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Osmium silsesquioxane as model compound and homogeneous catalyst for the dihydroxylation of alkenes

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Abstract

A homogeneous dihydroxylation catalyst was synthesised by complexation of osmium tetroxide (OsO_4) with a silsesquioxane ligand containing a tetrasubstituted olefin moiety. The advantage of this procedure consists in avoiding the presence of the highly toxic and volatile OsO_4 in solution during the dihydroxylation reaction. The Os–silsesquioxane complex was used as a homogeneous catalyst and as a model of the catalytic site of the heterogeneous analogue. The homogeneous catalyst gave 84% conversion with 99% selectivity for the dihydroxylation of cyclopentene and 99% conversion with 99% selectivity for the dihydroxylation of cyclohexene.

Keywords: Dihydroxylation of alkenes; Osmium tetroxide; Silsesquioxanes; Homogeneous catalysis; Model compound

1. Introduction

Osmium tetroxide (OsO_4) is generally considered the best catalyst for the *cis*-dihydroxylation of double bonds (Fig. 1) [1–4]. The disadvantage of using this compound as homogeneous catalyst lies in its high volatility and toxicity [5]. Therefore, many attempts have been carried out to immobilise osmium tetroxide on different supports [6–8]. Recently, Jacobs and co-workers reported an efficient and robust heterogeneous catalyst obtained by binding OsO_4 to a tetrasubstituted olefin covalently linked to a silica support [9,10]. The tetrasubstituted diolate ester which was obtained at one side of the osmium centre provided a stable connection between the osmium centre and the silica support, since it does not undergo hydrolysis under the reaction conditions applied. The remaining osmium co-ordination site is available for the catalytic reaction. The catalytic cycle is then reduced to the right part of the scheme in Fig. 1. This silica-supported Os-catalyst proved to be active in the dihydroxylation of a number of alkenes with *N*-methylmorpholine-*N*-oxide (NMO) as the oxidant [9,11] (NMO may be regenerated by oxidation with H_2O_2) [10]. Careful heterogeneity tests confirmed the absence of OsO_4 leaching. Given the relevance of these results, the preparation, characterisation and catalytic test of a silsesquioxane-based homogeneous analogue of this heterogeneous silica-supported catalyst becomes interesting in order to establish the surface chemistry unequivocally and to broaden the scope for immobilisation (e.g. silsesquioxane complexes of titanium have been successfully immobilised on MCM-41, yielding highly active, non-leaching heterogeneous catalysts) [12–14]. Silsesquioxanes [15] are compounds of general formula $(RSiO_{1.5})_a(H_2O)_{0.5b}$, where R is an hydrogen atom or an organic group and a and b are integer numbers ($a = 1, 2, 3, \ldots$; $b = 0, 1, 2, 3, \ldots$), which find applications as ligands for homogeneous catalysts and as model compounds for silica surfaces.

2. Experimental

2.1. Analytical methods

^{13}C NMR spectra were measured at 25 °C in $CDCl_3$ as solvent on a Varian Inova-300 (75.5 MHz, ^1H decoupled) and on a Bruker DPX-300 (75.5 MHz, ^1H decoupled).

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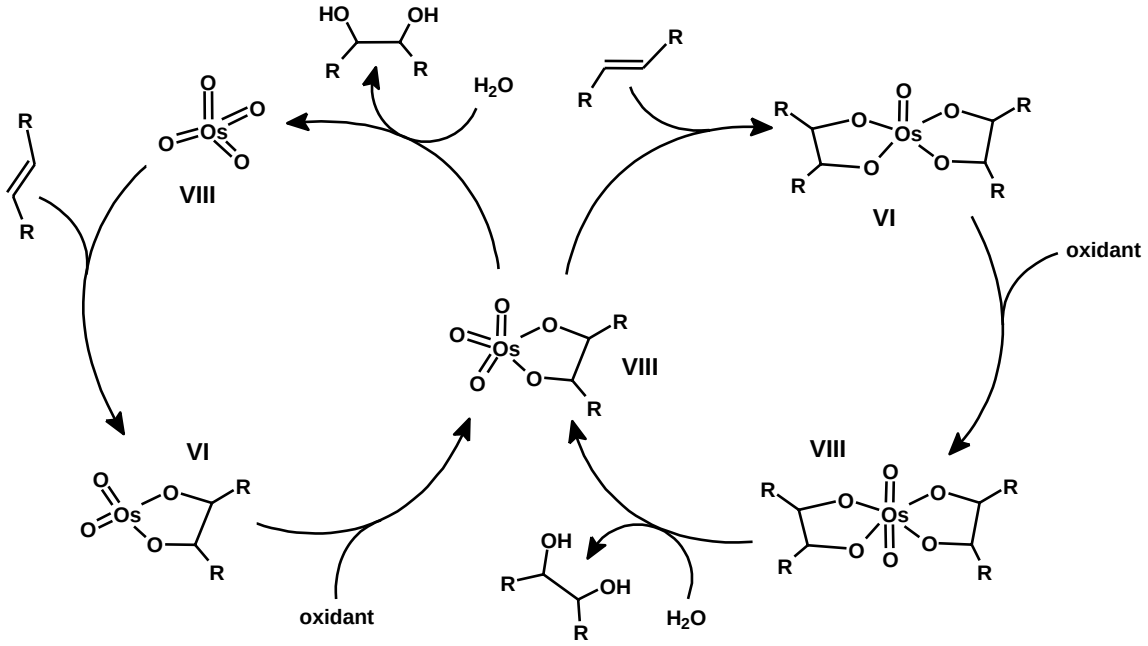

Fig. 1. Proposed catalytic cycles for the dihydroxylation of alkenes with OsO_4 as the catalyst.

Mass spectrometry analysis was performed on a Micromass Quattro LC–MS with ESI as ionisation technique and on a ThermoQuest Finnigan LCQ Deca equipped with ESI source and controlled by Xcalibur software. The desolvation temperature was set to 300 °C, the cone voltage to 20 V. The samples had a concentration of ∼0.01 mg of silsesquioxane-based compound diluted in 1 ml of methanol (or of a methanol/dichloromethane 1:1 mixture) with addition of a drop of acetic acid if necessary.

GC analysis was performed on a Hewlett-Packard 5890 equipped with a split/splitless capillary injector, FID detector and a Phenomenex Zebron ZB-5 column (30 m). In the temperature program, the temperature was set at 30 °C for 1 min, and then it was raised to 250 °C with a rate of 10 °C/min and hold at that temperature for 5 min.

GC–MS analysis was performed on a Finnigan Polaris Q ion trap mass spectrometer with a Trace GC. The GC was equipped with a HP1-MS column (25 m). The GC method started with a temperature of 40 °C for 2 min, then the temperature was raised to 200 °C at a rate of 10 °C/min and hold for 1 min. The ionisation technique for MS analysis was EI (70 eV).

2.2. Synthesis of compound *2*

2.0×10^{-3} moles of cyclopentyl silsesquioxane *a*7*b*3 **1** were dissolved in 70 ml of tetrahydrofuran (THF) and 2.2×10^{-3} moles of 3-aminopropyltrimethoxysilane, $(CH_3O)_3Si(CH_2)_3NH_2$, were dissolved in 50 ml of THF. The two solutions were mixed and allowed to react for 2 days at room temperature while stirring. The solvent was then removed under reduced pressure and the residue was washed with acetonitrile to remove any 3-aminopropyltrimethoxysilane that might still be present. The residue, in the form of a white gel, was redissolved in dichloromethane and dried again under reduced pressure yielding compound **2** as a white solid (1.484 g, corresponding to a yield of 78%). MS data, *m/z*: 958.22 (compound **2** + H^+, 100%), other peaks belonging to impurities with intensities <3%.

2.3. Synthesis of compound *B*

0.15 moles of 3,4-dimethylcyclohex-3-enyl ethyl carboxylate **A** were added to 250 ml of $10\%_{weight}$ NaOH solution in H_2O. Approximately 0.30 g of tetrabutylammonium bromide were added to the biphasic system to favour mixing between the ester **A** and water. The reaction mixture was stirred overnight under reflux to give a monophasic solution. The ethanol formed in the hydrolysis of compound **A** was removed from the solution under reduced pressure. H_2SO_4 1N was added to the solution until an acidic pH was reached: the carboxylic acid **B** precipitated as a white solid that was then dried overnight under reduced pressure. Total conversion of compound **A** to compound **B** was achieved. $^{13}C\{^1H\}$ NMR data: for compound **A**, δ: 14.32 (*11*), 18.87 (*7*), 19.01 (*8*), 25.96 (*6*), 31.12 (*5*), 33.84 (*2*), 40.33 (*1*), 60.20 (*10*), 124.02 (*4*), 125.29 (*3*), 176.00 (*9*); for compound **B**, δ: 19.05 (*7*), 19.17 (*8*), 25.80 (*6*), 31.05 (*5*), 33.64 (*2*), 40.14 (*1*), 123.94 (*4*), 125.59 (*3*), 182.04 (*9*).

2.4. Synthesis of compound *C*

4.0×10^{-2} moles of thionyl chloride ($SOCl_2$) were added to 1.6×10^{-2} moles of the carboxylic acid **B** and the solution obtained was stirred for 3 h and 30 min under reflux, while

the surface of the reaction mixture was flushed with N_2. Gaseous HCl leaving the reaction mixture through the reflux cooler was redirected into an aqueous solution of NaOH. The reaction mixture was dried under reduced pressure to remove the thionyl chloride still present. The remaining liquid contained the acid chloride **C** (∼70%) together with some carboxylic acid **B** (∼30%), as determined on the basis of ^{13}C NMR analysis. The sample was stored under N_2. $^{13}C\{^1H\}$ NMR data for compound **C**, δ: 19.04 (*7*), 19.33 (*8*), 25.38 (*6*), 30.74 (*5*), 33.15 (*2*), 41.31 (*1*), 123.51 (*4*), 125.58 (*3*), 171.81 (*9*).

2.5. Synthesis of compound *3*

1.6×10^{-3} moles of compound **2** were dissolved in a solution of 1.6×10^{-3} moles of triethylamine in 30 ml of dichloromethane. Subsequently, the solution was added to the mixture of acid chloride **C** and carboxylic acid **B** and stirred overnight at room temperature under N_2 flow. The solution was then concentrated to a volume of 5 ml under reduced pressure and 60 ml of acetonitrile were added: a white solid precipitated. The solid was washed with $0.8\%_{weight}$ $NaOH_{(aq)}$ to remove **B** and **C** that might still be present. The yield in compound **3** was ∼68%. MS data, *m/z*: 1094.15 (compound **3** + H^+, 13%), 1116.11 (compound **3** + Na^+, 100%), 1132.00 (compound **3** + K^+, 8%). $^{13}C\{^1H\}$ NMR data for compound **3**, δ: 9.36 (*12*), 18.84 (*7*), 18.98 (*8*), 23.26 (*11*) 26.56 (*6*), 31.14 (*5*), 34.54 (*2*), 41.47 (*1*), 42.33 (*10*), 124.09 (*4*), 125.48 (*3*), 175.76 (*9*); δ: 22.23 (ipso carbons of the cyclopentyl groups on the silsesquioxane), 27.03, 27.30 (multiplets; remaining carbons of the cyclopentyl groups on the silsesquioxane).

2.6. Synthesis of complexes *4* and *5*

4.0×10^{-5} moles of potassium osmate, $K_2OsO_2(OH)_4$, were dissolved in 2 ml of H_2O to give a dark-red solution. 8.0×10^{-4} moles of *N*-methylmorpholine-*N*-oxide (NMO) were dissolved in 0.5 ml of H_2O. The two aqueous solutions were mixed together with 4 ml of *tert*-butanol and the obtained pink solution was stirred overnight at room temperature. Upon addition of 0.1 ml of a 0.42 M aqueous solution of acetic acid the solution turned colourless. Next, 0.044 g (∼4×10^{-5} moles) of compound **3** and 7.6×10^{-4} moles of cyclohexene, previously dissolved in 5 ml of *tert*-butanol and 3 ml of dichloromethane, were added to the Os-containing solution: the solution immediately turned dark brown, indicating the formation of the Os-diolate. After stirring the reaction mixture for 3 days at room temperature, a sample was taken and analysed by MS. Then, dichloromethane was removed under reduced pressure from the homogeneous dark brown solution. Next, 15 ml of H_2O were added to the slightly turbid solution and a precipitate was formed. The solution was filtered on a folded paper filter and the grey-brown residue was collected (0.028 g, corresponding to ∼1.7×10^{-5} moles and, therefore, to a yield of ∼42% in Os–silsesquioxane complexes). MS data, *m/z*: 1470.60 (complex **5** + Na^+, 100%), 1418.47 (complex **4** + $3Na^+$, 18%), 1116.67 (compound **3** + Na^+, 21%), 1094.67 (compound **3** + H^+, 8%).

2.7. Catalytic test

0.014 g of the grey-brown solid (∼8.4×10^{-6} moles of Os–silsesquioxane complexes) were dissolved in 2.5 ml of dichloromethane and 5 ml of *tert*-butanol. To this solution, 4.0×10^{-3} moles of alkene (cyclopentene or cyclohexene), 2.0×10^{-3} moles of *n*-nonane (internal standard for GC analysis), 4.0×10^{-3} moles of NMO and 500 μl of H_2O were added. The yellow–brown solution was stirred at room temperature for 24 h. Samples for GC and GC–MS analysis were taken after 3, 6 and 24 h of reaction. MS analysis of the catalyst after the dihydroxylation of cyclopentene, *m/z*: 1456.53 (complex **6** + Na^+).

2.8. Safety precautions

All handling of osmium compounds was performed in a fume hood, while wearing a class P2 (particulate) respirator. The reactions in which OsO_4 was formed were carried out in sealed flasks or, if any gas was leaving the synthesis flask, it was led through a bottle containing oil, rich in unsaturated fatty acids, in order to trap any OsO_4 that might have been developed from the reaction mixture.

3. Results and discussion

3.1. Synthesis and characterisation of the Os–silsesquioxane

The synthesis of the silsesquioxane ligand for the Os-catalyst was performed analogously to that of the functionalised silica support described by Severeyns et al. [9]. Cyclopentyl silsesquioxane *a7b3* (**1**) [16] was used as the precursor for the synthesis of silsesquioxane **3**, which contains a tetrasubstituted olefin moiety to which OsO_4 can be anchored (Fig. 2). In the first step, silsesquioxane **1** was reacted with 3-aminopropyltrimethoxysilane to obtain the amino-functionalised silsesquioxane **2** as the only product (as assessed by means of ESI MS). In the second step, the amino group of silsesquioxane **2** was reacted with 3,4-dimethylcyclohex-3-enylcarbonyl chloride, **C**, to produce silsesquioxane **3**. The synthesis was performed under a N_2 flow and in the presence of a stoichiometric amount of triethylamine to remove HCl formed during the reaction. The formation of silsesquioxane **3** was confirmed by means of ESI MS and ^{13}C NMR analysis.

The acid chloride, **C**, was prepared by means of a three-step synthesis (Fig. 3): (1) Diels–Alder reaction of 2,3-dimethyl-1,3-butadiene with ethyl acrylate to give ethyl 3,4-dimethylcyclohex-3-enyl carboxylate,

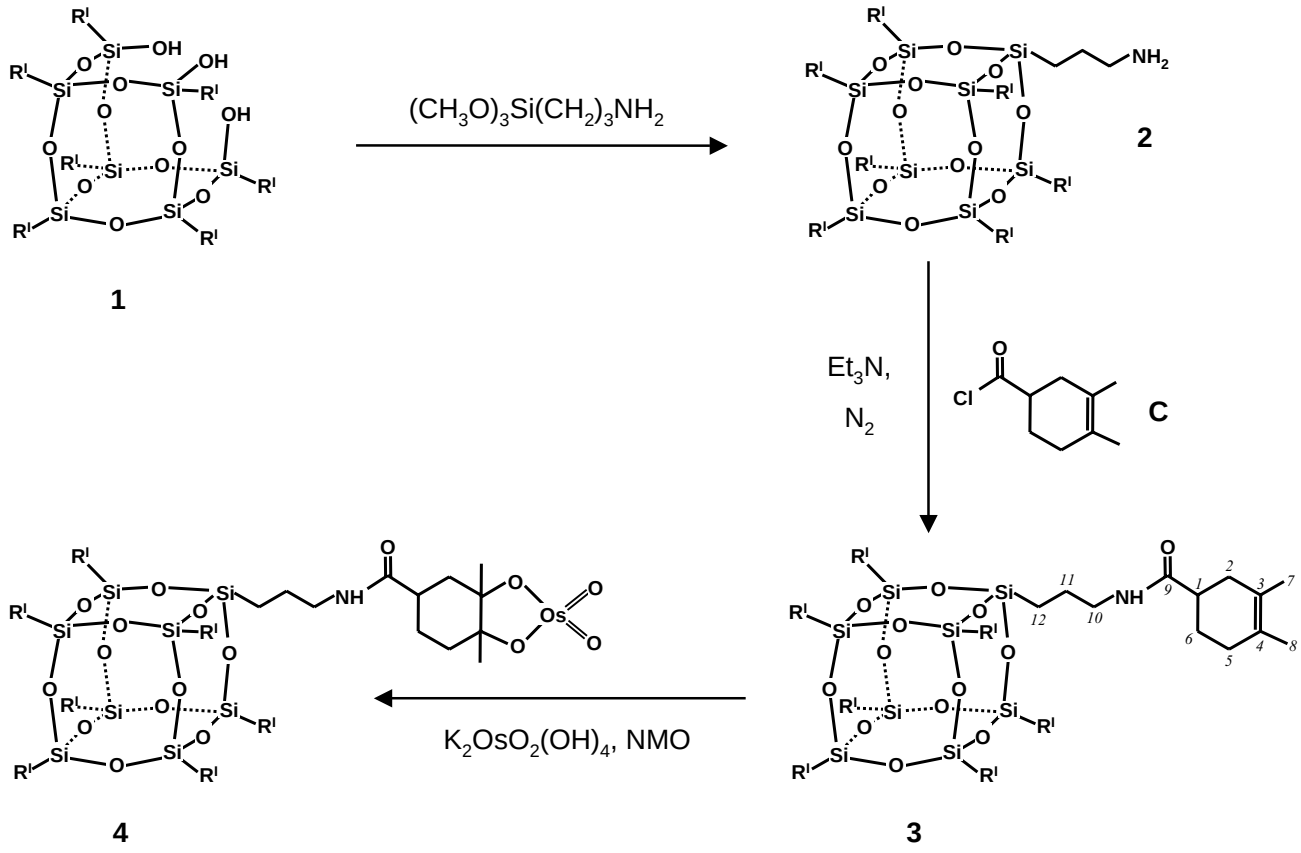

Fig. 2. Procedure for the preparation of the Os–silsesquioxane complex [R^I: cyclopentyl].

A [17]. (2) Hydrolysis of the ester, **A**, to produce 3,4-dimethylcyclohex-3-enyl carboxylic acid, **B**. (3) Conversion of the carboxylic acid, **B**, with $SOCl_2$ to obtain the desired acid chloride, **C**. The reaction was carried out under reflux and by flushing with N_2 to remove the HCl formed, which would otherwise attack the double bond in the cyclohexene ring. All steps of the synthesis of compound **C** were monitored by ^{13}C NMR analysis.

The actual catalytic complex is synthesised by the addition of OsO_4 to the double bond of the functionalised silsesquioxane **3** (in 1:1 molar ratio). To avoid the risks connected with the handling of OsO_4, potassium osmate $K_2OsO_2(OH)_4$ was used as osmium source [18]. In the case of the synthesis of the Os-silsesquioxane catalyst, care must be taken to avoid the reaction of the osmium centre with two instead of just one of the silsesquioxane ligands **3**, since this would lead to the formation of a stable, inactive bis-chelate complex. Therefore, a solution of potassium osmate was oxidised to OsO_4 with, initially, stoichiometric amounts of *N*-methylmorpholine-*N*-oxide (NMO), and then reacted with **3**. However, this reaction did not lead to the desired Os–silsesquioxane **4** as the oxidation of potassium osmate with NMO had not proceeded with a stoichiometric amount of the oxidant. Instead, a 20:1 excess of NMO was needed.

In order to prevent the formation of the bis-chelate while using an excess of NMO, **3** was added to the reaction mixture together with an excess of cyclohexene. The double bond of the cyclohexene would then compete with that of **3** for binding to the osmium centre. Being less sterically hindered and being in large excess (19:1) compared to **3**, cyclohexene will be favoured in reacting with the osmium centre and

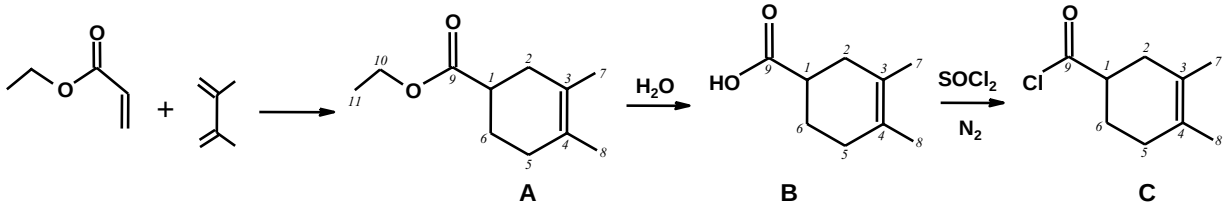

Fig. 3. Procedure for the synthesis of 3,4-dimethylcyclohex-3-enylcarbonyl chloride.

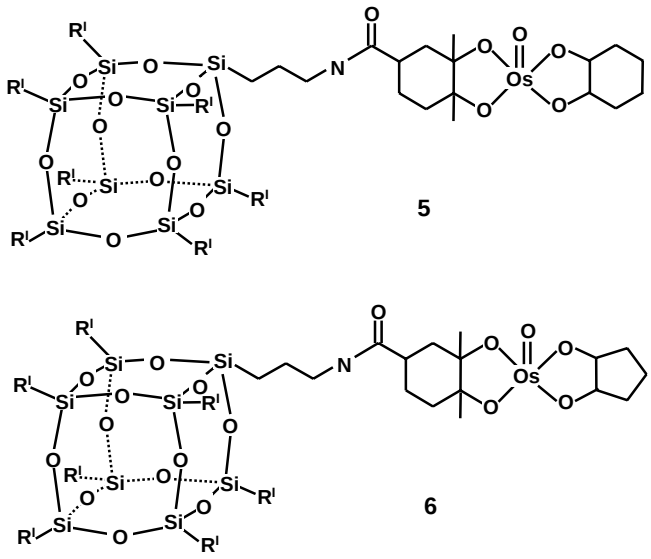

Fig. 4. Os–silsesquioxane complexes **5** and **6** [R^I: cyclopentyl].

will tend to occupy both catalytic sites. Cyclohexene is not a tetrasubstituted alkene, therefore its bond with the osmium centre is labile and in the presence of H_2O and of NMO it undergoes oxidative hydrolysis, yielding 1,2-cyclohexanediol and restoring the catalytic site on the osmium. This process proceeds according to the catalytic cycle for the dihydroxylation of alkenes (Fig. 1). As the concentration of cyclohexene in solution decreases, it becomes more likely that **3** binds to the osmium centre to produce complex **4** and the silesquioxane–Os–cyclohexane bisdiolate complex **5** (Fig. 4). This latter complex is characterised by an osmium centre bound on one side to the tetrasubstituted olefin of **3** and on the other side to cyclohexene. Cyclohexane diolate can be hydrolysed providing the catalytic site for dihydroxylation reactions, while a tetrasubstituted diolate is stable under the reaction conditions employed and, therefore, prevents the formation of free OsO_4 during the catalytic process.

The synthesis was monitored by means of ESI MS: after 3 days of reaction, **5** is the main product, with small amounts of **4** and of unreacted **3** (Fig. 5). A mixture of H_2O, Bu^tOH and CH_2Cl_2 was used as solvent during the synthesis: H_2O was needed to dissolve the potassium osmate and as reactant for the dihydroxylation of cyclohexene, CH_2Cl_2 was used to dissolve the silsesquioxane ligand **3** and Bu^tOH was used to obtain a monophasic solution. At the end of the reaction, dichloromethane was removed by evaporation under reduced pressure and H_2O was added, thereby, causing the precipitation of the silsesquioxane-based compounds that were then collected as a grey-brown powder.

3.2. Catalytic test

A catalytic dihydroxylation test of complex **5** was performed under the same reaction conditions used for testing the heterogeneous silica-supported analogue of the Os–silsesquioxane complex [9]. Two different substrates were investigated: cyclopentene and cyclohexene, the results being reported in Table 1. Conversions and selectivities were determined by GC and GC–MS analysis. The catalyst was active and very selective in the dihydroxylation of both substrates: after 3 h of reaction a $TON_{cyclopentene}$ of 130 and a $TON_{cyclohexene}$ of 414 were recorded. The higher conversion observed for cyclohexene as compared to cyclopentene is consistent with the complex between the

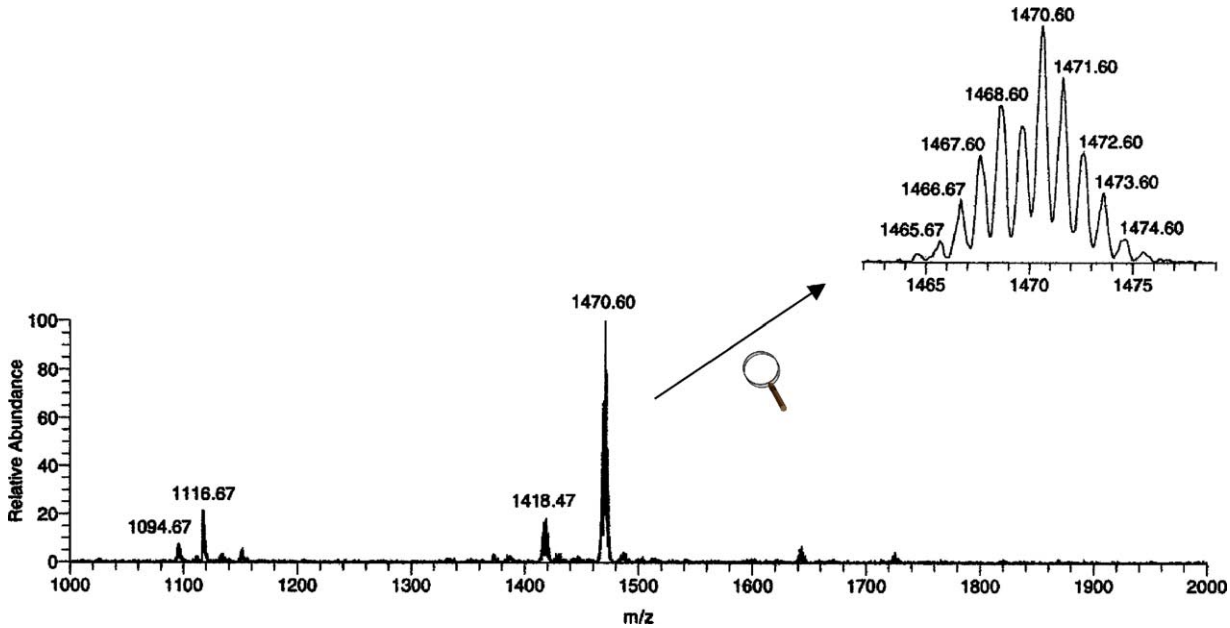

Fig. 5. ESI–MS analysis of the synthesis of Os–silsesquioxane complexes **4** (*m/z*: 1418.47) and **5** (*m/z*: 1470.60). The isotope pattern of osmium is clearly recognisable.

Table 1
Catalytic test of the Os–silsesquioxane in the dihydroxylation of cyclopentene and cyclohexene

Substrate	Time (h)	Conversion (%)	Selectivity (%)
Cyclopentene	3	36	99
	6	50	99
	24	84	99
Cyclohexene	3	99	99

osmium centre and the cyclopentene ring being geometrically more strained than the one involving cyclohexene, and its formation being, therefore, less favourable. The homogeneous Os–silsesquioxane showed similar trends but a higher activity than its silica-supported analogue [9]. For the dihydroxylation of cyclopentene, a conversion of 84% was achieved after 24 h of reaction, while with the silica-supported catalyst a conversion of 83% was obtained after 48 h. The difference in performance is even more evident for cyclohexene, for which total conversion is achieved after 48 h with the heterogeneous catalyst and after just 3 h with the Os-silsesquioxane catalyst.

After the dihydroxylation of cyclopentene proceeded for 24 h, the catalyst was analysed by means of ESI MS: complex **6** (Fig. 4) was the only Os-complex present in solution. This finding is in agreement with the proposed mechanism for the dihydroxylation reaction: the cyclohexane diolate of complex **5** was hydrolysed restoring the catalytic site, which was then active in the dihydroxylation of cyclopentene. The silsesquioxane ligand, bound to the osmium centre via a tetrasubstituted diolate, did not undergo hydrolysis and, therefore, prevented formation of the undesired OsO_4 in solution.

4. Conclusions

An Os–silsesquioxane complex was synthesised, characterised and tested for activity in dihydroxylation reactions. The complex provided a model for a silica-supported Os-catalyst. Careful monitoring of each reaction step helped to define possible surface reaction intermediates and to optimise the synthesis. Characterisation of the homogeneous Os–silsesquioxane confirmed the proposed nature of the heterogeneous catalytic site, where the osmium centre is on one face bound in a stable fashion to the silsesquioxane ligand and on the other face is available for catalysing the dihydroxylation of olefins. The dihydroxylations of cyclopentene and cyclohexene were used as test reactions. In both cases, the homogeneous catalyst displayed higher turnover frequencies than the heterogeneous one, while keeping the same selectivity (99%).

The Os-silsesquioxane catalyst can be separated from the reaction mixture by precipitation induced by removal of CH_2Cl_2 and addition of H_2O, and efficiently reused for further dihydroxylation reactions.

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