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Catalytic hydrogenation reactions by a monobenzene complex of ruthenium, $[Ru(\eta^6\text{-}C_6H_6)(CH_3CN)_3](BF_4)_2$, in biphasic medium

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Abstract

The water soluble monobenzene complex of ruthenium, $[Ru(\eta^6\text{-}C_6H_6)(CH_3CN)_3](BF_4)_2$ (**1**) is an effective catalyst or catalyst precursor for the hydrogenation of olefinic functions in benzene/H_2O biphasic medium. The catalyst can be recycled by simple decantation. Complex **1** is capable of catalyzing H/D exchange reaction between H_2 and D_2O. A two-loop reaction mechanism for the catalytic hydrogenation reactions with **1** is postulated. In this mechanism, water acts as the base to assist the heterolytic hydrogen cleavage in one of the loops, but is not an active participant in the other.

Key words: Ruthenium; Hydrogenation; Biphasic medium; Hydride

1. Introduction

The monoarene ruthenium complexes $[Ru(\eta^6\text{-}arene)L_3]^{2+}$ ($L = H_2O$, CH_3CN or NH_3) comprise an interesting class of molecules because they may help to bridge the gap between organometallic chemistry and so-called classical coordination chemistry. Although studies on the molecular structures, ligand-exchange kinetic and substitution reactions of these complexes have been documented [1], there has been little reported on their applications to catalysis. In this paper, we report the preliminary results of our studies of biphasic hydrogenation reactions with the monobenzene ruthenium complex, $[Ru(\eta^6\text{-}C_6H_6)(CH_3CN)_3](BF_4)_2$ (**1**). We are interested in catalysis in biphasic organic/aqueous systems because such systems provide an attractive solution to the problem of separation of products from precious metal-based catalysts in industrial catalysis with transition metal complexes [2].

2. Results and discussion

The catalytic activity of **1** in hydrogenation reactions was first studied in homogeneous acetonitrile solution, but it was found to be very low. It was then learned that addition of water to the acetonitrile solution of **1** enhanced the rate of hydrogenation reaction (runs 1 and 2, Table 1). Since **1** is soluble in water and is basically insoluble in non-polar organic solvents such as benzene, it was therefore decided to study hydrogenation reactions in a benzene/H_2O biphasic medium.

Results of catalytic hydrogenation of some organic substrates with **1** are shown in Table 1. In all the biphasic reactions (runs 3–18) except the hydrogenation of benzaldehyde (run 9), the catalyst remained in the aqueous layer while the organic substrates and products were in the organic phase. Therefore the catalyst could easily be recycled by simple decantation. It was recycled twice in the reduction of benzylideneacetone, and no loss of activity or selectivity was observed. In the hydrogenation of benzaldehyde (run 9), the catalyst had largely gone into the organic layer after the reaction because the organic phase became reddish brown while the aqueous layer turned almost colourless. It can be seen from Table 1 that in the hydrogenation of α,β-unsaturated ketones (runs 2–6), the catalyst showed high selectivity towards reduction of the carbon–carbon double bonds, giving the saturated ketones as the predominant products. In fact, the reduction of ketonic functions was found to be very sluggish (runs 7 and 8). Reduction of most olefins reported were fast, the reactions were practically com-

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TABLE 1. Catalytic hydrogenation with $[Ru(\eta^6\text{-}(C_6H_6)(CH_3CN)_3](BF_4)_2$ (1) [a]

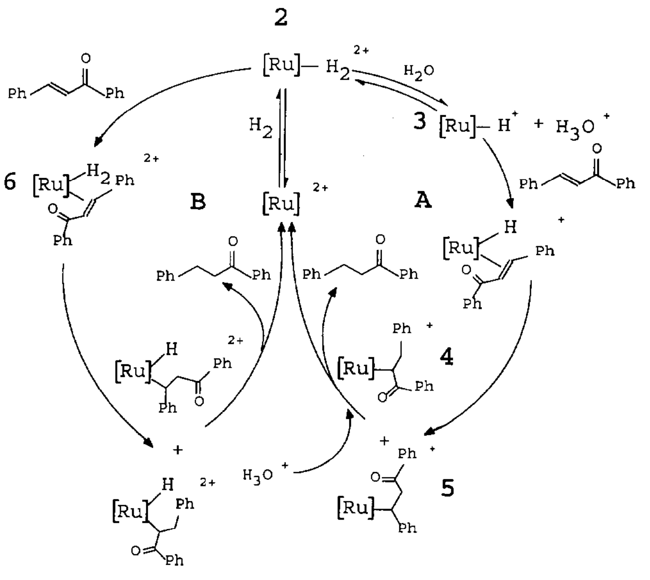
Run	Substrate	Solvent (ml/ml)	Product (% yield) [b]
1	benzylideneacetone	CH_3CN (10)	4-phenylbutan-2-one (2)
2	benzylideneacetone	CH_3CN/H_2O (10/2)	4-phenylbutan-2-one (15)
3	benzylideneacetone	C_6H_6/H_2O (5/5)	4-phenylbutan-2-one (87) 1-phenylbut-1-en-3-ol (1) 4-phenylbutan-2-ol (2)
4	benzylideneacetophenone	C_6H_6/H_2O (5/5)	1,3-diphenylpropan-1-one (98)
5	mesityl oxide	C_6H_6/H_2O (5/5)	methylisobutylketone (47)
6	cyclohex-1-en-2-one	C_6H_6/H_2O (5/5)	cyclohexanone (68) cyclohex-1-en-2-ol (1) cyclohexanol (2)
7	cyclohexanone	C_6H_6/H_2O (5/5)	cyclohexanol (5)
8	acetophenone	C_6H_6/H_2O (5/5)	1-phenylethanol (3)
9	benzaldehyde	C_6H_6/H_2O (5/5)	benzyl alcohol (30) [c]
10	cyclohexene	C_6H_6/H_2O (1/5)	cyclohexane (100)
11	1-octene	C_6H_6/H_2O (1/5)	n-octane (100)
12	1-decene	C_6H_6/H_2O (1/5)	n-decane (100)
13	styrene	C_6H_6/H_2O (1/5)	ethyl benzene (100)
14	norbornene	C_6H_6/H_2O (1/5)	norbornane (100)
15	dimethyl maleate	C_6H_6/H_2O (1/5)	dimethyl succinate (32)
16	1-dodecene	C_6H_6/H_2O (1/5)	n-dodecane (100)
17	1-dodecene [d]	C_6H_6/H_2O (1/5)	n-dodecane (44)
18	1-dodecene [e]	C_6H_6/H_2O (1/5)	n-dodecane (76)

[a] Reaction conditions: 1 = 1.5–2.0 × 10^{-5} mole; substrate/Ru = 1000; H_2 pressure 40 atm; temperature 110°C (runs 1–9), 90°C (runs 10–17); reaction time 4 h. [b] Based on substrate used. [c] The organic layer was reddish brown and the aqueous layer was colourless after the reaction. [d] Reaction time 2 h. [e] A drop of HBF_4 (50% in H_2O) was added; temperature 110°C.

pleted within 4 h. The catalyst was also found to be active for the reduction of dimethyl maleate (run 15) which is an electron deficient olefin, although the yield was not as good as the other alkenes. One reaction that is worth mentioning is the last entry in Table 1. It was observed that addition of a drop of 50% HBF_4 to the system had a detrimental effect on the hydrogenation of 1-dodecene; the yield of n-dodecane had dropped to 76% although the reaction temperature had been raised to 110°C.

In one of the hydrogenation experiments, biphasic hydrogenation reaction of benzylideneacetophenone with 1 was carried out in D_2O/benzene medium. It is hoped that analysis of distribution of deuterium in the hydrogenation product may shed some light on the role played by water in the catalysis. Analysis of the EI mass spectrum indicated that 14% of the reaction product, 1,3-diphenylpropan-1-one was monodeuterated with the small quantity (< 2%) of dideuterated product also present. The ^2H NMR spectrum of the product showed two peaks (in a 3.4 : 1 ratio) at 3.32 and 3.06 ppm. The former was due to the deuterium bonded to C-2 of 1,3-diphenylpropan-1-one while the other peak was due to deuterium attached to C-3. In the ^{13}C NMR spectrum of the reaction product, a small triplet attributable to deuterated C-2 of 1,3-dephenylpropan-1-one was found at 40.09 ppm (^1J(C–D) = 20.2 Hz); however the signal of deuterated C-3 was not observable, probably due to the much lower degree of deuteration at this carbon.

A tentative mechanism is proposed to explain the results of the benzene/D_2O biphasic hydrogenation of benzylideneacetophenone (Scheme 1). In the proposed mechanism, the precise nature of the bonding between



Scheme 1.

ruthenium and H_2 in **2** is not yet known. The intermediate **2** may be a metal dihydride formed by oxidative addition of dihydrogen molecule to ruthenium; it may be a non-classical η^2-H_2 ruthenium complex [3] or may even be an equilibrium mixture of both. It is well known that η^2-H_2 complexes can undergo rapid and reversible dissociation of H_2 [4] and may exhibit remarkable acidic character and be readily deprotonated by bases [5]. But it is also well established that neutral or cationic transition metal hydrides can be readily deprotonated [6]. For example, in their study of catalytic hydrogenation using cationic rhodium complexes, Schrock and Osborn had established that an equilibrium existed between the metal dihydride **A** and the monohydride **B** (x and y unknown, S = solvent) (eqn. 1).

$$\underset{\mathbf{A}}{[RhH_2L_nS_x]} \underset{}{\overset{-H^+}{\rightleftharpoons}} \underset{\mathbf{B}}{[RhHL_nS_y]} \qquad (1)$$

Both **A** and **B** are known as catalytically active species for hydrogenation and isomerization of olefins. The presence of a base shifted the equilibrium to the side of **B** [7]. In loop A of Scheme 1, **2** is deprotonated by base H_2O to generate the ruthenium hydride **3**. Coordination of benzylideneacetophenone to **3** followed by a hydride shift or insertion of the substrate across the Ru–H bond gives the two metal alkyls **4** and **5** in 3.4 : 1 ratio (see ^2H NMR data). Finally, attack of H_3O^+ on both **4** and **5** yields 1,3-diphenylpropan-1-one. Note that this product-generating step is also the deuterium-incorporating step if D_2O is used instead of H_2O. However, if loop A were the only catalytic pathway, a much higher percent deuterium incorporation in the hydrogenation product than that calculated from mass spectrum analysis would have resulted (*vide supra*). We therefore suggest that there may be a second catalytic pathway in operation. In this second pathway (loop B), water does not participate actively in the catalytic reaction. If **2** is a metal dihydride, then loop B is just the common dihydride mechanism analogous to the mechanism involving the Wilkinson's catalyst [8]. On the other hand, if **2** is a non-classical η^2-H_2 complex, then it reacts with the substrate to form **6** in which the η^2-H_2 and the π-bonded benzylideneacetophenone are *cis* disposed. Stepwise hydrogen transfer from the η^2-H_2 to the substrate will lead to the product. Bianchini *et al.* have recently reported a case of intramolecular reaction between *cis* disposed η^2-H_2 and σ-vinyl ligand in which hydrogen transfer from η^2-H_2 to the σ-vinyl ligand generated the alkene and the metal hydride [9]. We have to admit that at this stage the structure of [Ru] in Scheme 1 is also not yet known either.

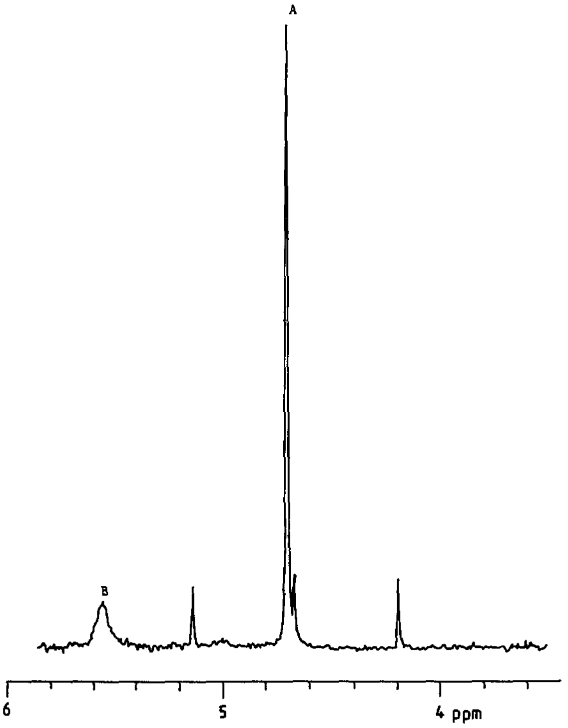
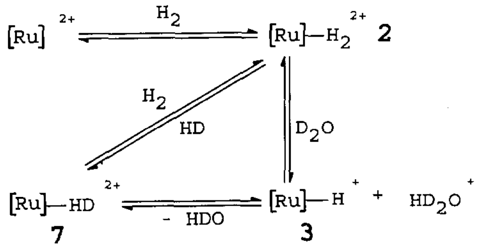


Fig. 1. ^1H NMR spectrum of HD produced in H/D exchange reaction between H_2 and D_2O. A: H_2 peak; B: water peak.

The two equilibrium steps in loop A have been established by a H/D exchange reaction between H_2 and D_2O using **1** as catalyst. A Wilmad pressure valve NMR tube (5 mm) was used for studying the **1**-catalyzed H/D exchange reaction. The NMR tube was filled to a height of 6 mm with a saturated D_2O solution of **2**. Over the D_2O solution was added a 25–30 mm column of benzene-d_6. The tube was then pressurized with H_2 (30 bar) and heated at 90°C for 20 h. The NMR spectrum was taken at room temperature. Since the column of D_2O solution was outside the receiver coil of the NMR instrument, the ^1H spectrum of the HD produced could be measured in the benzene-d_6 column without interference from the species in the D_2O solution. Figure 1 shows the ^1H NMR spectrum of the HD produced in the H/D exchange reaction, the triplet at 4.68 ppm with J(H–D) 42.6 Hz is due to HD. The HD/H_2 ratio (from NMR integration) was found to be 0.44.

Scheme 2 shows the mechanism through which H/D exchange between H_2 and D_2O can occur. In the mechanism, **2** is deprotonated by the base D_2O to generate the metal hydride **3**, and deuteration of **3** will form the HD-complex **7** which can produce HD by elimination. Kubas *et al.* have recently reported isotope exchange between H_2O and D_2 to produce HD in a solution of $W(CO)_3(P^iPr_3)_3(\eta^2\text{-}D_2)$ [10]. The similar H/D exchange reaction between D_2 and H_2O has also



Scheme 2.

been reported to be affected by the rhodium dideuteride species which was produced when [Rh(NBD)-$(PPhMe_2)_2]^+$ reacted with D_2 [7a].

It is also possible that water may have other roles to play other than acting as a base to deprotonate **2** as depicted in loop A of Scheme 2. One possibility is that water partially displaces the acetonitrile ligands of **1** to generate $[(\eta^6\text{-}C_6H_6)Ru(CH_3CH)_{3-n}(H_2O)_n]^{2+}$ which may be the active species or catalyst precursors for the hydrogenation reactions. In fact, NMR study has shown that in a D_2O solution of **1** at room temperature, *ca.* 65% of the coordinated acetonitrile has been displaced and three monobenzene ruthenium complexes were present in addition to **1**.

Our preliminary studies have shown that **1** is an effective catalyst or catalyst precursor for the hydrogenation of olefinic functions in organic/aqueous biphasic media. A tentative mechanism for the catalytic reaction has been proposed. Work aimed at unravelling the detailed mechanism is now in progress.

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