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Molecular hydrogen complexes in catalytic reactions: reactivity of neutral transition metal polyhydrides in the catalytic transfer hydrogenation of ketones

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Abstract

Transition metal polyhydrides are effective catalysts for the reduction of ketones by hydrogen transfer from 2-propanol at room temperature. The difference in the reactivity between $RuH_4(PPh_3)_3$ and $RuH_2(PPh_3)_4$ is discussed.

Introduction

The chemistry of transition metal polyhydrides is of current interest. Many known polyhydrides have been shown to contain nonclassical molecular hydrogen ligands (η^2-dihydrogen ligand) [1–5]. The variation in the coordination of the dihydrogen and the facile substitution of coordinated dihydrogen indicate that these polyhydrides have synthetic potential or should be active catalysts in catalytic reactions. We have reported the dehydrogenation of saturated alcohols in the absence of a hydrogen acceptor using $IrH_5(i\text{-}Pr_3P)_2$ as catalyst, during which the equilibrium between dihydrogen and dihydride was suggested to lead to the continuous evolution of dihydrogen in the catalytic cycle [6]. With this distinctive feature, it is proposed that the polyhydrides serve as an efficient catalyst in the transfer hydrogenation of ketones, with alcohol as the hydrogen donor under mild conditions. Here, the ketones are probably the hydrogen acceptors during the dehydrogenation of alcohols, which greatly favors the reaction. Although the transfer hydrogenation of ketones catalyzed by transition metal complexes have been extensively studied [7], the transfer hydrogenation of ketones from 2-propanol promoted by the molecular hydrogen complexes have not been reported.

Results and discussion

We found that $RuH_4(PPh_3)_3$ (**1**) is a very effective catalyst for the reduction of cyclic ketones by H transfer from i-PrOH at room temperature. When 4-methyl-

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Table 1

Hydrogenation of various cyclic ketones at room temperature [a]

Ketone	Catalyst [b]	Reaction time (h)	Conversion [c] (%)	Alkylcyclohexanol *cis* : *trans*
4-methylcyclohexanone	**A**	0.5	79	33 : 67
		1.0	91	33 : 67
		2.0	97	32 : 68
		5.0	97	29 : 71
		24.0	99	26 : 74
	B	24.0	33	30 : 70
	C	5.0	15	48 : 52
		24.0	95	41 : 59
2-methylcyclohexanone	**A**	5.0	40	
		24.0	70	62 : 38
	B	24.0	39 [d]	67 : 33
	C	24.0	4	–
4-t-butylcyclohexanone [d]	**A**	24.0	99	24 : 76
	B	24.0	< 1	
	C	24.0	6	

[a] Reaction conditions: substrate/catalyst = 100 : 1, ketone/i-PrOH = 1 : 3, T = 25 °C. [b] **A** = $RuH_4(PPh_3)_3$, **B** = $RuH_2(PPh_3)_4$, **C** = $IrH_5(i\text{-}Pr_3P)_2$. [c] The conversion and *cis/trans* ratio of products were determined by GLC and ^1H NMR. [d] Reaction in benzene.

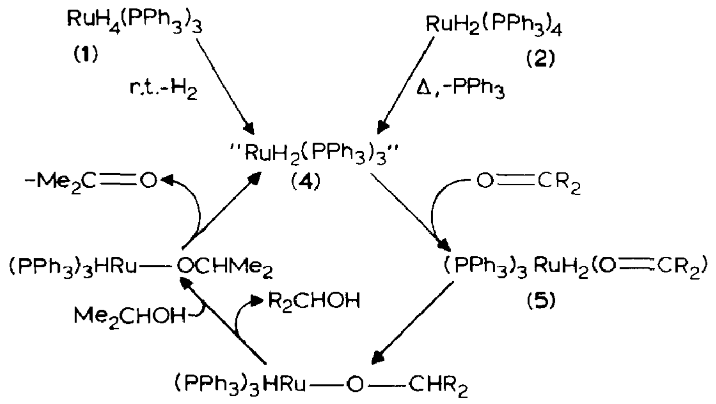
cyclohexanone in 3 equivalent amounts of 2-propanol with 1.0% of **1** was stirred at 25 °C under argon for 0.5 h, 4-methylcyclohexanol was obtained in 33 : 67 *cis/trans* ratio and in 78% yield. After 2 h, 97% of the 4-methylcyclohexanone had been converted to 4-methylcyclohexanol in the same *cis/trans* ratio. The hydrogenation reaction of various cyclic ketones are given in Table 1. When $IrH_5(i\text{-}Pr_3P)_2$ (**3**) was used the initial rate of hydrogenation of 4-methylcyclohexanone was slightly lower than that of **1**, but a similar overall conversion in 24 h was observed. Compared with **1**, however, $RuH_2(PPh_3)_4$ (**2**) gave only 32% of 4-methylcyclohexanol in 24 h under identical conditions.

Table 2

Hydrogenation of cyclic ketones at 83 °C [a]

Ketone	Catalyst [b]	Conversion (%)	Turnover number	Alkylcyclohexanol *cis* : *trans*
4-methyl-cyclohexanone	**A**	97.0	577	26 74
	B	96.1	576	25 75
	C	96.4	570	39 61
2-methyl-cyclohexanone	**A**	91.2	559	46 54
	B	94.1	576	30 70
	C	69.0 [c]	413	75 25
4-t-butyl-cyclohexanone [d]	**A**	97.1		24 76
	B	98.9		21 79
	C	94.8 [e]		43 57

[a] Reaction conditions: substrate/catalyst = 600 : 1, t = 24 h, T = 83 °C, ketone/i-PrOH = 1 : 3. [b] See footnote *b* to Table 1. [c] t = 48 h. [d] Substrate/catalyst = 50 : 1. [e] t = 96 h.



Scheme 1

The molecular hydrogen complex **1** shows greater reactivity than complex **2** in the catalytic reduction of ketones, but the stereoselectivity of the products remains unchanged. The unhindered alkyl-substituted cyclohexanone yields high proportions of the corresponding *trans* alcohols on reduction by complexes **1** and **2**, whereas sterically hindered 2-methylcyclohexanone gives mainly the *cis* alcohol. When 2-methylcyclohexanone and 0.16 mole% of $IrH_5(i\text{-}Pr_3P)_2$ in 2-propanol was refluxed at 83° C for 24 h, the *cis*-alcohol was obtained in 75% yield as shown in Table 2.

The higher activity of the polyhydrides under mild conditions is probably because of the ready substitution of the coordinated η^2-dihydrogen which can be regarded as a good leaving group in the catalytic reaction at low temperature. We suggest that the reaction of complexes **1** and **2** probably proceeds via the same intermediate by the dissociation of η^2-dihydrogen and triphenylphosphine ligands, respectively, although at room temperature the loss of H_2 is favored. Therefore, the catalytic activities of **1** and **2** are almost identical under reflux at 83° C in 2-propanol for 24 h because of enhanced PPh_3 dissociation in the reaction of **2**. The results are shown in Table 2.

The mechanism of H transfer is postulated as Scheme 1.

For a better understanding of the differences in these reactions, the stoichiometric reaction of 1 or 2 with cyclohexanone in a sealed tube was monitored by ^1H and ^{31}P NMR spectroscopy in C_6D_6. At low temperature (10–25° C), the intermediate "$RuH_2(PPh_3)_3$" (**4**) [8] formed from η^2-H_2 or PPh_3 dissociation was observed (^1H δ -17.79 q, *J* 26.6 Hz; ^{31}P δ 57.5 s). As the reaction temperature was raised, the ^{31}P NMR signal of the solution containing **1** and cyclohexanone appeared at δ 55.6 (broad s) and 74.6 (broad s), the ^1H resonance appeared at δ -10.2 (q, *J* 40.0 Hz) and -24.9 (broad s), and cyclohexanol (^1H δ 3.56 ppm) was formed. From a comparison experiment, these signals, attributable to the coordination of cyclohexanone were assumed to be due to $(RuH_2(PPh_3)_3L)$ (**5**) and $(RuH_2(PPh_3)_2L_2)$ (**6**) [9] (L = cyclohexanone). However, under the same conditions, only a small amount of the analogue was generated in the reaction of **2**. Finally, at 65–80° C, the mixture was found to contain for **1**, **5** (28%), **6** (35%), **1** (6%), **2** (5%); for **2**, **5** (16%), **6** (27%) **2** (27%). These results indicate that the reaction rate of **1** is higher than (**2**) owing to the readiness of η^2-H_2 dissociation at low temperature. We believe that the higher reactivity of the transition metal polyhydride for the hydrogenation reaction of unsaturated compounds under mild conditions provides possibilities in its application, especially, to asymmetric hydrogenation, a study of which is in progress.

Experimental

All the reactions were carried out under prepurified nitrogen or argon using Schlenk techniques. The complexes (**1**), (**2**) [10] and (**3**) [11] were prepared by published methods. The 2- and 4-methylcyclohexanones were purchased from Tokyo Kasei Chemical Co. and purified by distillation under nitrogen. 4-t-Butylcyclohexanone was prepared by published procedures [12]. ^{1}H NMR spectra were recorded on a Varian EM-360 or Varian XL-200 spectrometer. IR spectra were recorded on a Shimadzu IR-440 instrument. Mass spectra were recorded on a Finnigan 4021 GC/MS/DC instrument. GC were determined on a Shangfen 102G with 10% polyethylene glycol column supported on 102 silanized white support.

Procedure for the catalytic reduction of ketones: 0.5–1.0 ml of 2-propanol solution containing 1.0–6.0 mmole of cyclic ketones and 0.01 mole of catalyst were stirred magnetically in a Schlenk tube at 25°C for 24 h. The conversion and stereoselectivity were monitored by GLC. The colorless liquid obtained after distillation under vacuum was used for the characterization by IR, NMR and MS spectroscopy.

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