



# Catalytic isomerization of allylic alcohols promoted by complexes $[\text{RuCl}_2(\eta^6\text{-arene})(\text{PTA-Me})]$ under homogeneous conditions and supported on Montmorillonite K-10

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## ARTICLE INFO

### Article history:

Received 3 August 2012

Received in revised form 22 October 2012

Accepted 22 October 2012

Available online 1 November 2012

### Keywords:

Ruthenium catalysts

Supported catalysts

Montmorillonite

Redox isomerizations

Allylic alcohols

## ABSTRACT

The mononuclear arene-ruthenium(II) derivatives  $[\text{RuCl}_2(\eta^6\text{-arene})(\text{PTA-Me})]$  (arene =  $\text{C}_6\text{H}_6$  (**3a**), *p*-cymene (**3b**), 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$  (**3c**),  $\text{C}_6\text{Me}_6$  (**3d**)), containing the ionic phosphine ligand 1-methyl-3,5-diaza-1-azonia-7-phosphaadamantane chloride (PTA-Me), have been synthesized and fully characterized. These complexes were evaluated as potential catalysts for the redox isomerization of allylic alcohols. Among them, best results in terms of activity were obtained with complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) which, in combination with  $\text{K}_2\text{CO}_3$  (2.5 equiv. per Ru), was able to selectively isomerize a number of allylic alcohols  $\text{RCH}(\text{OH})\text{CH}=\text{CH}_2$  (R = H, aryl, alkyl or heteroaryl group) into the corresponding carbonyl compounds  $\text{RC}(=\text{O})\text{CH}_2\text{CH}_3$  in refluxing THF (TOF values up to  $800\text{ h}^{-1}$ ). Complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) was adsorbed onto the Montmorillonite K-10 clay, and the resulting solid proved also active in the isomerization of the model substrate 1-octen-3-ol. In addition, it could be easily separated from the reaction media by simple filtration and reused several times (up to 11 consecutive runs) with retention of its efficiency.

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## 1. Introduction

The redox isomerization of allylic alcohols catalyzed by transition-metal complexes has emerged in recent years as a useful and straightforward synthetic route to carbonyl compounds (Scheme 1, path a), which conveniently replaces the classical two-step sequential oxidation/reduction reactions (Scheme 1, path b or c). Besides step and atom economy, one advantage of the redox isomerization is to avoid the use of toxic and/or expensive oxidation and reduction reagents. Hence, considerable efforts have been devoted to the development of efficient catalytic systems for this process, with those based on ruthenium, rhodium and iridium showing nowadays the best performances [1]. The transformation is based on the well-known ability of transition-metals to assist the migration of carbon-carbon double bonds, that is, the catalyst turns the allylic alcohol into an enol which readily tautomerizes into the corresponding carbonyl compound [2].

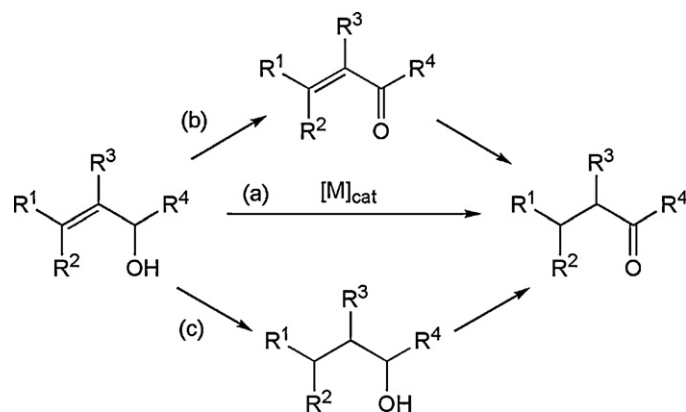
With the gradual availability of efficient and selective catalysts, this relatively simple reaction is beginning to be applied in multi-step syntheses of structurally elaborated substrates of high added value. In this context, we must highlight the preparations

of the naturally occurring pheromones muscone [3] and (+)-iso-exo-brevicomin [4], the marine alkaloid (–)-brevisamide [5], the fragrance Florhydral® [6] and the antitumor agent (–)-FR182877 [7], all of them including a redox isomerization step. The interest of the pharmaceutical industry for the large scale production of the analgesic drugs hydromorphone and hydrocodone by catalytic isomerization of the naturally occurring opiates morphine and codeine also deserves to be mentioned [8]. In addition, remarkable results have been recently obtained in the development of asymmetric versions of this reaction, excellent enantiomeric excesses being achieved in some instances [3,9].

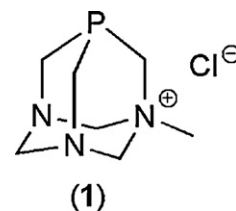
On the other hand, a very important aspect for large-scale chemical processes is the availability of efficient methods for catalyst separation and recycling [10]. In this context, most efforts devoted to achieve recyclable systems for the catalytic isomerization of allylic alcohols have focused on water-soluble complexes, the use of water as solvent allowing the easy separation of the reaction products from the catalyst by simple liquid–liquid extraction (or by decantation if a biphasic medium is employed) [1]. In this way, the active species can be re-used in further catalytic cycles. Best results in this field have been obtained with the hydrosoluble arene-ruthenium(II) derivative  $[\text{RuCl}_2(\eta^6\text{-p-cymene})\{\text{P}(\text{OCH}_2\text{CH}_2\text{NMe}_3)_3\}][\text{SbF}_6]_3$ , containing a phosphite-ammonium ligand, which could be used for at least 10 consecutive runs without significant loss of activity [11].

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**Scheme 1.** The redox isomerization of allylic alcohols.



**Fig. 1.** Structure of the ionic phosphine ligand PTA-Me (**1**) employed in this work.

Immobilization on insoluble solids supports is also a common strategy to overcome the intrinsic separation problems associated with homogeneous catalysts [10]. However, to date, this method has been scarcely applied in the redox isomerization of allylic alcohols. In this context, Majoral and co-workers have described the grafting of the organometallic fragments  $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]$  and  $[\text{RhCl}(\text{cod})]$  (cod = 1,5-cyclooctadiene) on the surface of phosphine-ended dendrimers [12]. The resulting systems were able to isomerize selectively 1-octen-3-ol into octan-3-one and could be recycled (up to four times), but their activities were relatively low (TOF up to  $12\text{ h}^{-1}$ ).  $\text{PdCl}_2$  impregnated on different polymers was also employed to promote redox isomerization processes [13]. However, the requirement of a hydrogen atmosphere resulted in low selectivities toward the desired carbonyl compounds, due to the occurrence of hydrogenation and hydrogenolysis reactions in competition [14]. A much more general, selective, and efficient system (TOF up to  $6400\text{ h}^{-1}$ ), consisting of a rhodium complex immobilized onto a ligand–polymer support, has been recently reported by Bergens and co-workers [15]. Unfortunately, despite the remarkable efficiency showed by this polymeric material, its recycling was not demonstrated.

In our group, we supported an arene-ruthenium(II) complex on the surface of functionalized silica-coated ferrite nanoparticles [16]. The resulting heterogeneous catalyst was able to convert selectively and efficiently several allylic alcohols into the corresponding aldehydes or ketones (TOF up to  $253\text{ h}^{-1}$ ). In addition, this magnetic material was easily separated with the aid of external magnet and could be reused in three further catalytic runs. However, the preparation of the support was rather tedious and simpler alternatives are desirable. This fact, along with a recent study by Martín-Matute and co-workers demonstrating the utility of cationic Rh(I) complexes supported onto the mesoporous aluminosilicate AISBA-15 for this catalytic transformation (TOF up to  $48\text{ h}^{-1}$ ; up to five consecutive runs after simple separation of the catalyst by filtration) [17], prompted us to explore more readily available inorganic solids as supports [18]. In particular, we directed our attention to the smectite-type laminar clay Montmorillonite, whose combination of cation exchange, intercalation and swelling properties has been largely exploited for the immobilization of metal catalysts in the last decades [19]. Ionic complexes are known to be readily adsorbed on the surface of this clay through electrostatic interactions or, alternatively, they can be intercalated into its interlaminal spacing, leading in both cases to robust heterogenized systems.

Thus, herein we describe the preparation of mononuclear arene-ruthenium(II) complexes  $[\text{RuCl}_2(\eta^6\text{-arene})(\text{PTA-Me})]$  containing the ionic phosphine ligand 1-methyl-3,5-diaza-7-phosphaadamantane chloride **1** (abbreviated as PTA-Me; see Fig. 1)

[20], the catalytic activity of these complexes in the redox isomerization of allylic alcohols under homogeneous conditions, and the heterogenization of the most active one, namely  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$ , onto the commercially available and inexpensive Montmorillonite K-10 clay. As the reader will see, the resulting solid proved also active in the isomerization process and showed an excellent recyclability.

## 2. Experimental

### 2.1. General information

All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Organic solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of compounds PTA-Me (**1**) [21],  $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$  (**2a–d**) [22], 1-(2-naphthyl)-2-propen-1-ol (**4h**) [23], 1-(3-methoxyphenyl)-2-propen-1-ol (**4i**) [24], 1-(4-methoxyphenyl)-2-propen-1-ol (**4j**) [25], 1-(4-chlorophenyl)-2-propen-1-ol (**4k**) [26], 1-(4-fluorophenyl)-2-propen-1-ol (**4l**) [27], 1-(2-furyl)-2-propen-1-ol (**4m**) [26], (5*R*)-5,9-dimethyl-1,8-decadien-3-ol (**4n**) [18b] and (*E/Z*)-5,9-dimethyl-1,4,8-decatrien-3-ol (**4o**) [28], which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. NMR spectra were recorded on Bruker DPX300 or AV400 instruments. Chemical shifts are given in ppm, relative to internal tetramethylsilane ( $^1\text{H}$  and  $^{13}\text{C}$ ), and external 85% aqueous  $\text{H}_3\text{PO}_4$  solutions ( $^{31}\text{P}$ ). DEPT experiments have been carried out for all the compounds reported in this paper. The elemental C, H, and N analyses and FAB mass spectra were provided by Analytical Services of the University of Sevilla. ICP-MS analyses and powder X-ray diffraction (XRD) patterns were provided by the Scientific-Technical Services of the University of Oviedo. GC measurements were made on a Hewlett-Packard HP6890 equipment using a Supelco Beta-Dex<sup>TM</sup> 120 (30 m length; 250  $\mu\text{m}$  diameter) or HP-INNOWAX (30 m length; 250  $\mu\text{m}$  diameter) column. GC/MSD measurements were performed on Agilent 6890 N equipment coupled to a 5973 mass detector (70 eV electron impact ionization) using a HP-1MS column.

### 2.2. Synthesis of complexes $[\text{RuCl}_2(\eta^6\text{-arene})(\text{PTA-Me})]$ (arene = $\text{C}_6\text{H}_6$ (**3a**), *p*-cymene (**3b**), 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ (**3c**), $\text{C}_6\text{Me}_6$ (**3d**))

A suspension of the corresponding dimeric precursor  $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$  (**2a–d**) (0.5 mmol) in tetrahydrofuran (30 mL) was treated with the phosphine ligand PTA-Me (0.250 g, 1.2 mmol) at room temperature for 24 h. Concentration of the resulting solution to ca. 10 mL followed by the addition of 50 mL of diethyl ether precipitated an orange solid, which was washed with diethyl ether (3  $\times$  10 mL) and dried *in vacuo*. (**3a**): Yield: 78% (0.357 g); Anal. Calcd for  $\text{RuCl}_2\text{C}_{13}\text{H}_{21}\text{Cl}_3\text{N}_3\text{P}$  (457.73  $\text{g mol}^{-1}$ ): C, 34.11; H, 4.62; N, 9.18%. Found: C, 33.98; H, 4.73; N, 9.03%; IR (KBr)  $\nu = 422$  (m), 579 (w), 569

(s), 743 (s), 812 (s), 834 (s), 897 (s), 929 (s), 982 (s), 1023 (s), 1087 (s), 1124 (s), 1251 (m), 1277 (m), 1301 (s), 1430 (s), 1451 (s), 1509 (w), 2984 (m), 3032 (m)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = -21.3$  (s) ppm;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = 2.87$  (d, 3H,  $^4J_{\text{PH}} = 2.1$  Hz, NMe), 4.26–5.15 (m, 12H,  $\text{PCH}_2\text{N}$  and  $\text{NCH}_2\text{N}$ ), 5.92 (d, 6H,  $^3J_{\text{PH}} = 1.0$  Hz,  $\text{C}_6\text{Me}_6$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = 48.2$  (s, NMe), 48.4 (d,  $^1J_{\text{PC}} = 19.6$  Hz,  $\text{PCH}_2\text{N}$ ), 55.9 (d,  $^1J_{\text{PC}} = 15.8$  Hz,  $\text{PCH}_2\text{N}^+$ ), 69.1 (d,  $^3J_{\text{PC}} = 6.0$  Hz,  $\text{NCH}_2\text{N}$ ), 80.7 (d,  $^3J_{\text{PC}} = 3.0$  Hz,  $\text{NCH}_2\text{N}^+$ ), 88.1 (d,  $^2J_{\text{PC}} = 3.0$  Hz,  $\text{C}_6\text{H}_6$ ) ppm; MS (FAB)  $m/z = 422.0$  (100%) [ $\text{M}^+$ ]. (**3b**): Yield: 93% (0.478 g); Anal. Calcd for  $\text{RuCl}_2\text{H}_{29}\text{Cl}_3\text{N}_3\text{P}$  (513.83  $\text{g mol}^{-1}$ ): C, 39.74; H, 5.69; N, 8.18%. Found: C, 39.66; H, 5.81; N, 8.05%; IR (KBr)  $\nu = 481$  (m), 553 (m), 575 (s), 633 (m), 675 (m), 752 (s), 772 (s), 816 (s), 849 (m), 874 (m), 898 (s), 928 (s), 989 (s), 1147 (w), 1255 (m), 1306 (s), 1366 (w), 1394 (m), 1420 (m), 1457 (m), 3515 (m)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = -22.5$  (s) ppm;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = 1.24$  (d, 6H,  $^3J_{\text{HH}} = 7.1$  Hz,  $\text{CHMe}_2$ ), 2.07 (s, 3H, Me), 2.72 (sept, 1H,  $^3J_{\text{HH}} = 7.1$  Hz,  $\text{CHMe}_2$ ), 2.86 (s, 3H, NMe), 4.20–5.14 (m, 12H,  $\text{PCH}_2\text{N}$  and  $\text{NCH}_2\text{N}$ ), 5.88 (br, 4H, CH of cym) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = 15.9$  (s, Me), 19.7 (s,  $\text{CHMe}_2$ ), 29.5 (s,  $\text{CHMe}_2$ ), 46.5 (s, NMe), 46.7 (d,  $^1J_{\text{PC}} = 18.9$  Hz,  $\text{PCH}_2\text{N}$ ), 54.0 (d,  $^1J_{\text{PC}} = 15.9$  Hz,  $\text{PCH}_2\text{N}^+$ ), 67.8 (d,  $^3J_{\text{PC}} = 5.5$  Hz,  $\text{NCH}_2\text{N}$ ), 79.0 (d,  $^3J_{\text{PC}} = 3.3$  Hz,  $\text{NCH}_2\text{N}^+$ ), 84.7 and 87.8 (d,  $^2J_{\text{PC}} = 4.9$  Hz, CH of cym), 96.7 and 106.3 (s, C of cym) ppm. (**3c**): Yield: 81% (0.405 g); Anal. Calcd for  $\text{RuCl}_2\text{H}_{27}\text{Cl}_3\text{N}_3\text{P}$  (499.81  $\text{g mol}^{-1}$ ): C, 38.45; H, 5.44; N, 8.41%. Found: C, 38.35; H, 5.57; N, 8.31%; IR (KBr)  $\nu = 474$  (m), 570 (s), 638 (m), 741 (s), 769 (m), 813 (s), 891 (m), 939 (s), 1007 (s), 1314 (s), 1377 (m), 1409 (m), 1451 (s), 1535 (m), 3343 (w), 3513 (w)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = -25.4$  (s) ppm;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = 2.22$  (s, 9H, Me), 2.80 (s, 3H, NMe), 4.19–4.70 (m, 6H,  $\text{PCH}_2\text{N}$ ), 4.90–5.10 (m, 6H,  $\text{NCH}_2\text{N}$ ), 5.46 (s, 3H, CH of mes) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = 17.9$  (s, Me), 47.8 (d,  $^1J_{\text{PC}} = 18.9$  Hz,  $\text{PCH}_2\text{N}$ ), 48.3 (s, NMe), 55.8 (d,  $^1J_{\text{PC}} = 15.8$  Hz,  $\text{PCH}_2\text{N}^+$ ), 69.2 (d,  $^3J_{\text{PC}} = 5.3$  Hz,  $\text{NCH}_2\text{N}$ ), 80.7 (d,  $^3J_{\text{PC}} = 3.8$  Hz,  $\text{NCH}_2\text{N}^+$ ), 85.8 (d,  $^2J_{\text{PC}} = 3.8$  Hz, CH of mes), 103.3 (d,  $^2J_{\text{PC}} = 2.3$  Hz, C of mes) ppm; MS (FAB)  $m/z = 464.0$  (100%) [ $\text{M}^+$ ]. (**3d**): Yield: 77% (0.417 g); Anal. Calcd for  $\text{RuCl}_2\text{H}_{33}\text{Cl}_3\text{N}_3\text{P}$  (541.89  $\text{g mol}^{-1}$ ): C, 42.11; H, 6.14; N, 7.75%. Found: C, 42.24; H, 6.18; N, 7.69%; IR (KBr)  $\nu = 574$  (m), 754 (m), 813 (m), 897 (m), 930 (m), 982 (m), 1018 (m), 1092 (s), 1130 (m), 1245 (w), 1303 (m), 1389 (m), 1457 (m), 3396 (m), 3513 (w)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = -25.4$  (s) ppm;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = 2.01$  (d, 18H,  $^4J_{\text{PH}} = 1.1$  Hz,  $\text{C}_6\text{Me}_6$ ), 2.68 (d, 3H,  $^4J_{\text{PH}} = 1.9$  Hz, NMe), 4.01–4.85 (m, 12H,  $\text{PCH}_2\text{N}$  and  $\text{NCH}_2\text{N}$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta = 15.0$  (s,  $\text{C}_6\text{Me}_6$ ), 47.0 (d,  $^1J_{\text{PC}} = 12.1$  Hz,  $\text{PCH}_2\text{N}$ ), 47.6 (s, NMe), 55.4 (d,  $^1J_{\text{PC}} = 16.6$  Hz,  $\text{PCH}_2\text{N}^+$ ), 69.1 (d,  $^3J_{\text{PC}} = 6.0$  Hz,  $\text{NCH}_2\text{N}$ ), 80.6 (d,  $^3J_{\text{PC}} = 3.0$  Hz,  $\text{NCH}_2\text{N}^+$ ), 97.6 (d,  $^2J_{\text{PC}} = 1.5$  Hz,  $\text{C}_6\text{Me}_6$ ) ppm; MS (FAB)  $m/z = 506.1$  (100%) [ $\text{M}^+$ ].

### 2.3. General procedure for the catalytic isomerization of allylic alcohols using complex $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$ (**3a**)

In a sealed tube, under nitrogen atmosphere, the ruthenium complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) (0.02–0.1 mmol; 0.5–2.5 mol% of Ru) and  $\text{K}_2\text{CO}_3$  (0.05–0.25 mmol; 1.25–6.25 mol%) were added to a solution of the corresponding allylic alcohol **4a–o** (4 mmol) in tetrahydrofuran (4 mL), and the resulting mixture stirred at 75 °C for the indicated time (see Table 4 and Scheme 3). The course of the reaction was monitored by taking regularly samples of ca. 10  $\mu\text{L}$  which after dilution with dichloromethane (3 mL) were analyzed by GC. After the reaction was finished, the mixture was cooled to room temperature leading to the partial precipitation of **3a**. The solid was separated by filtration and the reaction product isolated by solvent removal and chromatographic work-up of the residue on silica-gel using a mixture of EtOAc–hexane (1:10) as eluent. The identity of the resulting carbonyl compounds **5a–o** was assessed by comparison of their retention times with those of commercially available pure samples (Sigma–Aldrich or

Acros Organics), by their fragmentation in GC/MS, and/or NMR spectroscopy.

### 2.4. General procedure for the support of complex $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$ (**3a**) in Montmorillonite K-10

Prior to its use, Montmorillonite K-10 (Sigma–Aldrich) was dried for 24 h at 110 °C. Under an inert atmosphere, the appropriate amount of complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) (0.1, 0.2, 0.3, 0.4 or 0.5 mmol) was dissolved in 15 mL of dichloromethane. To the resulting solution, 1 g of the clay was then added and the mixture stirred at room temperature for 4–24 h. After this time, the suspension was filtered off and the solid washed with dichloromethane (3  $\times$  15 mL) and vacuum-dried. The weight percentage of Ru in the resulting heterogeneous catalysts **MK10-3a-x** was determined by ICP-MS. Solids **MK10-3a-x** were further characterized by XRD and IR spectroscopy (see Section 3).

### 2.5. General procedure for catalytic isomerization of 1-octen-3-ol (**4a**) into octan-3-one (**5a**) using the heterogeneous catalysts **MK10-3a-x**

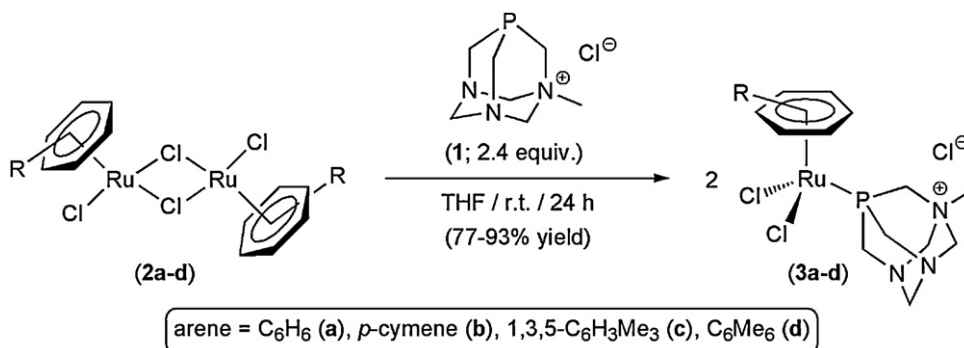
In a sealed tube, under nitrogen atmosphere, the appropriate amount of the corresponding heterogeneous catalyst **MK10-3a-x** (0.5 mol% of Ru) and  $\text{K}_2\text{CO}_3$  (6.9 mg, 5 mmol; 1.25 mol%) were added to a solution of 1-octen-3-ol (**4a**) (0.618 mL, 4 mmol) in tetrahydrofuran (4 mL), and the resulting mixture stirred at 75 °C for the indicated time (see Table 7). The course of the reaction was monitored by taking regularly samples of ca. 10  $\mu\text{L}$  which after dilution with dichloromethane (3 mL) were analyzed by GC. The heterogeneous catalyst **MK10-3a-x** was then separated by filtration and the reaction product isolated by solvent removal and chromatographic work-up of the residue on silica-gel using a mixture of EtOAc–hexane (1:10) as eluent. The identity of the resulting octan-3-one (**5a**) was assessed by GC, by comparison of its retention time with that of a commercially available pure sample.

### 2.6. Recycling of the heterogeneous catalyst **MK10-3a-2.5**

In a sealed tube, under nitrogen atmosphere, the heterogeneous catalyst **MK10-3a-2.5** (0.2 g; 1.25 mol% of Ru) and  $\text{K}_2\text{CO}_3$  (17.3 mg, 1.25 mmol; 2.5 equiv. per Ru) were added to a solution of 1-octen-3-ol (**4a**) (0.618 mL, 4 mmol) in tetrahydrofuran (4 mL), and the resulting mixture stirred at 75 °C until complete transformation of **4a** into **5a** (confirmed by GC analysis of aliquots). The reaction mixture was then cooled to room temperature, the solid filtered off, washed with hexanes (3  $\times$  5 mL) and vacuum-dried. To the solid, THF (4 mL) and a new load of 1-octen-3-ol (**4a**) (0.618 mL, 4 mmol) were then added, and the mixture heated again at 75 °C for the indicated time (see Fig. 4).

## 3. Results and discussion

Our study began with the synthesis of the mononuclear ruthenium(II) derivatives  $[\text{RuCl}_2(\eta^6\text{-arene})(\text{PTA-Me})]$  (arene =  $\text{C}_6\text{H}_6$  (**3a**), *p*-cymene (**3b**) [29], 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$  (**3c**),  $\text{C}_6\text{Me}_6$  (**3d**)). They were generated in high yields (77–93%) through a classical chloride bridges splitting reaction in the corresponding dimeric precursors  $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-arene})\}_2]$  (**2a–d**) [22] upon treatment with 2.4 equivalents of the ligand PTA-Me (**1**) in tetrahydrofuran, at room temperature, for 24 h (Scheme 2). Compounds **3a–d**, isolated as air-stable orange solids, were fully characterized by means of elemental analyses, IR, multinuclear NMR spectroscopy and mass spectrometry (FAB technique), the data obtained being fully consistent with the proposed structures (details are given in Section 2). In particular, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of these derivatives exhibit



**Scheme 2.** Synthesis of the mononuclear Ru(II) complexes [RuCl<sub>2</sub>(η<sup>6</sup>-arene)(PTA-Me)] (**3a–d**).

a singlet resonance at  $\delta_p$  –21.5 to –25.4 ppm, strongly deshielded with respect to that of the free phosphine PTA-Me ( $\delta_p$  = –84.6 ppm), thus supporting the selective *P*-coordination of **1** to ruthenium [30]. Their <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra also show the expected signals for the η<sup>6</sup>-coordinated arene groups and the PTA-Me ligand. For the latter, characteristic N-Me singlet resonances were observed at  $\delta_H$  2.68–2.87 (a doublet with <sup>3</sup>J<sub>PH</sub> = 1.9–2.1 Hz for **3a** and **3d**) and  $\delta_C$  46.5–48.3 ppm.

The ability of complexes [RuCl<sub>2</sub>(η<sup>6</sup>-arene)(PTA-Me)] (**3a–d**) to promote the redox isomerization of allylic alcohols in homogeneous phase was evaluated employing 1-octen-3-ol (**4a**) as model substrate. Since this catalytic reaction usually requires of a base [1], our initial efforts focused on finding the most appropriate one for carrying out the process. To this end, we studied the isomerization of **4a** with complex [RuCl<sub>2</sub>(η<sup>6</sup>-*p*-cymene)(PTA-Me)] (**3b**) in the presence of different alkali metal carbonates, hydroxides and *tert*-butoxides. Experiments were carried out at 75 °C employing 4 mmol of 1-octen-3-ol, 2 mol% of complex **3b**, tetrahydrofuran as the solvent (1 M solutions of the allylic alcohol) and 5 mol% of the corresponding base (2.5 equiv. per Ru). The results obtained from this initial screening are collected in Table 1.

As expected, performing the catalytic reaction in the absence of base did not yield appreciable amounts of the desired octan-3-one (**5a**) after 2 h of heating (entry 1), thus confirming the need of a basic media. Deprotonation of the hydroxyl group of the allylic alcohol, thereby enhancing its coordinating ability, is a requisite commonly proposed in the literature for this reaction [1,2]. As shown in Table 1, the introduction of a base in the medium allows the isomerization process to proceed, with those containing the bulkier and less polarizing cations K<sup>+</sup> and Cs<sup>+</sup> being the most effective. In particular, the best results were obtained with K<sub>2</sub>CO<sub>3</sub> (entry 4) and CsOH·H<sub>2</sub>O (entry 9), which allowed the selective and quantitative conversion of 1-octen-3-ol (**4a**) into octan-3-one (**5a**) after only 45 min of heating (TOF = 67 h<sup>–1</sup>). Based on these results, inexpensive K<sub>2</sub>CO<sub>3</sub> was chosen as the base for the rest of our studies. Concerning the [Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio, we have found that the isomerization reaction of **4a** also proceeds when equimolar amounts of complex **3b** and K<sub>2</sub>CO<sub>3</sub> are employed, but a longer time (3 h) is in this case needed to completion (entry 12). As shown in entry 13, increasing the amount of K<sub>2</sub>CO<sub>3</sub> to 4 equiv. per Ru resulted counterproductive, due probably to the partial decomposition of the active species under these strongly basic conditions. Consequently, a [Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio of 1:2.5 was adopted for the rest of our studies.

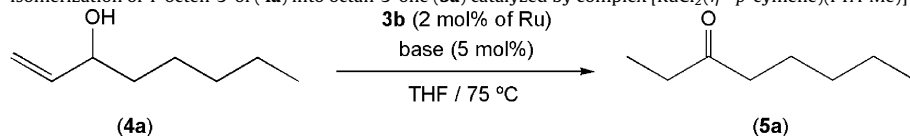
Using this optimal [Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio, the catalytic activity of the four complexes synthesized, i.e. [RuCl<sub>2</sub>(η<sup>6</sup>-arene)(PTA-Me)] (arene = C<sub>6</sub>H<sub>6</sub> (**3a**), *p*-cymene (**3b**), 1,3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub> (**3c**), C<sub>6</sub>Me<sub>6</sub> (**3d**)), in the isomerization of the model alcohol 1-octen-3-ol (**4a**) was compared. As shown in Table 2, all of them were found to be active and selective catalysts in the isomerization process, providing octan-3-one (**5a**) as the unique reaction product. However,

appreciable differences in activity were observed in function of the arene ligand present in the complex. The rate order observed (C<sub>6</sub>H<sub>6</sub> > *p*-cymene > 1,3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub> > C<sub>6</sub>Me<sub>6</sub>) indicates clearly that higher performances are found for the less sterically demanding and electron-rich arenes [31]. Thus, the highest rate was achieved with the benzene derivative [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**), which led to the quantitative formation of **5a** after only 30 min of heating (TOF = 100 h<sup>–1</sup>; entry 1). At this point, we must note that, when the same reaction was performed in the presence of free benzene (50 equiv. per mol of Ru), the performance of [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**) remained almost unaltered (entry 5 vs 1). This fact confirms that release of the arene ligand does not take place during the catalytic event, and that the required vacant sites for coordination of substrate are generated by the expected dissociation of the chloride ligands from the metal. On the other hand, it is also worthy of note that [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**) retains its high catalytic activity at low metal loadings. Thus, using only 0.5 mol% of this complex, quantitative formation of octan-3-one was observed by GC after 35 min, allowing to improve the TOF of the process up to 343 h<sup>–1</sup> (entry 6).

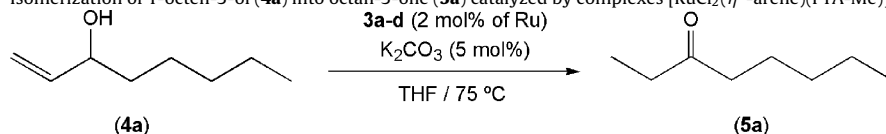
The isomerization of **4a** into **5a** by means of complex [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**) was also studied in other organic solvents (1,4-dioxane, toluene, 1,2-dichloroethane, methanol and ethanol), as well as in water. The results obtained are collected in Table 3. Thus, although quantitative conversions were in all cases reached using a metal loading of 0.5 mol%, none of these solvents allowed to improve the result previously obtained in THF (entry 3). Apparently, the performance of [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**) is optimal in aprotic media of intermediate polarity (entries 3–4). Some experiments were also performed in THF at different concentrations of the substrate (from 0.1 M to 2 M), but no marked differences in activity and selectivity were observed. In contrast, remarkably poorer results were obtained lowering the reaction temperature (e.g. at 55 °C only 60% of conversion of 1-octen-3-ol was observed after 4 h of heating).

Noteworthy, the reaction profile of this isomerization process is characterized by an induction period of several minutes (see Fig. 2), indicating the slow formation of the real active species in the catalytic cycle. Moreover, deactivation of the active species does not occur after total consumption of the substrate 1-octen-3-ol (**4a**). Thus, after a regular catalytic test, a faster reaction was observed upon addition of a second charge of **4a** (quantitative formation of **5a** after only 20 min), with the sigmoidal shape of the graph suggesting that generation of the active species still continues during the reaction. As the formation of metal(0) nanoparticles is known to be particularly favored in basic alcoholic media [32], these observations raised the question on the real homogeneous or heterogeneous nature of the catalytic reaction. To shed light on this point, the isomerization of **4a** was performed in the presence of mercury [33] and no major difference in activity was

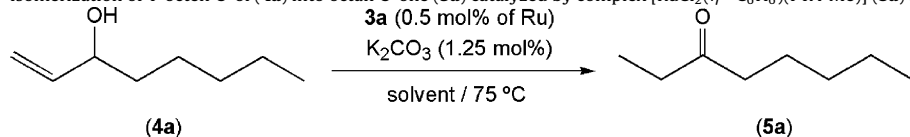


**Table 1**Isomerization of 1-octen-3-ol (**4a**) into octan-3-one (**5a**) catalyzed by complex  $[\text{RuCl}_2(\eta^6\text{-p-cymene})(\text{PTA-Me})]$  (**3b**).<sup>a</sup>

| Entry           | Base                            | Time   | Yield (%) <sup>b</sup> | TOF (h <sup>-1</sup> ) <sup>c</sup> |
|-----------------|---------------------------------|--------|------------------------|-------------------------------------|
| 1               | –                               | 2 h    | 0                      | 0                                   |
| 2               | Li <sub>2</sub> CO <sub>3</sub> | 2 h    | 5                      | 1                                   |
| 3               | Na <sub>2</sub> CO <sub>3</sub> | 2 h    | 15                     | 4                                   |
| 4               | K <sub>2</sub> CO <sub>3</sub>  | 45 min | 100                    | 67                                  |
| 5               | Cs <sub>2</sub> CO <sub>3</sub> | 1.25 h | 100                    | 40                                  |
| 6               | LiOH·H <sub>2</sub> O           | 2 h    | 4                      | 1                                   |
| 7               | NaOH                            | 2 h    | 60                     | 15                                  |
| 8               | KOH                             | 1 h    | 100                    | 50                                  |
| 9               | CsOH·H <sub>2</sub> O           | 45 min | 100                    | 67                                  |
| 10              | NaO <sup>t</sup> Bu             | 2 h    | 5                      | 1                                   |
| 11              | KO <sup>t</sup> Bu              | 2 h    | 100                    | 25                                  |
| 12 <sup>d</sup> | K <sub>2</sub> CO <sub>3</sub>  | 3 h    | 100                    | 17                                  |
| 13 <sup>e</sup> | K <sub>2</sub> CO <sub>3</sub>  | 3 h    | 40                     | 7                                   |

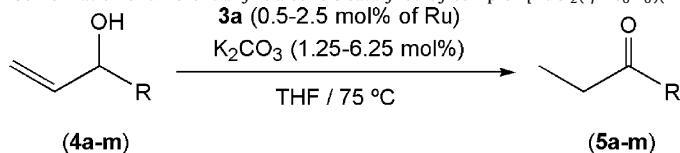
<sup>a</sup> Reactions performed under N<sub>2</sub> atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (**4a**) (1 M in THF). [1-octen-3-ol]:[Ru]:[base] ratio = 100:2:5.<sup>b</sup> Yield of octan-3-one (**5a**) determined by GC (uncorrected GC areas).<sup>c</sup> Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.<sup>d</sup> Reaction performed employing a [1-octen-3-ol]:[Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio of 100:2:2.<sup>e</sup> Reaction performed employing a [1-octen-3-ol]:[Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio of 100:2:8.**Table 2**Isomerization of 1-octen-3-ol (**4a**) into octan-3-one (**5a**) catalyzed by complexes  $[\text{RuCl}_2(\eta^6\text{-arene})(\text{PTA-Me})]$  (**3a–d**).<sup>a</sup>

| Entry          | Catalyst                                                                                     | Time   | Yield (%) <sup>b</sup> | TOF (h <sup>-1</sup> ) <sup>c</sup> |
|----------------|----------------------------------------------------------------------------------------------|--------|------------------------|-------------------------------------|
| 1              | $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$ ( <b>3a</b> )                  | 30 min | 100                    | 100                                 |
| 2              | $[\text{RuCl}_2(\eta^6\text{-p-cymene})(\text{PTA-Me})]$ ( <b>3b</b> )                       | 45 min | 100                    | 67                                  |
| 3              | $[\text{RuCl}_2(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{PTA-Me})]$ ( <b>3c</b> ) | 1 h    | 100                    | 50                                  |
| 4              | $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)(\text{PTA-Me})]$ ( <b>3d</b> )                 | 2.5 h  | 75                     | 15                                  |
| 5 <sup>d</sup> | $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$ ( <b>3a</b> )                  | 35 min | 100                    | 86                                  |
| 6 <sup>e</sup> | $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$ ( <b>3a</b> )                  | 35 min | 100                    | 343                                 |

<sup>a</sup> Reactions performed under N<sub>2</sub> atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (**4a**) (1 M in THF). [1-octen-3-ol]:[Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio = 100:2:5.<sup>b</sup> Yield of octan-3-one (**5a**) determined by GC (uncorrected GC areas).<sup>c</sup> Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.<sup>d</sup> Reaction performed in the presence of 50 equiv. per Ru of free benzene.<sup>e</sup> Reaction performed employing a [1-octen-3-ol]:[Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio of 100:0.5:1.25.**Table 3**Isomerization of 1-octen-3-ol (**4a**) into octan-3-one (**5a**) catalyzed by complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) in different solvents.<sup>a</sup>

| Entry | Solvent            | $\epsilon^b$ | Time   | Yield (%) <sup>c</sup> | TOF (h <sup>-1</sup> ) <sup>d</sup> |
|-------|--------------------|--------------|--------|------------------------|-------------------------------------|
| 1     | 1,4-Dioxane        | 2.3          | 2 h    | 100                    | 100                                 |
| 2     | Toluene            | 2.4          | 2.5 h  | 100                    | 80                                  |
| 3     | THF                | 7.6          | 35 min | 100                    | 343                                 |
| 4     | 1,2-Dichloroethane | 10.4         | 45 min | 100                    | 267                                 |
| 5     | Ethanol            | 24.6         | 1 h    | 100                    | 200                                 |
| 6     | Methanol           | 32.7         | 1 h    | 100                    | 200                                 |
| 7     | Water              | 80.1         | 24 h   | 100                    | 8                                   |

<sup>a</sup> Reactions performed under N<sub>2</sub> atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (**4a**) (1 M in the appropriate solvent). [1-octen-3-ol]:[Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio = 100:0.5:1.25.<sup>b</sup> Dielectric constant of the solvent at 25 °C.<sup>c</sup> Yield of octan-3-one (**5a**) determined by GC (uncorrected GC areas).<sup>d</sup> Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.

**Table 4**Isomerization of different allylic alcohols catalyzed by complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**).<sup>a</sup>

| Entry | Substrate                                             | mol% of <b>3a</b> | Time   | Yield (%) <sup>b</sup> | TOF (h <sup>-1</sup> ) <sup>c</sup> |
|-------|-------------------------------------------------------|-------------------|--------|------------------------|-------------------------------------|
| 1     | R = <sup>n</sup> Pent ( <b>4a</b> )                   | 0.5               | 35 min | 100 (91)               | 343                                 |
| 2     | R = <sup>n</sup> Bu ( <b>4b</b> )                     | 0.5               | 1 h    | 100 (90)               | 200                                 |
| 3     | R = <sup>n</sup> Pr ( <b>4c</b> )                     | 0.5               | 1 h    | 93 (82)                | 186                                 |
| 4     | R = Et ( <b>4d</b> )                                  | 0.5               | 45 min | 100 (89)               | 267                                 |
| 5     | R = Me ( <b>4e</b> )                                  | 0.5               | 15 min | 100 (88)               | 800                                 |
| 6     | R = H ( <b>4f</b> )                                   | 2.5               | 4.5 h  | 78 (65)                | 7                                   |
| 7     | R = Ph ( <b>4g</b> )                                  | 0.5               | 20 h   | 100 (92)               | 10                                  |
| 8     | R = 2-Naphthyl ( <b>4h</b> )                          | 0.5               | 22 h   | 98 (87)                | 9                                   |
| 9     | R = 3-C <sub>6</sub> H <sub>4</sub> OMe ( <b>4i</b> ) | 0.5               | 20 h   | 88 (75)                | 9                                   |
| 10    | R = 4-C <sub>6</sub> H <sub>4</sub> OMe ( <b>4j</b> ) | 0.5               | 20 h   | 100 (93)               | 10                                  |
| 11    | R = 4-C <sub>6</sub> H <sub>4</sub> Cl ( <b>4k</b> )  | 0.5               | 20 h   | 92 (80)                | 9                                   |
| 12    | R = 4-C <sub>6</sub> H <sub>4</sub> F ( <b>4l</b> )   | 0.5               | 20 h   | 100 (91)               | 10                                  |
| 13    | R = 2-Furyl ( <b>4m</b> )                             | 2.5               | 36 h   | 82 (73)                | 1                                   |

<sup>a</sup> Reactions performed under N<sub>2</sub> atmosphere at 75 °C using 4 mmol of the corresponding allylic alcohol **4a-m** (1 M in THF) and the quantity of complex **3a** indicated in each case.  $[\text{K}_2\text{CO}_3]:[\text{Ru}]$  ratio = 2.5:1.

<sup>b</sup> Yield of the resulting carbonyl compounds **5a-m** determined by GC (uncorrected GC areas). Isolated yields after are given in brackets.

<sup>c</sup> Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.

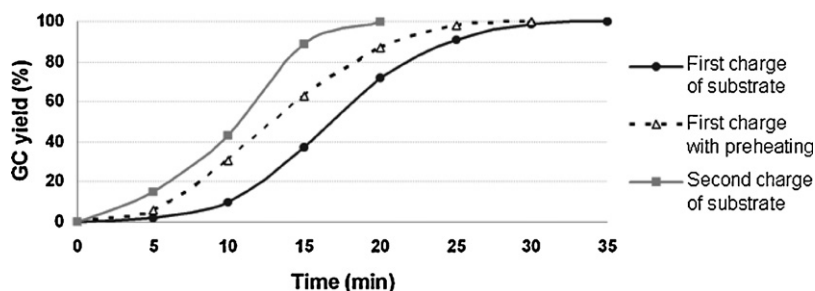
observed. This fact discards a heterogeneous process involving metallic nanoparticles as the active species. On the other hand, a diminution of the induction period was observed when complex **3a** was preheated with K<sub>2</sub>CO<sub>3</sub> prior to the addition of the allylic alcohol (see Fig. 2), suggesting that the dichloride complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) may be initially transformed into the carbonate one  $[\text{Ru}(\text{CO}_3)(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  [34]. A faster substitution of the carbonate ligand by the substrate, in comparison with that of the chlorides in **3a**, could then explain the reduction of the induction period.

To further define the scope of this catalytic transformation, other allylic alcohols were subjected to the combined action of  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) and K<sub>2</sub>CO<sub>3</sub> (Table 4). Reactions were performed in all cases in THF (1 M solutions) at 75 °C using a  $[\text{K}_2\text{CO}_3]:[\text{Ru}]$  ratio of 2.5:1. Thus, as observed for 1-octen-3-ol (**4a**), related aliphatic substrates **4b-e** could be efficiently converted into the corresponding ketones **5b-e** within 1 h of heating (entries 2–5), leading to a maximum TOF value of 800 h<sup>-1</sup> for the isomerization of 3-buten-2-ol (**4e**) into butan-2-one (**5e**) (entry 5). Allylic alcohol (**4f**) itself also participated in the reaction, albeit a longer reaction time (4.5 h) and a higher metal loading (2.5 instead of 0.5 mol% of Ru) were in this case needed to generate propionaldehyde (**5f**) in high yield (entry 6). This result is not surprising since a lower reactivity of primary vs secondary alcohols has been previously observed with other catalytic systems [35]. The gradual decomposition of the catalyst into an inactive metal-carbonyl compound by

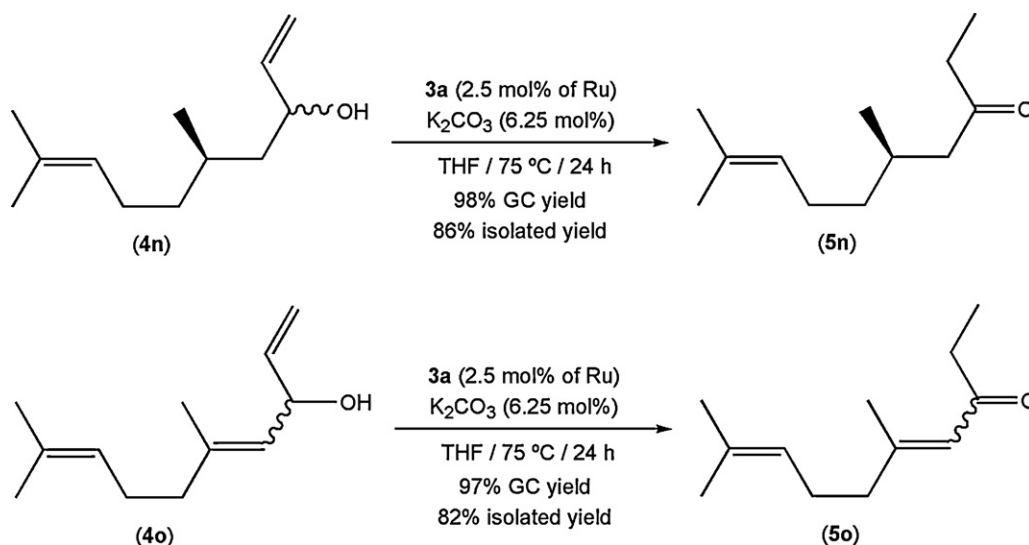
decarbonylation of the aldehyde may be responsible of this effect [36].

As shown in entries 7–12, complex **3a** (0.5 mol%) was also effective in the isomerization of the aromatic substrates **4g-l**, thus confirming the generality of this catalytic transformation. However, due probably to the steric congestion associated with the presence an aromatic ring in  $\alpha$ -position to the alcohol unit that disfavors their coordination to the metal, longer reaction times (20–22 h) were in these cases required to attain good conversions [37]. Using a ruthenium loading of 2.5 mol%, isomerization of the heteroaromatic substrate 1-(2-furyl)-2-propen-1-ol (**4m**) was also possible, leading to a maximum conversion of 82% after 36 h of heating. The lower reactivity of this substrate is probably associated to the competitive coordination of the furyl and olefin units onto the active ruthenium species.

Furthermore,  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) was also successfully employed in the chemoselective isomerization of allylic alcohols **4n** (1:1 mixture of diastereoisomers) and **4o** (1:1 mixture of *E/Z* stereoisomers) derived from the naturally occurring aldehydes (*R*)-(+)-citronellal and citral, respectively, into the known ketones **5n-o** [18b,38] (Scheme 3). Interestingly, although **4o** presents two carbon-carbon double bonds in  $\alpha$ -position with respect to the alcohol group, only the isomerization of the mono-substituted one was observed, leading to the exclusive formation of the enone **5o** as a 1:1 mixture of the corresponding *E* and *Z* isomers. In both cases the Me<sub>2</sub>C=CHCH<sub>2</sub>— unit remained unaltered.



**Fig. 2.** Isomerization of 1-octen-3-ol (**4a**) into octan-3-one (**5a**) catalyzed by complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) under optimized conditions (1 M solution in THF, at 75 °C using a  $[\text{4a}]:[\text{Ru}]:[\text{K}_2\text{CO}_3]$  ratio of 100:0.5:1.25): yield of octan-3-one (**5a**) as a function of time.



**Scheme 3.** Isomerization of allylic alcohols **4n–o** by complex [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**).

**Table 5**  
Ruthenium content in the solids.

| Entry | Ru initial <sup>a</sup> | % Ru (exp.) <sup>b</sup> | % Ru (theor.) <sup>c</sup> | MK10-3a-x <sup>d</sup> |
|-------|-------------------------|--------------------------|----------------------------|------------------------|
| 1     | 0.1 mmol                | 0.7%                     | 1.0%                       | MK10-3a-0.7            |
| 2     | 0.2 mmol                | 1.5%                     | 1.9%                       | MK10-3a-1.5            |
| 3     | 0.3 mmol                | 2.0%                     | 2.7%                       | MK10-3a-2.0            |
| 4     | 0.4 mmol                | 2.5%                     | 3.4%                       | MK10-3a-2.5            |
| 5     | 0.5 mmol                | 3.1%                     | 4.1%                       | MK10-3a-3.1            |

<sup>a</sup> Quantity of complex [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**) employed for the impregnation of 1 g of Montmorillonite K-10.

<sup>b</sup> Weight percentage of ruthenium in the resulting solids determined by ICP-MS.

<sup>c</sup> Maximum weight percentage of ruthenium that can be incorporated in the solid (calculated from the quantity of **3a** employed in each case).

<sup>d</sup> Name given to the solid (x refers to the amount of ruthenium incorporated).

Once demonstrated the synthetic potential of [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**), we proceeded to support this complex onto the commercial clay Montmorillonite K-10 (Sigma–Aldrich). The immobilization process was carried out by the classical solvent-impregnation method [39]. Thus, colored dichloromethane (15 mL) solutions containing 0.1, 0.2, 0.3, 0.4 and 0.5 mmol of [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**) were prepared under nitrogen atmosphere and treated with 1 g of the clay, previously dried at 110 °C to eliminate adsorbed water, for 4 h. Almost complete discoloration of the solutions was observed when 0.1–0.4 mmol of **3a** were employed. In contrast, starting from 0.5 mmol of **3a**, the loss of the initial orange color of the solution was much less pronounced even after

**Table 6**  
Powder XRD data for Montmorillonite K-10 and solids MK10-3a-x.

| Entry | Solid                | 2θ <sup>a</sup> | d <sup>b</sup> |
|-------|----------------------|-----------------|----------------|
| 1     | Montmorillonite K-10 | 8.8874°         | 9.950 Å        |
| 2     | MK10-3a-0.7          | 8.9658°         | 9.863 Å        |
| 3     | MK10-3a-1.5          | 8.9554°         | 9.875 Å        |
| 4     | MK10-3a-2.0          | 8.9381°         | 9.894 Å        |
| 5     | MK10-3a-2.5          | 8.9562°         | 9.888 Å        |
| 6     | MK10-3a-3.1          | 8.9220°         | 9.912 Å        |

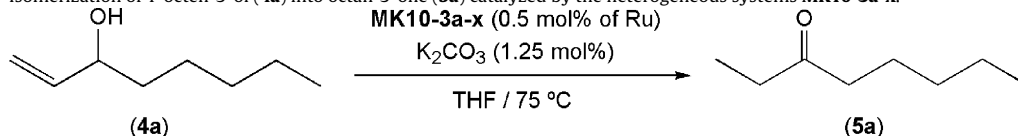
<sup>a</sup> The (0 0 1) diffraction line.

<sup>b</sup> Interlaminar (basal) distance.

24 h of stirring. This fact suggests that saturation of the clay takes place with this quantity of the complex. The suspensions generated in the impregnation process were then filtered off and the resulting solids washed with dichloromethane and dried under vacuum.

The IR spectra obtained for these solids confirmed the incorporation of complex [RuCl<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(PTA-Me)] (**3a**) to the clay since, in addition to the strong absorption bands characteristics of the Montmorillonite K-10 support, others of lower intensity at 1437 and 749 cm<sup>-1</sup> attributable to **3a** were also observed. The weight percentage of ruthenium present in the solids was determined by ICP-MS measurements (see Table 5). As expected, the ruthenium content increased with the quantity of complex **3a** initially present in solution. Thus, the weight percentage of Ru varied from 0.7% (starting from 0.1 mmol of **3a**; solid MK10-3a-0.7 in entry 1) to

**Table 7**  
Isomerization of 1-octen-3-ol (**4a**) into octan-3-one (**5a**) catalyzed by the heterogeneous systems MK10-3a-x.<sup>a</sup>



| Entry | Catalyst    | Time (h) | Yield (%) <sup>b</sup> | TOF (h <sup>-1</sup> ) <sup>c</sup> |
|-------|-------------|----------|------------------------|-------------------------------------|
| 1     | MK10-3a-0.7 | 8        | 97 (89)                | 24                                  |
| 2     | MK10-3a-1.5 | 5        | 100 (95)               | 40                                  |
| 3     | MK10-3a-2.0 | 4        | 100 (96)               | 50                                  |
| 4     | MK10-3a-2.5 | 3        | 100 (95)               | 67                                  |
| 5     | MK10-3a-3.1 | 9        | 76 (60)                | 17                                  |

<sup>a</sup> Reactions performed under N<sub>2</sub> atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (**4a**) (1 M in THF). [1-octen-3-ol]:[Ru]:[K<sub>2</sub>CO<sub>3</sub>] ratio = 100:0.5:1.25.

<sup>b</sup> Yield of octan-3-one (**5a**) determined by GC (uncorrected GC areas). Isolated yields are given in brackets.

<sup>c</sup> Turnover frequencies ((mol product)/(mol Ru)/time) were calculated at the time indicated in each case.

3.1% (starting from 0.5 mmol of **3a**; solid **MK10-3a-3.1** in entry 5). However, we must note that, in all cases, the actual content in ruthenium is slightly lower than the maximum value calculated from the amount of **3a** employed [40], indicating that part of the added complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) has not been attached to the solid support, well because it was not adsorbed by the clay initially, or by a problem of leaching during the washings with dichloromethane.

Solids **MK10-3a-x** were further characterized by powder X-ray diffraction, the diffractograms obtained showing in all the cases an insignificant shift in the (001) diffraction line with respect to that of the pure clay (see Table 6). For illustrative purposes, XRD patterns of samples of the Montmorillonite K-10 employed in this study and the solid **MK10-3a-0.7** are shown in Fig. 3. The small variations of the basal distances with respect to the pure clay, calculated from the (001) diffraction line by the Bragg equation (Table 6), suggest that complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) is mainly adsorbed on the external surface of the clay through electrostatic or H-bonding interactions [41], rather than intercalated into its interlaminar spacing [42].

Once characterized, the catalytic activity of **MK10-3a-x** in the redox isomerization of 1-octen-3-ol (**4a**) was then explored under the optimized conditions described above for  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) under homogeneous conditions (i.e. 1 M solution of 1-octen-3-ol in THF, a ruthenium loading of 0.5 mol%, 1.25 mol% of  $\text{K}_2\text{CO}_3$  as the base, and a working temperature of 75 °C). The amount of solids **MK10-3a-x** needed to fit with the metal loading of 0.5 mol% was calculated according to the ICP-MS measurements collected in Table 5.

As shown in Table 7, all of the heterogeneous systems prepared were able to promote the selective isomerization of **4a** into **5a** in high yields. However, they were comparatively less effective than the unsupported complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) (TOF values of 17–67 vs 343  $\text{h}^{-1}$ ). Thus, under heterogeneous conditions, the best results were found with **MK10-3a-2.5**, which was able to generate quantitatively the desired octan-3-one (**5a**) after 3 h of heating (entry 4). Remarkably, the TOF value attained with this system ( $67 \text{ h}^{-1}$ ) was slightly higher than that reported by Martín-Matute and co-workers for the isomerization of **4a** with a cationic Rh(I) complex anchored onto the mesoporous aluminosilicate AISBA-15 in THF at 80 °C ( $48 \text{ h}^{-1}$ ) [17]. We must also note that,

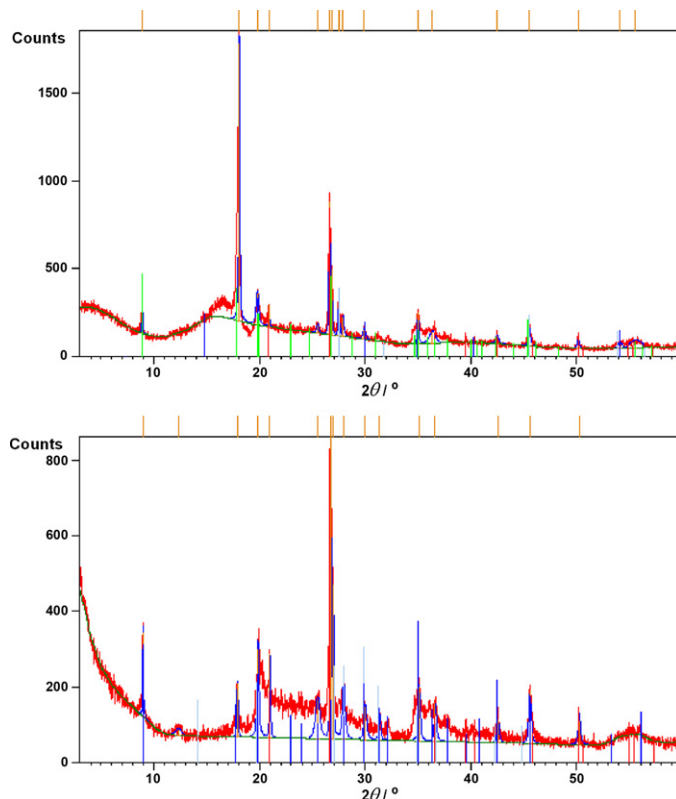


Fig. 3. Powder XRD patterns of Montmorillonite K-10 pure (top) and solid **MK10-3a-0.7** (bottom).

as a general trend, an increase of the catalytic activity of the solids **MK10-3a-x** with the weight percentage of ruthenium present in the sample was observed (see entries 1–4). However, with **MK10-3a-3.1**, which features the largest content of ruthenium, this trend failed (entry 5 vs entries 1–4). Steric hindrance as a consequence of the proximity between the metal centers on the surface of the clay may be responsible for this anomaly since, as commented previously, saturation of this solid was observed during impregnation with complex **3a**.

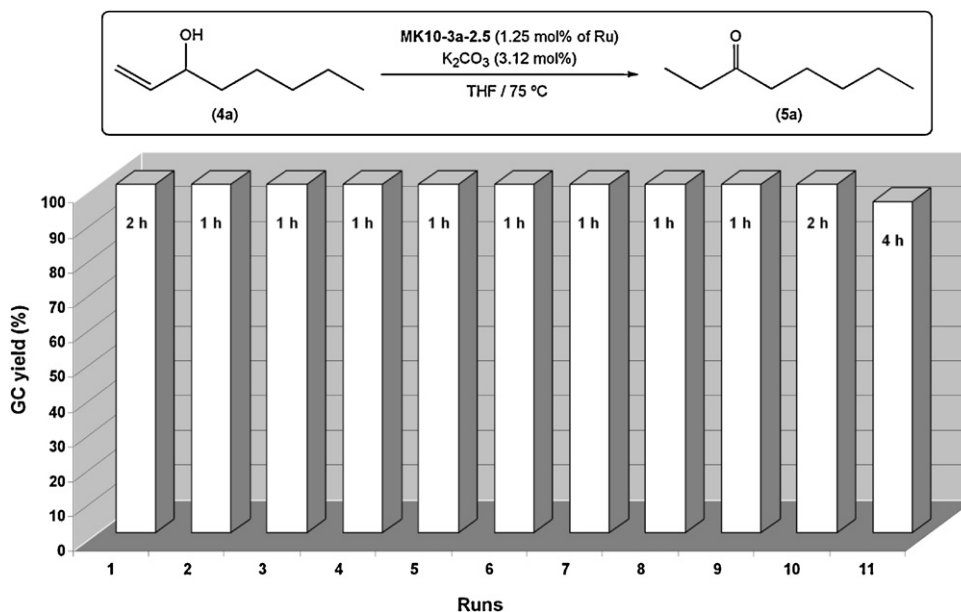


Fig. 4. Reuse of the heterogeneous system **MK10-3a-2.5** in the isomerization of 1-octen-3-ol (**4a**) into octan-3-one (**5a**).



Finally, the recycling of the most active system **MK10-3a-2.5** was investigated, using again the isomerization of 1-octen-3-ol (**4a**) into octan-3-one (**5a**) as model reaction. As shown in Fig. 4, performing the catalytic process with a ruthenium loading of 1.25 mol% [43], **MK10-3a-2.5** could be effectively reused in at least eleven consecutive runs after a simple filtration and washing of the solid with hexanes. In complete accord with the induction period observed for  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**) under homogeneous conditions (see Fig. 2), conversion of **4a** into **5a** proceeded faster in the second run than in the first one (1 vs 2 h). From there, the performance of **MK10-3a-2.5** remained stable without appreciable loss of activity until the tenth recycling cycle. In the eleventh one, more than 90% conversion was still reached after 4 h of heating, thus leading to a cumulative TON of 872. We also determined the Ru content in solution after the first reaction cycle by ICP-MS, and found that it was only ca. 28 ppm. The excellent recyclability of **MK10-3a-2.5**, superior to that shown by the related heterogeneous system Rh(I)/AISBA-15 described by Martín-Matute and co-workers (up to 5 consecutive cycles) [17], along with the low metal leaching observed attest for the high stability and lifetime of our Ru-based supported catalyst.

#### 4. Conclusion

In summary, a new catalytic system for the selective isomerization of allylic alcohols into carbonyl compounds under homogeneous conditions has been developed by the aid of the ruthenium(II) complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**). This ionic species was successfully immobilized onto the smectite-type clay Montmorillonite K-10 and used as a heterogeneous catalyst in the redox isomerization process. Remarkably, although the activity of the heterogeneous system was comparatively lower than that of the unsupported complex  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)(\text{PTA-Me})]$  (**3a**), it could be reused for a large number of runs, with negligible loss of the catalytic activity. Overall, our results, along with those previously reported by Martín-Matute and co-workers [17], clearly demonstrate the great potential of inorganic solids supports for the development of robust heterogeneous catalysts able to promote the synthetically useful isomerization reaction of allylic alcohols.

#### Acknowledgments

Financial support by the Ministerio de Economía y Competitividad of Spain (Projects CTQ2010-14796/BQU and CSD2007-00006) is gratefully acknowledged. L.M.-R. also thanks the Spanish Government and the European Social Fund for the award of a PhD grant (FPI program).

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