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Does the rate of competing isomerisation during alkene metathesis depend on pre-catalyst initiation rate?†

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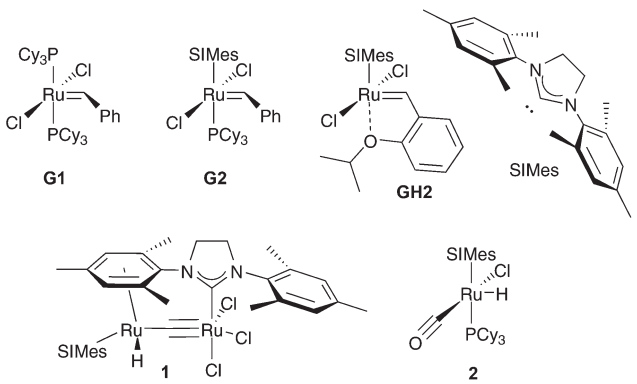
Experimental studies of the ring-closing metathesis reaction of 1,8-nonadiene and the ROMP reaction of cycloheptene show that the rate of isomerisation is not correlated to the initiation rate of the pre-catalyst, and that the absence of phosphine leads to a greatly increased rate of isomerisation. A range of pre-catalysts and solvents were probed and it is proposed that the isomerisation is mediated by a ruthenium hydride complex; our results are consistent with the rate-determining formation of such a species, which might be trapped *in situ* by tricyclohexylphosphane.

Introduction

Alkene metathesis has become a staple technique in organic chemistry,[1] allowing in particular the elegant syntheses of a number of cycloalkenes in natural product chemistry.[2,3] These advances have largely been stimulated by the development of user-friendly ruthenium-based pre-catalysts, initially complexes such as **G1**, and subsequently complexes including **G2** and **GH2** which bear *N*-heterocyclic carbene (NHC) ligands.[4,5]



However, competitive alkene isomerisation can compromise the effectiveness of this technique, *via* the non-productive consumption of valuable starting materials and the production of side products that can be very difficult to separate from the target. In most cases, these occur by isomerising terminal alkenes to internal alkenes,[6] or by bringing alkene functionality into conjugation with other functional groups.[7] Various researchers have approached this problem, seeking to understand its origin and provide means by which it can be suppressed. Others have exploited this process in synthetic applications.[8] Wagener has explored these competing reactions,[9] and implicated ruthenium hydride species in these processes *via* deuterium labelling experiments.[10] Nolan and Prunet proposed a mechanism based on C–H abstraction in the propagating carbene,[11] while researchers at Sasol have proposed and detected thermal decomposition of ruthenacyclobutanes *via* allylruthenium species.[12,13] Other researchers have identified and characterised various species, such as dinuclear **1** and [RuCl(H)(CO)(PCy_3)(SIMes)] (**2**), from the decomposition of ruthenium-based pre-catalysts under various conditions;[14–19] these have been implicated in isomerisation processes, and reagents such as benzoquinone (*inter alia*) have been proposed to remove such species efficiently from reaction mixtures.[20] Nolan and co-workers have characterised the product of an interesting indenylidene to η^5-indenyl rearrangement,[21] and shown that (with heating) the resulting complex can isomerise alkenes.[22] We have studied and compared three key mechanisms using *in silico* methods.[23] It was discovered that the ruthenium hydride pathway, based on a series of hydroruthenation/β-hydride elimination steps from [RuCl(H)(CO)(SIMes)] (**3**), constituted the lowest energy pathway (Scheme 1). The presence of [RuCl(H)(CO)(PCy_3)(SIMes)] (**2**), formed *in situ*, was observed during kinetic studies of the RCM of 1,8-nonadiene, indicating strongly that this complex is a potential isomerisation pre-catalyst. Notably, the highest barrier encountered was the barrier to phosphine dissociation from the 16e complex to yield an active 14e species.

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† Electronic supplementary information (ESI) available: Concentration/time plots for experiments presented in this manuscript, initiation rate data for **Zhan1B**. See DOI: 10.1039/c4dt00007b

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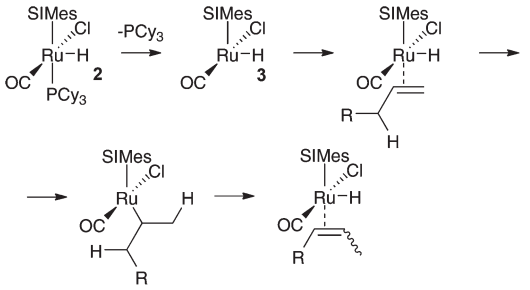

Scheme 1

Very recently, Fogg and co-workers have conducted interesting benchmarking studies, evaluating the isomerisation activity of complexes **1** and **2** (*inter alia*).[24] They concluded that neither of these species were sufficiently active to account for the observed levels of isomerisation in a model reaction; however, [RuCl(H)(CO)(PPh_3)$_3$], which bears more labile phosphine ligands, was found to be a highly active isomerisation catalyst. In addition, added PCy_3 was found to inhibit the isomerisation activity.

Our working hypothesis at this stage is that 14e [RuCl(H)(CO)(SIMes)] **3** is formed at some stage during the reaction, by a mechanism that is yet to be fully established; *i.e.* the 14e species is generated directly, and only manifests as 16e **2** when trapped by tricyclohexylphosphane in a subsequent step. A tentative mechanism for the formation of species such as **2** has been proposed by Dinger and Mol,[18] but this has not yet been supported with computational or experimental work. Our hypothesis might then explain both the detection of **2** by ^{1}H NMR spectroscopy and the measured sluggish reactivity of **2** as an isomerisation catalyst. In Fogg's experiments the entire stock of **2** that is charged to the reaction must first undergo an initiation process to which there is a significant energetic barrier.[23] Once formed, **3** might be trapped by tricyclohexylphosphane, which dissociates from **2** slowly to reform the active species **3**, or can directly react with alkene present in the reaction mixture. Under typical reaction conditions (*i.e.* $\leq$ *ca.* 5 mol% levels of pre-catalyst), the concentration of alkene will exceed that of phosphine significantly.

We therefore sought to explore various aspects of reaction conditions in order to begin to elucidate the factors that control isomerisation processes that occur during metathesis chemistry.

Results and discussion

Experimental approach

A series of kinetic reactions were used to elucidate the effects of pre-catalyst and reaction conditions on isomerisation processes, as kinetic profiles yield considerably more information than single-point yield or conversion determinations. The RCM reaction of 1,8-nonadiene was selected for this study. Cycloheptene has a thermodynamic effective molarity (EM_T)[25] of *ca.* 50 mmol L^{-1}; when metathesis reactions are conducted at *ca.* 10^{-1} mol L^{-1}, a mixture of cycloheptene, 1,8-cyclotetradecadiene, and higher oligomers are produced.[23,26,27] Notably, under the mild conditions used for these experiments, isomerisation processes are responsible for the consumption of a considerable proportion of the initial substrate charge (typically 10–50% in a matter of hours), and therefore comprise a *major* pathway in these reactions.

Metathesis reactions under the conditions selected here (0.5 mol L^{-1} 1,8-nonadiene, 3 mol% pre-catalyst, 298 K) occur on a timescale that is convenient for the collection of detailed concentration/time profiles by ^{1}H NMR spectroscopy. Ruthenium carbene species can be tracked by inspection and integration of the low field region of the ^{1}H NMR spectrum (*ca.* 16–20 ppm). The relatively low temperature avoids thermally-triggered decomposition of the ruthenium species. 1,3,5-Trimethoxybenzene was added as an internal standard.[27] Oligomer concentrations cannot be accurately quantified, as these species comprise a mixture of linear and cyclic species of various lengths.[26] Their signals cannot be deconvoluted from the signals corresponding to 1,8-nonadiene using 1D ^{1}H spectra (the 1D [^{1}H, ^{1}H] geTOCSY technique has been used effectively in this role). All solvents were dried over activated 4 Å molecular sieves, and degassed by sparging with inert gas (nitrogen or argon). The water content was determined by Karl-Fischer titrometry to be $\leq$10 ppm.

The diene concentration for all reactions was *ca.* 500 mmol L^{-1}. Plots are typically presented for cycloheptene and cyclohexene (at minimum), for reasons of clarity. For full concentration/time profiles for all components (cycloheptene, cyclohexene, cyclic dimer, ethene), please see the ESI.† The remaining mass balance (*i.e.* the organic material unaccounted for as cycloalkene, ethene, or cyclic dimer) comprises a mixture of diene and oligomer.

The concentration of cyclohexene is used to report on the degree of isomerisation in the reaction. The RCM of 1,7-octadiene is known to be fast, complete and irreversible, even at 4 mol L^{-1};[26,27] the assumption is made here that 1,7-nonadiene, the immediate product of 1,8-nonadiene isomerisation, undergoes RCM much faster than oligomerisation (*i.e.* this too has a high EM). Therefore, the relative rates of isomerisation can be inferred from the relative rates of cyclohexene production.

Pre-catalyst structure

Initially, a series of pre-catalysts was systematically explored, covering a range of common motifs. Bis(phosphine) complex **G1** is known to initiate rapidly[28,29] and its use tends to result in very little isomerisation.[30] The addition of pre-catalyst to a benzene-d_6 solution of 1,8-nonadiene produced a high concentration of ethene rapidly, along with an equilibrium concentration of cycloheptene (*ca.* 60 mmol L^{-1}) (Fig. 1). As the ethene concentration slowly decreased, the cycloheptene concentration increased slightly, suggesting that ethene build-up and retention was suppressing further conversion. Negligible quantities of cyclohexene and cyclic dimer were produced. Inspection of the low field region allowed identification and

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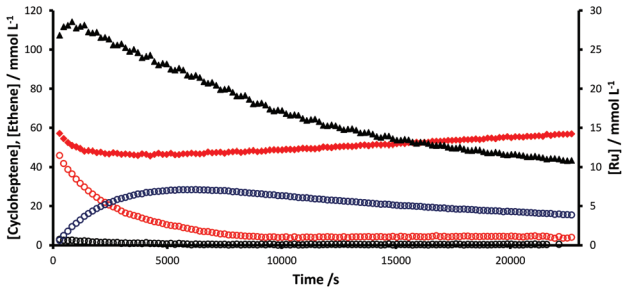
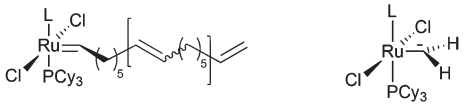


Fig. 1 Concentration/time profile for the RCM of 1,8-nonadiene (0.5 mol L^{-1} in benzene-d_6) by **G1** (3 mol%) at 298 K, showing ethene (black triangles), cycloheptene (red diamonds), **G1** (black open circles), alkylidene (red open circles) and methylidene (blue open circles).

quantification of the various ruthenium species, showing rapid initiation of the pre-catalyst,[29] an initial high concentration of alkylidenes **4a**, and a growing population of methylidene **5a** which then decreased gradually.



4a L = PCy_3
4b L = SIMes

5a L = PCy_3
5b L = SIMes

The chemical shift of the alkylidene (Ru=C*H*R) proton was consistent with that reported for alkylidenes derived from linear 1-alkenes.[31] The alkylidene decay followed excellent first order kinetics (k_{obs} = 2.78 × 10^{-4} s^{-1}) while no hydride species were detected in the high field region. The mass balance of ruthenium species is not maintained in these reactions (*ca.* 20% is lost after 1 h, 33% after 2 h, and 50% after 5 h), but the final fate of the ruthenium complex is unknown. These results suggest that either (i) no hydride species form under these conditions or that (ii) those hydride species that do form are not active enough to isomerise appreciable quantities of substrate. Fogg has reported the sluggish isomerisation ability of $[RuCl(H)(CO)(PCy_3)_2]$,[24] although it is unclear whether this is a consequence of slow initiation or slow isomerisation.

Second generation complex **G2** was examined next. This commercially-available complex represents one of the most commonly-deployed metathesis complexes in organic synthesis. Significant isomerisation was observed in the 1,8-nonadiene RCM experiment, to the point that cyclohexene concentration outstripped cycloheptene concentration (Fig. 2). Quantities of cyclic dimer were also produced. The pre-catalyst initiation was much slower than for **G1** and incomplete even after 5 h, consistent with what is known about the initiation of this species.[28,29] Alkylidene and methylidene populations could be tracked *via* the low field region of the ^{1}H NMR spectrum. Again, significant proportions of the ruthenium population are unaccounted for, part of which must comprise the isomerisation agent. Interestingly, the isomerisation process accelerated as the reaction reached the equilibrium concentration of cycloheptene, suggesting that isomerisation

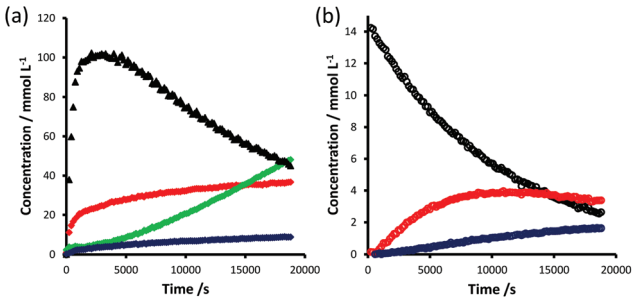
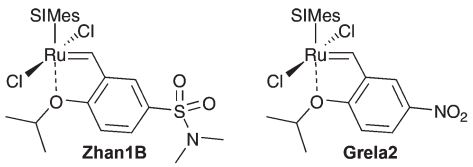


Fig. 2 Concentration/time profile for the RCM of 1,8-nonadiene (0.5 mol L^{-1} in benzene-d_6) by **G2** (3 mol%) at 298 K, showing (a) ethene (black triangles), cycloheptene (red diamonds), cyclohexene (green diamonds), and cyclic dimer (blue diamonds); and (b) **G2** (black circles), alkylidene (red circles) and methylidene (blue circles).

predominantly occurs after the productive metathesis has finished. Notably, the acceleration in isomerisation rate appeared to occur as a population of methylidene increased.

Both **G1** and **G2** bear 'throw-away' phosphine ligands, which have been implicated in the decomposition mechanism of some metathesis pre-catalysts, *via* nucleophilic attack of the 14e methylidene intermediate.[14] Phosphine-free **GH2** and more rapidly initiating analogues **Zhan1B** and **Grela2** were therefore tested, to determine if they led to reduced or increased rates of isomerisation, and whether the pre-catalyst initiation rate affected the isomerisation rate.



In all three cases, isomerisation was far more rapid than exhibited by G2 (Fig. 3); within *ca.* 4 hours, one third of the starting material had been consumed by isomerisation processes. In each case, the equilibrium concentration of cycloheptene was reached rapidly.

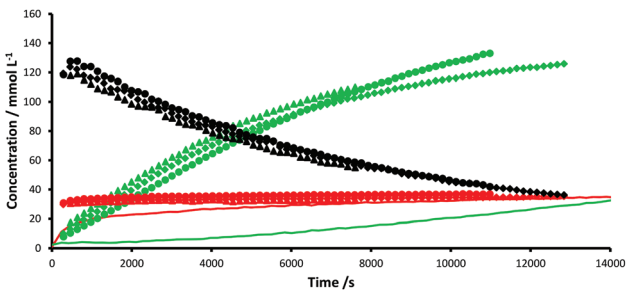


Fig. 3 Concentration/time profile for the RCM of 1,8-nonadiene (0.5 mol L^{-1} in benzene-d_6) by **GH2** (circles), **Zhan1B** (triangles) and **Grela2** (diamonds) (3 mol%) at 298 K, showing ethene (black), cycloheptene (red), and cyclohexene (green); the lines represent concentration/time profiles for cycloheptene (red) and cyclohexene (green) from Fig. 2 (using **G2**).

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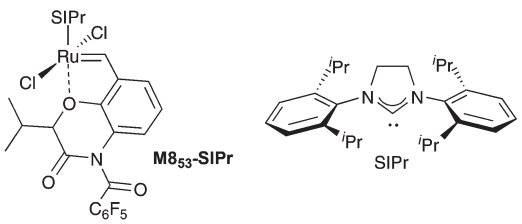
Clearly, the absence of a phosphine ligand does not preclude isomerisation. Indeed, the lack of phosphine in the reaction mixture may actually serve to prevent capture of the postulated active 14e hydride species **3** and thus promote the isomerisation. Computational studies have suggested that, during the initiation of **2**, the phosphine dissociation event (to yield **3**) is highly endergonic (22.9 kcal mol^{-1}).[23] Phosphine dissociation from **G2** has been shown to present similar yet slightly higher barriers; Jensen and co-workers have estimated this barrier at 23.7 kcal mol^{-1} using detailed DFT calculations, while Grubbs and co-workers reported an experimental value of 23.0 ± 0.4 kcal mol^{-1}.

The Hoveyda-type catalysts considered here have very different initiation rate constants, covering a 10-fold range (at 298 K in DCM solution: 0.026 L mol^{-1} s^{-1} for **GH2**, 0.132 L mol^{-1} s^{-1} for **Zhan1B**, 0.317 L mol^{-1} s^{-1} for **Grela2**); initiation rates for **GH2** and **Grela2** have been reported previously,[32,33] while the initiation rate of **Zhan1B** was measured for this work (see the ESI† for full details). This difference in initiation rate is reflected in the concentration/time profiles of the pre-catalyst concentrations in these experiments (see the ESI†); the concentrations of methylidene and propagating carbene cannot be monitored under these conditions, as these 14e alkylidene species are not detectable by NMR spectroscopy.[34] Unfortunately, this also precluded detection of ruthenium hydride species and insights into the mass balance of ruthenium species. The fact that isomerisation rate is unrelated to initiation rate (and therefore the concentration of 14e ruthenium species) is somewhat surprising, and suggests that the rate is limited by some other species or process.

Finally, the reactivity of **$M8_{53}$-SIPr** was explored (initiation rate constant of 0.571 L mol^{-1} s^{-1}).[33] This complex bears the SIPr ligand, rather than SIMes; complexes bearing the SIPr ligand are frequently more active in the metathesis of less hindered alkenes, but are less efficacious for the synthesis of tri- and tetra-substituted alkenes.[35–37]



When this pre-catalyst was tested in the RCM of 1,8-nonadiene, significantly more isomerisation occurred, consuming half of the starting material in less than 2 hours, leading to consumption of some of the cycloheptene formed initially (Fig. 4). While this complex is known to initiate very rapidly, this alone cannot explain the increased rate of isomerisation, as **GH2**, **Zhan1B** and **Grela2** all lead to the same rate of isomerisation (*vide supra*). The difference must therefore be due to the different NHC ligand present on the pre-catalyst (*i.e.* SIPr *versus* SIMes); this difference must be a result of either faster

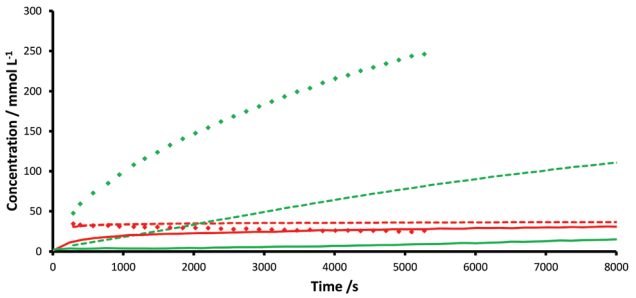


Fig. 4 Concentration/time profile for the RCM of 1,8-nonadiene (0.5 mol L^{-1} in benzene-d_6) by **$M8_{53}$-SIPr** (3 mol%) at 298 K, showing cycloheptene (red diamonds) and cyclohexene (green diamonds); for comparison, the corresponding profiles with **G2** (solid lines, from Fig. 2) and **GH2** (dashed lines, from Fig. 3) are presented on the same scale.

formation of the SIPr-containing hydride complex, its higher activity, or a combination of these two factors.

These results suggest strongly that the structure of the isomerisation catalyst depends on that of the pre-catalyst; the isomerisation agent is not common in all of the experiments studied herein. The ancillary ligands present on the metathesis pre-catalyst therefore influence those present on the isomerisation agent, and in so doing (a) determine the activity of this agent, and/or (b) the rate of its formation (both in the order SIPr > SIMes > PCy_3). Further work is necessary in order to separate these two different effects. Banti *et al.* have shown that the isomerisation activity of [RuCl(H)(CO)(PCy_3)(L)] complexes (in neat 1-octene at 100 °C) decreases in the order SIMes > PCy_3 > SIPr, but that the NHC-bearing complexes are only active at higher temperatures.[19] Fogg has shown that the SIMes-bearing hydride **2** is more active for allylbenzene isomerisation than its phosphine-bearing congener at lower temperatures (40–80 °C in DCM or toluene).[24] For catalysts with the same non-dissociating ligands (*i.e.* NHC, two chloride ligands, and an alkylidene) we have shown here that the initiation rate has *no effect* on the rate of the isomerisation process, despite the demonstrably different concentrations of ruthenium that have been delivered into the reaction.

Solvent effects

Further experiments were conducted to explore the effect of reaction conditions on isomerisation activity. In particular the effect of solvent was probed, as this has been shown to influence the rate of metathesis,[27,38,39] although this typically occurs predominantly *via* changes to the pre-catalyst initiation rate.[40,41]

Reactions were conducted with **G2** in chloroform-*d*, dichloromethane-d_2 and toluene-d_8. There were clear solvent effects on the rate of isomerisation, with toluene leading to far less isomerisation than dichloromethane (Fig. 5).

Water is unlikely to be the cause of this difference in reactivity; not only is metathesis under aqueous conditions well documented,[42] but the use of undried chloroform-*d* (containing *ca.* 30 ppm water, as determined by Karl Fischer titrometry) led to only a slight reduction in metathesis rate but a

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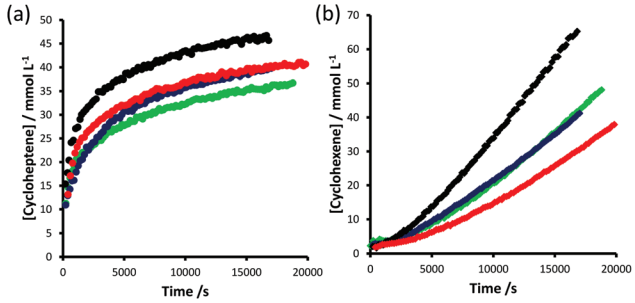

Fig. 5 Concentration/time profiles showing (a) cycloheptene and (b) cyclohexene from the RCM of 1,8-nonadiene (0.5 mol L^{-1} at 298 K with 3 mol% **G2**) in benzene-d_6 (green), chloroform-*d* (blue), dichloromethane-d_2 (black) and toluene-d_8 (red).

significant reduction in isomerisation rate (see the ESI†). In addition, the relative rates of isomerisation (DCM > benzene ≈ chloroform > toluene) do not mirror the relative rates of initiation (toluene > benzene > DCM > chloroform),[41] supporting the view that this difference is not simply a consequence of the rate of formation of the 14e metathesis-active species. This is consistent with the results reported above for the pre-catalysts which have different initiation rates but converge on the same active species after one turnover.

RCM *versus* ROMP

Methylidene complexes, generated in the presence of ethene or when terminal alkenes undergo metathesis, have been implicated as the most fragile ruthenium alkylidenes, and the most likely sources of isomerisation-active decomposition agents.[15] The ROMP of cycloheptene was therefore probed, as this avoids the production of methylidene complexes.

When a sample of cycloheptene (500 mmol L^{-1} in benzene-d_6) was exposed to **G2** (3 mol%) under the same conditions as the RCM reactions, ROMP was rapid, leading to equilibrium concentrations of cycloheptene (*ca.* 90 mmol L^{-1}) and cyclic dimer (*ca.* 45 mmol L^{-1}) (Fig. 6). Isomerisation processes occurred, but at a much lower rate. Inspection of the alkylidene region revealed no methylidene (**5b**), smooth consumption of the pre-catalyst, and production of the ruthenium alkylidene intermediate (**4b**). The mass balance between pre-catalyst and alkylidene was excellent, with only *ca.* 5% of the ruthenium population unaccounted for after *ca.* 4 hours (see the ESI†).

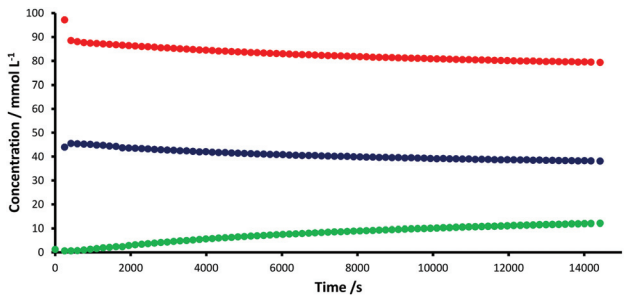

Fig. 6 Concentration/time profile for the ROMP of cycloheptene (0.5 mol L^{-1} in benzene-d_6) by **G2** (3 mol%) at 298 K, showing cycloheptene (red), cyclohexene (green), and cyclic dimer (blue).

This reaction was repeated and *ca.* 50 mmol L^{-1} 1,7-octadiene added after 15 minutes; this substrate undergoes almost instantaneous, complete and irreversible RCM to yield cyclohexene plus ethene.[27,43] Methylidene was now generated by diene turnover, appearing in the low field region of the ^{1}H NMR spectrum; mass balance in the alkylidene region was not reached, and isomerisation now began (see the ESI†). In addition, very little ethene was observed, consistent with its consumption by reaction with the alkylidene to form diene. It seems likely that the key precursor to an active isomerisation catalyst is indeed the methylidene complex produced upon diene turnover in RCM.

Conclusions

The progress of a model ring-closing metathesis reaction under mild conditions has been monitored using ^{1}H NMR kinetic experiments. The degree of isomerisation has been found to depend on the nature of the propagating species, *i.e.* the ligand retained by the ruthenium throughout the metathesis cycle. **G1** leads to no isomerisation, while all NHC-bearing pre-catalysts produce cyclohexene as a side product. Hoveyda-type complexes (**GH2**, **Zhan1B** and **Grela**) produce cyclohexene more rapidly than **G2**, despite the active species being the same, yet at a rate that was independent of the pre-catalyst initiation rate. **M8$_{53}$-SIPr** generated cyclohexene faster than SIMes-bearing complexes. These results suggest an isomerisation process mediated by a ruthenium complex that forms *in situ* and is not part of the metathesis cycle; if isomerisation was a result of side-reactions occurring during the RCM reaction (such as those proposed by Nolan and Prunet,[11] or researchers at Sasol)[12,13] then more rapid initiation would lead to more rapid isomerisation due to the higher population of ruthenium species in the cycle when initiation is rapid. Similarly, while solvent effects were evident, these were not the same as those on the rates of pre-catalyst initiation.[41]

Experiments with the corresponding ROMP reaction (of cycloheptene) under similar conditions resulted in very little isomerisation until a portion of 1,7-octadiene was added; isomerisation processes then occurred much more quickly.

These results suggest strongly that the active isomerisation agent is generated from the 14e methylidene species. In the presence of phosphine, which can trap both 14e methylidene and 14e hydride, the isomerisation might be somewhat suppressed, explaining the higher isomerisation rates in the presence of the Hoveyda-type complexes. The phosphine dissociation events from methylidene complex [$RuCl_2(PCy_3)$-(SIMes)(=CH_2)] (**5**)[29] and hydride complex [RuCl(H)(CO)(PCy_3)-(SIMes)] (**2**)[23] are known to be slow; a rate could not be measured for the former. However, the lack of dependence of isomerisation rate on initiation rate suggests that the

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formation of the active hydridocarbonyl species may be rate-determining for isomerisation.

Further experimental and theoretical studies into the mechanism of formation of the active ruthenium hydride are currently underway in our laboratories.

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