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Ruthenium clay catalyzed chemoselective hydrogenation of unsaturated esters, epoxides, sulfones and phosphonates [1]

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Abstract

Ru-clays were prepared using montmorillonite–PPh_2 or montmorillonite–bpy and $RuCl_3 \cdot H_2O$. The clays obtained were found to be effective catalysts for the reduction of unsaturated esters, epoxides, sulfones and phosphonates. © 1998 Elsevier Science S.A.

Keywords: Hydrogenation; Ruthenium; Clay

1. Introduction

There is substantial interest in immobilized transition metal catalysts, because they are capable of combining the advantages of homogeneous and heterogeneous catalysis. The catalyst is easily removed after reaction, a high yield of the products can often be obtained, and the lifetime of the catalyst is good in some cases. From the variety of possible supports for hydrogenation reactions, the option for clays comes from their capacity to mimic to some extent, but at a much lower cost, the properties of a rare noble metal and to make possible synthesis with improved selectivity [1]. The immobilization of a metal complex in a clay structure modifies the chemical and physical forces acting in the interlayer space of the clay and this can result in improved catalytic specificity [2].

We have been examining the catalytic activity of metals immobilized on clays for different processes [3–9]. Montmorillonite–bipyridinyl palladium (II) was used for the reductive carbonylation of nitroarenes to urethanes [3] the oxidative carbonylation of aliphatic mono, di- and triamines [4] and for the sterospecific synthesis of β, γ-unsaturated acids [5]. Rhodium–montmorillonite was an effective catalyst for the hydroformylation of vinylsilanes [6] and allyl acetates [7].

We now wish to report the preparation of ruthenium supported on clay and the use of this new system, as a catalyst, for the selective reduction of functionalized olefins.

2. Results and discussion

Ruthenium complexes, fixed between the interlayers of clays by cation exchange, were reported previously and their catalytic activity already investigated [10–12]. Λ-Ru(2,2′-bipyridyl)$_3^2$-montmorillonite [10] is efficient for the oxidation of alkyl phenyl sulfides to optically active sulfoxides and Ru(1,10-phenanthroline)$_3^2$-pillared montmorillonite is the catalyst precursor for the selective reduction of the carbon∧carbon double bond of unsaturated ketones [11]. $RuCl_2(H)_2(AsPh_3)_2$ intercalated in montmorillonite is reported to be active for the hydrogenation of jojoba oil and castor oil [12]. Our approach was to use either phosphine or bipyridine as the ligands to attach to the clay, and these ligands serve as the link for binding ruthenium to the clay. Two methods were used for the preparation of ruthenium clay, one involving the reaction of $Si(OMe)_3(CH_2)_3Cl$ with OH groups present in the clay, followed by the addition of $KPPh_2$ [13], and subsequent treatment with $RuCl_3 \cdot H_2O$ (Scheme 1, catalyst **1**). In the second method the clay, in its acidic form, is reacted with $SOCl_2$, followed by treatment with *n*-BuLi and bipyridine [14], and finally by addition of $RuCl_3 \cdot H_2O$ (Scheme 1, catalyst **2**).

The Ru-clays obtained were analyzed for ruthenium

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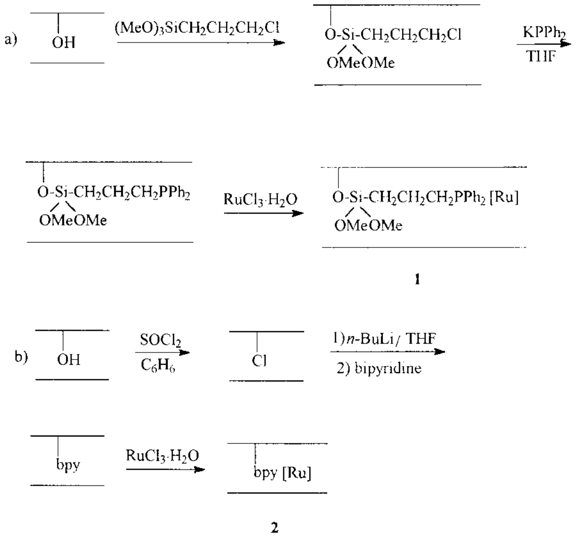
[1] Dedicated to Professor Peter Maitlis, a splendid person who has made outstanding contributions to science. We have learned so much from him.



Scheme 1.

content by flame emission with 0.17 mmol Rug^{-1} and 0.018 mmol Rug^{-1} found for **1** and **2**, respectively.

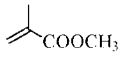
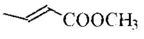
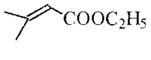
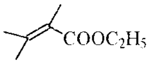
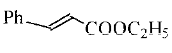
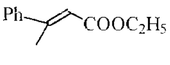
The IR spectra of both Ru-clays show strong absorptions due to the montmorillonite. For catalyst **1** the 2880–2900 cm^{-1} band can be assigned to the carbon–hydrogen stretch from the propyl group attached to the phosphorus atom and the enhanced absorption at 697 cm^{-1}, compared to pure K-10 montmorillonite, is typical of the substitution pattern of an aromatic phosphine.

In the CP/MAS ^{31}P NMR spectrum of the ligand bound to the clay, a signal at -17.6 ppm was assigned to the phosphorus in siloxypropyldiphenylphosphine, which is close to the value (-16 ppm) reported for the same ligand grafted on silica [15]. The NMR study also indicates the presence of a P (*V*) species (32.7 ppm) [15]. After the coordination of ruthenium the spectrum shows a broad peak at 32 ppm and the signal at -17.6 ppm disappeared. It is known that the coordination of Ru to phosphorus produces the shift of the ^{31}P signal in the upper field region (40 ppm) [16] and a similar shift takes place in the case of Pd coordinated to phosphine on clay [17].

X-Ray powder diffraction showed a basal region expansion (d_{001}) of 13.36 Å for **1** from 9.6 Å in the dehydrated sodium montmorillonite.

For catalyst **2**, the IR spectrum of the clay containing the dipyridyl ligand, before complexation of the metal, indicated the characteristic absorption of bipyridine in the region of 1562–1438 cm^{-1}. After treatment with $RuCl_3 \cdot H_2O$ a sharp absorption at 1642 cm^{-1} was observed. It is known that dipyridyl ligands coordinated

Table 1
Reduction of unsaturated esters using **1** and **2** as catalysts[a]

No.	Substrate	Catalyst	Pressure (psi H_2)	Time (h)	Conv. (Yield)[b] (%)
1.		**1** **2**	300	22	100 (87) 100 (91)
2.		**1** **2**	600	45	100 (85) 100 (91)
3.		**1** **2**	600	40 45	- 100
4.		**1** **2**	600	40	- -
5.[c]		**1** **2**	800	52 63	100 (85)[d] 21
6.[c]		**1** **2**	800	24	100 (84)[d] 100

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[a] Reaction conditions: substrate (2.0 mmol); 30 mg **1** or **2** (0.005 mmol Ru); temperature: 75°C; benzene (8.0 ml).

[b] Determined by ^{1}H NMR using an internal standard.

[c] 1 mmol substrate.

[d] Isolated yield.

to ruthenium are characterized by the sharp 1600 cm^{-1} peak [18] and, once the ligand is fixed on a solid support, a shift of the band can take place. In this particular case the peak corresponding to bipyridine is overlaped with the band near 1642–1633 cm^{-1} displayed by montmorillonite. The basal region expansion (d_{001}) for **2** was 14.11 Å.

It is important to note that, when Ru-clays were used in the catalysis process, no leaching of Ru was observed. The recycling capacity of the catalyst (both **1** and **2**) was tested by reusing the Ru-clays three times consecutively without loss of activity.

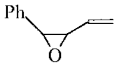
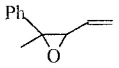
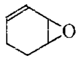
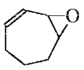
An investigation was made on the effectiveness of **1** and **2**, for the selective reduction of the double bond of unsaturated esters, a reaction of substantial interest in organic chemistry [19–21].

The hydrogenation of methyl methacrylate catalyzed by Ru-clays **1** and **2** with a substrate to catalyst ratio of 370:1 showed complete conversion to the corresponding propionate ester in 22 h at 300 psi H_2 and 75°C. Clays **1** and **2** had comparable catalytic activity for the selective reduction of double bond of methyl methacrylate and methyl crotonate (Table 1, entries 1 and 2).

The two catalysts behaved differently when both terminal hydrogens of the double bond are replaced by methyl groups, as in the case of ethyl 3-methyl-2-butenoate: **1** is inactive towards the substrate even at 600 psi H_2, while **2** catalyses the hydrogenation in 45 h (Table 1, entry 3). Neither **1** or **2** was effective for the hydrogenation of ethyl 2,3-dimethyl-2-butenoate [22] (Table 1, entry 4). In contrast with the increased activity of **2** for the reduction of carbon=carbon double bond in ethyl 3-methyl-2-butenoate, **1** is the catalyst of choice for ethyl *trans* cinnamate: 100% conversion resulting in the formation of ethyl 3-phenylpropanoate in 85% isolated yield (Table 1, entry 5). Catalyst **2** gave only 21% conversion of ethyl *trans* cinnamate to the saturated ester, the rest being unreacted starting material. Ru-clay **1** is also effective in the case of ethyl *trans*-*β*-methylcinnamate with 100% conversion to the saturated ester (Table 1, entry 6). The activity displayed by **2** for this substrate is similar to that of catalyst **1** (Table 1, entry 7).

The hydrogenation reactions were performed in benzene and, in the crude mixture, cyclohexane, obtained from the reduction of aromatic ring, was observed. Several other solvents were used for the hydrogenation reaction with **1** as the catalyst. Reaction of methyl methacrylate catalyzed by **1** in methylene chloride gave complete conversion to methyl 2-methylpropionate, while in the reaction using methanol as the solvent, the starting material was recovered and only traces of hydrogenated product were found. To make sure that the Ru-clay system is the active catalyst, the reaction of

Table 2
Reduction of unsaturated epoxides using **1** as the catalyst[a]

No.	Substrate	Pressure (psi H_2)	Time (h)	Conversion[b] (%)	Isolated Yield[c] (%)
1.		500	24	100	60
2.		300	24	100	30[d]
3.		500	48	100	16[e]
4.		500	19	100	50[d]

[a] Reaction conditions: 1 mmol substrate; 30 mg **1** (0.005 mmol Ru); temperature: 75°C; 8 ml benzene as solvent.
[b] Conversion determined from ^1H NMR.
[c] By-products obtained: entry 1: benzyl ethyl ketone (10%); entry 2: 2-methyl-2-phenyl-butanal (30%) and 2-phenyl-3-pentanone; entry 3: cyclohexanone (84%); entry 4: cycloheptanone (50%).
[d] Yield determined by ^1H NMR using an internal standard.
[e] Yield determined by GC with an internal standard.

methyl methacrylate at 300 psi H_2 and 75°C using Fluka K-10 montmorillonite, without any metal, was tested in which case no reaction was observed. The use of $RuCl_3 \cdot H_2O$, as the catalyst, for the same substrate, in benzene, gave only 27% conversion to methyl 2-methylpropionate. It was also demonstrated that the solid obtained by stirring a dry THF solution of K-10 montmorillonite and $RuCl_3 \cdot H_2O$, under nitrogen, and then washing with water and THF, followed by drying in vacuo, does not give any reduction of methyl methacrylate.

Catalyst **1** was also tested for the selective hydrogenation of the double bond of vinyl epoxides (Table 2), a reaction which occurs using palladium or rhodium on carbon for butadiene monoxide [23] and with homogeneous palladium and iridium catalysts [24].

Good selectivity was obtained for 2-phenyl-3-vinyloxirane [25], which afforded, at 500 psi H_2, 2-ethyl-3-phenyl-oxirane in 60% isolated yield (Table 2, entry 1). In the case of 2-methyl-2-phenyl-3-vinyloxirane [25], an appreciable amount of saturated aldehyde (2-methyl-2-phenyl butanal) together with 2-phenyl-3-pentanone was obtained in addition to the saturated epoxide, which represented only 30% of the products (Table 2, entry 2). The hydrogenation reaction of 1,3-cyclohexadiene monoxide [22] at 500 psi H_2 gave cyclohexene oxide in 16% yield, the principal product being cyclohexanone (Table 2, entry 3). In the case of 1,3-cycloheptadiene monoxide [26] the yield of cycloheptene oxide was good (50%) (Table 2, entry 4) with the accompanying product being cycloheptanone. Cycloheptene oxide is obtained in lower yield (33%) when 1,3-cycloheptadiene monoxide is reduced at 300 psi H_2.

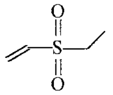
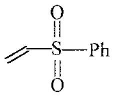
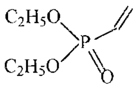
The catalytic activity of **1** was investigated for two other classes of functionalized compounds α, β-unsaturated sulfones and phosphonates (Table 3).

Ethyl vinyl sulfone and phenyl vinyl sulfone (Table 3, entries 1 and 2) afforded diethyl sulfone and ethyl phenyl sulfone in 64% and 94% yield, respectively. The use of ruthenium clay for the reduction of the carbon=carbon double bond in sulfones compares favorably with commonly used hydride reagents such as $NaBH_4$ or $[(PPh_3)\ CuH]$ [27–29] or with the catalyst generated from the reaction of $[(Bu^t_2PH)_3PdPBu^t_2]_2$ with O_2 in THF [30]. The hydrogenation also proceeded readily for diethyl vinyl phosphonate (100% conversion and 90% yield) (Table 3, entry 3), but the reaction is of limited scope as the presence of another substituent at the carbon=carbon double bond inhibits reduction (e.g., α-phenyl-substituted vinyl diethylphosphonate or diethyl 1-propenylphosphonate did not react).

3. Conclusion

$RuCl_3$, immobilized on clay by means of phosphine or bipyridine containing units, showed good catalytic activity for the reduction of α,β-unsaturated esters and unsaturated sulfones but was less selective for unsaturated epoxides and not generally efficient for

Table 3
Reduction of unsaturated sulfones and phosphonates using **1** as the catalyst[a]

No.	Substrate	Time (h)	Conversion[b] (%)	Isolated Yield (%)
1.[c]		66	80	64[d]
2.		63	100	94
3.		22	100	90

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[a] Reaction conditions: substrate (0.5 mmol); **1** (30 mg, 0.005 mmol Ru); temperature: 125°C for sulfones and 100°C for phosphonate; pressure: 500 psi H_2; 8 ml benzene as solvent.

[b] Conversion determined by ^1H NMR.

[c] 1 mmol substrate used.

[d] Yield determined by GC with an internal standard.

phoshonates. It is an attractive method because of facile separation and reuse of the catalyst.

4. Experimental

All solvents were dried and distilled by standard methods prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 and XL 300 spectrometers; a Bomen MB 100-C15 spectrometer was used for FT-IR spectra and a Varian 3400 Chromatograph for GC analyses. The substrates were purchased from Aldrich Chemical and were used as received. The substrates which were not commercially available were synthesized by literature methods (i.e., ethyl 2,3-dimethyl crotonate, 2-phenyl-3 vinyl-oxirane, 2-methyl-2-phenyl-3-vinyl-oxirane, 1,3-cyclohexadiene monoxide and 1,3-cycloheptadiene monoxide) [22,25,26]. Physical data for all starting materials and products are in accord with literature data.

4.1. Synthesis of Ru-clays

Synthesis of **1**: H–montmorillonite was prepared from montmorillonite K-10 (Fluka) by treatment with saturated NaCl solution followed by 0.1 N HCl solution. It was dried in air and then in vacuum. H–montmorillonite (4 g) was suspended in benzene (40 ml), $(MeO)_3SiCH_2CH_2CH_2Cl$ (5 ml, 0.027 mol) was added and the mixture was refluxed for 12 h. The clay was extracted (Soxhlet) with toluene for 24 h, and dried [13]. The clay (2.5 g) was then suspended in dry THF (30 ml), $KPPh_2$ (4 mmol, 8 ml 0.5 M solution in THF) was added dropwise and the mixture was refluxed overnight under nitrogen [13]. The excess $KPPh_2$ was quenched with methanol and the clay was subjected to extraction with methanol for 24 h and then toluene for additional 24 h, and subsequently dried in vacuum. The dried montmorillonite (0.8 g) was suspended in THF (15 ml), 20.7 mg (0.1 mmol) of $RuCl_3 \cdot H_2O$ was added and the mixture was stirred for 8 h under N_2 and then washed with water and THF and vacuum dried affording clay containing 0.017 mmol g^{-1} Ru (determined by flame emission, wavelength 372.8 nm).

Synthesis of **2**: H–montmorillonite (7 g) was suspended in dry benzene (50 ml), and reacted with $SOCl_2$(10 ml, 0.13 mol) under reflux for 24 h [14]. The chloromontmorillonite obtained was filtered and dried under vacuum. Chloromontmorillonite (2 g) was reacted with excess *n*-butyllithium (3.5 ml, 5.6 mmol, 1.6 M in hexane) at -78°C in dry THF. The solution was stirred at 0°C for 4 h and then allowed to warm to room temperature and stirred for 1 h. Bipyridine (1.185 g, 7.6 mmol) was added and the mixture was refluxed for 4 h [14]. The reaction mixture turned purple during refluxing. It was then cooled to room temperature and air was bubbled through the solution until it became yellow. The montmorillonite was washed with THF, ethyl acetate and benzene followed by Soxhlet extraction with THF for 24 h. The solid obtained was dried under vacuum and then 41.5 mg of $RuCl_3 \cdot H_2O$ (0.2 mmol) was added to 2 g of bipyridine–montmorillonite suspended in THF and the mixture was stirred for 8 h under nitrogen. The resulting Ru-clay was thoroughly washed with water and THF to remove excess $RuCl_3$ and dried in vacuo. The Ru content was determined to be 0.18 mmol g^{-1} (flame emission).

4.2. General procedure for the hydrogenation reactions

A mixture of unsaturated substrate (2 mmol) and Ru-clay, **1** or **2**, (30 mg–0.005 mmol Ru) in 8 ml benzene (8 ml) were placed in a 45-ml autoclave. The autoclave was purged three times with H_2 and then pressurized to the desired level. The reactor was then placed in an oil bath and maintained at constant temperature. After the appropriate reaction time, the autoclave was cooled to room temperature, excess H_2 gas was released and the reaction mixture was filtered through Celite and the solvent was removed by rotary evaporation. The products were purified by vacuum distillation or column chromatogaphy.

Acknowledgements

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