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Ruthenium Dihydride $RuH_2(PPh_3)_2((R,R)$-cyclohexyldiamine) and Ruthenium Monohydride $RuHCl(PPh_3)_2((R,R)$-cyclohexyldiamine): Active Catalyst and Catalyst Precursor for the Hydrogenation of Ketones and Imines

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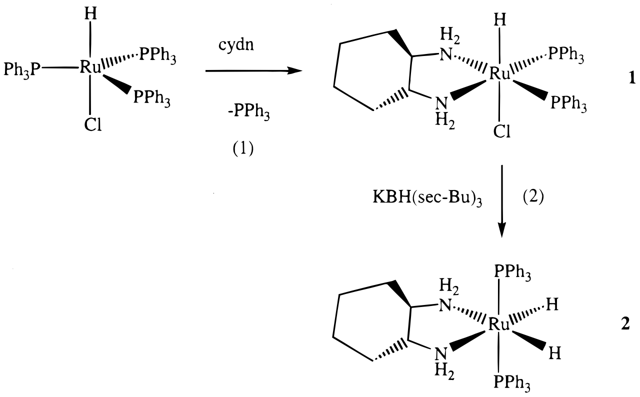
Summary: The new monohydride $RuHCl(PPh_3)_2(R,R$-cydn), with base added, and dihydride $RuH_2(PPh_3)_2$-(R,R-cydn), in the absence of base, catalyze the hydrogenation of a wide variety of ketones and some imines at 3 atm of H_2 and 20 °C with high turnover numbers. The mechanism is thought to involve the concerted dihydrogen transfer from cis hydride and N−H groups to the substrate followed by heterolytic dihydrogen splitting.

Noyori and co-workers have reported $RuCl_2(PPh_3)_3$/diamine and $RuCl_2$(diphosphine)(diamine) systems, which are precursors for the generation of what appears to be some of the most active catalysts for the homogeneous and asymmetric hydrogenation of ketones in a 2-propanol/base mixture.[1−3] They suspected that monohydride or dihydride species were the active and selective catalysts in these systems, but they were unable to isolate and characterize these (see footnote 16 of ref 3). In related work they[4,5] and others[6] have provided evidence that the bifunctional Ru−H/N−H motif, a hydride and amine coordinated cis on ruthenium(II), plays an important role in the hydrogenation of ketones and imines by transfer of hydrogen from 2-propanol or $[HNEt_3][HCO_2]$. Our interest in ruthenium hydride and dihydrogen chemistry[7−9] and in protonic−hydridic NH···HM bonds[10,11] led us to study the nature of the ruthenium hydrides that might be present in the Noyori $RuCl_2(PPh_3)_3$/diamine/KOH/2-propanol catalytic system.

Scheme 1



This has led to the discovery that the dihydride $Ru(H)_2(PPh_3)_2$(cydn) (**2**; cydn = (*R,R*)-cyclohexyldiamine) is a very active ketone and imine hydrogenation catalyst, while the monohydride complex $Ru(H)(Cl)(PPh_3)_2$(cydn) (**1**) is inactive. Ruthenium dihydrides $RuH_2(L)(PPh_3)_3$ (L = H_2, N_2,[12] vacant site[13]) are catalysts for the hydrogenation of cyclohexanone in THF and the transfer hydrogenation of cyclopentanone from 2-propanol solvent. To the best of our knowledge, catalysts based on ruthenium dihydride complexes with two amino ligands are unprecedented.

When an equimolar mixture of $RuHCl(PPh_3)_3$ and cydn in tetrahydrofuran is stirred at room temperature under a nitrogen atmosphere, the substituted complex $RuHCl(PPh_3)_2$(cydn) (**1**) is formed quantitatively (Scheme 1, eq 1).[14] A similar reaction with ethylenediamine yields $RuHCl(PPh_3)_2$(en), as will be described elsewhere. The ^1H and $^{31}P\{^1H\}$ NMR spectra are consistent with a structure containing mutually cis hydride and phosphorus nuclei. The structure of **1** as shown in Scheme 1 has been confirmed in a preliminary X-ray diffraction study.

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(14) **1**: THF (2 mL) was added to $RuHCl(PPh_3)_3$ (300 mg, 0.31 mmol) and (*R,R*)-*trans*-cyclohexyldiamine (36 mg, 0.32 mmol) and the mixture stirred for 6 h under nitrogen. The resulting solution was filtered and hexanes (10 mL) added to the filtrate, precipitating a yellow solid. Yield: 224 mg, 94%. ^1H NMR (δ): −17.99 (t), $^2J_{HP} = 25.7$ Hz, 1H (RuH); 0.45 ppm (br), 2H (NH); 2.38 ppm (br), 2H (NH). $^{31}P\{^1H\}$ NMR (δ): 70.6 (s). IR: 1987 cm^{-1}.

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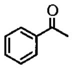
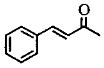
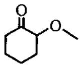
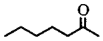
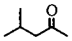
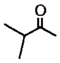
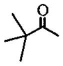
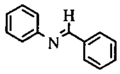
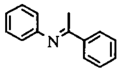
Table 1. Catalytic Hydrogenations Using $RuH_2(PPh_3)_2$(*R*,*R*-cydn) (2) and H_2 Gas[a]

Entry	Substrate	S:C ratio	% Conversion	Time (hr)
1		5000	100	<12
2		5000	100	<8
3		5000	100	<8
4		3600	100	<12
5		4000	100	<12
6		5000	100	<12
7		3600	100	<12
8		5000	87	48
9		500	100	<4
10		280	66	48

[a] Neat substrate except for entries 3, 9, and 10, where benzene was used as the solvent. The product of entry 3 is exclusively the allyl alcohol PhCH=CHCH(OH)Me.

In the presence of catalytic amounts of a base such as sodium hydroxide or sodium isopropoxide under H_2 gas (3.5 atm) at 20 °C, complex **1** (**1**:base = 1:10) facilitates the efficient hydrogenation of neat ketones and imines to alcohols and amines, respectively (results similar to those of Table 1). In the absence of a base, no hydrogenation was observed, clearly demonstrating that the hydrido chloro species **1** is not the true catalyst.

When a mixture of **1** (50 mg, 65 μmol), acetone (4 mg, 67 μmol), and potassium isopropoxide (7 mg, 65 μmol) in C_6D_6 (0.7 mL) was stirred under hydrogen gas (3.5 atm) for 30 min, the ^1H NMR spectrum showed complete conversion of the ketone to 2-propanol and the presence of the novel dihydride species $Ru(H)_2(PPh_3)_2$(cydn) (**2**). The pure, bright yellow dihydride was prepared by stirring equimolar amounts of **1** and potassium tri-*sec*-butylborohydride in tetrahydrofuran for 12 h under a nitrogen atmosphere at room temperature (Scheme 1, eq 2) and then isolated.[15] The triplet at −18.3 ppm with J_{HP} = 27 Hz for the hydride in the ^1H NMR spectrum and the singlet at 67.2 ppm in the $^{31}P\{^1H\}$ NMR spectra of this complex in C_6D_6 are consistent with trans phosphines and cis hydrides. The single-crystal X-ray structure of the complex is shown in Figure 1.[16] The complex is chiral and approximately C_2 symmetric. The two Ru−H bond lengths are 1.53(2) and 1.62(3) Å. The Ru(1)−N(2) bond length of 2.284(2) Å is longer than that of Ru(1)−N(1) (2.225(3) Å). The RuH···HN distances of 2.8−3.4 Å are too long for significant hydrogen bonding in the solid state. The solid state (Nujol) infrared spectrum of **2** shows two sharp ν_{Ru-H} peaks at 1833 and 1844 cm^{-1} and four sharp ν_{NH} signals in the range 3266−3337 cm^{-1}, also in keeping with a lack of intramolecular hydrogen bonding.

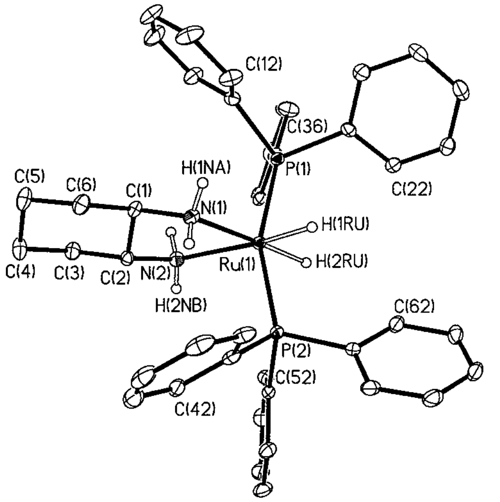


Figure 1. Molecular structure and atomic numbering of complex **2**.

A sealed solution of complex **2** in benzene-d_6 under deuterium gas resulted in the rapid disappearance (within 5 min) of both the NH (2.04 ppm) and hydride (−18.3 ppm) chemical shifts. A series of four triplets at −18.25, −18.23, −18.22, and −18.20 ppm with J_{HP} = 27 Hz in the hydride region of the ^1H NMR spectrum is observed after a 60% decrease in the intensity of the hydride signal. These are due to some of the isotopomers of **2** with one hydride, one deuteride, and with zero to four deuterium atoms in place of the diamine N−H. The rapid H/D exchange observed for both the hydrides and NH moieties when a solution of **2** is exposed to D_2 gas is suggestive of an equilibrium between dihydride and dihydrogen tautomers where the dihydrogen species is too low in concentration to be detected (see eq 6, Scheme 2). Such a mechanism has been proposed for H/D exchange in iridium hydride−amine complexes[17] and has been observed directly for osmium hydride−thiol/dihydrogen−thiolate complexes.[18] No deuteration of either the hydride or NH moieties is observed for complex **1**. The dihydrogen tautomer would be disfavored in this case because the hydride in **1** is less basic, being trans to chloride.

Complex **2** readily catalyzes the hydrogenation of neat ketones to the alcohols under 3 atm of H_2 gas at 20 °C without the addition of a base. For example, neat acetophenone (4.1 g, 34 mmol) was quantitatively hydrogenated to (*S*)-phenethyl alcohol (60% ee) in less than 8 h by use of catalyst **2** (5 mg, 0.0068 mmol).

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(15) **2**: THF (2 mL) was added to **1** (200 mg, 0.27 mmol) and potassium tri-*sec*-butylborohydride (200 mg of 1 M solution) and the mixture stirred for 6 h under nitrogen. The resulting mixture was filtered and evaporated to dryness, and the solids were extracted with diethyl ether (10 mL). The ether solution was concentrated to 2 mL and hexanes (5 mL) added, precipitating a bright yellow solid. Yield: 142 mg, 74%. ^1H NMR (δ): −18.25 ppm (t), $^2J_{HP}$ = 27.0 Hz, 2H (RuH); 2.04 ppm (d), 2H (NH). $^{31}P\{^1H\}$ NMR (δ): 67.2 ppm (s).

(16) Crystals of $C_{42}H_{46}N_2P_2Ru$ (**2**) were obtained by layering a diethyl ether solution of the complex with hexanes: M_r = 741.82, monoclinic, space group $P2_1$, a = 8.9595(2) Å, b = 17.7941(6) Å, c = 112.1757(4) Å, β = 103.688(2)°, V = 1885.99(10) Å^3, d = 1.306 g cm^{-3}, Z = 2, T = 150(1) K, 17 210 reflections collected, $R(F)$ = 0.0369 and $R_w(F^2)$ = 0.0648 for 7972 independent reflections.

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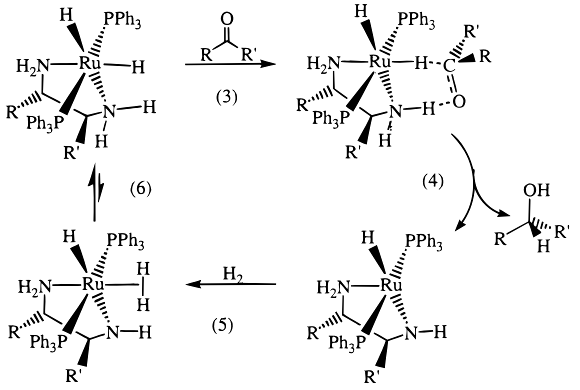
Scheme 2



Benzene was used as the solvent for the α,β-unsaturated ketone, and the product was exclusively the allyl alcohol. The same selectivity for the ketone over the olefin was reported by Okhuma et al.[2] Our study demonstrates that deactivated and sterically congested ketones such as *tert*-butyl methyl ketone (pinacolone) can also be readily hydrogenated using this procedure. The high conversions shown for the dialkyl ketones are unprecedented and attest to the enhanced activity of these catalysts under the current conditions. The hydrogenation of the aldimine and the ketimine in benzene by use of **2** also proceeded under notably mild conditions (Table 1).

One equivalent of acetophenone reacts with **2** in C_6D_6 in the absence of dihydrogen to give an intermediate currently under study. When the resulting solution was then exposed to H_2 gas, the ^{1}H NMR spectrum shows the presence of phenethyl alcohol and regenerated **2**.

These observations would be consistent with the proposed mechanism shown in Scheme 2. The first steps in the catalytic cycle (eqs 3 and 4) involves the concerted transfer of the hydride to the carbonyl carbon and NH proton to the oxygen as proposed also for the RuH(η^6-arene)(NH$_2$LNTs) catalysts.[4,5] Steps 5 and 6 are proposed on the basis of the H/D exchange results mentioned above.

This direct hydrogenation mechanism, in which the dihydride catalyst is regenerated from H_2 gas, differs significantly from the transfer hydrogenation process reported for the series of RuH(η^6-arene)(NH$_2$LNTs) complexes, in which a hydrogen-donor solvent such as an alcohol or triethylammonium formate is required for the regeneration of the monohydride catalyst. However, in both of these classes of complexes, the presence of a *cis*-M−H···H−N bifunctional motif seems to be a key feature for the activity of these catalysts.

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Supporting Information Available: Text giving complete characterization data for complexes **1** and **2** and X-ray crystallographic tables for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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