CATALYTIC HYDROGENATION OF 1-HEXENE WITH RuCl₂(TPPMS)₃(DMSO).
PART I: AQUEOUS BIPHASIC SYSTEM

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Abstract
RuCl₂(TPPMS)₃(DMSO) (complex I) shows good catalytic 1-hexene hydrogenation activity in toluene/water biphasic medium under moderate conditions, reaching 90% conversion in 5 h, with good hydrogenation selectivity and low isomerization products. The effect of various parameters (temperature, H₂ pressure, reaction time, substrate/catalyst ratio, added electrolytes and other additives) on the hydrogenation reaction were studied. Complex (I) shows good stability in the reaction medium and can be reused several times.

Keywords: Ruthenium, biphasic catalysis, hydrogenation

INTRODUCTION

Biphasic catalysis is helping modern industrial chemistry with organic solvent substitution, catalysts reuse, better product separation, or use of water as solvent [1]. The use of transition metal complexes with water soluble ligands such as sulfonated phosphines has increased [2-3]. For example, soluble rhodium complexes [4] have been used in propene hydroformylation [5-6], using

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water-soluble phosphine ligands [7]. Different ruthenium complexes with triphenylphosphine sulfonate (TPPMS, TPPDS, TPPTS) in biphasic medium have good hydrogenation activity [8]. In our laboratory, hydrogenation reactions have been carried out with Ru(DMSO)$_2$Cl$_2$ (9) and RuCl$_2$(η$^5$-C$_5$H$_5$)(TPPMS)$_2$ [10] in aqueous biphasic systems; more recently RuCl$_2$(TPPMS)$_3$(DMSO) [11] (complex I, see Fig. 1) has been synthesized and characterized, and its hydrogenation catalytic activity in biphasic toluene/water is reported here. In Part II of this series, the catalytic reaction in biphasic organic/ionic liquid will be reported.

Fig. 1. Proposed structure for the RuCl$_2$(TPPMS)$_3$(DMSO) complex

EXPERIMENTAL

Materials and methods

Reagents

RuCl$_3$·3H$_2$O (Strem Chem. Co), Ph$_3$P (Aldrich Chem. Co.), H$_2$ and Ar (Gases Industriales de Venezuela) were obtained commercially and used directly. The liquid substrates used in catalysis were distilled before use; ethanol, toluene and H$_2$O were purified as described in the literature [12].
Syntheses

Triphenylphosphine monosulfonate (TPPMS) was synthesized by Ahrland’s modified method [13]. To 20 mL of 30% sulfuric acid at 0 °C, 10 g (3.8 mmol) of triphenylphosphine were added slowly with stirring. The mixture was slowly heated on a water bath for 2 h and then added to a beaker with 100 g of ice; at room temperature the solution was neutralized with 50% aqueous sodium hydroxide. A white solid product was filtered and re-crystallized from hot water. Yield: 1.11 g (80%); decompose above 300 °C. FTIR (KBr pellet, cm⁻¹): ν(O-H) 3,444 cm⁻¹ (broad hydration band), ν(C=C) 1,626 cm⁻¹, νₐ(P-C) 1,434 cm⁻¹, νₐ(C-SO₃⁻) 1,397 cm⁻¹, νₛ(C-SO₃⁻) 1,196 cm⁻¹, νₛ(P-C) 995 cm⁻¹. The ¹H-NMR spectrum in water-d₂, δ (ppm): phenyl sulfonate, 7.57 (doublet of doublet, 2 H), 7.26 – 7.23 (multiplet, 12 H), 4.8 (broad singlet, water protons). ¹³C-NMR spectrum, δ (ppm): for the sulfonated ring: 142.6 (C-SO₃, J = 5.9 Hz); 137.8 (P-Cipso, J = 10 Hz), 135.6 (P-Cortho, J = 17.8 Hz), 129.5 (P-Cmeta, J = 20.1 Hz), 129.60 (P-Cparapara); for the non-sulfonated rings: 134.9 (P-Cipso, J = 6.5 Hz), 133.6 (P-Cortho, J = 19.4 Hz), 128.4 (P-Cmeta, J = 7.4 Hz), 129 (P-Cpara); the assignments were confirmed using NMR bidimensional experiments: HMQC, HMBC [14]. ³¹P-NMR spectrum: –3.5 p.p.m (triplet, J = 19 Hz, P-CH coupling according to reported values [15]), (85% phosphoric acid reference). Mass spectrum: [M⁺], m/e = 364 (I = 100%); and [M⁺+1], 365 (14). The following fragmentation pattern was observed: C₆H₄⁺, 76 (28); C₁₂H₈P⁺, 183 (8); HP(C₆H₅)₂⁺, 186 (3); PC₁₂H₇SO₃⁺, 262 (5).

Complex (I) was prepared according to the reported method [11]. A TPPMS suspension (2.6 g, 6.63 mmol) in toluene (50 mL) was refluxed under Ar with RuCl₂(DMSO)₄ (1.0 g, 2.21 mmol) for 4 h. The orange solid produced was suction filtered. Yield: 1.89 g (70%). m.p.: 150 °C (dec.) UV-Vis. electronic spectrum: λmax, nm (ε, M⁻¹ cm⁻¹) 199(34,740), 252(21,110), 427(286). The two UV absorptions are assigned to /G8C/G3A/G8C*/Gd/G3A/G2F/G46/G4B/G44/G55/G4A/G48/G10 transfer transitions respectively. The visible absorption is a /G3A/Gd transition typical of ruthenium(II) phosphine complexes. FTIR: ν(O-H) 3447 cm⁻¹ (broad hydration band), ν(C=C) 1,632 cm⁻¹, νₐ(P-C) 1,432 cm⁻¹, νₐ(C-SO₃⁻) 1,396 cm⁻¹, νₛ(C-SO₃⁻) 1,198 cm⁻¹, νₛ(P-C) 1,096 cm⁻¹. The ¹H-NMR spectrum in water-d₂, δ (ppm): 8.2 – 7.2 (multiplet, 42 H) and 3.34 (multiplet, 6 H). ¹³C-NMR spectrum, δ (ppm): for the sulfonated ring: (P-C); 129.7; 129.4; 128.9; 133.7; 143.1 133.5 (C-SO₃⁻); for the non-sulfonated rings: 135.9 (P-C); 133.9; 133.8; 129.4; for DMSO: 39.1 ppm. ³¹P-NMR spectrum: 38.4 ppm (axial P) and 56.7 ppm (equatorial P). Mass spectrum: [M⁺][¹⁰¹Ru]-[CH₃ClNa₃], m/e = 1220.4 (I = 100%); and the ruthenium isotope [M⁺+4][¹⁰⁴Ru]-[CH₃ClNa₃], 1224.1(59), the ratio confirming a monometallic complex. The following fragmentation pattern was observed: C₆H₆⁺, 66.05 (23.7); C₅H₄⁺, 76.6 (25.4); C₁₂H₈P⁺, 183.32 (37.4); HP(C₆H₅)₂⁺, 186.35 (28.7); PC₁₂H₇SO₃⁺, 263.43 (29.6).
Physical measurements

The UV-Vis electronic absorption spectrum of complex (I) in H₂O was recorded in a Shimadzu UV/Vis UVmini-1240 spectrophotometer. The vibrational spectrum (5,000 – 400 cm⁻¹, KBr pellet) was recorded in a FTIR Perkin-Elmer 1725X spectrophotometer. Room temperature ¹H, ¹³C and ³¹P-NMR spectra in water-d₂ solutions were taken on a Bruker Advance DRX 400-MHz spectrometer with TMS as internal standard; ³¹P-NMR chemical shifts relative to 85 % H₃PO₄. Mass spectra were recorded on a Hewlett-Packard System 5988A GC-MS spectrometer using chemical ionization with isobutene.

Catalytic tests

Catalytic tests were made in a 125 cm³ Parr reactor with internal glass liner, heating unit, temperature and stirring control and sampling valve. Conditions for a typical trial: toluene (20 mL), H₂O (20 mL), 1-hexene or olefin (1 mL), complex (I) (20 mg, substrate/catalyst molar ratio, S/C = ca. 500:1), H₂ pressure (250 – 1,250 psi range), temperature (50 °C - 120 °C range), 1,600 rpm stirring rate to insure thorough mixing and emulsion formation. Reaction products were analyzed in a PE, Autosystem GC, using a 3 m column (0.6 cm diameter) of 10% tricresyl phosphate on Cromosorb P (80 - 100 mesh), with H₂ carrying gas and TC detector.

RESULTS AND DISCUSSION

Effect of pressure and temperature

The temperature effect on the hydrogenation reaction is shown in Fig. 2. There is catalytic activity from room temperature, increasing gradually to complete reaction at 100°C (95% n-hexane and small quantity of 2-hexenes). There is some activity decrease at 120°C, probably due to the start of complex decomposition. 80°C was selected as the optimum temperature. The change in H₂ pressure (250 to 1250 psi, at 80°C) did not give an appreciable effect on 1-hexene hydrogenation, the conversion remains fairly constant (ca. 95% after 500 psi, with a decrease below 250 psi), with low isomerization conversion, favoring cis-2-hexene. 500 psi H₂ pressure was selected as the optimum pressure. A preliminary kinetic study shows a pseudo first order rate constant with respect to substrate of \( k_{\text{obs}} = 7.4 \times 10^{-3} \text{ min}^{-1} \).
**Substrate/catalyst ratio effect**

As the substrate/catalyst ratio is increased in the range studied, there is a slight decrease in hydrogenation conversion for the 5 h reaction time used. A 500/1 ratio was selected as the optimum for the other studies.

**Additive effect (acid, bases and electrolytes)**

The aqueous phase pH effect on 1-hexene hydrogenation, (pH = 1-14, HCl addition in the acid range and NaOH addition in the basic range) did not show a considerable effect on the catalytic activity; n-hexane formation remains high (above 80% conversion) and the isomerization reaction remains low (below 10%, favoring the cis-2-hexene isomer). The effect of adding some electrolytes: NaCl, KCl, Na₂SO₄ and K₂SO₄ (0.2 mol L⁻¹) is shown in Fig. 3. Following the reaction in time and using the system without additive as reference, the added electrolytes with Na⁺ as counterion show faster conversion, and maintain a high conversion, but the added electrolytes with K⁺ counterion are noticeably slower and maintain a lower conversion after 300 min. Assuming micellar catalysis
[16], in which the water soluble complex intervenes, the electrolytes will have a charge effect on the micellar interphase, apparently being more favorable the association of the smaller Na$^+$ ion than the K$^+$ ion, thus attenuating electrostatic repulsion of the charged hydrophilic surface [17] and favoring the catalytic activity [18].

**Fig. 3.** Electrolytes effect on 1-hexene hydrogenation. T 80°C, 500 psi H$_2$ pressure, S/C: 500/1, 1600 rpm stirring rate, 5 h reaction time, constant total ionic strength ■ without additive, ● NaCl, ▲ KCl, ▼ Na$_2$SO$_4$, ◆ K$_2$SO$_4$

**TPPMS and DMSO addition effect**

The effect of adding excess ligands (TPPMS and DMSO, *ca.* 5 molar excess) is similar for the two ligands, showing a notable reduction in the hydrogenation rate, being somewhat higher for the TPPMS ligand at longer times. It is presumed that complex (I) acts as a catalytic precursor and the active coordinatively unsaturated catalytic species is produced by the equilibrium: RuCl$_2$L$_4$ $\rightleftharpoons$ RuCl$_2$L$_3$ + L (L = TPPMS (three ligands) or DMSO (one ligand)). Ligand excess in solution will displace the equilibrium to the left and compete with the substrate for the vacant coordination site.
Catalyst reuse

The catalytic activity for several consecutive reuses of the aqueous phase was studied and is presented in Fig. 4. The aqueous phase which concentrates the Ru complex, is decanted after each catalytic run and recovered under Ar. Fresh toluene plus substrate is added and the biphasic system is run again under the pre-selected reaction conditions. The catalytic behavior observed for six consecutive reruns indicate that the activity is maintained and for 5 hours total reaction time, the total percent hydrogenation conversion is still high (95 to 98%); the main product is still 1-hexane (about 90%) and below 10% of isomerization products (favoring cis-2-hexene). Some activity decrease is observed after several consecutive reuses, probably due to some complex decomposition or loss on separation and handling.

![Graph showing consecutive reuses of catalytic precursor](image)

**Fig. 4.** Consecutive reuses of catalytic precursor. Temperature 100ºC, 500 psi H₂ pressure, S/C: 500:1, 1600 rpm stirring rate, 5 h total reaction time. Columns from left to right refer to n-hexane, 1-hexene, cis-2-hexene, trans-2-hexene, respectively

Hydrogenation of other substrates

The catalytic activity in the biphasic medium has been extended to other unsaturated substrates (Cyclohexene and crotonaldehyde; 80ºC, 500 psi H₂ pressure, S/C: 500:1, and 5 h reaction time). Cyclohexene gives 64% cyclohexane conversion and crotonaldehyde gives 34% 1-butenol conversion as
the main product, showing some carbonyl hydrogenation selectivity. Complex (I) shows moderate activity for hydrogenation of propionaldehyde, \(\alpha,\beta\)-unsaturated aldehydes and ketones [19].

**CONCLUSIONS**

RuCl\(_2\)(TPPMS)\(_3\) (DMSO) shows good 1-hexene hydrogenation activity in biphasic toluene/water systems (turnover number = 1.70 min\(^{-1}\)). The activity is sensitive to electrolytes added and to the presence of ligand excess. The aqueous phase catalyst can be recovered and reused several times maintaining catalytic activity, indicating some potential for practical applications.

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**REFERENCES**

14. HMQC: Heteronuclear Multiple Quantum Correlation and HMBC: Heteronuclear Multiple Bond Correlation.