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Dimerisation of cyclooctene using Grubbs' catalysts

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ABSTRACT

The dimerisation of cyclooctene (COE) to 1,9-cyclohexadecadiene, a molecule of interest to the fragrance industry, has been achieved using ruthenium catalysts in organic solvents with significantly better selectivities (47–74%) and yields (39–60%) than previously reported (34% and 30%, respectively). Grubbs' first and second generation catalysts, the Hoveyda–Grubbs' catalyst and a phosphonium alkylidene catalyst were tested in a range of organic solvents and ionic liquids (ILs), including 1:1 IL/dichloromethane mixtures and biphasic IL+ pentane systems. The best results (74% selectivity, 60% yield) were obtained using Grubbs' first generation catalyst in 1,2-dichloroethane. The formation of trimer, tetramer and other higher molecular mass products were found to be favoured at low catalyst loadings (<8.5 mol%) and high concentration of cyclooctene (>0.77 mM). Studies of metathesis reactions using 1,9-cyclohexadecadiene as substrate indicated that the monomer–dimer and monomer–trimer reactions are faster than the dimer–dimer reaction. The use of IL media allowed for the recyclability of the catalyst, although a drop in the yield of dimer generally occurred after the first run. Heterogeneized catalysts, where the IL-catalyst system was immobilised onto silica, resulted in fast reactions leading to poor yields of dimer.

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1. Introduction

Olefin metathesis is a popular and useful reaction which occurs when two olefins exchange alkylidene fragments in the presence of certain transition-metal compounds [1]. This can result in several different outcomes [2]; cross-metathesis (CM) involving the straight swapping of groups between two acyclic olefins; ring-closing metathesis (RCM) the closure of large rings; ringopening metathesis (ROM), formation of dienes from cyclic and acyclic olefins; ring-opening metathesis polymerisation (ROMP), the polymerisation of cyclic olefins, and acyclic diene metathesis polymerisation (ADMET), the polymerisation of acyclic dienes. The metathesis reaction is reversible and forms both the *cis* and *trans* isomers. It allows the synthesis of well-defined, functionalised polymers and complex architectures, including medium sized and large ring structures [3].

Until the 1980s, metathesis reactions were carried out using catalysts based on transition metal salts such as WCl_6/Bu_4Sn , MoO_3/SiO_2 and Re_2O_7/Al_2O_3 [4]. Although limited due to their sensitivity to many functional groups, these catalysts have been commercially employed widely. A family of well-defined

catalysts of general formula [M(=CHR)(=NAr)(OR')₂] (M = Mo or W), developed by Schrock and co-workers showed high activity over a diverse range of olefins [5]. However, the development of the Grubbs' 1st generation catalyst in 1995, 1 (Scheme 1), is mainly credited with putting olefin metathesis at the forefront of organic synthesis [6]. Subsequently, the more stable second generation Grubbs' catalysts were reported [7], such as 2 (Scheme 1), containing a NHC ligand with bulky side groups. However, these catalysts are homogeneous and subsequently have two major disadvantages; namely their poor recyclability and difficulty in removing ruthenium waste from the final products. Following this, Hoveyda and co-workers developed the Hoveyda-Grubbs' third generation catalysts (e.g., catalyst 3, Scheme 1) [8]. These catalysts are based on a release and return olefin metathesis mechanism and are commonly referred to as 'boomerang catalysts', as the styrenyl ligand can readily detach from the metal centre, allowing metathesis to take place, then reattach to the metal after the reaction. Since the development of these catalysts, there have been significant improvements in catalyst design, based on Grubbs' catalysts, for metathesis reactions [9]. In particular, of interest to the present research, are the ionic phosphonium catalysts [{Ru=CH(PCy₃)}(H₂IMes)Cl₂][X] (H₂IMes = 1,3bis(mesityl)-2-imidazolidinylidene; $X = B(C_6F_5)_4$, BF₄, BPh₄, OTf (4, Scheme 1)) which have been found to have superior activity to Grubbs' catalysts in some instances. Specifically, the RCM of 5,5-dicarbethoxy-2-methyl-l,7-octadiene using these ionic catalysts gave approximately 90% conversion, compared with only 5%

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Scheme 1. Grubbs' first (1) and second (2) generation catalysts, Hoveyda–Grubbs' catalyst (3) and phosphonium alkylidene catalyst (4).

conversion using catalyst **2** [10]. Recently, the utilisation of ionic catalysts has been combined with ionic liquids to provide an effective recyclable catalytic system. The charged state of the catalyst enhances the ability of the ionic liquid to retain the catalyst on recycle and reduces the leaching into the organic phase [11]. In addition, ionic liquids have been found to be suitable media for metathesis reactions using conventional Grubbs' catalysts [12]. For example, the dimerisation of 1-octene to form 7-tetradecene using the Hoveyda–Grubbs' catalyst has been reported to give improved yields and selectivities when ionic liquids are used, in comparison to conventional solvents or in solventless conditions [12b,c].

In this paper, the use of Grubbs' catalysts is investigated for the dimerisation of cvclooctene (COE) to 1.9-cvclohexadecadiene (Scheme 2) in both organic solvents and ILs. 1,9-Cyclohexadecadiene has potential as an intermediate for macrocyclic musk compounds [13]. Muscone for example is the principal odour constituent of musk pod; however, due to its rare occurrence in nature, many synthetic routes have been developed [14]. In addition, 1,9-cyclohexadecadiene can also be used in the production of Animusk[®] [13a]. Therein, COE is ultimately obtained from butadiene and then used to produce 1,9-cyclohexadecadiene through a self-metathesis reaction. Finally, after selective epoxidation of one of the double bonds, followed by its rearrangement, Animusk® is produced (Scheme 2). Selectivity in the dimerisation process is problematic with trimer, tetramer and higher molecular mass polymers being formed readily. Previous research focusing on the dimerisation of cycloolefins has been limited due to the fast polymerisation and low selectivities. The formation of cyclic derivatives vs. linear polymers is generally favoured at higher temperatures and lower reactant concentrations, but also depends on a variety of factors such as solvent, reaction time and catalyst [15]. Dimerisation of $C_7 - C_{10}$ cycloolefins was reported by Warwel et al.



Scheme 2. Dimerisation of COE to 1,9-cyclohexadecadiene, which is used in the production of Animusk[®].

[16] using Soxhlet extraction and a heterogeneous (rhenium heptoxide/aluminium oxide/tetramethyltin) catalyst in n-hexane at 35–50 °C. With the exception of the C_8 (COE) ring, all ring sizes were found to produce reasonable selectivities and yields of the corresponding dimers (59-80% selectivity, 58-68% yield). However, in the case of COE, a significantly reduced selectivity (34%) and yield (30%) of the dimer was obtained. Dimerisation of COE has also been carried out using cyclic olefins and open-chain olefins together [17], using WOCl₄/Al(C₂H₅)₂Cl (8.6% yield after 24 h) or $WOCl_4/Sn(C_4H_9)_4$ (3.4% yield after 14 min) as catalyst. It was found that WOCl₄/Sn(C₄H₉)₄ leads to more selective reactions, whereas $WOCl_4/Al(C_2H_5)_2Cl$ had a higher thermal stability. However, products of higher molecular weight were dominant and due to the low concentration of the dimer, it was impossible to separate the products. More recently, tandem Ir/Mo catalyst systems have been used for the dehydrogenation and subsequent oligomerisation of cyclooctene, with 0.7-15% of dimer found in the mixtures of cycloalkenes obtained [18]. Despite the increasing popularity of Grubbs' ruthenium catalysts for olefin metathesis, currently there are no reports of their use on the dimerisation of cycloolefins.

2. Experimental

2.1. General

Cyclooctene, decane and solvents (dichloromethane, 1,2dichloroethane, ethyl acetate, 2-propanol, benzene and pentane) were obtained from Aldrich, distilled and/or dried over activated molecular sieves, degassed with nitrogen for 1–2 h and stored under a nitrogen atmosphere. Methanol and tetrahydrofuran were collected from a MBRAUN manual solvent purification system, under nitrogen and dried over activated molecular sieves (85 °C). All other reagents were obtained from Aldrich and used as received.

NMR spectra were performed on either a Bruker Avance DRX (300 MHz) or DPX (500 MHz) spectrometer. GC-FID samples were analysed using a Hewlett Packard 6890 GC fitted with an RTX-5 column (30 m, 0.25 µm diameter). GC–MS (Perkin Elmer Turbo Mass) was performed using a PE5MS column (length, 30 m;

thickness, 0.25 $\mu m;$ IDO, 0.32 mm). Decane was used as internal standard for GC analysis.

2.2. Ionic liquids

The ionic liquids [A][NTf₂] (A=1-butyl-3-methylimidazolium (C₄mim), 1-butyl-1-methyl-pyrrolidinium (C₄Pyr), 1-butyl-2,3-dimethylimidazolium (C₄dmim); $NTf_2 = N(CF_3SO_2)_2$) and [C₄mim][X] (X=PF₆, CF₃SO₃ (OTf)) were prepared in-house from the corresponding bromide salts and LiNTf2 or NaX $(X = PF_6, OTf)$ following methods similar to those previously described [19]. Analogous procedures were also used to prepare $[A][NTf_2]$ (A = methyl(trioctyl)ammonium (N_{8.8.8.1}), tetradecyl(trihexyl)phosphonium (P_{6.6.6.14})), using the chloride salts [N_{8,8,8,1}]Cl and [P_{6,6,6,14}]Cl, which were obtained from Aldrich and Cytec, respectively. The ILs were dried for 24-48 h under high vacuum at 60–70 °C prior to use, the resulting ILs typically containing a residual water content of <0.02 wt% as determined by Karl Fischer titration. They were stored and handled in a glove box or under nitrogen atmosphere. The results of the catalytic reactions were reproducible when different batches of IL were used, and no attempts were made to determine the residual content of halide or 1-methylimidazole in the ILs. The presence of such impurities, however, have been shown to have an effect in the self-metathesis of 1-octene in ILs [12c].

2.3. Catalysts

Catalysts **1**, **2** and **3** were obtained from Aldrich, stored and handled in a glove box, and used without further purification. Catalyst **4** and its precursor $[(Ru \equiv C)(PCy_3)(H_2IMes)Cl_2]$ were prepared following literature procedures [10], as summarised below. Feist's Ester was also synthesised as previously reported [20].

[(Ru=C)(PCy₃)(H₂IMes)Cl₂]: Grubbs' 2nd generation catalyst [2] (1.0 g, 1.178 mmol) was weighed in a glove box and dissolved in dry dichloromethane (10 cm³). To this, a solution of Feist's Ester (0.2 g, 1.178 m mol) in dichloromethane (5 cm³) was added. The resulting solution was stirred under nitrogen for 15 h, after which the solvent was removed under vacuum. The resulting brown residue was dissolved in pentane (15 cm³) and sonicated for 10 min. The solid was then filtered and repeatedly washed with cold pentane, forming a light brown solid which was dried under vacuum (0.69 g, 75%). ¹H NMR (300 MHz, CDCl₃, δ): 6.96 (s, 2H, Mes-*m*H), 6.89 (s, 2H, Mes*m*H), 4.07 (m, 4H, (CH₂)₂ bridge in H₂IMes), 2.54 (s, 6H, Mes-oCH₃), 2.49 (s, 6H, Mes-oCH₃), 2.29 (s, 3H, Mes-*p*CH₃), 2.24 (s, 3H, Mes*p*CH₃), 1.88 (m, P(C₆H₁₁)₃), 1.65 (m, P(C₆H₁₁)₃), 1.17 (m, P(C₆H₁₁)₃). ³¹P NMR (300 MHz, CDCl₃, δ): 35.4 (s).

[{Ru=CH(PCy₃)}(H₂IMes)Cl₂][OTf] (**4**): A solution of triflic acid (0.039 g, 0.259 mmol) in dichloromethane (5 cm^3) was added to a solution of $[(Ru=C)(PCy_3)(H_2IMes)Cl_2]$ (0.2 g, 0.259 mmol) in dichloromethane (5 cm^3) , and the mixture stirred for 30 min. The solvent was removed under vacuum, and the resulting solid suspended in pentane (15 cm³) and stirred for 10 min. The pentane was then decanted, leaving a brown solid which was dried under vacuum (0.18 g, 90%). The product obtained was used without further purification. However, fast degradation of 4 was observed in CDCl₃ by ¹H NMR, most likely producing [H₂IMesH][OTf] [21] and other unidentified product(s). Attempts to obtain a better ¹H NMR spectrum and/or study the degradation of 4 in solution in detail were not made. The major product in the ¹H NMR spectrum after dissolution of the catalyst in CDCl₃ corresponded well with the spectroscopic data previously reported for 4 [10]. After 72 h in solution, the signals for 4 had disappeared leaving only those attributed to [H₂IMesH][OTf] [21] plus other PCy₃-containing impurities. ¹H NMR (300 MHz, CDCl₃, δ): [fresh solution; signals attributed to [H₂IMesH][OTf] are indicated with *; the approximate **4**:[H₂IMesH][OTf] ratio is 2:1]: 18.43 (s, 1H, Ru = CH)⁴, 7.06 (s, 4H, Mes-*m*H)⁴, 7.00 (s, 4H, Mes-*m*H)^{*}, 4.52 (s, 4H, (CH₂)₂ bridge in H₂IMesH)^{*}, 4.11 (s, 4H, (CH₂)₂ bridge in H₂IMes)⁴, 2.41 (s, 12H, Mes-oCH₃)⁴, 2.39 (s, 6H, Mes-*p*CH₃)⁴, 2.37 (s, 12H, Mes-oCH₃)^{*}, 2.32 (s, 6H, Mes-*p*CH₃)^{*}, 1.94 (broad m, P(C₆H₁)₃)^{4+other}, 1.77 (broad m, P(C₆H₁)₃)^{4+other}, 1.36 (broad m, P(C₆H₁)₃)^{4+other}.

2.4. ICP analyses

ICP analyses were performed at the ASEP unit in Queen's University, Belfast. Samples to determine the amount of catalyst dissolved in various solvents were prepared by adding 5.4 mg (0.007 mmol) of 1 and 10 mL of solvent (dichloromethane, methanol, hexane, benzene, ethyl acetate, tetrahydrofuran, 2-propanol or 1,2-dichloroethane) into a Schlenk flask, under nitrogen. The mixtures were stirred for 10 min and then passed through a sintered glass funnel. Any undissolved catalyst remaining on the funnel was washed with dichloromethane (5 mL) into a crucible. The dichloromethane was allowed to evaporate and the remaining residue in the crucible was submitted for ICP-MS analysis. A sample was also analysed where the catalyst was dissolved in dichloromethane and no filtration was undertaken, giving a value of 268 ppm. Compared to this standard the % of undissolved Ru in each solvent was: dichloromethane (4%), 1,2-dichloroethane (13%), ethyl acetate (15%), methanol (18%), benzene (27%), tetrahydrofuran (48%), 2-propanol (49%) and pentane (84%). ICP analyses to determine the loss of Ru in reactions using catalyst **3** or 4 in IL/dichloromethane or IL/pentane were carried out on the IL/catalyst phase after three recycles, and the results compared to the standard. Prior to analysis, the organic solvent was removed, as described in Section 2.8, and the samples dried under high vacuum for ca. 24 h.

2.5. Dimerisation of COE in organic solvents

To 0.066 mmol of catalyst [1 (54 mg), 2 (56 mg), 3 (41 mg) or 4 (60 mg)] into a Schlenk flask, under nitrogen, 100 mL of solvent (dichloromethane, methanol, hexane, benzene, ethyl acetate, tetrahydrofuran, 2-propanol or 1,2-dichloroethane) were added, followed by degassed cyclooctene (0.1 mL, 0.77 mmol) and decane (0.1 mL, 0.51 mmol). The reaction mixtures were stirred at *r.t.*, for 24 h, under nitrogen. Samples (1 mL) for GC analysis were taken every 10 min for the first hour and subsequently every hour for 8 h. Finally, a 24 h sample was taken. Each sample was quenched with tert-butylhydroperoxide (TBHP, 2 drops), diluted with diethyl ether (1 mL) and filtered through a silica plug prior to being submitted for GC analysis.

For experiments at different catalyst loadings, the reactions were carried out as above, in dichloromethane, using 14, 27, 54 and 108 mg (2.2, 4.3, 8.5 and 17.1 mol%, respectively) of catalyst **1**. The same procedure was also used for reactions at different substrate concentrations, using 0.01, 0.05, 0.1, 0.2 and 1 mL (0.077, 0.35, 0.77, 1.54 and 7.7 mmol, respectively) of COE and 0.01, 0.05, 0.1, 0.2 and 1 mL, respectively, of decane.

2.6. Reactions involving 1,9-cyclohexadecadiene

For the reaction of COE and 1,9-cyclohexadecadiene, Grubbs' 1st generation catalyst **1** (54 mg, 0.066 mmol) was weighed into a Schlenk flask, under nitrogen. Distilled dichloromethane (100 mL) was added, followed by degassed cyclooctene (0.1 mL, 0.77 mmol), 1,9-cyclohexadecadiene (0.2 mL, 0.77 mmol) and decane (0.1 mL, 0.51 mmol). The reaction mixture was stirred, at *r.t.*, for 24 h, under nitrogen. Samples for GC analysis were obtained as described above for the dimerisation of COE. The reaction using only

1,9-cyclohexadecadiene was carried out in the same way but without adding COE.

2.7. Dimerisation of COE in ILs or IL/dichloromethane

Catalyst **1** (5.4 mg, 0.007 mmol), **3** (4.1 mg, 0.007 mmol) or **4** (6.0 mg, 0.007 mmol) was weighed into a Schlenk flask, under nitrogen. To this was added the corresponding IL (10 mL), followed by degassed COE (10 μ L, 0.077 mmol) and decane (10 μ L, 0.051 mmol). The reaction mixture was stirred, at *r.t.*, for 24 h, under nitrogen. Samples (1 mL) for GC analysis were taken every 10 min for the first hour and subsequently every hour for 8 h. Finally, a 24 h sample was taken. Each sample was quenched with TBHP (2 drops), diluted with diethyl ether (1 mL) and filtered through a silica plug prior to being submitted for GC analysis. For reactions in 1:1 IL/dichloromethane, the same procedure was followed but using 5 mL of IL and 5 mL of degassed dichloromethane instead of 10 mL of IL.

2.8. Recycling of catalyst **3** or **4** in IL/dichloromethane or IL/pentane

Catalyst **3** (4.1 mg, 0.007 mmol) or **4** (6.0 mg, 0.007 mmol) was weighed into a Schlenk flask, under nitrogen. To this was added ionic liquid ($[C_4Pyr][NTf_2]$ or $[C_4mim][NTf_2]$, 5.0 mL) and the corresponding organic solvent (degassed dichloromethane or pentane, 5 mL), followed by degassed COE (10 μ L, 0.077 mmol) and decane (10 μ L, 0.051 mmol). The reaction mixture was stirred, at *r.t.*, for 6 h, under nitrogen. The organic solvent was removed under vacuum (dichloromethane) or *via* a syringe (pentane). The IL layer was then extracted with pentane (3 × 10 mL). The combined pentane washes were reduced under vacuum and submitted for GC analysis. To begin a new reaction fresh dichloromethane or pentane and substrates were added to the IL. This process was repeated up to three times for each catalyst.

2.9. Preparation of supported catalyst 3

Catalyst **3** (41 mg, 0.066 mmol) was weighed into a Schlenk flask, under nitrogen. To this was added dichloromethane (5 mL), $[C_4 mim][NTf_2]$ (0.1 mL) and pre-dried Davicat sp 550-10654 silica, pH 4 (0.2 g). This was stirred for 10–15 min and the dichloromethane removed under vacuum. Further drying under vacuum (4–5 h) produced the supported catalyst as a green powder.

2.10. Dimerisation of COE with supported catalyst **3** and recycling of the catalyst

Catalyst **3** was immobilised onto silica as described above and used directly. To this was added pentane (20 mL), COE (10μ L, 0.077 mmol) and decane (10μ L, 0.051 mmol). The reaction mixture was stirred, at *r.t.*, for 6 h, under nitrogen. After 6 h the pentane layer was removed, *via* a syringe and the supported catalyst was washed with pentane ($3 \times 20 \text{ mL}$). The combined pentane washes were reduced under vacuum and submitted for GC analysis. To begin a new reaction fresh pentane and substrates were added to the silica. This was repeated twice for a total of 3 reactions.

3. Results and discussion

3.1. Dimerisation of COE in dichloromethane with catalyst 1

The dimerisation of COE was studied using dichloromethane as solvent and Grubbs' 1st generation catalyst **1** in the first instance. The reaction was initially screened as a function of catalyst loading and was carried out using 0.77 mM of COE at *r.t.*, for 8 h (see ESI). It was observed that as the loading of catalyst **1** in dichloromethane



Scheme 3. Proposed routes for formation of dimer (D), trimer (Tri) and tetramer (Tet) starting from COE (M = monomer).

was increased from 2.2 mol% to 17.1 mol%, the yield of dimer increased from 49% to 69%. However, only a limited increase in dimer yield (3%) was obtained on doubling the catalyst loading from 8.5 mol% to 17.1 mol%. Therefore, 8.5 mol% was used in further experiments as it provided the best balance between activity and yield. These observations are as expected, with a higher catalyst loading there is a lower amount of monomer available to polymerise into products of higher molecular mass.

As previously stated, dilute conditions are used to favour the low molecular weight products and to prevent the formation of polymer. The selectivity/yield to dimer was therefore investigated as a function of the COE concentration from 0.07 to 7.70 mM at a constant catalyst concentration of 6.6 \times 10^{-4} M (8.5 mol%). All reactions were found to result in >98% COE conversion with an average initial rate of 0.023 (mols COE)(mols cat)⁻¹ s⁻¹ (see ESI). A small increase in dimer production was observed on increasing the COE concentration from 0.39 to 0.77 mM from 51 to 60% yield; however, thereafter, the yield significantly reduces up to a COE concentration of 7.70 mM forming only 28% yield of dimer. These observations are expected as there will be a critical amount of COE present such that COE dimerisation is favoured due to the slower dimer+COE and dimer + dimer reactions (Scheme 3). However, at high concentrations of COE, the dimer concentration will also be significant which will favour further oligomerisation and thus a reduction in the dimer yield.

In summary, under optimised conditions with catalyst **1** in dichloromethane (8.5 mol% of catalyst, 0.77 mM of COE, at *r.t.* for 8 h; Table 1, entry 1a), 99% conversion of COE and a 60% yield of 1,9-cyclohexadecadiene was achieved with the ratio of dimer:trimer:tetramer being 63:30:7, respectively. In comparison with previous reports using Re_2O_7/Al_2O_3 catalyst activated by SnMe₄ where the dimer was obtained with 34% selectivity at 90% conversion [16], a significant improvement is found. In order to gain an understanding of the processes involved in the formation of the trimer and tetramer compared with dimer and their relative rates, the dimer was used as a substrate both in the presence and absence of COE. Scheme 3 shows four proposed routes for the formation of the dimer, trimer and tetramer whereby:

- (a) two monomers of COE react to form dimer;
- (b) a monomer of COE reacts with the dimer forming trimer;
- (c) a monomer of COE reacts with the trimer producing the tetramer; or
- (d) two dimers react to produce tetramer.

Fig. 1a shows the time course from the reaction of COE and 1,9-cyclohexadecadiene. As the COE and dimer react, both trimer and tetramer products are formed with the trimer being the dominant product. Fig. 1b shows the result from the self-metathesis of 1,9-cyclohexadecadiene. After a short induction period, the dimer reacts to again form both trimer and tetramer. In addition, a

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Table 1

Summary of the results for the self-metathesis reaction of COE (entry 1*a*), the reaction between COE and 1,9-cyclohexadecadiene (dimer, entry 1*b*) and the self-metathesis reaction of the dimer (entry 1*c*).^a

Entry	Initial rate ^b		Conversion of COE (%)	Yield of dimer (%)	Ratio of C	Ratio of COE, dimer, trimer and tetrar		
	COE	Dimer			COE	Dimer	Trimer	Tetramer
1a	0.021	-	99	60	-	63	30	7
1b	0.022	0.009	94	-	-	47	36	17
1c	-	0.003	-	_	9	48	32	11

^a All reactions carried out using 0.77 mM of substrate, 8.5 mol% of catalyst **1**, at *r.t.*, for 8 h in dichloromethane. All data obtained by GC analysis.

^b (mols COE)(mols cat)⁻¹ s⁻¹.

small amount of COE is also produced via the dissociation of the dimer. Although only dimer is present at the start of the reaction, more trimer than tetramer is formed, indicating that dimer decomposition and subsequent reaction of the monomer with dimer is faster than dimer-dimer reaction (route (d), Scheme 3). It is, therefore, likely that the tetramer formed is also due to the reaction of the monomer with trimer (route (c), Scheme 3) and there is little reaction via the direct reaction of two dimer molecules. This may be due to steric hindrance as the monomer should be able to bind to the Ru centre more easily than the dimer and thus this reaction dictates the pathway observed. In addition, the presence of trans olefins in the dimer makes this molecule less reactive towards the Ru centre than the monomer, with a highly reactive *cis*-olefin [9]. This is exemplified by comparing the initial rates of reaction (Table 1). It is clear that the reactivity of the dimer both with itself and with the monomer is significantly slower than that of the monomer with itself; and that the monomer rate is not significantly altered by the presence of the dimer.

During the course of these reactions the dimer, 1,9-cyclohexadecadiene, can be observed in three isomeric forms, namely *cis-cis*, *trans-trans* and *cis-trans*. As found in previously reported studies, the isomeric ratio of the *cis-cis:cis-trans:trans-trans* isomers was found to be 0.2:0.6:0.2 [16].

3.2. Solvent studies

Solvents are known to have a significant effect on both rates of reaction and the reaction selectivity [1a,22]. In order to examine the effect of catalyst solubility and stability in a variety of solvents as well as the effect of polarity and protic/aprotic nature of the solvent, the dimerisation of COE was performed using catalyst 1 in 1,2-dichloroethane, benzene, ethyl acetate, pentane, tetrahydrofuran, 2-propanol and methanol. The results of this study are summarised in Table 2 (entries *2a*, *2e*, *2h*, *2k*, *2n*–2*q*). Moderate to good activity was observed in all solvents, with the exception of methanol, where no reaction occurred. Tetrahydrofuran resulted in a low conversion of COE (35%); however, no dimer was

produced and polymeric products were observed. 2-Propanol also had a low overall conversion of COE (30%) and an extremely slow initial rate; however, some dimer (58% selectivity) albeit with a poor yield (15%) was obtained. In this case, trimer and tetramer were also present and the reaction was dominated by polymeric products. In contrast, the use of pentane resulted in good conversion of COE (55%) and good selectivity to dimer was found (63%) but the overall dimer yield was only 30%. Four solvents resulted in COE conversions of >90% namely ethyl acetate, benzene, 1,2dichloroethane and dichloromethane: of which ethyl acetate has the lowest initial rate, 0.013 (mols COE)(mols cat) $^{-1}$ s⁻¹. Furthermore, ethyl acetate also resulted in the lowest COE conversion (92%) after 8 h and it produced the smallest dimer yield (45%) of this group of solvents. Dichloromethane and benzene produce similar results with initial rates of 0.021 and 0.019 (mols COE) (mols cat)⁻¹ s⁻¹, respectively. Both solvents also led to almost quantitative conversion of COE with a similar ratio of dimer:trimer:tetramer (63:30:7) and dimer yield (60%). 1,2-Dichloroethane also showed a high initial rate, $0.021 \text{ (mols COE)}(\text{mols cat})^{-1} \text{ s}^{-1}$, and resulted in 100% conversion of COE with a high selectivity and yield of dimer (74% selectivity, 60% yield) and only a small trimer selectivity (16%). Of the solvents studied, 1,2-dichloroethane was found to give the highest selectivity and yield of the desired dimer product.

One reason why the reaction does not proceed well in some solvents may be due to catalyst solubility and/or stability (*i.e.*, colour changes can be observed throughout the reactions). In dichloromethane, the catalyst **1** dissolved rapidly in the solvent forming a purple solution which slowly turned brown during the course of the reaction. Whereas a similar colour change is often attributed to catalyst reaction, it the present case may be indicative of catalyst decomposition/poisoning as, thereafter, no significant reaction was observed. Analogous colour changes were also observed in the other solvents used, but tetrahydrofuran showed the fastest rate, with solutions turning brown only after a few minutes, possibly due to the high coordinating ability of tetrahydrofuran. In addition, in some solvents the catalyst was only found to be partially soluble and this contributed to the low



Fig. 1. Distribution of products (as determined by GC) during (a) the reaction of COE and 1,9-cyclohexadecadiene (0.77 mM each) and (b) the self-metathesis reaction of 1,9-cyclohexadecadiene (0.77 mM). Both reactions carried out in dichloromethane using catalyst **1** (8.5 mol%) at *r.t.* (■ COE, ● dimer, ▲ trimer, ▼ tetramer).

Table 2
Kinetic data for the dimerisation of cyclooctene. ^a

Entry	Solvent	Catalyst	Initial rate ^b	Conversion of COE (%)	Yield of dimer (%)	Ratio of dimer, trimer and tetram		nd tetramer
						Dimer	Trimer	Tetramer
2a	Diclhoro-methane	1	0.021	99	60	63	30	7
2b	Diclhoro-methane	2	0.032	100	50	55	32	14
2c	Diclhoro-methane	3	0.010	98	47	48	37	15
2d	Diclhoro-methane	4	0.031	97	43	68	25	7
2e	1,2-Dichloro-ethane	1	0.021	100	60	74	16	10
2f	1,2-Dichloro-ethane	2	0.033	100	43	64	29	7
2g	1,2-Dichloro-ethane	3	0.027	100	58	64	32	4
2h	Benzene	1	0.019	98	60	63	30	7
2i	Benzene	2	0.032	100	45	50	33	17
2j	Benzene	3	0.032	100	39	47	37	16
2k	Pentane	1 ^c	0.010	55	30	63	25	13
21	Pentane	2	0.031	94	49	54	33	14
2m	Pentane	3 ^{c,d}	0.029	95	48	54	34	12
2n	Ethyl acetate	1	0.013	92	45	65	30	5
20	Tetrahydrofuran	1	0.009	35	-	-	-	-
2р	2-Propanol	1 ^c	0.001	30	15	58	37	5
2q	Methanol	1 ^c	0.000	0	0	-	-	-

^a All reactions performed using 0.77 mM of COE and 8.5 mol% catalyst, at *r.t.* for 8 h. All data obtained by GC analysis.

^b (mols COE)(mols cat)⁻¹ s⁻¹.

^c The catalyst did not fully dissolve.

^d Estimated concentration of catalyst **3** in solution is 4.6×10^{-5} M.

activity found. ICP studies following catalyst dissolution showed that only 42 ppm of Ru dissolved in pentane; 136 ppm and 139 ppm were found in 2-propanol and tetrahydrofuran, respectively. Better solubility was found in benzene (196 ppm), methanol (220 ppm), ethyl acetate (229 ppm) and 1,2-dichloroethane (231 ppm); with dichloromethane giving the best solubility (257 ppm).

Solubility alone cannot explain the variation in the solvent effect. It is clear that protic solvents do not favour the reaction as both primary and secondary alcohols are found to result in the lowest activity. Degradation of Grubbs' catalysts in the presence of protic functionalities has previously been reported, in particular, ruthenium hydrido carbonyl species have been isolated upon reaction with primary alcohols [23]. Regarding polarity, both nonpolar and polar solvents can result in high conversion and similar selectivity, for example dichloromethane and benzene. Therefore, the polarity per se is not the important factor. However, the initial rate in benzene is slightly slower than in 1,2-dichloroethane or dichloromethane, in agreement with previous observations that more polar solvents lead to higher initiation rates [22b]. The coordinating ability of each solvent to the metal centre of the catalyst is a contributing factor. 1,2-Dichloroethane, dichloromethane, benzene and pentane will only weakly coordinate to the ruthenium centre whereas the oxophilic centre will coordinate strongly to the oxygen lone pairs in tetrahydrofuran, 2-propanol, methanol and ethyl acetate. This may hinder the olefin binding to the metal centre to form the metallacyclobutane intermediate which is critical for the metathesis reaction [1]. These effects are consistent with those reported previously for the metathesis of 1-octene, where low conversions have been found in tetrahydrofuran or alcohols compared to less coordinating solvents such as toluene [12c,22a,24]. Herein, the combination of low coordinating ability and high solubility indicates why 1,2-dichloroethane shows the highest activity for the COE conversion.

3.3. Catalyst studies

Of clear importance is the overall activity of the catalyst. In order to maximise the yield of dimer, a balance in the activity of the catalyst must be obtained between too little COE conversion with high selectivity to the dimer and too high a COE conversion such that it is not possible to control the oligomerisation. A comparison of the catalysts **1**, **2** and **3** in 1,2-dichloroethane, dichloromethane, benzene and pentane is shown in Table 2 (entries 2a-2c and 2e-2m). With the exception of catalyst **1** in pentane, all catalysts resulted in \geq 94% conversion of COE; however, a significant variation in dimer selectivity and yield was observed. In all cases, the dimer was found to be the dominant product and significant selectivity was observed compared with the trimer and tetramer. However, in only one case, that of catalyst **1** in 1,2-dichloroethane, was a sufficiently high yield (82%) and selectivity (74%) towards the dimer obtained.

The activity results herein are comparable with those reported previously for Grubbs' catalysts over a range of metathesis reactions [7,25]. In most cases, as well as for COE dimerisation, catalysts **2** and **3** were found to be more active than **1**, with the exception of the reaction in dichloromethane (entry *2c*, Table 2). However, due to this high activity, increased polymerisation of COE is observed and consequently less yield dimer is obtained. Therefore, although catalysts **2** and **3** have been found to have better activity for numerous reactions they are too active, compared with **1**, for the selective dimerisation of COE. Catalyst **1** provides a balance in being able to activate the monomer but not have too high an activity to over oligomerise the monomer or further react the dimer.

3.4. Dimerisation of COE in ILs

In order to examine the possibility of recycling the catalyst, a range of ionic liquids were also examined for the dimerisation of COE using catalysts **1** and **3** as a function of the anion with a common cation ($[C_4mim]$ anion; anion = $[NTf_2]^-$, $[PF_6]^-$, $[OTf]^-$) and of the cation with a common anion (Cation $[NTf_2]$; cation = $[C_4Pyr]^+$, $[C_4dmim]^+$, $[N_{8,8,8,1}]^+$ and $[P_{6,6,6,14}]^+$). The reactions were performed in either pure IL or in a equivolume IL/dichloromethane homogeneous mixture. The dichloromethane was required in the case of catalyst **1** which had a low solubility in the ILs. In contrast, catalyst **3** was, in general, soluble in the ILs and the addition of dichloromethane did not make a substantial difference to the results. Although reaction was observed in all ionic liquids, significant polymerisation was found with the exception of those ILs based on $[NTf_2]^-$. Overall, the best results were obtained with catalyst **3** in $[C_4mim][NTf_2]/dichloromethane$

Та	bl	e	3

Recyc	le experiments f	or the	e dimerisation of	cyc	looctene in	IL/dichloromet	hane and	IL	/pentane 1	1:1	1 mixtures. ^a	
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Entry Solvent		Catalyst	talyst Run Initial rate ^b Conversion of COE (%) Yield of dimer (%)		Yield of dimer (%)	Ratio of dimer, trimer and tetrame			
							Dimer	Trimer	Tetramer
За	[C ₄ Pyr][NTf ₂]/diclhoromethane	3	1	0.032	100	32	46	37	17
3b	[C ₄ Pyr][NTf ₂]/diclhoromethane	3	2	0.032	99	23	44	37	18
3c	[C ₄ Pyr][NTf ₂]/diclhoromethane	3	3	0.032	99	17	44	38	19
3d	[C ₄ Pyr][NTf ₂]/pentane	3	1	0.032	100	19	47	36	8
Зе	[C ₄ Pyr][NTf ₂]/pentane	3	2	0.032	100	15	46	37	17
3f	[C ₄ Pyr][NTf ₂]/pentane	3	3	0.032	99	14	43	38	17
3g	[C ₄ Pyr][NTf ₂]/diclhoromethane	4	1	0.032	99	61	70	32	11
3h	[C ₄ Pyr][NTf ₂]/diclhoromethane	4	2	0.032	98	59	60	31	9
3i	[C ₄ Pyr][NTf ₂]/diclhoromethane	4	3	0.029	87	50	56	23	7
3j	[C ₄ Pyr][NTf ₂]/pentane	4	1	0.024	69	41	87	11	2
3k	[C ₄ Pyr][NTf ₂]/pentane	4	2	0.020	58	0	0	0	0
31	[C ₄ Pyr][NTf ₂]/pentane	4	3	0.019	54	0	0	0	0
3m	[C4mim][NTf2]/diclhoromethane	3	1	0.032	100	22	46	36	17
3n	[C ₄ mim][NTf ₂]/diclhoromethane	3	2	0.032	99	21	45	37	18
30	[C ₄ mim][NTf ₂]/diclhoromethane	3	3	0.032	99	17	44	37	19
Зр	[C ₄ mim][NTf ₂]/pentane	3	1	0.032	100	15	48	36	16
Зq	[C ₄ mim][NTf ₂]/pentane	3	2	0.032	100	15	44	37	18
3r	[C ₄ mim][NTf ₂]/pentane	3	3	0.032	100	12	40	37	18

^a All reactions performed using 0.77 mM of COE and 8.5 mol% catalyst, at *r.t.* for 6 h. All data obtained by GC analysis.

^b (mols COE)(mols cat)⁻¹ s⁻¹.

and $[C_4Pyr][NTf_2]/dichloromethane, which yielded 22% and 32% of dimer, respectively, at 100% conversion of COE after 6 h. Similar initial rates (0.032 (mols COE))(mols cat)⁻¹ s⁻¹) and dimer:trimer:tetramer selectivities (46:37:17, respectively) were found in both cases.$

Recycle experiments were performed using IL/dichloromethane solutions and biphasic reactions IL + pentane with $[C_4Pyr][NTf_2]$ or $[C_4 mim][NTf_2]$, using catalyst **3**. In the biphasic reactions the catalyst was observed to reside in the lower IL phase while the pentane remained as a separate upper layer. After each run, the organic solvent was removed from the mixture under vacuum (dichloromethane) or via decantation (pentane). The IL layer was then extracted with pentane before fresh organic solvent was added. Table 3 summarises the results obtained. For the IL/dichloromethane systems (entries 3a-3c and 3m-3o), a good initial rate, 0.032 (mols COE)(mols cat)⁻¹ s⁻¹ was observed for all runs with ~99% conversion of COE found in 6 h. As indicated above, catalyst degradation was observed after this reaction time, which partly explain the sharp decrease in the yield of dimer found in subsequent runs (i.e., from 32 to 17% and from 22 to 17% in [C₄Pyr][NTf₂]/ dichloromethane and [C₄mim][NTf₂]/dichloromethane, respectively). In comparison, similar initial rates and conversions of COE were obtained using pentane (entries 3d-3f and 3p-3r) and although less dimer was produced in the first run, a less pronounced decrease in the yield of dimer in the 2nd and 3rd runs was observed (19-14% and 15-12% yield in [C₄Pyr][NTf₂]/pentane and [C₄mim][NTf₂]/pentane, respectively). Although less dimer is formed using [C₄mim][NTf₂], the activity of the catalyst over the three runs shows less deactivation in the case of the imidazolium based ionic liquid. This is consistent with the ICP results (Table 4). These indicated that, on recycle, there was an average loss in Ru in the [C₄Pyr][NTf₂] systems of ca. 26%, but this was less significant in the case of [C₄mim][NTf₂] (13% and 3% in IL/dichloromethane and IL/pentane, respectively). In order to limit the loss of catalyst, the ionic catalyst 4 was also examined using [C₄Pyr][NTf₂].

Catalyst **4** was prepared following published methods [10] and used without further purification, but fast degradation was noted in CDCl₃ by ¹H NMR (see Section 2). Whereas **4** has been reported to be relatively stable, formation of $[H_2IMesH]^+$ has been observed during the reaction of analogous Ru

carbides with acids containing weakly coordinating anions such as $[B(C_6F_5)]_4^-$ or $[OTf]^-$ [26]. Although the degradation of **4** in solution has not been studied in detail, herein, it is possible that the protonated carbide $[(Ru=CH)(PCy_3)(H_2IMes)Cl_2]^+$ also forms in the process. For example, it has been shown that the osmium analogue $[(Os=CH)(PCy_3)_2Cl_2][OTf]$ is obtained by reaction of $[(Os=C)(PCy_3)_2Cl_2]$ and HOTf [27].

The dimerisation of COE was performed using catalyst 4 and [C₄Pyr][NTf₂] and dichloromethane or pentane, Table 3, entries 3g–3l. For comparison, the reaction in pure dichloromethane was also carried out (Table 2, entry 2d). As in the case of catalyst 3, in the presence of [C₄Pyr][NTf₂]/dichloromethane, entries 3g-3i, a good initial rate of \sim 0.031 (mols COE)(mols cat)⁻¹ s⁻¹ was found in all reactions; however, a drop in the conversion of COE was observed on the 3rd run from 99% to 87%. Reasonable yields of dimer were found for all runs although a drop was noted on recycle from 61% to 50%. Interestingly, the ionic liquid was found to increase the dimer yield over that of the pure dichloromethane (Table 2, entry 2d) possibly reflecting the increased viscosity and lowering of the diffusion coefficient which limits the activity of the catalyst. In contrast, in the biphasic reaction (Table 3, entries 3*i*–3*l*), although reaction did occur, significantly reduced initial rates and COE conversions were observed (~0.021 (mols COE)(mols $(cat)^{-1} s^{-1}$, ~60% conversion after 6 h). In this case, recycle of the catalyst/IL led to some reaction but a drop in dimer yield from 41% to 0% from the first to second reactions, with only polymeric material and some cracking products formed after the first run. Disappointingly, ICP analysis has shown there to be an average loss of ruthenium of 40% in the reactions using ionic catalyst 4 (Table 4). This change in the concentration of the catalyst has been shown herein to have a significant effect on the dimer formed. The results of all the recycle experiments reported in Table 3 are consistent with the observation that a reduction in the catalyst loading decreases the dimer in favour of higher molecular weight products.

3.5. Heterogeneized catalysts

In an attempt to further improve the catalyst recyclability, the IL-catalyst **3** system was supported on silica using the 'supported

Table 4

Leaching of Ru (%) after three recycl	les, using catalyst 3 or 4 in IL/dic	lhoromethane and IL/pentane mixtures.	. Data obtained by ICP analysis.4
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Solvent	Catalyst	Catalyst Ru content (ppm)		Difference	Ru loss (%)
		Before	After		
[C ₄ Pyr][NTf ₂]/diclhoromethane	3	51	43	8	22
[C ₄ mim][NTf ₂]/diclhoromethane	3	39	33	6	13
[C ₄ Pyr][NTf ₂]/pentane	3	57	52	5	30
[C ₄ mim][NTf ₂]/pentane	3	17	17	~0.08	3
[C ₄ Pyr][NTf ₂]/diclhoromethane	4	9	4	5	44
[C ₄ Pyr][NTf ₂]/pentane	4	8	3	5	38

^a ICP studies were carried out on the IL/catalyst phase after three recycles, with each reaction performed in a 1:1 mixture of IL/diclhoromethane or IL/pentane, using 0.77 mM of COE and 8.5 mol% catalyst, at *r.t.* for 6 h. The organic solvent was removed under vaccum (dichloromethane) or *via* a syringe (pentane), and the samples dried under vacuum for 24 h, prior to analysis.

ionic liquid phase' (SILP) concept. This method has been extensively researched in recent years for many different catalysts in a variety of reactions [28]. Catalyst 3 (8.5 mol%) was supported using [C₄mim][NTf₂] and Davicat sp 550-10654 silica, pH 4. The recycling of the supported catalyst was then examined for the dimerisation of COE (0.77 mM of COE at r.t, 6 h per run), using pentane as the solvent. In all cases, high COE conversions were found: however, extremely low vields of dimer were observed (run 1 (5.4%), run 2 (0.6%) and no dimer was observed by the 3rd run) with polymeric material formed during reaction. The use of the IL-silica system without catalyst produced little reaction showing that the presence of the catalyst is indeed needed for the reaction, and also indicating that accessibility to the catalyst may be the issue in this case (i.e., the effective catalyst concentration is reduced, favouring polymerisation over dimerisation). The reaction in biphasic $[C_4 mim][NTf_2]$ /pentane (Table 3, entries 3p-3r) also shows good conversion of COE and recyclability, but gives better yields of dimer (15–12%) than the heterogeneous systems, again indicating that accessibility to the catalyst may be hindered when supported on the silica. Compared with the reaction in pentane using catalyst **3** (Table 2, entry 2m), the reactions using the supported catalyst were faster, with ca. 100% conversion of COE in the first two runs observed after only 10 min. This indicates that there is little leaching of the ruthenium catalyst into the organic phase.

4. Conclusions

The dimerisation of COE to form 1,9-cyclohexadecadiene has been achieved with high selectivity (74%) and yield (60%) using Grubbs' catalyst 1 in 1,2-dichloroethane. This is a significant improvement on previous work where the yield and selectivity to the dimer was limited to 30% and 34%, respectively. Good results are also obtained in other organic solvents (ethyl acetate, benzene, dichloromethane and pentane) and/or using other Ru catalysts (2-4), with yields of dimer ranging between 39 and 60% and selectivities of 47-68% (all at >92% conversion). Reactions performed in tetrahydrofuran or alcohols were found to be poor due to a combination of strong solvent coordination and/or poor catalyst solubility/stability. In general, low catalyst loadings (<8.5 mol%) and high concentration of COE (>0.77 mM) decreased the yield of dimer, favouring the production of higher molecular mass products, such as the trimer and tetramer. Studies of metathesis reactions starting from 1,9-cyclohexadecadiene indicate that the monomer-dimer and monomer-trimer reactions are faster than the dimer-dimer reaction, possibly due to the difficulty of the dimer to bind to the Ru centre compared with the monomer, less sterically hindered. The dimerisation of COE was also examined in ionic liquid media for the first time in order to improve the recyclability of the catalyst. The best results were obtained in 1:1 mixtures of IL/dichloromethane or in biphasic IL+pentane $(IL = [C_4Pyr][NTf_2], [C_4mim][NTf_2])$ using catalyst **3** or **4**. Although

the catalysts remained active after three recycles, a drop in the yield of dimer was observed after the first run due to loss of catalyst between cycles. The IL-assisted immobilisation of catalyst **3** onto silica resulted in fast reactions leading to poor yields of dimer.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.09.005.

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