Hydrogenation of Aromatic Ketones Catalyzed by (η^5-$C_5(CH_3)_5$)Ru Complexes Bearing Primary Amines

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Summary: The rapid hydrogenation of simple aromatic ketones is accomplished by using a combination of (η^5-$C_5(CH_3)_5$)Ru complexes and primary amines as a catalyst in 2-propanol. In particular, 1,2-diamines with primary and tertiary amino groups at both ends exhibit a significant ligand acceleration effect. Isotope-labeling experiments using D_2 and 2-propanol-d_n reveal that 2-propanol participates in the activation of H_2 based on a metal/NH bifunctional effect to facilitate the hydrogenation. Asymmetric hydrogenation of prochiral simple ketones with the chiral version of the catalysts provides optically active secondary alcohols with up to 95% ee.

Well-defined chiral transition metal catalysts having a metal/NH bifunctional synergetic effect have been recently developed for the enantioselective catalytic reduction of carbonyl compounds[1a] and imines[1b] to give optically active alcohols and amines.[1−4] Particularly, chiral Ru complexes $RuCl_2$(chiral diphosphine)(chiral 1,2-diamine)[2] and RuCl(Tsdpen)(η^6-arene)[3] (TsDPEN: *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine) combined with a base have proven to effect practical asymmetric hydrogenation or transfer hydrogenation as catalysts with an excellent reactivity and stereoselectivity as well as a wide range of substrates. Although both catalyst systems have a characteristic NH functionality, the catalytic performance of the two catalyst systems differs greatly. For example, the Ru−phosphine/diamine complexes readily react with H_2, leading to effective hydrogenation catalysts, while the Ru−arene/Tsdiamine complexes hardly react with H_2 but instead react with 2-propanol or formic acid to generate transfer hydrogenation catalysts. This remarkable difference in the reactivity may be attributable to the electronic properties on the central Ru metal; the former catalyst has an electron-donating phosphorus ligand, but the latter one has an electron-withdrawing tosylamido ligand. We found that Cp*Ru−1,2-diamine complexes (Cp* = pentamethylcyclopentadienyl, η^5-$C_5(CH_3)_5$), which are isoelectronic to the Ru arene transfer hydrogenation catalyst,[3] are highly effective catalysts for the hydrogenation of ketones. We now report the

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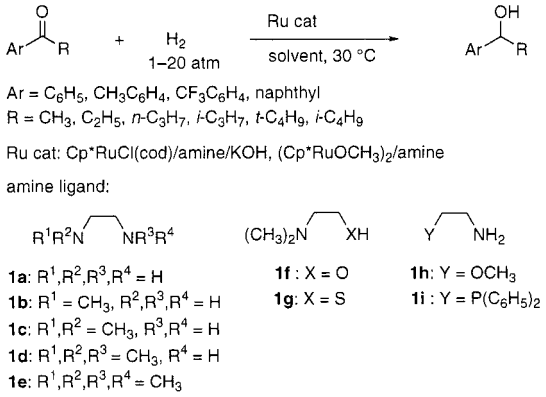
Table 1. Hydrogenation of Acetophenone Catalyzed by Cp*Ru−Amine (1) Complexes[a]

run	Cp*Ru(II)	amine (**1**)	P_{H_2}, atm	conv, %[b]	TOF, h^{-1} [c]
1	Cp*RuCl(cod)	**1a**	1	41	
2	Cp*RuCl(cod)	**1b**	1	98	
3	Cp*RuCl(cod)	**1c**	1	100	100
4	Cp*RuCl(cod)	**1d**	1	57	
5	Cp*RuCl(cod)	**1c**	0		0
6	Cp*RuCl(cod)	**1c**	10		520
7	Cp*RuCl(cod)	**1c**	20		1170[d]
8	$(Cp^*RuOCH_3)_2$	**1c**	10		100[e]
9	$(Cp^*RuOCH_3)_2$	**1c**	10		150[e,f]

[a] The reaction was carried out at 30 °C in 2-propanol unless otherwise noted. The molar ratio of acetophenone:Ru:**1**:KOH is 100:1:1:1 for runs 1−4, 1000:1:1:1 for runs 5−7, and 500:1:1.5:0 for runs 8−9. The reaction time is 1.0 h unless otherwise noted. [b] Determined by ^1H NMR spectroscopy. [c] See text. [d] 0.5 h. [e] 2.0 h. [f] In ethanol.

Scheme 1



synthesis and structures of the Cp*Ru complexes as well as their catalytic activity and some mechanistic considerations for the hydrogenation of ketones.

We first examined the ligand-acceleration effect of several amine ligands for the hydrogenation of acetophenone (Scheme 1). The reaction was carried out in 2-propanol containing acetophenone, Cp*RuCl(cod),[5] amine (**1**), and KOH (cod = 1,5-cyclooctadiene, acetophenone:Ru:**1**:KOH = 100:1:1:1) under atmospheric pressure of H_2 and at 30 °C for 1 h. The reaction proceeded very slowly without any amine, to give 1-phenylethanol in <1% yield. However, the screening test with a range of amines under otherwise identical conditions revealed that *N*,*N*-dimethylethylenediamine (**1c**) displayed the highest rate enhancement to afford the product quantitatively (Table 1, runs 1−4). It is noteworthy that *N*-methylethylenediamine (**1b**) worked equally well, and ethylenediamine (**1a**) or *N*,*N*,*N*′-trimethylethylenediamine (**1d**) gave only modest yields, while *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**1e**) did not promote the reaction at all. These results strongly suggest that the amino NH group plays a crucial role for the catalysis. This may be seen from the fact that 2-(dimethylamino)ethanol (**1f**) and 2-(dimethylamino)-ethanethiol (**1g**) were ineffective. Furthermore, a tertiary amino group at the other terminus in **1c** most likely contributes to the rate enhancement, as is clear from the results obtained using benzylamine (3%), 2-methoxyethylamine (**1h**, 2%), 2-(diphenylphosphino)-ethylamine (**1i**, 16%), and 2-picolylamine (37%).

The hydrogen pressure strongly influences the rate of the reaction, as shown in Table 1 (runs 3, 5−7). When the reaction was carried out in 2-propanol containing the combined catalyst at 30 °C with a substrate/catalyst molar ratio (S/C) of 1000 (Ru:**1c**:KOH = 1:1:1), the initial rate of the reaction was 100 TOF (TOF: turnover frequency, moles of product per mole of catalyst per hour, h^{-1}) under atmospheric pressure of H_2 and increased to 1170 h^{-1} at 20 atm of H_2. Notably, in the absence of H_2, the hydrogenated product was hardly obtainable, indicating that this reductive transformation is a net hydrogenation. However, the present catalyst system was totally inactive for the hydrogenation of a simple olefin or acetylene such as styrene or phenylacetylene.

Cp*RuCl(cod)/**1c** is a useful catalyst precursor, which possibly gives in situ an active catalyst, Cp*Ru(amido) complex, upon treatment with KOH as observed in the RuCl(Tsdpen)(η^6-arene) catalyst system.[3] Unfortunately, all attempts to isolate this amido complex using either Cp*RuCl(cod) or $(Cp^*RuCl)_4$[6] and **1c** in the presence of KOH or $(Cp^*RuOCH_3)_2$[7] and **1c** have been unsuccessful. Also, similar trials to isolate the Ru hydride complex, Cp*RuH(amine), in the presence of H_2 resulted in the formation of polynuclear Ru hydride clusters[8] without **1c**, which are inert to this hydrogenation. Nevertheless, a combined catalyst system of Cp*RuCl(cod)/**1c**/KOH or $(Cp^*RuOCH_3)_2$/**1c** showed high activity in the presence of ketonic substrates.

2-Propanol or ethanol is the best solvent choice for this hydrogenation, while use of aprotic solvents such as DMF, THF, acetonitrile, and CH_2Cl_2 resulted in moderate to low yields. Isotope-labeling experiments using partially deuterated 2-propanol and D_2 revealed that 2-propanol participates in the H_2 activation to generate a Ru hydride species. The reaction of *tert*-butyl phenyl ketone with 1 atm of H_2 in $(CH_3)_2CDOH$ (solvent/substrate molar ratio of 25) containing the combined catalyst system Cp*RuCl(cod)/**1c**/KOH (S/C = 100) gave no deuterated product, indicating that 2-propanol is hardly dehydrogenatively oxidized under the reaction conditions. When the reaction was performed with D_2 in $(CH_3)_2CHOH$ under otherwise identical conditions, the deuterated product was obtained with 7% of D incorporated at the benzylic position. ^2H NMR analysis of this reaction in toluene-d_8 showed that a considerable amount of $(CH_3)_2CHOD$ is formed, and this H/D exchange rate is faster (146 TOF) than the product formation (33 TOF) (Supporting Information). Notably, the reaction with D_2 in $(CH_3)_2CHOD$ provided an alcoholic product with greater than 90% deuterium content at the benzylic carbon. These results clearly show that a rapid exchange of hydrogen atoms between H_2 and ROH occurs reversibly prior to the reduction of the ketones. This scrambling caused by the catalyst in 2-propanol proceeds possibly via interconversion of Cp*Ru(amido)(η^2-H_2)[9] and Cp*Ru(amine)H, in which 2-propanol participates in the H_2 activation through the formation of a hydrogen-bonding network,[10,11] as shown

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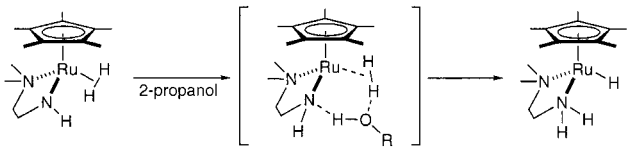


Figure 1. Postulated intermediate for the effective activation of dihydrogen.[9−11]

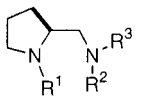
Table 2. Asymmetric Hydrogenation of Various Aryl Ketones, ArCOR, Catalyzed by a Catalyst System, Cp*RuCl(cod)/(*S*)-2a/KOH[a]

Ar	R	conv, %[b]	ee, %[c]	config[d]
C_6H_5	CH_3	>99	72	*R*
C_6H_5	C_2H_5	94	79	*R*
C_6H_5	*n*-C_3H_7	>99	79	*R*
C_6H_5	*i*-C_3H_7	94	73	*R*
C_6H_5	*t*-C_4H_9	99	81	*R*
C_6H_5	*i*-C_4H_9	98	95	*R*
o-$CH_3C_6H_4$	CH_3	87	85	*R*
m-$CH_3C_6H_4$	CH_3	70	72	*R*
o-$CF_3C_6H_4$	CH_3	>99	66	*R*
m-$CF_3C_6H_4$	CH_3	99	66	*R*
1-naphthyl	CH_3	97	79	*R*
2-naphthyl	CH_3	98	64	*R*

[a] The reaction was carried out at 30 °C for 6−18 h under 10 atm of H_2 using a 0.1−0.6 M solution of the ketone in 2-propanol. Ketone:Ru:(*S*)-**2a**:KOH = 100:1:1:1. [b] Conversion was determined by ^{1}H NMR. [c] Determined by GLC analysis or HPLC analysis. See Supporting Information. [d] Determined from the sign of rotation of the isolated product.

in Figure 1. Such an effective activation of η^2-H_2 by H_2O or $N(C_2H_5)_3$ additives has been considered in an olefin hydrogenation reaction with a cationic Ru hydridotris(pyrazolyl)borate complex and results in a significant improvement in the catalytic activity.[12]

Encouraged by the marked acceleration in the reaction in 2-propanol, we then tried asymmetric hydrogenation of simple ketones using a chiral version of the Ru catalyst (Table 2). We found that an isolable Cp*RuCl((*S*)-**2a**) effects asymmetric hydrogenation of alkyl phenyl ketones to provide the corresponding *R* alcohols with good to excellent ee's. Among the chiral diamine ligands tested, a chiral diamine, (*S*)-**2**, derived from L-proline showed the highest enantioselectivity for the hydrogenation of acetophenone. The stereoselective outcome of the reaction was delicately influenced by the structures of the ketones and catalysts. The enantioselectivity was noticeably increased by increasing the bulkiness of the alkyl group from methyl to isobutyl. The reaction of phenyl isobutyl ketone was achieved in up to 95% ee. Notably, (*S*)-**2a** and (*S*)-**2b** with the NH group at the side chain provided the (*R*)-1-phenylethanol with 72% and 13% ee's, respectively, while (*S*)-**2c** and (*S*)-**2d** with the NH group at the pyrrolidine ring provided the (*S*)-1-phenylethanol with 40% and 13% ee's, respectively, irrespective of their backbone structure. On the other hand, the chiral diamine, (*S*)-**2e**, with two NH functionalities at both N termini gave a low enantioselectivity (3% ee, (*R*)), presumably because the opposite selectivities caused by the two NH groups counteract each other.



chiral diamines

2a: $R^1 = C_2H_5$, R^2, R^3 = H
2b: $R^1 = CH_3$, R^2 = 1-naphthyl, R^3 = H
2c: R^1 = H, R^2, $R^3 = -(CH_2)_4-$
2d: R^1 = H, R^2, $R^3 = CH_3$
2e: R^1 = H, R^2, R^3 = H

To gain a deeper insight into the enantioselective reaction, the preformed catalyst, Cp*RuCl((*S*)-**2a**), was prepared by mixing an equimolar amount of Cp*RuCl(cod) and (*S*)-**2a** in toluene at reflux temperature or more conveniently from 1/4(Cp*RuCl)$_4$ and (*S*)-**2a** in diethyl ether at room temperature. A single-crystal X-ray analysis (Supporting Information) shows that the complex has a distorted pseudo-octahedral coordination environment with Cp*, NR_3, RNH_2, and Cl ligands as observed in the RuCl(η^6-*p*-cymene)(Tsdpen) complex.[3d] We would expect the Ru hydride complex to be generated with retention of configuration with the *R*-Ru(II) center[3d] by a *D*cb mechanism upon the treatment of the preformed catalyst with KOH in the presence of H_2. Thus, the preformed catalyst promotes the asymmetric hydrogenation of acetophenone in 2-propanol containing KOH to give a chiral alcohol with almost the same enantiomeric purity as does the in situ generated catalyst. The aryl ketones approach the H−Ru−N−H linkage in the hydride−amine complex to form a six-membered cyclic transition state,[3i,4k] in which steric repulsion between the ethyl group of the ligand and the substituent of the ketone is minimized. To our knowlegde, this is the first example of homogeneous asymmetric hydrogenation of carbonyl compounds catalyzed by phosphine ligand-free chiral transition metal complexes.[13]

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Supporting Information Available: Experimental procedures for the hydrogenation, HPLC or GLC behavior, isotope-labeling experiments, and data concerning the single-crystal X-ray analysis of Cp*RuCl((*S*)-**2a**). This material is available free of charge via the Internet at http://pubs.acs.org.

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