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Catalytic cycloisomerisation of 1,6-dienes in ionic liquids

Xiaowei Miao [a], Joanna Feder-Kubis [b], Cédric Fischmeister [a,*], Juliusz Pernak [b], Pierre H. Dixneuf [a,*]

[a] *UMR 6226-CNRS-Université de Rennes 1, Institut Sciences Chimiques de Rennes, Catalyse et Organométalliques, Campus de Beaulieu, Av. du général Leclerc, 35042 Rennes Cedex, France*
[b] *Poznań University of Technology, Poznań, Poland*

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Abstract

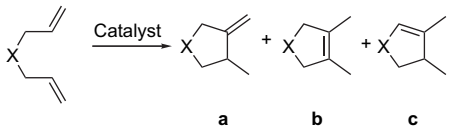
The ruthenium and palladium catalysed cycloisomerisation of 1,6-dienes in [bdmim][PF_6], a room temperature ionic liquid (RTIL), is presented. The catalytic system comprising of [$RuCl_2(COD)]_n$ in the presence of ^{i}PrOH was found to be particularly *efficient* and *selective* for the cycloisomerisation of the *N*,*N*-diallyltosylamide. This system can be reused several times without loss of performances and displays catalytic activity after a long storage period in the IL.

Keywords: Cycloisomerisation; 1,6-Dienes; Ionic liquids; Ruthenium; Palladium; Recycling

1. Introduction

Transition metal catalysed cycloisomerisation of 1,6-dienes constitutes a powerful and atom economic route for the synthesis of carbo- and heterocyclic compounds (Scheme 1).[1]

Several organometallic complexes based on Ti,[2] Rh,[3] Ru,[4] Ni[5] and Pd[6] have already been described as efficient catalysts for this transformation. Until recently, high catalyst activity and regioselectivity for the five-membered products (**a**, **b** and **c**, Scheme 1) were the major concerns but asymmetric versions of this transformation are now reported with enantiomeric excess up to 80%.[5,7]



Scheme 1. Catalytic cycloisomerisation of 1,6-dienes.

Room temperature ionic liquids (RTILs)[8] are now commonly used as medium to perform homogeneous organometallic catalysis[9,10] especially because when the catalysts show a strong affinity for the ionic liquid it is possible to extract very easily the reaction products and to reuse the catalysts. This strategy was reported for the cycloisomerisation of 2,2-diallylmalonates using palladium catalysts in [bmim][PF_6] (1-butyl-2-methyl imidazolium hexafluorophosphate) allowing catalyst recycling over several runs but with significant variations in the product distribution.[11]

Herein we report the cycloisomerisation of two 1,6-dienes in [bdmim][PF_6] (1-butyl-2,3-dimethyl imidazolium hexafluorophosphate) using ruthenium and palladium precatalysts. We show that the ruthenium catalyst can be reused several times with very high efficiency and selectivity for the cycloisomerisation of *N*,*N*-diallyltosylamide in this ionic liquid, whereas chiral ionic liquids (CILs), if they allow efficient cycloisomerisation, do not induce enantioselectivity.

2. Results and discussion

Several rhodium, ruthenium and palladium complexes have been tested in the ionic liquid [bdmim][PF_6] (1-butyl-2,3-dimethyl imidazolium hexafluorophosphate) aiming at the selective

* Corresponding authors. Tel.: +33 (0)2 23235998; fax: +33 (0)2 23236939.
E-mail addresses: cedric.fischmeister@univ-rennes1.fr (C. Fischmeister), pierre.dixneuf@univ-rennes1.fr (P.H. Dixneuf).

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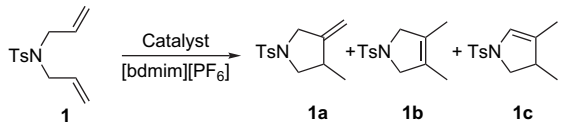
preparation of the *exo*-methylenecyclopentane **1a** (Scheme 2, Table 1).



Scheme 2. Catalytic cycloisomerisation of *N*,*N*-diallyltosylamide in [bdmim][PF_6].

Among the complexes tested, $RhCl_3\cdot 3H_2O$, $RuCl_3\cdot H_2O$ and RuCl(Cp*)(COD) showed very poor activity. On the other hand, the Wilkinson catalyst $RhCl(PPh_3)_3$ afforded very good conversion but the selectivity was in favour of the endocyclic product **1c** and the isomerised starting material $CH_3CH{=}CH{-}N(Ts){-}CH_2CH{=}CH_2$ **1d** was also detected (entry 2). The ruthenium polymer $[Ru(O_2CH)(CO)_2]_n$ with ^{i}PrOH also afforded high conversion with a selectivity in favour of the product **1b** (entry 6). $[RuCl_2(COD)]_n$ in pure ^{i}PrOH was reported by Itoh to be an efficient catalyst for the cycloisomerisation of 1,6-dienes to five-membered cycles with a good selectivity for the *exo*-methylenecyclopentane derivatives.[4d] We have evaluated this catalytic system by adding ^{i}PrOH (120 equiv/Ru, optimised conditions) to the ruthenium complex dissolved in the ionic liquid resulting in the selective formation of **1a** that was obtained in 95% isolated yield (entry 5).[12] No conversion was observed in a blank test without ^{i}PrOH under the same experimental conditions. It must be noted that under conventional conditions ($[RuCl_2(COD)]_n$ in pure ^{i}PrOH) the product **1a** is obtained in 65% yield and 86% purity[4a] demonstrating the benefit of using an ionic liquid as the reaction media.

The ionic palladium complex $[Pd(MeCN)_4](BF_4)_2$[7b] was found to be more efficient than the ruthenium based system since it afforded very good activity and selectivity for **1a** under milder conditions (40 °C) using a lower catalyst loading (entry 7).

This initial catalyst screening led us to focus our efforts on the recyclability of $[RuCl_2(COD)]_n$/^{i}PrOH and $[Pd(MeCN)_4](BF_4)_2$ in [bdmim][PF_6]. With the $[RuCl_2(COD)]_n$/^{i}PrOH system, ^{i}PrOH acts as a hydride source allowing the formation of a Ru–H species.[4d] We reasoned that addition of ^{i}PrOH should be necessary only at the beginning of the recycling test (i.e., first run). Thus, when the first run was completed, the organic products were extracted with toluene and the medium was reloaded with fresh substrate only. The second run showed an important loss of conversion but the regioselectivity remained very high for **1a** (Table 2). The next two runs did not show a drop in conversion as we could expect and the activity seemed to be somehow constant. At this point it became obvious that ^{i}PrOH is necessary to ensure high conversions. Indeed addition of ^{i}PrOH in a fifth run allowed restoring a high conversion of 99% with a selectivity remaining fairly high for the desired product **1a** (run 5, Table 2).

Table 1
Catalyst screening for the cycloisomerisation of **1** in [bdmim][PF_6][a]

Entry	Catalyst (mol %)	Conv.[b]	Yield (%)	Selectivity[b]		
				1a	**1b**	**1c**
1	$RhCl_3\cdot 3H_2O$ (5)	5	—	5		
2	$RhCl(PPh_3)_3$ (5)	>99	—			87
3	$RuCl_3\cdot H_2O$ (5)	0	—			
4	RuClCp*(COD) (5)	20	—	20		
5	$[RuCl_2(COD)]_n$ (5)+^{i}PrOH[c]	>99	96	>98		
6	$[Ru(O_2CH)(CO)_2]_n$ (2.5)+^{i}PrOH[c]	>99	93[d]		86	14
7	$[Pd(MeCN)_4](BF_4)_2$[e] (2.5)	>99	90	>98		

[a] All reactions were carried out at 90 °C for 16 h.
[b] Conversions and selectivity (%) determined by GC.
[c] 120 equiv/Ru.
[d] Isolated yield of (**1b**+**1c**), 14 h.
[e] 40 °C.

Table 2
Ruthenium catalyst recycling in [bdmim][PF_6][a]

Run	^{i}PrOH[b]	Conv.[c]	**1a**[c]	**1c**[c]
1	120	>99	>95	2
2	0	24	21	2
3	0	33	30	
4	0	36	32	
5	120	>99	85	9

[a] $[RuCl_2(COD)]_n$ 5 mol %, 90 °C for 16 h.
[b] equiv/Ru.
[c] Conversions and selectivity (%) determined by GC.

The above results suggested that only a portion of the initially introduced $[RuCl_2(COD)]_n$ complex was activated by ^{i}PrOH during the first run. Thus, the recycling test was repeated by adding ^{i}PrOH along with fresh substrate after completion and workup of each run. As foreseen, this resulted in a second run with a high conversion and selectivity for **1a**. This procedure was repeated and finally allowed to perform seven consecutive runs with very good yields and full selectivity for **1a** (Table 3).

Table 3
Catalyst recycling in the cycloisomerisation of **1** with $[RuCl_2(COD)]_n$/^{i}PrOH in [bdmim][PF_6][a]

Run	Conv.[b] (selectivity)	Isolated yield of **1a** (%)
1	>99 (100)	97
2	>99 (100)	94
3	>99 (100)	93
4	>99 (100)	96
5	>99 (100)	98
6	>99 (100)	93
7	98 (100)	96
8	92	90
9[c]	60	56

[a] $[RuCl_2(COD)]_n$ 5 mol %, ^{i}PrOH 120 equiv/Ru, 90 °C for 16 h.
[b] Conversions and selectivity (%) determined by GC.
[c] After 45 days.

After the eighth run was completed and the workup procedure was performed as described earlier, the resulting ionic liquid was stored for 45 days under an inert atmosphere. It is noteworthy that this solution showed catalytic activity upon addition of fresh substrate and ^{i}PrOH. These results demonstrate that although the catalytic activity over the consecutive runs is partially due to catalyst recycling, the ionic liquid phase acts essentially as a reservoir of ruthenium catalyst precursor.

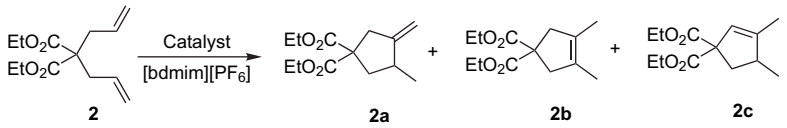
The recyclability of $[Pd(MeCN)_4](BF_4)_2$ was also evaluated for the cycloisomerisation of **1** using the above mentioned procedure except that no ^{i}PrOH is required with this complex. In this case two consecutive runs were possible with good conversions and selectivity. The third and fourth runs showed a drop in conversion and selectivity for the *exo*-methylenecyclopentane **1a** was strongly affected (Table 4).

Table 4
Cycloisomerisation of **1** with $[Pd(MeCN)_4](BF_4)_2$: catalyst recycling[a]

Run	Conv.[b]	Selectivity for **1a**[b]	Isolated yield of **1a** (%)
1	>99	97	90
2	>99	93	90
3	95	72	68
4	95	71	60

[a] $[Pd(MeCN)_4](BF_4)_2$, 2.5 mol %, 40 °C for 16 h.
[b] Conversions and selectivity (%) determined by GC.

The transformation of compound **2** was attempted using $[RuCl_2(COD)]_n$/^{i}PrOH and $[Pd(MeCN)_4](BF_4)_2$ catalysts in [bdmim][PF_6] (Scheme 3).



Scheme 3. Catalytic cycloisomerisation of diethyl diallylmalonate in [bdmim][PF_6].

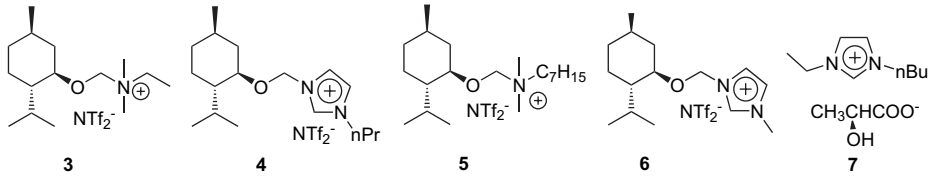


Figure 1. Chiral ionic liquids tested for the cycloisomerisation of **1**.

$[RuCl_2(COD)]_n$/^{i}PrOH afforded 99% conversion with a 52:47 ratio of **2a** and isomerised starting material $CH_3CH{=}CH{-}C(CO_2Et)_2{-}CH_2CH{=}CH_2$ **2d**. $[Pd(MeCN)_4](BF_4)_2$ led also to 99% conversion but the reaction mixture was composed of the three products **2a/2b/2c** in a ratio 24:40:26. These results constitute another example of the dependence of this transformation to the experimental conditions and to the substrate. Indeed, it is generally observed that under conventional reaction condition (pure ^{i}PrOH), compound such as **2** usually leads to high selectivity whereas lower selectivity is obtained with compound **1**.[4a]

Having reached two important objectives (efficiency and selectivity) for the cycloisomerisation of compound **1** in IL, we were interested in the enantioselective version of this reaction for which examples remain scarce.[5b,c,7] Recently, ee's up to 80% have been reported for the cycloisomerisation of **2** with cationic nickel complexes [Ni(allyl)(COD)][Y] and chiral monodentate phosphoramidite ligands.[5b,c] Due to their diversity and easy access,[13] chiral ionic liquids (CILs) are attracting interest in the domain of enantioselective transformations[14] and very promising results have been reported.[15] Having demonstrated the possibility to use $[RuCl_2(COD)]_n$/^{i}PrOH and $[Pd(MeCN)_4](BF_4)_2$ in IL, we have performed the cycloisomerisation of **1** using those catalysts in a series of (CILs) chiral ionic liquids **3**–**7** (Fig. 1).

With $[RuCl_2(COD)]_n$/^{i}PrOH at 90 °C, as it was the case with [bdmim][PF_6], the menthol based ammonium or imidazolium chiral ionic liquids **3**–**6** provided very good conversion and selectivity for **1a** (full conversion, isolated yields ≥75%), however, no enantioselectivity could be observed. CIL **7** bearing a chiral anion totally inhibited the reaction. The palladium catalyst $[Pd(MeCN)_4](BF_4)_2$ was also tested in CILs for the cycloisomerisation of **1**. The higher reactivity of this catalyst allowed running the reaction at much lower temperature than with the ruthenium based system. Using the chiral IL **3** at 20 or 0 °C, the reaction proceeded in 90 and 80% conversions, respectively,[16] but the product **1a** was again obtained as a racemic mixture. As shown in a recent example, the understanding of the interaction between the solvent and the solute or reaction intermediate, leading to the synthesis of tailor-made functional chiral ionic liquids, is a prerequisite for a high asymmetric induction by the reaction medium.[15a]

3. Conclusion

Two catalysts have been used for the cycloisomerisation of *N*,*N*-diallyltosylamide **1** in IL [bdmim][PF_6] allowing the efficient and selective formation of the *exo*-methylenecyclo pentane product **1a**. The catalytic system resulting from $[Ru(COD)Cl_2]_n$ and ^{i}PrOH in [bdmim][PF_6] was found to be more efficient and selective in the ionic liquid media than in pure ^{i}PrOH. This catalytic system can be reused for seven runs without decrease in conversion and selectivity provided ^{i}PrOH was added for each run. $[Pd(MeCN)_4](BF_4)_2$ was also found to be efficient under milder experimental conditions and afforded the *exo*-methylenecyclopentane **1a** with a high selectivity. The challenging use of CILs as stereoselectivity promoters was attempted but no enantioselectivity could be obtained.

4. Experimental

4.1. General

All the solvents were dried and distilled prior to use. $RhCl_3 \cdot xH_2O$, $RuCl_3 \cdot xH_2O$, were purchased from Jonhson Matthey and used as received. $[Pd(MeCN)_4](BF_4)_2$ was purchased from Alfa Aesar and stored under argon. $[RuCl_2(COD)]_n$,[17] $[Ru(O_2CH)(CO)_2]_n$,[18] RuClCp*(COD)[19] were obtained according to literature procedures. [bdmim][PF_6][10d] and CILs[15a] were prepared according to reported procedures. Flash chromatography purifications were performed on silica gel column (Merck Silica gel 60) using mixtures of heptane and diethylether as the eluant.

^{1}H NMR spectra were recorded on a BRUKER DPX 200 spectrometer. Gas chromatography analyses were performed on a Hewlett 5890 Packard Series II. HPLC analyses were performed on a Waters 1515 apparatus equipped with a Waters 2495 UV detector. 3-Methyl-4-methylene-1-tosylpyrrolidine **1a**: Daicel column Chiralpak AD, 0.46×25 cm, hexane/^{i}PrOH=95:5, 0.5 ml/min, λ=230 nm, 29 and 35 min.

4.2. Typical procedure for the cycloisomerisation of 1,6-heptadienes

The ionic liquid (1.5 ml) was first dried for 1 h at 90 °C under vacuum. Catalyst (5 mol % for $[RuCl_2(COD)]_n$ and 2.5 mol % for $[Pd(MeCN)_4](BF_4)_2$), degassed ^{i}PrOH (120 equiv/Ru) and diene (0.5 mmol) were then added under argon and the reaction mixture was stirred at 90 °C. The organic products were extracted with toluene (4×3 ml) and purified by flash column chromatography on silica gel (heptane/diethyl/ether, 8:2 (v/v)).

^{1}H NMR for products **1a**[4b] and **2a**[3a] were consistent with reported data.

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