CATALYTIC HYDROGENATION OF 1-HEXENE WITH 
RuCl\textsubscript{2}(TPPMS)\textsubscript{3}(DMSO) 
PART II: IONIC LIQUID BIPHASIC SYSTEM

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Abstract
RuCl\textsubscript{2}(TPPMS)\textsubscript{3}(DMSO) (complex (I)) is very soluble in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate (BMI.PF\textsubscript{6}). Complex (I) catalyzes 1-hexene hydrogenation (500 psi H\textsubscript{2} and 100°C) in a two-phase system, with 80% conversion in 24 h, with little substrate isomerization. Changes in catalytic behavior with temperature, pressure, time and substrate/catalyst relation are presented. Complex (I) shows good stability and can be reused several times with little activity loss.

Keywords: Ruthenium, biphasic catalysis, hydrogenation, ionic liquid

INTRODUCTION

Reaction products separation, catalyst recovery and use of organic solvents are disadvantages of industrial homogenous catalysis applications. Two-phase catalysis is an alternative, but some organometallic complexes are unstable in water, making attractive the use of other catalytic systems. Ionic liquids (IL’s) have useful physical characteristics as solvents in biphasic catalytic systems for
organometallic complexes [1-7]. In our laboratory we have studied new soluble precursors for biphasic catalysis: \( \text{RuCl}_2(\text{DMSO})_4 \) [8] \( \text{RuCl(\eta}^5-\text{C}_5\text{H}_5)(\text{TPPMS})_2 \) [9] and \( \text{RuCl}_2(\text{TPPMS})_3(\text{DMSO}) \) [10], being active in diverse unsaturated organic substrates hydrogenations. We report here 1-hexene hydrogenation with complex (I) in 1-\( n \)-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆) as ionic liquid medium.

**EXPERIMENTAL**

**Materials and methods**

RuCl₃·3H₂O (Strem Chem. Co), PPh₃ (Aldrich Chem. Co.), H₂ and Ar (Gases Industriales de Venezuela) were obtained commercially and used directly. Liquid substrates used in catalysis were distilled before use; all solvents were purified as described in the literature [11].

**Syntheses**

Triphenylphosphine monosulfonate (TPPMS) was synthesized by Ahrland’s method [12] and characterized as described previously [13]; the ionic liquid 1-\( n \)-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆) [14] and the catalytic precursor complex (I) were synthesized as reported in the literature [10].

**Catalytic tests**

Catalytic tests were done in a 50 mL Parr reactor with internal magnetic stirring. Conditions for a typical trial: 3 mL of BMI-PF₆, 1-hexene or olefin (1 mL, 8 mmol), complex (I) (20 mg, 0.015 mmol), substrate/catalyst molar ratio, S/C= 500:1, H₂ pressure: 250 to 1.000 psi range, temperature: 50°C to 120°C range, 1600 rpm stirring rate was held constant. 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 FID detector.
RESULTS AND DISCUSSION

Temperature effect

Temperature effect on 1-hexene hydrogenation is shown in Fig. 1. There is a gradual increase in \( n \)-hexane hydrogenation product to 77% conversion as the temperature increases from 60ºC to 100ºC, and a slight decrease at 120ºC (73% conversion). Isomerization products remain below 10% with a slight cis-2-hexene preference. An increase in temperature decreases the ionic liquid viscosity [1,15], probably allowing better contact between the substrate and catalytic precursor improving total conversion. At 120ºC, partial catalyst decomposition could lead to lower total conversion. Partial decomposition has also been observed for complex (I) in aqueous biphasic systems (toluene/water) [13].

![Fig. 1. Temperature effect on 1-hexene hydrogenation. 500 psi H\(_2\) pressure, S/C: 500/1, 1600 rpm stirring rate, 24 h reaction time. ■ \( n \)-hexane, ● 1-hexene, ▲ cis-2-hexene, ▼ trans-2-hexene](image)

Pressure effect

\( H_2 \) pressure effect on 1-hexene hydrogenation is shown in Fig. 2. The \( n \)-hexane hydrogenation product increases up to 500 psi \( H_2 \) pressure and levels off at higher pressures (ca. 75% conversion). At 100 psi pressure, the isomerization
reaction has higher activity (30% total isomerization conversion, cis-2-hexene preference) and then levels off (ca. 15% isomerization conversion) at higher H₂ pressures. It is possible that hydrogen concentration saturation is reached at 500 psi in the biphasic system.

**Fig. 2.** H₂ pressure effect on 1-hexene hydrogenation. 100°C, S/C: 500/1, 1600 rpm stirring rate, 24 h reaction time. ■ n-hexane, ● 1-hexene; ▲ cis-2-hexene, ▼ trans-2-hexene

**Other parameter studies**

The results of changing other parameters in 1-hexene hydrogenation are shown in Table 1. Varying the reaction time from 6 h to 24 h shows an increase in n-hexane conversion (to 91% conversion). The isomerization products remain fairly constant with time, indicating that these products occur early in the reaction. An increase in product conversion is observed when the [1-hexene]/[Ru] relation is smaller (R/C:250:1), but isomerization remains fairly low (ca.10%, favoring cis-2-hexene). Adding excess ligand (TPPMS, ca. 5 molar excess) shows a notable reduction in the hydrogenation reaction. A similar reduction is observed in the aqueous/toluene biphasic systems for the same complex [13]. It is presumed that excess ligand in solution competes with the substrate for the metal vacant coordination site.
### Table 1

Catalytic activity of 1-hexene hydrogenation under various modified conditions

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>[1-hexene]/[Ru] (mol/mol)</th>
<th>[L(^b)/[Ru]] (mol/mol)</th>
<th>Conv. (%)</th>
<th>Selectivity (%)</th>
<th>TOF(^c) (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hexane</td>
<td>cis-2-hexene</td>
<td>trans-2-hexene</td>
</tr>
<tr>
<td>6</td>
<td>500</td>
<td>1:1</td>
<td>70</td>
<td>57</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>500</td>
<td>1:1</td>
<td>82</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>24</td>
<td>500</td>
<td>1:1</td>
<td>91</td>
<td>77</td>
<td>10</td>
</tr>
<tr>
<td>24</td>
<td>500</td>
<td>5:1</td>
<td>47</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>24</td>
<td>250</td>
<td>1:1</td>
<td>98</td>
<td>89</td>
<td>7</td>
</tr>
<tr>
<td>24</td>
<td>1000</td>
<td>1:1</td>
<td>76</td>
<td>57</td>
<td>14</td>
</tr>
</tbody>
</table>

\(^a\) Catalysis performed at 100°C and 500 psi H\(_2\). \(^b\) TPPMS ligand excess. \(^c\) TOF calculated as mol of 1-hexene converted per mol of catalyst per hour.

**Fig. 3.** Consecutive reuses of catalytic precursor. Temperature 100°C, 500 psi H\(_2\) pressure, S/C: 500/1, 1600 rpm stirring rate, 24 h reaction time. Columns from left to right refer to n-hexane, 1-hexene, cis-2-hexene, trans-2-hexene, respectively.
Recycling of ionic liquid

The organic substrate is completely insoluble in the ionic medium, thus a simple decantation separates the catalytic precursor. The study of consecutive reuses for the catalytic precursor is shown in Fig. 3. There is a gradual decrease to about 70% total conversion after 6 reuses. The hexane product is favored (above 60% conversion) and smaller amounts of isomerization products (above 10% conversion for cis-2-hexene).

Hydrogenation of other substrates

Catalytic activity of complex \( \text{(I)} \) in cyclohexene and crotonaldehyde hydrogenation was tried (Reaction conditions: 100ºC, 500 psi \( \text{H}_2 \) pressure, S/C: 500:1, and 24 h reaction time). Cyclohexene gives 34% cyclohexane conversion, and crotonaldehyde shows 1-butanol as sole product with lower conversion (25%). For crotonaldehyde there is no apparent selectivity for the double bonds in ionic liquid, but the carbonyl bond gets hydrogenated in toluene/water [13]. Pure BMI·PF\(_6\) has a polymeric structure well organized with weak interactions [16], and this could affect reactions with other unsaturated substrates giving lower conversions than with 1-hexene. In general, the catalytic activity in the ionic liquid/organic substrate biphasic system is lower than in the biphasic toluene/water system [13], requiring longer times to achieve high conversions under similar reaction conditions.

CONCLUSION

Complex \( \text{(I)} \) shows good 1-hexene hydrogenation activity in ionic liquid media (BMI·PF\(_6\)). The complex shows good stability and can be reused at least six times with low catalytic activity loss, indicating some potential for practical applications.

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REFERENCES
