

Biphasic catalysis with $\text{RuCl}_2(\text{DMSO})(\text{TPPMS})_3$

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Abstract

A mononuclear $\text{RuCl}_2(\text{DMSO})(\text{TPPMS})_3$ complex (*1*) (TPPMS = triphenylphosphine monosulfonate) has been synthesized. Spectroscopic analysis by i.r., u.v.–vis., ^1H -, ^{13}C -, ^{31}P -n.m.r., cyclic voltammetry, m.s. analysis and MO calculations were in agreement with a possible octahedral structure. Biphasic ($\text{H}_2\text{O}/\text{PhMe}$) catalytic studies have shown good olefin hydrogenation activity by the complex at moderate temperature and pressure.

Introduction

One homogeneous catalysis limitation is catalyst reuse. Thus two-phase systems are an alternative to this problem. There is great interest in using water-soluble complexes in biphasic catalysis [1–3]. In our laboratory we have prepared the water-soluble $\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{TPPMS})_2$ [4] and $\text{RuCl}_2(\text{DMSO})_4$ [5] complexes with good catalytic activity in reactions of olefin, aldehyde and ketone hydrogenation. We now report the synthesis, characterization and catalytic activity in $\text{H}_2\text{O}/\text{PhMe}$ of the water-soluble $\text{RuCl}_2(\text{DMSO})(\text{TPPMS})_3$ (*1*) (TPPMS = triphenylphosphine monosulfonate) complex.

Experimental

Materials and methods

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Strem Chem. Co), Ph_3P (Aldrich Chem. Co.), H_2 and Ar (Gases Industriales de Venezuela) were obtained commercially and used directly. The substrates used in catalysis are all liquid and were distilled before use; EtOH, PhMe and H_2O were purified as described in the literature [6]. TPPMS was synthesized by Ahrland *et al.*'s method [7]. $\text{RuCl}_2(\text{DMSO})_4$ was prepared according to Wilkinson and co-workers [8a] as modified by Suarez *et al.* [8b].

$\text{RuCl}_2(\text{DMSO})(\text{TPPMS})_3(1)$

A TPPMS suspension (2.6 g, 6.63 mmol) in PhMe (50 cm^3) was refluxed under Ar with $\text{RuCl}_2(\text{DMSO})_4$ (1.0 g, 2.21 mmol) for 4 h. The orange solid produced was suction-filtered. Yield: 70%. m.p.: $150\text{ }^\circ\text{C}$ (dec.).

Physical measurements

The u.v.–vis. electronic absorption spectrum of (*1*) in H_2O was recorded on a LAMBDA 3 Perkin-Elmer spectrophotometer. The vibrational spectrum ($5000\text{--}400\text{ cm}^{-1}$, KBr pellet) was recorded on a FT-IR Perkin-Elmer 1725X spectrophotometer. Room temperature ^1H -, ^{13}C - and ^{31}P -n.m.r. spectra in water- d_2 solutions were taken on a Bruker Advance DRX 400-MHz spectrometer with TMS as internal standard; ^{31}P n.m.r. chemical shifts relative to 85% H_3PO_4 . Electrochemical experiments were performed using a BAS 100 B/W potentiostat. A one compartment cell with a three electrode configuration was employed, consisting of a working electrode (Pt, area = 0.40 cm^2), counter electrode (Pt gauze) and reference electrode. The potentials for aqueous solutions are quoted with respect to a home-made saturated calomel electrode (SCE). Cyclic voltammetric experiments were carried out at room temperature in $5.0 \times 10^{-6}\text{ mol cm}^{-3}$ aqueous solution (H_2O Millipore $18\text{ M}\Omega\text{-cm}^{-1}$) containing $1.0 \times 10^{-2}\text{ mol cm}^{-3}$ of LiClO_4 . Mass spectra were recorded on a Hewlett-Packard System 5988A g.c.-m.s. spectrometer using chemical ionization with isobutene.

Catalytic trials

Catalytic trials were done in a 125 cm^3 Parr reactor with an internal glass holder, heating unit, temperature and stirring control and sampling valve. The conditions used in a typical trial were: PhMe (30 cm^3), H_2O (30 cm^3), 1-hexene or olefin (3 cm^3), complex (*1*) (15 mg, substrate/catalyst molar ratio, S/C = ca. 500:1), H_2 pressure (250, 500 or 1000 psi) and temperature (100 or $70\text{--}180\text{ }^\circ\text{C}$ range). A 1600 rpm stirring rate was used 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

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phosphate on Cromosorb P (80–100 mesh), with H₂ carrying gas and TC detector.

Results and discussion

RuCl₂(DMSO)(TPPMS)₃

The u.v.–vis. electronic spectrum of (1) showed bands at: λ_{\max} (nm; ϵ , M⁻¹ cm⁻¹): 199 (34,740), 252 (21,110), 427 (286). The two u.v. absorptions are assigned to $\pi \rightarrow \pi^*$ (internal ligand) and Ru^{II}d $\pi \rightarrow$ L charge-transfer transitions respectively. The visible absorption is a d \rightarrow d transition typical of ruthenium(II) phosphine complexes [9]. The FT-IR spectrum shows bands characteristic of phenyl sulfonate groups and DMSO: $\nu(\text{O-H})$ 3447 cm⁻¹ (broad hydration band), $\nu(\text{C=C})$ 1632 cm⁻¹, $\nu_a(\text{P-C})$ 1432 cm⁻¹, $\nu_a(\text{C-SO}_3^-)$ 1396 cm⁻¹, $\nu_s(\text{C-SO}_3^-)$ 1198 cm⁻¹, $\nu_s(\text{P-C})$ 1096 cm⁻¹. The ¹H-n.m.r. spectrum in water-*d*₂ shows the following peaks: δ (p.p.m.) 7.8–6.8 (multiplet, 42H), corresponding to the phenyl group aromatic protons. The S-coordinated DMSO methyl protons [10] appear as a lower field (3.36–3.46 p.p.m. range) multiplet (6H). The DMSO methyl protons multiplet could be due to bound DMSO rotational restriction produced by steric interaction with phosphine groups, as confirmed by an nonbonded interatomic distance calculation between the DMSO methyl groups and the phosphine ligands [11]. Ligand exchange with DMSO-*d*₆ at room temperature shows a gradual intensity decrease of the 3.36–3.46 p.p.m. multiplet and a corresponding intensity increase of the free DMSO signal, the exchange being practically complete after 30 min. The ligand exchange rate was calculated using the free DMSO singlet time change (corrected for the DMSO impurity in DMSO-*d*₆) giving 6.45×10^{-4} s⁻¹ ($R^2 = 0.97$, for first order adjustment). ¹³C-n.m.r. shows the following peaks: δ (p.p.m.) for the sulfonated ring: 143.1 (P-C); 129.7; 129.4; 128.9; 133.7; 133.5 (C-SO₃⁻); for the non-sulfonated rings: 135.9 (P-C); 133.9; 133.8; 129.4; for DMSO: 39.1. ³¹P-n.m.r. for free TPPMS showed a peak at -3.5 p.p.m.; for complex (1) the observed signals are at 38.4 p.p.m. (axial P) and 56.7 p.p.m. (equatorial P) indicating two types of phosphorus environments. The $E_{1/2}$ for the Ru^{II}/Ru^{III} couple in aqueous solutions for complex (1) was observed at -424.5 mV *versus* SCE (100 mV s⁻¹). The diagnostic test of electrochemical reversibility seems to indicate a quasi-reversible system. Analysis of the current (*i.e.* $i_{p,a}/i_{p,c}$ ratios) and potential behavior with scan rate (10–500 mV s⁻¹) suggest one electron slow processes. The mass spectrum shows peaks at: [M⁺](¹⁰¹Ru)-[CH₃CINa₃], $m/e = 1220.4$ ($I = 100\%$); and the ruthenium isotope [M+4](¹⁰⁴Ru)-[CH₃CINa₃], 1224.1 (59), the ratio confirming a monometallic complex. The following fragmentation pattern was observed: C₅H₆⁺, 66.05 (23.7); C₆H₄⁺, 76.6 (25.4); C₁₂H₈P⁺, 183.32 (37.4); HP(C₆H₅)₂⁺, 186.35 (28.7); PC₁₂H₇SO₃⁺, 263.43 (29.6). The spectroscopic and mass spectrometric evi-

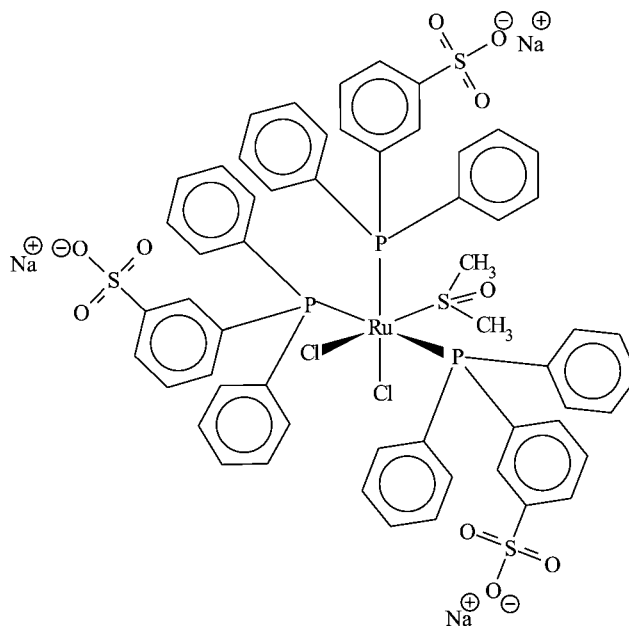


Fig. 1. RuCl₂(DMSO)(TPPMS)₃, calculated minimum energy structure [11 (footnote 1)].

dence supports the proposed structure shown in Figure 1, which corresponds to a minimum energy computational structure (I).

Catalytic results

RuCl₂(DMSO)(TPPMS)₃ exhibits catalytic activity for hydrogenation of unsaturated organic substrates (1-hexene, cyclohexene, butyraldehyde, crotonaldehyde, cinnamaldehyde and myrcene). 1-Hexene hydrogenation shows a high total conversion percentage within 1 h mainly to *n*-hexane with small *cis*- and *trans*-2-hexene isomerization products; isomer hydrogenation is much slower and after 3 h there is an equilibrium trend as shown in Figure 2. The hydrogenation results for other unsaturated organic substrates are given in Table 1, under higher H₂ pressure (1000 psi) and 5 h reaction time. Cyclohexene (a cyclic olefin) gives a high cyclohexane yield; carbonyl group hydrogenation, as in butyraldehyde, gives 67% 1-butanol. For crotonaldehyde and cinnamaldehyde (α,β -unsaturated substrates) the three expected reaction products are obtained, with some selectivity toward terminal olefin hydrogenation. For crotonaldehyde, carbonyl group hydrogenation is the main product (1-butenol), and internal double bond hydrogenation is the secondary product (1-butanol); on the other hand, for cinnamaldehyde, internal double bond hydrogenation is the main product (phenylprop-*anal*) probably due to an aromatic ring effect, and carbonyl group hydrogenation is the secondary product (phenylprop-*enol*). For both α,β -unsaturated substrates,

¹ Calculated results for (1) using PM3 semi-empirical MO model in units as given by the program: heat of formation, -1333.432 kJ mol⁻¹; HOMO energy, -4.88741122 eV; LUMO energy, -4.65634118 eV; dipole, 2.030×10^{-29} Cm (6.087 D), area, 752.74 Å²; vol., 824.96 Å³.

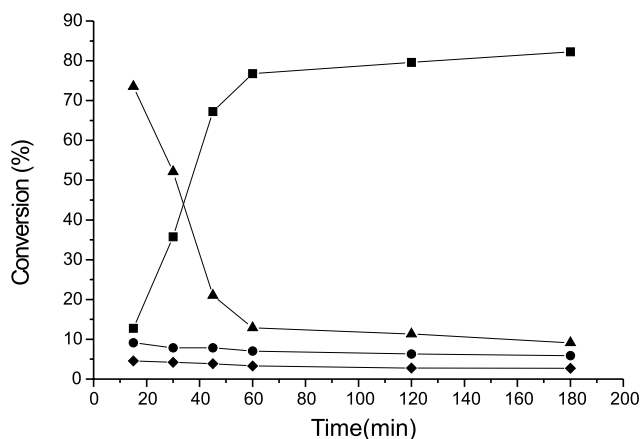


Fig. 2. Percent conversion of 1-hexene versus reaction time, $P = 500$ psi, $T = 100$ °C, substrate catalyst ratio = 500:1, stirring rate: 1600 rpm. (■) *n*-hexane, (▲) 1-hexene, (●) *cis*-2-hexene, (◆) *trans*-2-hexene.

Table 1. Unsaturated organic substrates hydrogenation

Substrate	Products	Conversión (%)
Cyclohexene	Cyclohexane	73.2
Butyraldehyde	1-Butanol	67.0
Crotonaldehyde	1-Butanal	25.0
	1-Butenol	30.0
Cinnamaldehyde	Butanol	5.0
	Phenylpropanal	41.1
	Phenylpropenol	21.5
Myrcene	Phenylpropanol	4.9
	2-Ethyl-6,6-dimethyl-1,5-hexadiene	98.0

Reaction conditions: H_2 pressure: 1000 psi, temp.: 100 °C, stirring rate: 1600 rpm, S/C: 500:1, total reaction time: 5 h.

the complete hydrogenation product is observed in smaller quantities, which indicates a more difficult reaction that requires more severe conditions or longer reaction times. In myrcene, only hydrogenation of the less substituted C=C double bond (2-ethyl, 6-dimethyl, 1,5-hexadiene) occurs. Biphasic catalysis with $RuCl(\eta^5-C_5H_5)(TPPMS)_2$ [4] reveals terminal double bond hydrogenation selectivity. More detailed catalytic and

kinetic studies with complex (1) are currently under way in our laboratories.

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