

Hydrogenation of α,β -unsaturated carbonyl substrates by use of $[\text{Ir}(\text{COD})(\text{PPh}_3)_2] \text{PF}_6$ in 1-butyl-3-methylimidazolium hexafluorophosphate

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Abstract

The biphasic selective hydrogenation α,β -unsaturated carbonyl substrates by use of $[\text{Ir}(\text{COD})(\text{PPh}_3)_2]\text{PF}_6$ in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM)(PF₆) is described and compared with the homogeneous system dissolved in pure toluene.

Key words: α,β -unsaturated aldehydes and ketones; biphasic catalysis; hydrogenation; ionic liquid; iridium.

Hidrogenación de substratos carbonílicos α, β insaturados usando $[\text{Ir}(\text{COD})(\text{PPh}_3)_2]\text{PF}_6$ en 1-butil-3-metil-imidazolin hezafluorofosfato

Resumen

La hidrogenación selectiva de sustratos carbonílicos α, β -insaturados se llevó a cabo en medio bifásico mediante el uso del complejo $[\text{Ir}(\text{COD})(\text{PPh}_3)_2][\text{PF}_6]$ inmovilizado en hexafluorofosfato de 1-butil-3-metilimidazolio [BMIM][PF₆] como precursor catalítico; los resultados se describen en comparación con el sistema homogéneo análogo, disuelto en tolueno.

Palabras clave: α,β -insaturados; catálisis bifásica; hidrogenación; iridio; líquidos iónicos; sustratos.

Introduction

The selective hydrogenation of α,β -unsaturated carbonyl compounds is of interest in organic synthesis and some of its applications to the production of fine chemicals for the fragrance and pharmaceutical industries (1, 2, 3). C=C bond hydrogenation

is thermodynamically favored over reduction of the C=O bond by about 35 KJ mol⁻¹ and from a kinetic point of view, the reactivity of the C=C bond toward hydrogenation is also higher than that of the C=O bond (4); these features may be utilized in the development of highly selective catalytic systems.

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A number of complexes of Ru, Rh and Ir have been used as catalysts for this important reaction (5). Iridium complexes generally display lower activities in comparison with those of ruthenium and rhodium and they have shown good selectivity for the hydrogenation of α,β -unsaturated aldehydes under optimum reaction conditions (6).

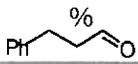
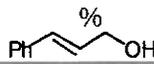
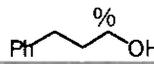
Catalyst separation from the products is frequently cited as a major problem in homogeneous catalytic processes and one way to resolve it is the use of liquid biphasic catalysts (7, 8). Indeed, we have previously reported the hydrogenation of *trans*-cinnamaldehyde in *aqueous*-biphasic media by use of water-soluble Ru and Os complexes containing sulfonated phosphine ligands (9, 11). An alternative very attractive approach is the introduction of ionic liquids as supports for immobilizing transition metal complexes in liquid phases; these novel polar solvents possess negligible vapor pressure, high stability, and the ability to dissolve a variety of organic and organometallic compounds over a wide temperature range, all of which results in environmental advantages of potential industrial applications (12).

In this communication we report some preliminary data on the hydrogenation of *trans*-cinnamaldehyde, 4-phenyl-3-buten-2-one, methyl-*trans*-cinnamate and (\pm)-carvone in a toluene/ionic liquid biphasic system under moderate reaction conditions, by use of a catalyst prepared by immobilization of the complex $[\text{Ir}(\text{COD})(\text{PPh}_3)_2][\text{PF}_6]$ (13) (**1**) (COD = 1,3-

cyclooctadiene) in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate $[\text{BMIM}][\text{PF}_6]$ (14). The performance of this ionic liquid-supported catalyst was compared to that displayed by $[\text{Ir}(\text{COD})(\text{PPh}_3)_2][\text{PF}_6]$ dissolved in pure toluene.

For *trans*-cinnamaldehyde (Table 1) the catalytic activity in homogeneous toluene solution is higher than those observed for the ionic liquid-supported catalysts. Also, a marked decrease in activity was observed on going from the PF_6^- to the BF_4^- anion, which is curious; there was no evidence of catalyst leaking into the organic phase in the ionic liquid mixtures. More interestingly, a switch in the selectivity was evidenced on going from the homogeneous system (88% selectivity for C=C bond hydrogenation) to the $[\text{BMIM}][\text{PF}_6]$ ionic liquid (53% selectivity for C=O bond hydrogenation). In both cases, the fully hydrogenated product, 3-phenylpropanol was also present in small amounts (7% in toluene, 18% in $[\text{BMIM}][\text{PF}_6]$). However, the reaction in $[\text{BMIM}][\text{BF}_4]$ was 100% selective for C=C bond hydrogenation. Although the experimental data available do not allow us to provide a clear explanation for this activity and selectivity shifts, the known sensitivity of $[\text{BMIM}][\text{PF}_6]$ toward hydrolysis by traces of water in the system may be playing a role; it is possible that under those conditions a small amount of undetected colloidal iridium particles is formed and they are responsible for the observed C=O hydrogenation.

Table 1
Homogeneous and biphasic hydrogenation of cinnamaldehyde by $[\text{Ir}(\text{COD})(\text{PPh}_3)_2][\text{PF}_6]$.

Solvent	% conv.	TOF (h^{-1})	% selectivity		
					
Toluene	53.5	321	88	5	7
$[\text{BMIM}][\text{PF}_6]$	36.5	218	29	53	18
$[\text{BMIM}][\text{BF}_4]$	16	96	100	—	—

Conditions: cat, 0.024 mmol; $[\text{BMIM}][\text{X}]$, 3 mL; toluene, 47 mL; 80 °C; 9,5 atm H_2 ; substrate, 2.4 mmol; 6 h.

In the case of 4-phenyl-3-buten-2-one, the catalytic activity is essentially the same in both the ionic liquid and in toluene (TOF *ca.* 600 h⁻¹) and both catalysts are highly selective for the hydrogenation of the C=C bond (90% in toluene; 98% in $[\text{BMIM}][\text{PF}_6]$) (see Scheme 1). For the α,β -unsaturated ester; methyl-*trans*-cinnamate, the activity in the ionic liquid (41% conv., TOF 246 h⁻¹) is lower than that in homogeneous phase (69%, TOF 415 h⁻¹), but in both cases, the C=C bond is exclusively hydrogenated without any indication of reduction of the ester group (Scheme 1).

(±)-Carvone is an interesting molecule, since it contains both exocyclic and endocyclic C=C bonds besides a C=O bond. As shown in Scheme 2, on going from the homogeneous to the ionic liquid system, the activity is reduced considerably, but the reaction in both cases is very selective for the hydrogenation of the C=C bonds, while the C=O bond remains untouched under these reaction conditions. Moreover, the exocyclic C=C bond is preferentially hydrogenated over the endocyclic C=C bond hydrogenation, which can be considered a normal trend.

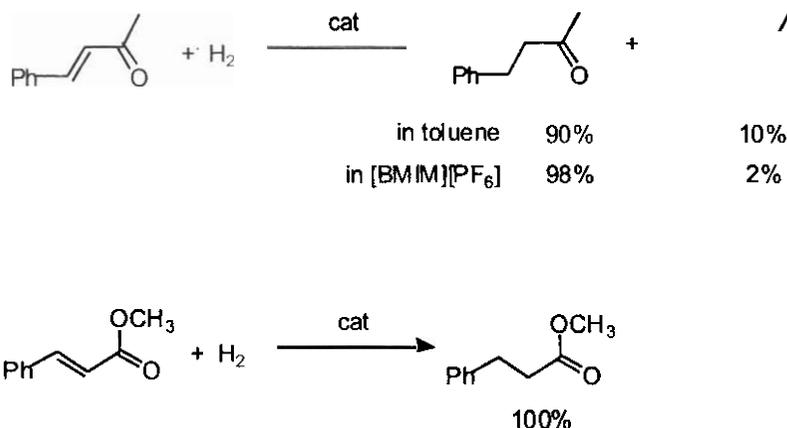
In summary, the use of the ionic liquid-supported biphasic catalyst $[\text{Ir}(\text{COD})(\text{PPh}_3)_2][\text{PF}_6]$ - $[\text{BMIM}][\text{PF}_6]$ for the se-

lective hydrogenation of α,β -unsaturated carbonyl substrates is reported. The catalytic activity tends to be lower in the supported system but high selectivities are achieved in most cases; the supported catalysts can be easily recovered and re-used without any significant changes in their properties. Further work is in progress in order to establish the scope of this reaction and to better understand the trends observed in C=C vs. C=O bond reactivity.

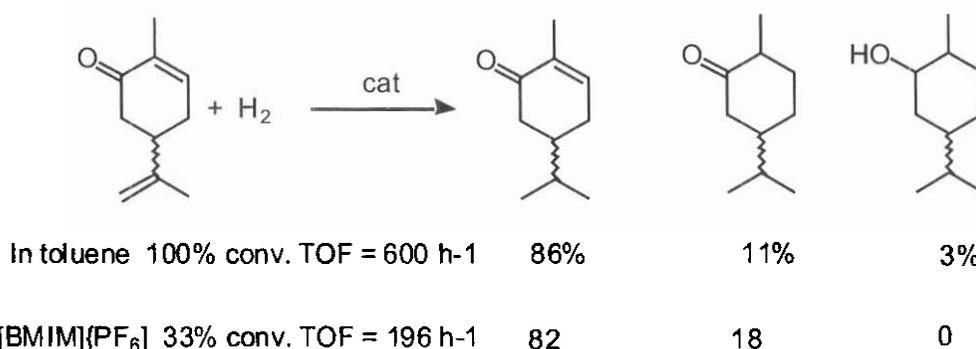
Experimental Section

The catalyst precursor $[\text{Ir}(\text{COD})(\text{PPh}_3)_2][\text{PF}_6]$ (COD = 1,3-cyclooctadiene) (13) and the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate $[\text{BMIM}][\text{PF}_6]$ (14) were synthesized by literature procedures. All other reagents were of commercial grade and were used without further purification.

Hydrogenation Runs. In a typical hydrogenation run, a solution of complex (0,024 mmol) in 3 mL $[\text{BMIM}][\text{PF}_6]$ and a solution of the substrate (2.4 mmol) in 47 mL of toluene were introduced in a glass-lined stainless steel autoclave (300 mL) (PARR instruments) equipped with internal stirring, temperature control unit and a sampling valve. Air was removed by purging three



Scheme 1. Homogeneous and biphasic hydrogenation of 4-phenyl-but-3-ene-2-one and methyl-*trans*-cinnamate catalyzed by $[\text{Ir}(\text{COD})(\text{PPh}_3)_2][\text{PF}_6]$. Conditions: cat, 0.024 mmol; toluene, 50 or 47 mL; $[\text{BMIM}][\text{PF}_6]$, 0 or 3 mL; 80°C; 9,5 atm H₂; substrate, 2.4 mmol; 6 h.



Scheme 2. Homogeneous and biphasic hydrogenation of (±)-carvone catalyzed by [Ir(COD)(PPh₃)₂][PF₆]. Conditions: cat, 0.024 mmol; toluene, 50 or 47 mL; [BMIM][PF₆], 0 or 3 mL; 80°C; 9,5 atm H₂; substrate, 2.4 mmol; 6 h.

times with hydrogen and the reactor was charged to the required pressure (9,5 atm) and heated to the chosen reaction temperature (80°C) under constant stirring at 430 rpm. During the catalytic test, the total pressure of the system was continuously adjusted to a constant value by making up from a high-pressure reservoir and reaction mixture samples were periodically taken through the sampling valve. The reaction was stopped after 6 hours, cooled down, the residual hydrogen was released and the products separated from the ionic liquid solution by decantation. The samples were analyzed by GC-MS analysis.

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