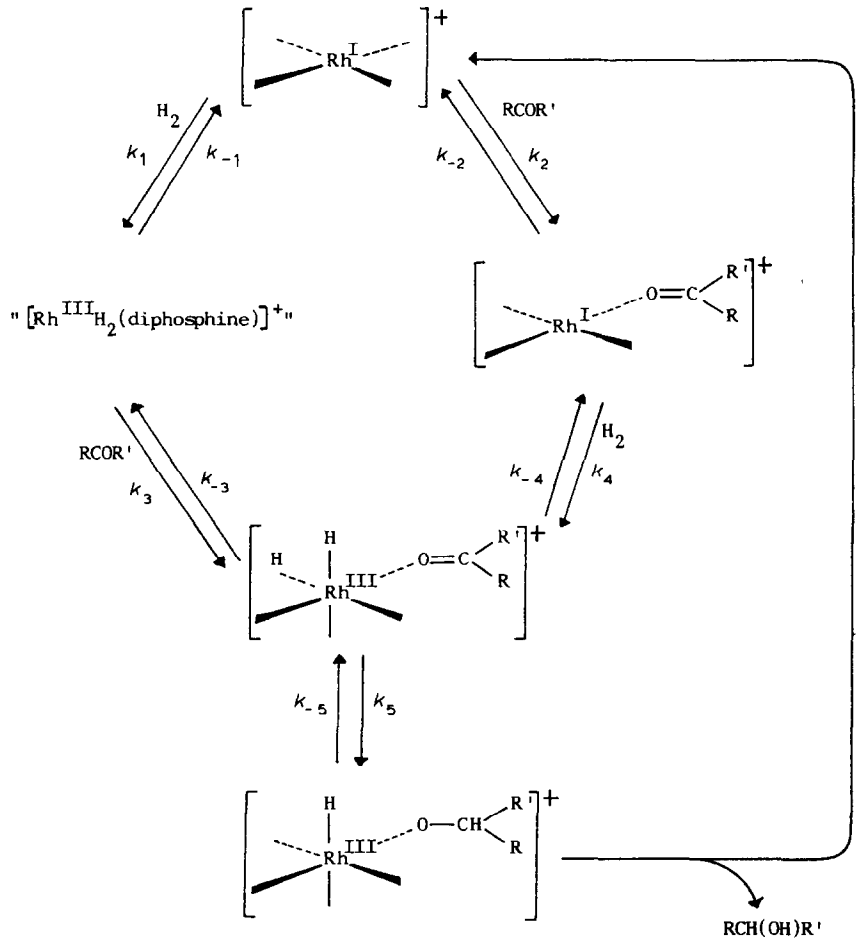
isomers. Attempts to isolate the similar Rh^{I} complex were unsuccessful due to its thermal instability.

The Ir^{I} complex $[Ir((i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2)(COD)]^+$ shows very poor activity as a catalyst for hydrogenation of $PhCOCONHCH_2Ph$. Note that the hydrido-alcoholato complex corresponds to the product of an oxidative addition of an alcohol which may be regarded as an intermediate in the dehydrogenation in an alcohol. Such hydrido-alkoxo complex has often been postulated as an intermediate complex in the catalytic ketone hydrogenation [3,27]. The iridium complex is the first example of such a hydrido-alkoxo complex of transition metal.

Catalytic reaction sequence

As a general reaction scheme of the catalytic hydrogenation one would consider two routes, one is a sequence involving an incipient oxidative addition of H_2 followed by the substrate coordination and subsequent intramolecular hydride migration leading to the hydrido-alkoxo species (the hydride route) and the other is a sequence starting from the formation of the ketone complex followed by the oxidative addition of H_2 and so on (the ketone route). The possible reaction sequences are illustrated in Scheme 1 (if the substrate is α-ketoamide, it acts as a bidentate which is not shown).

Obviously the catalytic hydrogenation of α-ketoamide proceeds through the ketone route owing to the kinetic ($k_2 > k_1$) and thermodynamic ($K_2 > K_1$) aspects.



(the diphosphine ligand is abbreviated)

SCHEME 1

The rate-determining step then comes after the substrate complex formation, either the H_2 oxidative addition (k_4) or the subsequent hydride migration (k_5). The rate law (eq. 2) suggests the H_2 oxidative addition step to be the rate-determining step. The observed very large negative entropy value (Table 3) is consistent with a mechanism involving such an association as the rate-determining step. The dominance of the ketone route was confirmed from the following observation. With a catalytic amount (1 mol%) of the dihydride complex "$[RhH_2(CyDIOP)]ClO_4$" prepared separately the hydrogenation of $PhCOCONHCH_2Ph$ was carried out under atmospheric pressure of dihydrogen at 25 °C. The reaction mixture was not entirely homogeneous at the beginning but the slurry gradually became a pale orange solution after several hours. The rate was found to be much slower (< 50% conversion during 27 h) than that effected with the precursor [Rh(CyDIOP)-

(NBD)]ClO_4 (100% conversion within 30 min), a result implying a very small k_3 value. Since k_1 is also small (see the preceding section), it is very likely that the hydride route is not operating in the catalysis. The reason why the cationic dihydride complex shows such a low activity toward the α-ketoamide is not clear at present, but we believe that the low reactivity is due to the polymeric structure described above.

Participation of monohydride species in the catalysis may be possible if heterolysis of dihydrogen molecule occurs at the oxidative addition step k_1 or k_4. Generally the monohydride formation is assisted by the presence of a base as the proton acceptor [28]. The ^1H NMR data of the polymeric hydride complexes we isolated exclude the formulation as a monohydride. For the ketone route, we do not have any direct experimental evidence related to this issue. However, we favor the dihydride formation rather than the heterolysis, since we could isolate the monohydrido-alkoxo Ir^I complex **7** which suggests the absence of such a heterolytic reaction.

The rate of the hydrogenation of simple ketones, cyclohexanone or benzophenone, catalyzed by [Rh((i-Pr)$_2$P(CH$_2$)$_4$P(i-Pr)$_2$)(NBD)]ClO_4 was found to follow a simple third-order expression (eq. 1). This apparent third-order rate law may be understood by assuming an equilibrium with a very small K value preceding the bimolecular rate-determining step. In this case also, only the ketone route may be operating as inferred from the following observation. The hydrogenation of cyclohexanone or benzophenone catalyzed by [Rh((i-Pr)$_2$P(CH$_2$)$_4$P(i-Pr)$_2$)(NBD)]ClO_4 (1 mol%, 1 atm H_2, 35 °C) proceeds much faster (100% yield within 20 min for cyclohexanone and within 1 h for benzophenone) compared to the formation of the dihydride complex "[RhH$_2$((i-Pr)$_2$P(CH$_2$)$_4$P(i-Pr)$_2$)]ClO_4" (about 30% yield during two days, see above).

The isolated dihydride complex again functions as a very poor catalyst for the hydrogenation of these simple ketones (< 40% yield during 24 h under a similar reaction conditions). Although we could not obtain the equilibrium constant K_2, ^{31}P NMR showed that the formation constant of the substrate complex in the case of simple ketones should be very small (vide supra). Thus if the subsequent H_2 oxidative addition is the rate-determining step, we obtain the following rate-equation (eq. 6) which agrees with the observed third-order expression. The observed unusual negative temperature dependence of the rate for the hydrogenation of simple ketones with the cationic Rh^I complex can be explained as follows. Namely, K_2 decreases as

$$r_0 = k_4[\text{Rh} \cdot \text{ketone}]_0[H_2]_0 \quad (5)$$

$$= k_4 K_2[\text{Rh}][\text{ketone}]_0[H_2]_0 \quad (6)$$

the temperature rises and simultaneously the increase in k_4 with the temperature rise is relatively small so that the product k_4K_2 decreases. Such an unusual negative temperature dependence of the reaction rate was reported for the oxidation of nitric oxide and well debated [29] and also reported for heterogeneous catalytic hydrogenation [30].

A large K_2 value implies the concentration of the substrate complex approaches that of the catalyst. Thus, in the case of the hydrogenation of the ketoamide, where a large K_2 value is involved as described above, the rate equation (eq. 2) corresponds with eq. 5. Thus the various kinetic aspects described above can be accommodated with the general scheme shown above.

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