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Catalytic hydrogenation reactions by *cis*-[Ru(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$][CF$_3$SO$_3$]$_2$ (6,6′-Cl$_2$bpy = 6,6′-dichloro-2,2′-bipyridine)

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Transition metal complexes of tertiary phosphines have been extensively used as catalysts for hydrogenation reactions. But unfortunately, under reducing conditions of hydrogenation, tertiary phosphines sometimes degrade through P–C oxidative addition [1], and this process is often responsible for catalyst deactivation. Contrary to the popularity of phosphine complexes, transition metal complexes containing nitrogen coordinating ligands such as 2,2′-bipyridine, 1,10-phenanthroline and their derivatives have not been widely explored as hydrogenation catalysts [2]. In view of the proclivity of phosphine ligands to be degraded by phosphorous–carbon bond cleavage during catalytic hydrogenation reactions, the application of nitrogen donor ligand containing transition metal complexes to homogeneous catalysis may eventually become significant. We report here that the ruthenium complex of (6,6′-Cl$_2$bpy), *cis*-[Ru(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$][CF$_3$SO$_3$]$_2$ (**1**) [3] is an active hydrogenation catalyst for carbonyl compounds and olefins.

Experimental

All solvents used were reagent grade and were distilled by standard procedures. All liquid substrates were distilled and all solid ones were recrystallized before use. High purity hydrogen gas (Hong Kong Oxygen) was used directly. The catalyst *cis*-[Ru(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$][CF$_3$SO$_3$]$_2$ (**1**) was prepared according to the literature [3]. Gas chromatography was carried out using a Perkin-Elmer Sigma 3B apparatus equipped with a FID. A 25 m×0.32 mm OV-1 capillary column or a 50 m×0.32 mm OV-17 capillary column was used for the analyses. ^{1}H and ^{13}C NMR spectra were obtained by use of a Jeol FX90Q spectrometer.

Hydrogenation reaction

All reactions were carried out in a 100 ml stainless steel autoclave. In a typical run, ~ 15 mg of **1**, 10 ml of THF, 0.6 ml of H$_2$O and 2.0–2.5 g substrate were mixed in the autoclave. After flushing with H$_2$ three times, the system was heated with stirring at 105 °C under 40 atm of hydrogen. At the end of the desired time, the reactor was cooled rapidly and the reaction mixture was analyzed by gas chromatography.

Results and discussion

Complex **1** was chosen as catalyst for the hydrogenation studies because it has been shown that the steric effect of the chloro groups at the *ortho* positions of 2,2,′-bipyridine circumvents the *cis–trans* isomerization of the complex [3]; and by the dissociation of the water ligands, it is possible to generate a ruthenium species with two *cis* vacant sites. In the course of a study of catalytic hydrogenation activity of **1**, it was found that careful exclusion of water from the reaction mixture had an unexpected effect. Rather than increasing the rate of hydrogenation, the reaction became very sluggish; but addition of a small amount of water greatly enhanced the rate of the reaction. Therefore it becomes obvious that water acts as a cocatalyst in the hydrogenation reactions catalyzed by **1**. Results of the water assisted catalytic hydrogenation of some organic substrates are shown in Table 1. In the hydrogenation of α,β-unsaturated ketones (runs 4–6), the carbon–carbon double bonds are reduced faster than the ketonic functionalities. In the cases of α,β-unsaturated aldehydes (runs 9 and 10), a higher selectivity toward the formation of the corresponding unsaturated alcohols is observed. Complete reduction of the olefins is effected in 4 h. In all of the reactions studied, **1** was recovered at the end of the reactions.

In a hydrogenation study of acetophenone, D$_2$O was added instead of H$_2$O; it was observed that the hydrogenation product, 1-phenylethanol showed an appreciable amount of deuterium incorporation. NMR integration showed that 30% and 70% of the α-carbons and hydroxyl groups were deuterated, respectively. The ^{1}H NMR spectrum of the product showed a doublet at 1.42 ppm (J(H–H) = 7.2 Hz) and a triplet at 1.40 ppm (J(D–H) = 1.2 Hz), corresponding respectively to the methyl protons of $>$CH–CH$_3$ and that of $>$CD–CH$_3$. In the ^{13}C NMR spectrum, the undeuterated α-carbon showed a doublet at 69.44 ppm (^{1}J(C–H) = 143.0 Hz)

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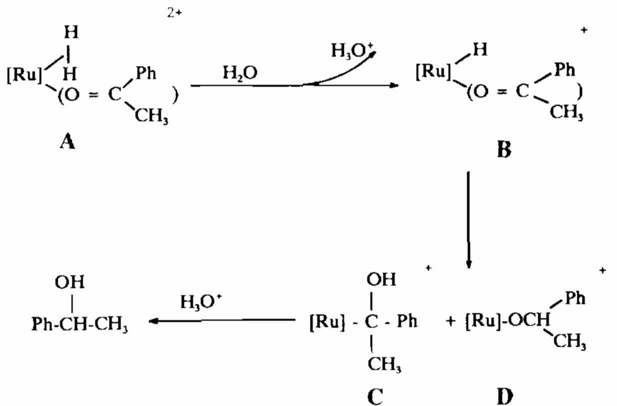
TABLE 1. Catalytic hydrogenation with **1**[a]

Run	Substrate	Product (% yield)[b]
1	Acetophenone	1-phenylethanol (90)
2	Benzophenone	benzhydrol (92)
3	Cyclohexanone	cyclohexanol (84)
4	Cyclohex-1-en-2-one	cyclohex-1-en-2-ol (5) cyclohexanone (21) cyclohexanol (37)
5	Mesity oxide	methylisobutylketone (77) 4-methylpentan-2-ol (9)
6	Benzylidenacetone	1-phenylbut-1-en-3-ol (4) 4-phenylbutan-2-one (54) 4-phenylbutan-2-ol (11)
7	Benzaldehyde	benzyl alcohol (78)
8	n-Butyl aldehyde	n-butanol (57)
9	Cinnamaldehyde	cinnamyl alcohol (48) 3-phenylpropanaldehyde (5) 3-phenylpropanol (5)
10	Crotonaldehyde	crotyl alcohol (60) n-butylaldehyde (4) n-butanol (14)
11	1-Octene[c]	n-octane (100)
12	Styrene[c]	ethyl benzene (100)

[a] Reaction conditions: $1 = 1.3 \times 10^{-3}$ mol, substrate/Ru = 1000, THF = 10 ml, $H_2O = 0.6$ ml, H_2 pressure 40 atm, temperature 105 °C, reaction time 10 h. [b] Based on substrate used. [c] Reaction time 4 h.



Scheme 1.

while the deuterated α-carbon showed a triplet at 69.00 ppm (^1J(C–D) = 21.4 Hz). Based on the results of this labelling experiment and the fact that the hydrogenation reaction is assisted by water, we suggest that the η^2-H_2 complex **A** [4] may be one of the intermediates during the catalysis (Scheme 1). It is well known that the η^2-H_2 ligand in molecular dihydrogen complexes may exhibit remarkable acidic character and be readily deprotonated by bases [5]. Therefore the η^2-H_2 ligand in **A** is heterolytically cleaved by water to form the metal hydride **B**, which by a hydride shift or insertion of the ketone across the Ru–H bond generates the metal hydroxyalkyl **C** and the metal alkoxide **D**. Finally, attack of H_3O^+ on both **C** and **D** yields 1-phenylethanol. Note that this product generating step is also the deuterium incorporating step if D_2O is used instead of H_2O. The reason for suggesting both the metal hydroxyalkyl **C** and metal alkoxide **D** intermediates is that we should have observed a much higher percent deuterium incorporation at the α-carbon of 1-phenylethanol if only the metal hydroxyalkyl **C** were present. Control experiments were performed to see the possible deuteration of the α-carbon and hydroxyl group of 1-phenylethanol with D_2O under reaction conditions identical to that of catalytic acetophenone hydrogenation. It was found that the hydroxyl group was readily deuterated but the α-carbon was not.

We have also studied the catalytic hydrogenation of organic substrates with **1** in aqueous organic two phase solvent systems, the results of which will be published elsewhere.

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