

Hydrogenation of aromatics with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{TPPDS})_2]$ in biphasic medium

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Abstract

$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{TPPDS})_2]$, $[\text{TPPDS} = \text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{SO}_3^-)_2]$ in biphasic (n-heptane/water) medium hydrogenates toluene, benzene and *m*-xylene (105 °C, 1400 psig H_2 , substrate/catalyst = 600:1, 4 h) and in toluene hydrogenation gives methylcyclohexane. Catalytic activity increases with temperature, H_2 pressure, ionic strength, and pH lower than 10. The catalytic water solution can be reused several times with little activity loss.

Introduction

Biphasic catalysis is a useful tool in modern industrial chemistry, with organic solvent substitution, catalysis reuse, better product separation, or use of water as solvent. Recently, the use of water-soluble transition metal complexes with sulfonated phosphine ligands has increased [1, 2]. For example, water soluble rhodium complexes [3] have been used in propene hydroformylation [4, 5]. Different ruthenium complexes with water soluble triphenylphosphine sulfonates in biphasic medium, show good hydrogenation activity [7]. Our laboratory has reported catalytic studies with ruthenium complexes in biphasic medium and ionic liquids (IL) in olefin hydrogenation and with other substrates [8–12]. Recently there has been interest in catalytically reducing the aromatic content in liquid fuels [13, 14]. $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{TPPDS})_2][\text{TPPDS} = \text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{SO}_3^-)_2]$ in biphasic medium is a good catalytic precursor for olefins and aromatic hydrogenation [15, 16]. Here we report aromatic hydrogenation with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{TPPDS})_2]$ in n-heptane/water biphasic medium.

Experimental

Materials and methods

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Strem), Ph_3P (Aldrich), H_2 and Ar (Gases Industriales de Venezuela) were obtained commercially and used as received. The liquid substrates used in catalysis were distilled before use; EtOH, n-heptane, toluene, xylenes and H_2O were purified as described in the literature [17].

TPPDS was synthesized by Ahrlund's method [18], modified thus. Recrystallized PPh_3 (12.0 g, 45 mmol),

was dissolved in concentrated H_2SO_4 (84 cm³) at room temperature with strong stirring. The mixture was cooled to 0 °C and fuming H_2SO_4 (65% SO_3 , 38 cm³) added dropwise. Room temperature stirring was continued for 24 h. The mixture was neutralized with NaOH (7.5 M, 0 °C) added dropwise, and the precipitated solid vacuum filtered off. MeOH (1.2 l) was added to the solid, the mixture refluxed for 30 min, filtered hot and the product was recrystallized from MeOH/EtOAc (1/3), then followed by hot water. Yield: 7.80 g (53%), decomposes above 300 °C. FTIR (Perkin-Elmer FT-IR 1725 X, KBr pellet), cm⁻¹: 3467 [$\nu(\text{O-H})$, broad hydration band], 3037, [$\nu(\text{C-H})$, aromatic], 1658 [$\nu(\text{C=C})$], 1471 [$\nu_a(\text{P-C})$], 1191 [$\nu_a(\text{C-SO}_3)$], 1133 [$\nu_s(\text{C-SO}_3)$], 1048 [$\nu_s(\text{P-C})$], 1014 [$\delta_p(\text{C-H})$], 817 [$\delta_{\text{op}}(\text{C-H})$] and 703 [*meta* disubstituted aromatics]. ¹H-n.m.r. (Bruker Avance DRX, 500 MHz) (δ (p.p.m.)), (see Diagram 1): 7.7 [H⁴, doublet, 2H, $J(\text{H-H})=7.5$ Hz]; 7.6 [H², doublet, 2H, $J(\text{P-H})=7.7$ Hz]; 7.2–7.4 [H⁵, H⁶, H⁸, H⁹, H¹⁰, multiplet, 9H]. ¹³C-n.m.r. (δ (p.p.m.)), (see Diagram 1): sulfonated rings: 142.9 [doublet, C³, $J=7.3$ Hz]; 137.1 [doublet, C¹, $J=10.3$ Hz]; 136.3 [doublet, C², $J=17.3$ Hz]; 130.1 [doublet, C⁶, $J=22$ Hz]; 129.6 [doublet, C⁵, $J=6.4$ Hz]; 126.2 [singlet, C⁴]; nonsulfonated ring: 134.6 [doublet, C⁷, $J=6.7$ Hz]; 133.8 [doublet, C⁸, $J=20$ Hz]; 129.8 [singlet, C¹⁰]; 129.1 [doublet, C⁹, $J=7.5$ Hz]. ³¹P-n.m.r. (δ (p.p.m.)): -4.9 [triplet, 1P]; -36.6 [weak singlet, phosphine oxide]; Mass spectrum (Hewlett-Packard 5988 A GC/MS): [M^+], $m/e=484$; phosphine with water molecules; m/e , 363 (-SO₃Na loss) and 262 (two -SO₃Na loss).

Preparation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{TPPDS})_2]$

To a refluxing solution of TPPDS (2 g, 4.2 mmol) in EtOH (25 cm³) was slowly added a solution of $\text{RuCl}_3 \times$

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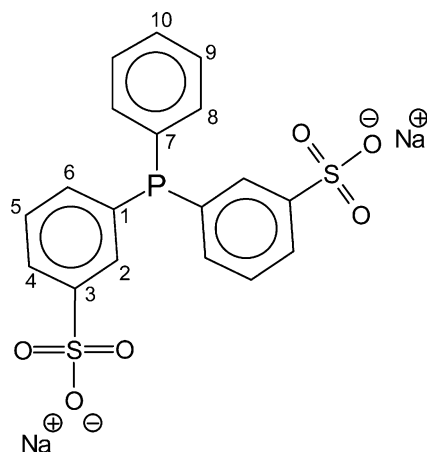


Diagram 1. Triphenylphosphine disulfonate (TPPDS) numbering system.

3H₂O (0.25 g, 1.0 mmol) in EtOH (20 cm³). Refluxing was continued for 30 min, then freshly distilled cyclopentadiene (2.5 cm³) in EtOH (15 cm³) was added and the mixture was refluxed for 3 h. A light brown solid precipitated on cooling and addition of Et₂O. This was filtered off and washed with EtOH and n-hexane. Electronic spectrum: λ_{\max} (nm; ϵ , M⁻¹ cm⁻¹): 206(18512), 262(2168.5), 638(889.5). FTIR cm⁻¹: 3467 [ν (O–H), broad hydroxyl band], 3037 [ν (C–H), aromatic], 1633 [ν (C=C)], 1471 [ν_a (P–C)], 1191 [ν_a (C–SO₃)], 1133 [ν_s (C–SO₃)], 1048 [ν_s (P–C)], 1014 [δ_p (C–H)], 817 [δ_{op} (C–H)] and 703 [*meta* disubstituted aromatics]. ¹H-n.m.r. [δ (p.p.m.)]: 4.9 [singlet, 5H, cyclopentadienyl ring]; 8 [multiplet, 26H]. Mass spectrum: [M^+], $m/e=1134$; other fragments are shown in Table 1, which are consistent with the proposed [Ru(η^5 -C₅H₅)Cl(TPPDS)₂] structure (See Figure 1).

Catalytic trials

Catalytic trials were done in a 125 cm³ Parr reactor with internal glass liner, heating unit, temperature and

Table 1. Observed MS fragments for [Ru(η^5 -C₅H₅)Cl(TPPDS)₂]

Observed MS fragment	m/z
RuCpCl(TPPDS) ₂ ⁺	1134
RuCpCl(TPPDS) ₂ ⁺ -Na	1112
RuCpCl(TPPDS) ₂ ⁺ -3Na	1090
RuCpCl(TPPDS) ₂ ⁺ -Cp	1069
RuCpCl(TPPDS) ₂ ⁺ -2SO ₃ Na	929
RuCpCl(TPPDS) ₂ ⁺ -4SO ₃ Na	726
RuCpCl(TPP) ₂ ⁺ -Cl	691
RuCpCl(TPPDS) ₂ ⁺ -TPPDS	668
RuCp(TPP) ₂ ⁺ -Cp	626
RuCpCl(TPPDS) ₂ ⁺ -Cl, Cp	568
RuCpCl(TPPDS) ₂ ⁺ -2TPPDS	202
RuCpClH ⁺ -Cl	166

stirring control and sampling valve. Conditions for a typical trial: n-heptane (20 cm³), H₂O (20 cm³), toluene or liquid aromatic compound (1 cm³), Ru complex (21 mg), substrate/catalyst = *ca.* 600:1, H₂ pressure (250–1400 psi), temperature (50–120 °C), 1600 rpm stirring rate to ensure thorough mixing and emulsion formation; reaction time, 4 h. 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

The results of varying hydrogen pressures on the toluene hydrogenation reaction are given in Figure 2. At 105 °C and H₂ pressures below 1200 psi, the catalytic activity is slow, reaching between 20% and 30% conversion after 4 h, but there is an important increase at 1400 psi. giving a 65% conversion after 4 h. Toluene hydrogenation is efficient in biphasic n-heptane/water medium, giving methylcyclohexane as the sole product. The H₂ pressure dependence suggests that ruthenium hydride complex is necessary in the catalytic cycle.

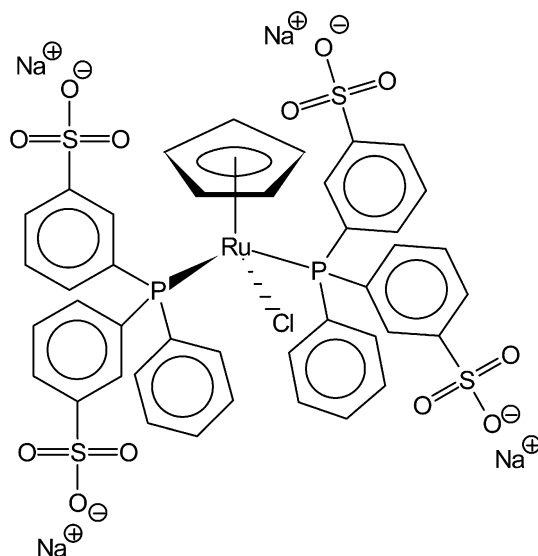


Fig. 1. Proposed structure for [Ru(η^5 -C₅H₅)Cl(TPPDS)₂].

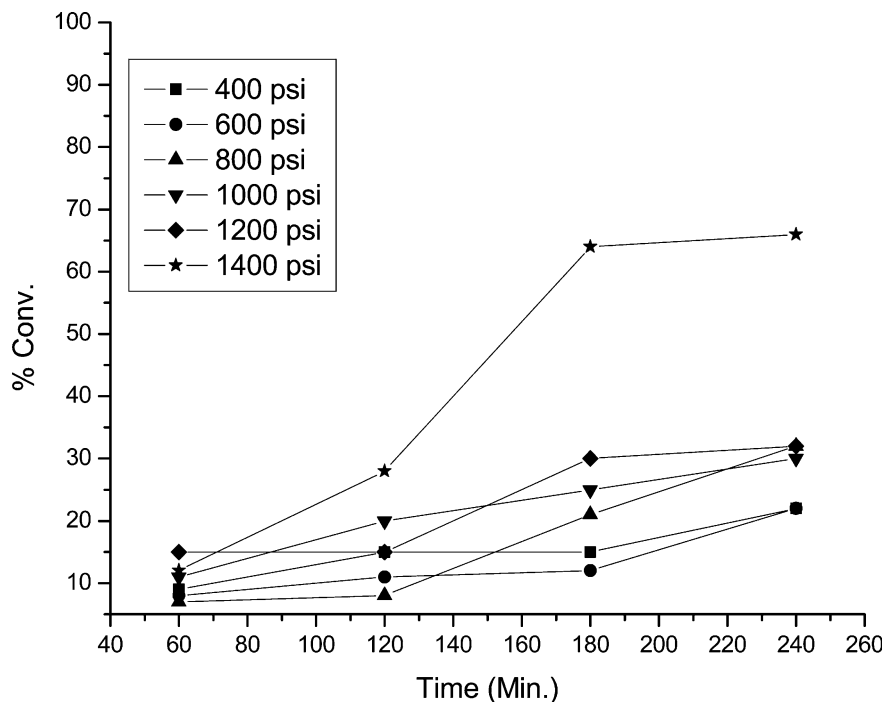


Fig. 2. Toluene hydrogenation with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{TPPDS})_2]$. H_2 pressure effect. Toluene (1 cm^3); n-heptane (20 cm^3), H_2O (20 cm^3), Ru complex (21 mg), S/C = ca. 600:1, Temperature: 105°C ; 1600 rpm stirring rate.

The effects of temperature are shown in Figure 3. At 55°C and 1400 psi H_2 pressure, the reaction is very slow, indicating that the Ru complex precursor requires activation, with a probable induction period necessary to give the active catalytic species. The best results are obtained at 105°C (65% conversion after 4 h), with the percent conversion decreasing at 125°C , probably due to complex decomposition occurring at higher temperatures.

The results of varying the substrate/catalyst ratio (S/C) are shown in Figure 4. The amount of substrate was kept constant (1 cm^3) and variable Ru complex amounts were used. The optimum S/C ratio was 600/1 (65% conversion after 4 h), with a reproducible marked decrease for S/C of 700, probably due to a reduced number of active species. For lower S/C values, lower % conversions were observed, even though there was relatively more Ru complex present. The catalytic

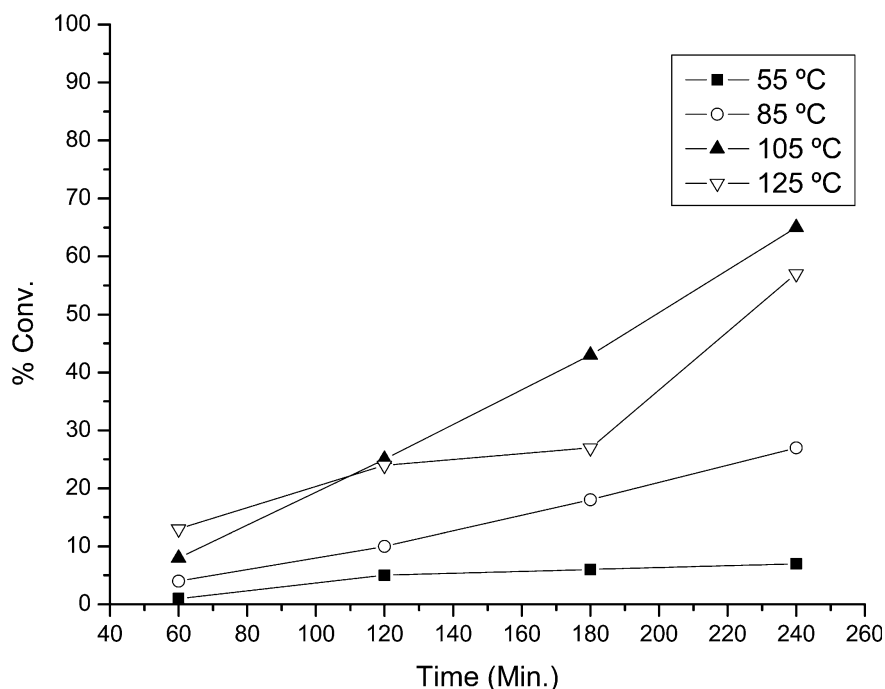


Fig. 3. Toluene hydrogenation with $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{TPPDS})_2]$. Temperature effect. Toluene (1 cm^3); n-heptane (20 cm^3), H_2O (20 cm^3), Ru complex (21 mg), S/C = ca. 600:1, $p(\text{H}_2)$: 1400 psi; 1600 rpm stirring rate.

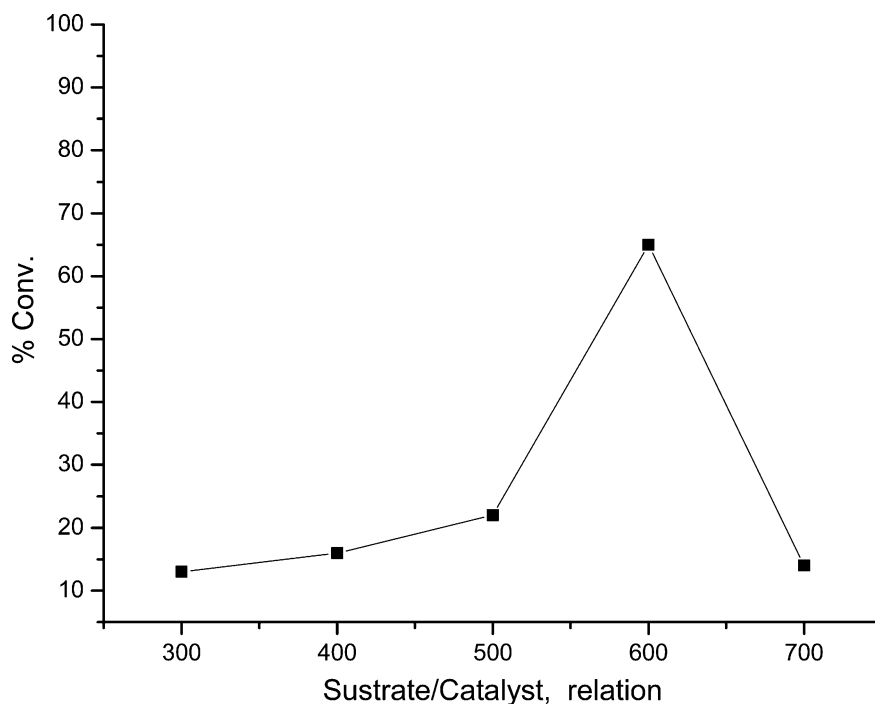


Fig. 4. Toluene hydrogenation with [Ru(η^5 -C₅H₅)Cl(TPPDS)₂]. Substrate/catalyst (S/C) ratio effect. Toluene (1 cm³); n-heptane (20 cm³), H₂O (20 cm³), Ru complex (variable), p(H₂): 1400 psi; Temp.: 105 °C; 1600 rpm stirring rate, 4 h.

reaction is expected to occur at the organic/water inter-phase and more Ru complex could compete with the substrate for the reaction sites, even though due to the small amount of Ru complex used, saturation is not expected.

The results of varying pH are shown in Figure 5. The best results were obtained from neutral pH to pH 10,

(80% conversion at 4 h), but low (pH 4) and high (pH 12) values gave much lower reaction. At low pH, SO₃⁻ group protonation in the phosphine ligands could lead to less water soluble intermediates. At very high pH, the OH⁻ anions could strongly compete for the vacant sites on the Ru intermediate, but the hydroxyruthenium intermediates could be the more reactive

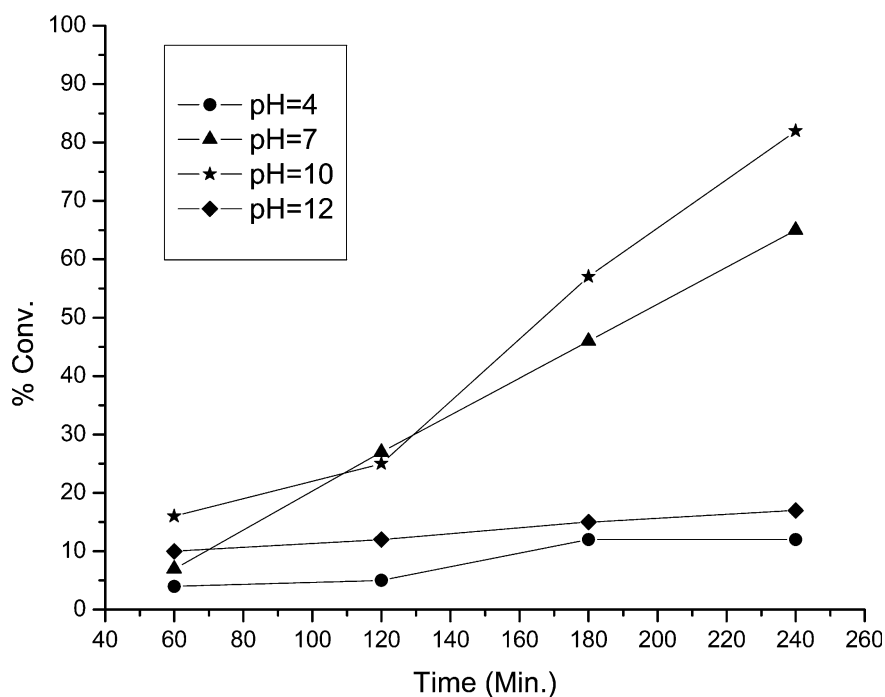


Fig. 5. Toluene hydrogenation with [Ru(η^5 -C₅H₅)Cl(TPPDS)₂]. Water pH effect. Toluene (1 cm³); n-heptane (20 cm³), H₂O (20 cm³), Ru complex (21 mg), p(H₂): 1400 psi; Temp.: 105 °C; S/C=600:1; 1600 rpm stirring rate.

species at pH 10. A higher conversion rate was observed when the water layer ionic strength was increased from 0.1 to 0.4 by adding soluble NaCl and KCl electrolytes, the latter salt giving better conversions. This behavior seems to imply that micelle formation in the biphasic system is being stabilized by the charged species being added.

The Ru complex also shows hydrogenation activity with benzene (43% conversion to cyclohexane) and with *m*-xylene (25% conversion to 1,3-dimethylcyclohexane) under the same reaction conditions used in toluene hydrogenation. The separated water layer containing the Ru complex (u.v.-vis spectra monitored, under Ar) can be recycled at least four times without apparent catalytic activity loss. Test reactions in the presence of liquid mercury do not show any significant activity changes, indicating that metallic ruthenium is not the catalytic phase.

Conclusions

[Ru(η^5 -C₅H₅)Cl(PPDS)₂] is a good catalytic precursor for aromatic hydrocarbon (toluene, benzene and *m*-xylene) hydrogenation in biphasic, n-heptane/water medium under relatively mild conditions. The water system can be recycled several times maintaining good catalytic activity.

Acknowledgements

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