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# Selective linear dimerization of 1,3-butadiene by palladium compounds immobilized into 1-*n*-butyl-3-methyl imidazolium ionic liquids

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## Summary

Palladium (II) compounds (palladium dichloride, acetate and acetylacetonate) in conjunction with triphenylphosphine dissolved in 1-butyl-methyl imidazolium tetrafluoroborate, hexafluorophosphate or trifluoromethanesulfonate are able to dimerize butadiene into 1,3,6-octatriene in a typical two-phase catalytic reaction with 100% selectivity. The reaction product is easily separated from the reaction mixture by simple decantation, and the recovered ionic liquid catalyst solution can be reused several times without significant changes in catalytic activity or selectivity.

## Introduction

Octatrienes have wide range of applications such as comonomer in $\alpha$-olefin copolymers,[1] plasticizers,[2] adhesive compounds,[3] fragrances[4] and building blocks for organic synthesis[5]. In this respect various methods have been developed in the last years for the synthesis of such compounds, especially for 1,3,6 and 1,3,7-octatriene. These methods are mainly based on the catalytic homogeneous dimerization of 1,3-butadiene by transition metal complexes of Ni[6] and Pd.[7] However, since these octatrienes rapidly polymerize in the presence of air,[7] the use of synthetic processes that require distillation or other thermal separation techniques are not recommended. Moreover, it is well known that the separation of the products from the reaction mixture is still one of the basic problem of homogeneous organometallic catalysis. This problem can be overcome by the use of two-phase catalytic systems. Indeed, it has been reported that palladium (II) compounds dissolved in acetonitrile and containing isooctane as cosolvent dimerize selectively 1,3-butadiene to 1,3,7-octatriene in a two-phase catalytic system.[8] We and others have recently demonstrated that various transition metal catalyst precursors dissolved in ionic liquids based on the 1,3-dialkyl imidazolium cation are able to perform several reactions such as hydrogenation[9] and oligomerization[10] of olefins in typical two-phase catalytic reactions. The conversions and selectivities achieved in these catalytic reactions are similar to those obtained with the same catalyst precursors in homogeneous media. Moreover the catalytic ionic liquid mixture can be reused several times without significant changes on catalytic activity and selectivity. We wish to report here that

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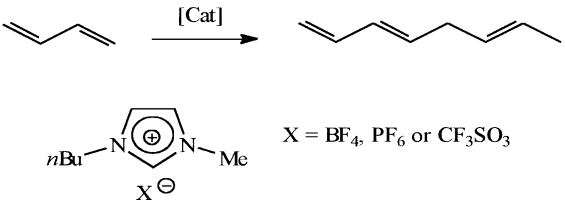
palladium (II) complexes dissolved in 1-butyl-3-methyl imidazolium ionic liquids are able to dimerize selectively 1,3-butadiene to 1,3,6-octatriene in a typical two-phase catalytic reaction.

## Results and Discussion

The palladium (II) catalyst precursors chosen for this study (Table 1) are classically used in the dimerization of 1,3-butadiene in homogeneous media and they have been immobilized in 1-butyl-3-methyl imidazolium based molten salts by simple mixing of the complexes with the ionic liquid at room temperature. In all the cases only 1,3,6-octatriene has been obtained in the organic phase (Scheme 1).

The results obtained with various catalyst precursors are summarized in Table 1. Note that butadiene conversion in homogeneous media (THF) with $PdCl_2$ catalyst precursor is significantly lower than conversions achieved with this palladium compound immobilized in the ionic liquid (entries 1 and 2 respectively). Moreover, under the homogeneous reaction conditions metallic palladium is obtained at the end of the reaction. There are not great differences on the butadiene conversion with the various palladium catalyst precursors immobilized or with the three ionic liquids (compare entries 2 to 8). However, in the absence of triphenylphosphine butadiene conversion is less than 5% and metallic palladium was observed at the end of the reaction. The best results on butadiene conversion were obtained with $PPh_3/[Pd] \approx 4$. Using $PPh_3/[Pd]$ inferior or superior to 4 butadiene conversion decreases dramatically. The role of triphenylphosphine in these systems can be rationalized in terms of stabilization of the catalytic active species, as already pointed out earlier for similar palladium catalyzed C-C bond forming reactions.[11] This behavior associated with the high selectivity achieved with the palladium compounds immobilized in the ionic liquid suggests that the mechanism of butadiene dimerization in this two-phase catalysis is similar to those generally accepted for homogeneous systems.[12]

Scheme 1.



X = $BF_4$, $PF_6$ or $CF_3SO_3$

The reaction temperature is also essential for butadiene conversion. Below 70°C or above 90°C the conversion decreases substantially (down to 8%). Moreover, above 110°C, products such as vinyl cyclohexene, resulting from thermal homo Diels-Alder reactions were also formed.[7d,13]

The increase of the catalyst concentration in the ionic liquid also decreases butadiene conversion. This behaviour is probably related to an increase of the viscosity of the reaction medium that impedes stirring and therefore mass transfer between the phases is reduced. In this respect, when stirring is stopped, butadiene conversion decreases to zero.

Table 1. Butadiene conversion and turnover frequencies (TOF) on butadiene dimerization by palladium compounds.

| Entry | Catalyst Precursor | Ionic Liquid/ Cosolvent | Gas (atm) | Conv.[a] (%) | TOF[b] ($h^{-1}$) |
|---|---|---|---|---|---|
| 1. | $PdCl_2$ | THF | --- | 1.5 | 6.0 |
| 2 | $PdCl_2$ | BMI[c].$BF_4$ | --- | 12.7 | 49.2 |
| 3 | $PdCl_2$ | BMI.PF6 | --- | 11.3 | 46.8 |
| 4 | $PdCl_2$ | MBI.$CF_3SO_3$ | --- | 11.0 | 46.2 |
| 5 | $[Pd(OAc)_2]_3$[d] | BMI.$BF_4$ | --- | 10.7 | 43.2 |
| 6 | $Pd(acac)_2$[e] | BMI.$BF_4$ | --- | 11.5 | 48.6 |
| 7 | $PdCl_2(PhCN)_2$ | BMI.$BF_4$ | --- | 8.3 | 37.2 |
| 8 | $PdAnM(PPh_3)_2$[f] | BMI.$BF_4$ | --- | 8.6 | 37.8 |
| 9 | $PdCl_2$ | BMI.$BF_4$/cyclohexane | --- | 8.4 | 34.2 |
| 10 | $PdCl_2$ | BMI.$BF_4$/THF | --- | 1.4 | 6.0 |
| 11 | $PdCl_2$ | BMI.$BF_4$ | $CO_2$ (5) | 12.5 | 48.6 |
| 12 | $PdCl_2$ | BMI.$BF_4$ | $CO_2$ (10) | 5.5 | 27.0 |
| 13 | $PdCl_2$ | BMI.$BF_4$ | Ar (5) | 9.6 | 40.2 |
| 14 | $PdCl_2$ | BMI.$BF_4$ | Ar (10) | 9.6 | 40.2 |

a) butadiene conversion; b) Turnover frequency (TOF): mole of butadiene converted by mole of palladium per hour; c) BMI= 1-n-butyl-3-methyl imidazolium; d) OAc= acetate; e) acac= acetylacetonate; f) AnM= maleic anhydride.

The use of polar cosolvent is detrimental for the catalytic activity (see entry 10). In fact, under this reaction condition, the catalyst precursor is extracted by the THF from the ionic phase and metallic palladium was observed at the end of the reaction.

It is known that the use of carbon dioxide pressure on the dimerization and telomerization of dienes in both homogeneous[14] and two-phase[15] reactions increases the catalytic selectivity. This, however, was not observed in our system (entries 11-14). Contrarily, with higher carbon dioxide pressure (entry 12), butadiene conversion decreases. This behavior can be associated with the saturation of the ionic phase by the gas thus making difficult the dissolution of the diene into the ionic liquid.

It is important to note that the palladium compounds are almost completely retained in the ionic phase, as determined by atomic absorption analysis of the two phases after the catalytic reaction. Moreover, the recovered ionic catalyst solution can be reused several times without significant changes on the catalytic activity or selectivity.

In summary we have shown that butadiene dimerization can be performed with classical palladium catalyst precursors immobilized in ionic liquids with activities similar to those obtained in homogeneous media. Moreover, the selectivity in 1,3,6-octatriene is higher than that obtained with the classical homogeneous catalysis and the product can be easily separated from the reaction mixture by decantation.

## Experimental

### General

Manipulations were performed under dry, oxygen-free argon using standard techniques. Solvents were dried and distilled under argon prior to use. Proton and carbon shifts (δ/p.p.m., *J*/Hz), are down field relative to external $SiMe_4$. Mass spectra were obtained with GC-MS HP5988A (EI, 70 eV). The palladium contents in both ionic and organic phases were determined by atomic absorption analysis using a Perkin Elmer 2380, HGA 400, atomic absorption spectrometer with graphite tube atomizer. The reaction products were analyzed by gas chromatography on a Varian 3400 CX chromatograph equipped with an LM1 column 20 m x 0.25 mm x 0.2 μm, and FID detector; $N_2$ was the carrier (1 mL/min); the temperature program was from 50°C (5 min) to 180°C (15 min) at a heating rate of 10°C / min.

$[Pd(OAC)_2]_3$,[16] $Pd(acac)_2$,[17] $PdCl_2(PhCN)_2$,[18] $PdAnM(PPh_3)_2$[19] and the ionic liquids[9a] were prepared according to literature procedures. The butadiene was distilled under argon and stored over molecular sieves (3 Å). All other reagents were obtained from commercial sources and were used as received without further purification.

The catalytic reaction was performed with 10 mL (125 mmol) of liquid butadiene, 0.1 mmol of the catalyst precursor in 3 mL (15mmol) of the ionic liquid in the presence of triphenylphosphine for 3h at 70°C.

### *Catalytic Experiments*

In a typical experiment, palladium catalyst precursor (0.1 mmol) and triphenylphosphine (105 mg, 0.4 mmol) were dissolved in the ionic liquid (3 mL) affording and light yellow solution. This solution and butadiene (10 mL, 125 mmol) were introduced, under argon atmosphere, into a 100 mL stainless steel autoclave with a magnetic stirring bar. The autoclave was heated at 70°C for 3h. The autoclave was then cooled and degassed. The crude reaction mixture contained two-phases, was decanted and the upper phase was analyzed. Butadiene conversion and product selectivity were determined by capillary gas chromatography using benzene as internal standard. The remaining light yellow catalytic mixture can be reused several times. The product has been identified as 1,3,6-octatriene by CG-MS.[20]

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