Photocatalysis of $RhCl(PCy_3)_2$ for Cyclohexane Dehydrogenation: Thermal Dissociation of C–H Bond and Photoelimination of H_2

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Catalytic cyclohexane dehydrogenation, yielding cyclohexene and dihydrogen, proceeded under photoirradiation on either a three-coordinated complex, $RhCl(PCy_3)_2$ (Cy=cyclohexyl), or a dihydride complex, $RhClH_2(PCy_3)_2$, with almost the same turnover frequencies (8.4 or 8.6, respectively) attained by use of a cut-filter (UV-27) under refluxing conditions (354 K). $RhCl(PCy_3)_2$ in cyclohexane gave stoichiometric amounts of cyclohexene and $RhClH_2(PCy_3)_2$ at 354 K; the latter complex yielded little H_2 even at 373 K in toluene. A photocatalysis cycle for cyclohexane dehydrogenation with $RhCl(PCy_3)_2$ is proposed, where cyclohexene is yielded by thermal C–H bond dissociation and dihydrogen is photoeliminated from $RhClH_2(PCy_3)_2$, regenerating the original complex.

Functionalization of saturated hydrocarbons under mild conditions is one of the most challenging targets in catalytic chemistry. A lot of advances in the C–H bond activation have been made regarding saturated hydrocarbons with transition-metal complexes.[1] Remarkable photocatalytic activities for alkane dehydrogenation (Eq. 1) were found with Vaska-type rhodium complexes $RhCl(CO)(PR_3)_2$.[2]

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2 \qquad (1)$$

Flash photolysis studies revealed the role of a three-coordinated intermediate $RhCl(PR_3)_2$ (R=Ph, *p*-tolyl, and Me), generated from $RhCl(CO)(PR_3)_2$ under photoirradiation.[3] An electronic absorption band effective in CO dissociation was assigned by extended Hückel molecular orbital calculations to metal-to-ligand charge transfer (m.l.c.t.) from HOMO to a certain unoccupied orbital, antibonding with respect to the Rh–C bond.[4] Moreover, thermocatalytic dehydrogenation of cyclooctane was achieved with the Wilkinson complexes $RhCl(PR_3)_3$ (R=Ph, C_6H_4Me-*p* or R_3=$MePh_2$),[5] for which the key role of $RhCl(PR_3)_2$ was elucidated kinetically.[6]

Formation of $RhClH(C_6H_{11})(PMe_3)_2$ in cyclohexane[3c,3d] or of $RhClH_2(P^iPr_3)_2$ and $H_2[Rh(P^iPr_3)_2Cl]_2$ in cyclooctane[7] offers us pertinent suggestions on the reaction mechanism of photocatalytic alkane dehydrogenation. In the present study, $RhCl(PCy_3)_2$ is reacted with cyclohexane under thermal and photocatalysis conditions, with attention being paid to C–H bond splitting and H_2 elimination processes (Chart 1).

Experimental

All manipulations were carried out under Ar or N_2 atmosphere. Stable complexes $RhCl(PCy_3)_2$[8] and $RhClH_2(PCy_3)_2$[9] were prepared by the published methods. Cyclohexane of reagent grade was dried and deaerated over metallic sodium and benzophenone by refluxing under N_2 flow.

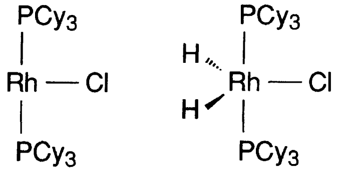


Chart 1.

Photocatalytic dehydrogenation of cyclohexane was carried out under boiling and refluxing conditions (354 K) in a cylindrical quartz cell (diameter 45 mm, cell length 80 mm), which was irradiated by a xenon lamp (2 kW, external-type, Ushio) or an ultra high-pressure Hg lamp (500 W, external-type, Ushio) utilizing cut-off filters: UV-27, UV-29, UV-32, UV-36, and L-42 (Kenko), where the L-42 filter was specified to cut off wavelengths <420 nm (50% transmittance at 420 nm). The amount of gas evolved was measured by a gas buret (10 cm^3). The reaction products were analyzed by gas chromatography using active carbon and PEG-20M columns for gas- and liquid-phase products, respectively. The UV/vis spectrum of $RhClH_2(PCy_3)_2$ complex was recorded on a UV-365 (Shimadzu) spectrometer.

Thermal reactivities of $RhCl(PCy_3)_2$ with cyclohexane and of $RhClH_2(PCy_3)_2$ in toluene were investigated in situ in an NMR tube under an argon atmosphere. ^1H and $^{31}P\{^1H\}$ spectra were recorded on JEOL GX 400 and JNM 90Q spectrometers, respectively, operating in the FT mode. ^{31}P chemical shifts were referred to an external standard of 85 % H_3PO_4, whereas ^1H spectra were referenced internally to the toluene-d_8 solvent and converted to the TMS scale.

Results and Discussion

Photocatalytic Dehydrogenation of Cyclohexane. Photocatalytic cyclohexane dehydrogenation proceeded with $RhClH_2(PCy_3)_2$ through a UV-29 filter, giving a total turnover number of 8.1 at the first (after 1.5 h) and 12.0 at the second (after 3 h) stage, respectively (Fig. 1). Since this complex decomposed gradually under reaction conditions (vide infra), the turnover frequency decreased from 10.8 h^{-1} (the first stage initially) to 5.1 h^{-1} (the first stage finally) and to 3.4 h^{-1} (the second stage). Without photoirradiation, little dihydrogen evolved even at refluxing conditions (354 K).

Wavelength Dependence of Photocatalytic Activity. Figure 2 shows the electronic absorption

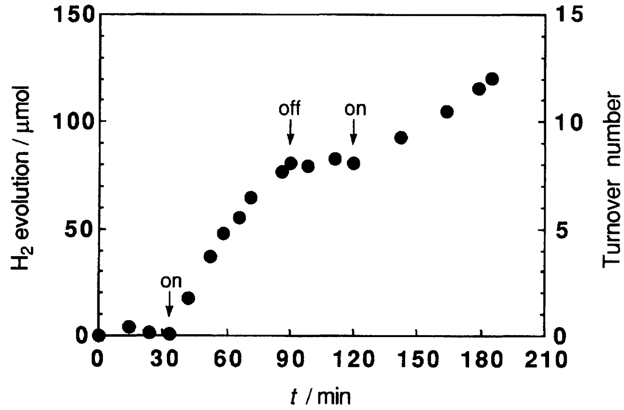


Fig. 1. Time-course plot for photocatalytic dehydrogenation of cyclohexane with $RhClH_2(PCy_3)_2$; catalyst concentration 10 μmol per 100 cm^3 cyclohexane, reaction temperature 354 K (reflux), cut-filter UV-29, and ultra high-pressure Hg lamp (500 W) light source.

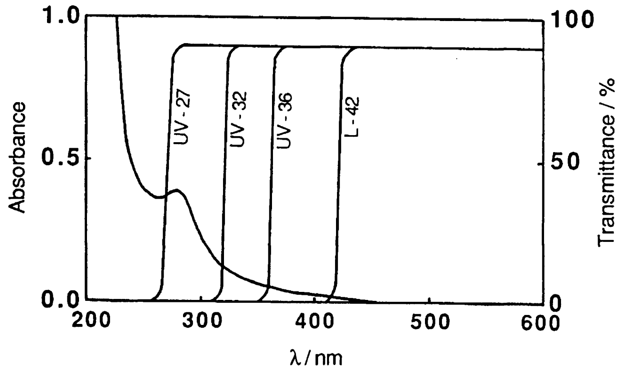


Fig. 2. UV-vis spectrum of $RhClH_2(PCy_3)_2$ with reference to transmission characteristics of the cut-off filters; catalyst concentration 5.0 μmol per 100 cm^3 toluene and cell length 10 mm.

spectrum of $RhClH_2(PCy_3)_2$ together with transmission characteristics of cut-filters used for the photoreaction. The photocatalytic reaction rates were dependent on wavelength and increased in the order of L-42<UV-36<UV-32<UV-27 (Table 1). The UV-27 filter gave a high rate, whereas little H_2 evolution was observed with the L-42 filter.

Wavelength dependence was investigated in a similar manner for the photocatalytic activity of $RhCl(PCy_3)_2$. Photoirradiation was indispensable for $RhCl(PCy_3)_2$ to dehydrogenate cyclohexane catalytically, as observed for $RhClH_2(PCy_3)_2$. The photoreaction rates of these complexes were almost the same at each wavelength region (Table 1). It seems reasonable to assume, therefore, that both $RhClH_2(PCy_3)_2$ and $RhCl(PCy_3)_2$ lie on the same photoreaction cycle.

Stoichiometric coincidence of dihydrogen with cyclohexene was excellent. Neither cyclohexadiene nor benzene was ever detected by GC analysis. Little dehydrogenation from the PCy_3 ligand itself under the reaction conditions was observed; this absence would be attributed at least partly to the low concentration of the PCy_3-coordinated complex (0.1 mM (1 mM=1 mmol dm^{-3})).

Table 1. Wavelength Dependence on the Rate of Cyclohexane Dehydrogenation with $RhCl(H)_2(PCy_3)_2$ and $RhCl(PCy_3)_2$ [a]

Cut-filter	$RhCl(H)_2(PCy_3)_2$		$RhCl(PCy_3)_2$	
	H_2 [b]	C_6H_{10}	H_2	C_6H_{10}
	μmol	μmol	μmol	μmol
UV-27	86	74	84	72
UV-32	47	39	48	52
UV-36	34	20	35	34
L-42	ca.0	ca.0	ca.0	ca.0

a) $RhCl(H)_2(PCy_3)_2$ 10 μmol, $RhCl(PCy_3)_2$ 10 μmol, cyclohexane 100 cm^3, 354 K (reflux), Xe lamp (2 kW) light source, reaction period 1 h. b) Contribution of catalytic H_2 evolution from C_6H_{12} with $RhCl(H)_2(PCy_3)_2$ can be estimated by subtracting the H_2 amount of its dihydrido ligand (10 μmol) from the observed values.

Reactivity of $RhCl(PCy_3)_2$ with Cyclohexane. Photocatalysis for cyclohexane dehydrogenation with these PCy_3-coordinated complexes should contain the processes of C–H bond splitting and H_2 elimination.

When the cyclohexane solution of $RhCl(PCy_3)_2$ was heated at 354 K, the color changed from violet to yellow, indicating a structural change of the complex. As shown in Fig. 3, the dihydrido complex, $RhClH_2(PCy_3)_2$ (δ_P=50.3 ppm, $^1J_{Rh-P}$=114.6 Hz, δ_H=−22.6 ppm, $^1J_{Rh-H}$=27.4 Hz, $^2J_{P-H}$=13.7 Hz, identified by the authentic sample), was gradually formed as a sole product when $RhCl(PCy_3)_2$ (δ_P=47.5 ppm, $^1J_{Rh-P}$=196.5 Hz) in cyclohexane was heated at 354 K. In addition, a stoichiometric quantity of cyclohexene was detected by GC analysis from the cyclohexane solution of $RhCl(PCy_3)_2$ after its refluxing for 0.5 h. A selective reaction process (Eq. 2) under thermal conditions was thus confirmed.

$$RhCl(PCy_3)_2 + C_6H_{12} \rightarrow RhClH_2(PCy_3)_2 + C_6H_{10} \quad (2)$$

As observed in Fig. 3(c), free PCy_3 (δ_P=10.0 ppm) was liberated by thermal decomposition of PCy_3-coordinated complexes; this release would be attributed at least partly to the gradual decrease of turnover frequency (Fig. 1).

A subtle difference between $RhCl(PCy_3)_2$ and $RhCl(P^iPr_3)_2$ in cyclohexane thermolysis is to be noted, since the former could dehydrogenate solvent cyclohexane in a stoichiometric manner and, moreover, $RhClH_2(PCy_3)_2$ was selectively formed during the reaction.[10] Both selective performance of Eq. 2 and low reactivities of PCy_3-coordinated complexes would be correlated to the remarkable bulkiness of the PCy_3 ligand.

Reductive Elimination of H_2 from $RhClH_2(PCy_3)_2$. After the heat treatment of $RhClH_2$-

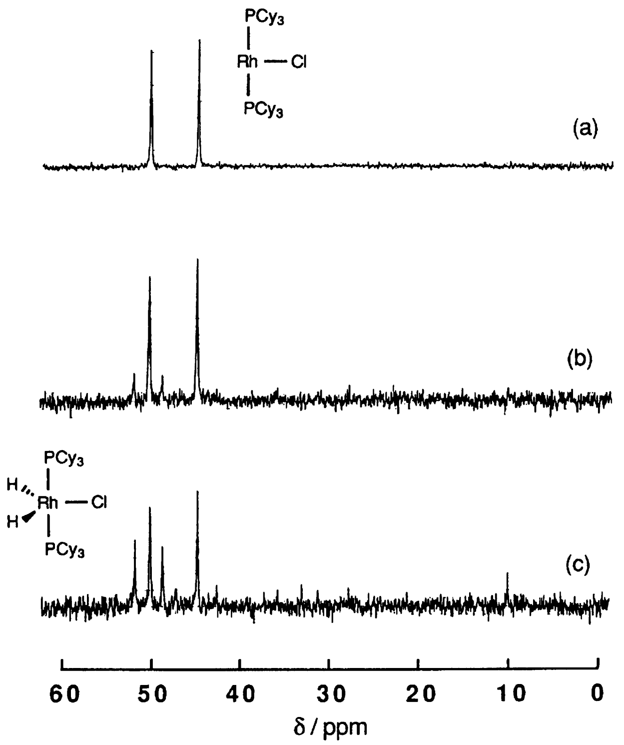
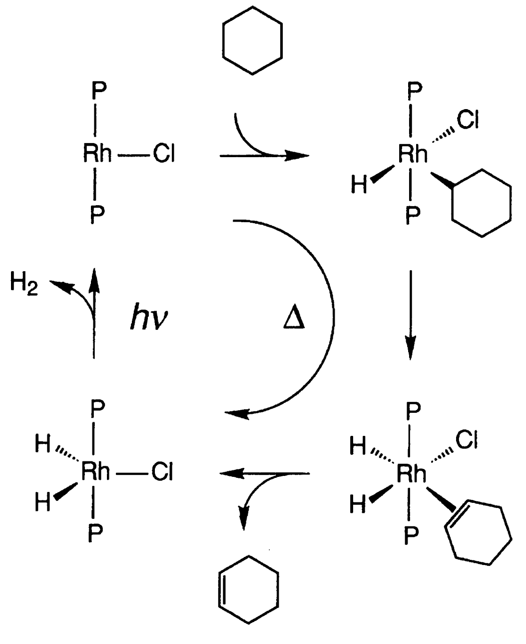


Fig. 3. Formation of $RhClH_2(PCy_3)_2$ from RhCl-$(PCy_3)_2$ in cyclohexane solution; $^{31}P\{^1H\}$ NMR spectra taken at 298 K for the samples before (a) and after the 0.5 h- (b) or 1.0 h- (c) heat treatment at 354 K.



Scheme 1.

$(PCy_3)_2$ in toluene at 373 K for 0.5 h, a trace amount of dihydrogen was detected by GC analysis. The charged amount of $RhClH_2(PCy_3)_2$ was recovered, as ascertained by ^1H and ^{31}P NMR analyses. Photoelimination of H_2 from dihydrido complexes has frequently been pointed out,[11] which is in conformity with our results on photocatalytic dehydrogenation of cyclohexane with $RhClH_2(PCy_3)_2$ or $RhCl(PCy_3)_2$ under refluxing conditions (Fig. 1 and Table 1).

Thermal reductive elimination of H_2 from $RhClH_2$-$(PR_3)_2$ was claimed to be rather facile for electron-withdrawing aryl-phosphine ligands, e.g., such as PPh_3 and $P(p\text{-tolyl})_3$, in contrast to the cases with electron-donating alkyl-substituted phosphine ligands, e.g., $PEtPh_2$ and $PMePh_2$.[6] The observed difficulty in thermal H_2 elimination from $RhClH_2(PCy_3)_2$ can be well interpreted in terms of the electron-donating property of PCy_3.

Proposal of Photocatalysis Cycle for Alkane Dehydrogenation. A reaction mechanism for photocatalytic dehydrogenation of cyclohexane with $RhCl(PCy_3)_2$ or $RhClH_2(PCy_3)_2$ is now proposed (Scheme 1). Thermal steps consist of (1) C–H bond splitting of cyclohexane with $RhCl(PCy_3)_2$, (2) elimination of β-hydrogen from the cyclohexyl ligand, and (3) formation of $RhClH_2(PCy_3)_2$ and cyclohexene. A photoreactive step follows: (4) H_2 dissociation from $RhClH_2(PCy_3)_2$ and regeneration of $RhCl(PCy_3)_2$.

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10) Heat treatment of $RhCl(P^iPr_3)_2$ (19 mM) in cyclohexane at 363 K for 3 h gave only a small amount of cyclohexene (<0.5 mM) but a lot of product complexes, including $RhClH_2(P^iPr_3)_2$ (2.7 mM), $H_2[Rh(P^iPr_3)_2Cl]_2$ (0.9 mM), $RhCl_2H(P^iPr_3)_2$ (3.6 mM), $[(^iPr_2)P(\eta^2\text{-MeC=CH}_2)]Rh(\mu\text{-Cl}_2)Rh(P^iPr_3)_2H_2$ (1.9 mM), and $H_2(P^iPr_3)_2Rh(\mu\text{-H}_2)Rh(P^iPr_3)_2HCl$ (1.5 mM).[7]

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