

5. Conclusions and Recommendations

The advancement in homogeneous catalysis depends on the ability to predict the chemical properties of catalysts and the ability to synthesise these catalysts. The aim of this study was to attempt to identify the electronic and steric properties of the precatalyst ligands that determine the characteristics of phosphine ligated Grubbs-type precatalysts for alkene metathesis by means of molecular modelling. Additionally, it was found from literature that there is no easy method to determine the electronic and steric properties of the precatalyst ligands in existence. An investigation of the literature showed that the possibilities for synthesising a wide range of phosphine ligands are almost unlimited.

A preliminary experimental investigation into the feasibility of synthesising the new potential ligands that were identified at the start of this thesis was done. In terms of the cost effectiveness and environmental impact, the synthesis method has to be reconsidered. The flammability, high delivery costs as well as the toxicity of the phosphines have to be taken into account when considering these types of ligands. A new precatalyst obtained by using a new ligand has to show a remarkable improvement over the current commercially available precatalysts to justify the additional cost to synthesise the new ligand. The preliminary experimental study also showed that the final step in the synthesis did not proceed as reported in literature.¹ The reason for this is currently not very clear. This also serves as an additional reason to rethink the use of these ligands for the Grubbs-type precatalysts.

The molecular modelling study raised several questions regarding the current approach to theoretical studies. The theoretically obtained structures correlated well with the XRD data (**Table 3.2**). The experimentally determined dissociation energies correlated well with those determined via molecular modelling (**Table 3.3**). Comparing dissociation energies (**Figure 3.5**) to determine which potential precatalysts merit further investigation also proved to be an unsuitable method of investigation. It was also shown that great care should be taken to avoid model ligand and substrate systems (**Figure 3.6**). If all the shortcomings of a simplified system are not taken into consideration, some very suspect conclusions might be drawn from the obtained energy profiles. The energy profiles of **A1** to **A28** (**Figures 3.7, 3.8, 3.10, 3.11, 3.12, 3.13** and **3.14**) also raised questions about the real meaning of the difference in the energy barriers. Although there are differences, the trends are essentially the same. In an effort to determine whether there is an ideal energy range wherein the values of a 'good' catalyst will be found, the precatalyst **A105** was studied (**Figures 3.16, 3.17** and **3.18**). It was hoped that this precatalyst, known to show low catalytic activity,² would provide the answer to this question. The energy values of **A105** were very similar to the two commercial precatalysts **A1** and **A2**, and this led to the study of the precatalyst

A106. The hope that the poor donating ability³ of $\text{P}(\text{OCH}_2\text{CCl}_3)_3$ (**Table 3.8**) would lead to a vastly different energy trend for **A106** was realised. However, this difference in the energy values failed to provide a definitive answer to the question of where on the potential energy surface the 'bad area' for catalysis lies. Precatalyst **A103**, which is a newly reported precatalyst, has energy values that are similar as well as higher than those of **A106**. This raised questions about the whole molecular modelling method of determining only the primary metathesis energy values.

Since the electronic investigation provided unexpected results and showed that finding a fast, effective method of determining which ligand merits further study is not as easy, some steric aspects were studied. The possibility of agostic stabilised metallacyclobutane rings was studied (**Table 3.9**). There was no evidence that the commercially available precatalysts (**A1**, **A2** and **A103**) have any real difference in their metallacyclobutane rings when compared to the low activity precatalysts (**A105**, **A106** and **A107**). Next, the ability of the ligands to shield the metal centre was studied. The expectation was that a trend would be found that might shed some light on the differences between the catalytic steps of the precatalysts. No clear trend could be determined (**Figure 3.25**). While the atoms bonded directly to the metal already shielded it very well; when the shielding of the metal by the complete ligands in the various steps of the mechanism was compared to the calculated Gibbs free energy values, no clear correlation could be found. The difference in the shielding was very small in most cases and cannot on its own account for the vast differences in the activity of the precatalysts. The main conclusions of the theoretical investigations were that future studies should be broadened to include the solvent effects, isomerisation, secondary metathesis and deactivation routes.

In order to determine whether the solvent will really provide a deeper understanding of the energy values, the solvent effects of **A1** to **F1** were determined with the COSMO^{4,5} (conductor-like screening model) continuum solvation model⁶ available in Materials Studio's DMol³ DFT code using the dielectric constant of 1-octene. The solute molecule forms a cavity within the dielectric continuum of permittivity, ϵ , which represents the solvent (**Figure 5.1**).⁴⁻⁶ The charge distribution of the solute polarises the dielectric medium. The response of the dielectric medium is described by the generation of screening (or polarisation) charges on the cavity surface.⁴⁻⁶ COSMO provides the electrostatic contribution to the free energy of solvation. In addition, there are non-electrostatic contributions to the total free energy of solvation that describe the dispersion interactions and cavity formation effects.⁴ The difference between the calculated gas phase and solvent effect ΔG energy values is illustrated in **Figure 5.2**. What becomes apparent from the comparison is that the energy values do not differ by more than 6 kJ.mol^{-1} . The only exception is the transition state **E-D**, where the difference is $16.49 \text{ kJ.mol}^{-1}$. The absence of major differences when solvent effects are taken into account, at least in this small data sample, does seem to indicate that solvent effects on their own will probably also not provide the clear-cut answers that are desired.

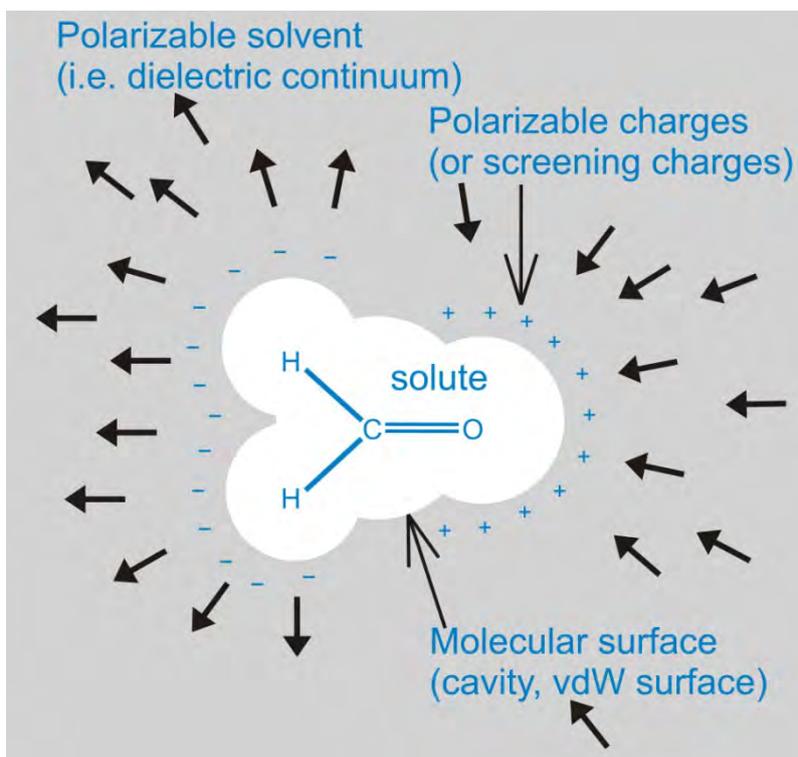


Figure 5.1 The COSMO continuum solvation model.^{4,5}

The energy values of the secondary metathesis route should be fairly easy to determine theoretically. The main difficulty is that the deactivation routes and therefore the source of the hydrides necessary for isomerisation of 1-octene are currently still very poorly understood, as has already been pointed out in **Chapter 3**. One way to study this would be to try to simplify the complete metathesis reaction. This could be done in several different ways. The first would be to study the secondary metathesis process on its own, experimentally. This could be done by performing metathesis reactions with pure 2-, 3- or 4-octene as well as with a mixture of the octenes. Since these isomers of 1-octene are the products of the isomerisation process, this might shed some light on how the secondary metathesis affects the total catalytic activity. This leaves the big problem of the deactivation mechanism. One of the big problems, as was pointed out in **Scheme 3.9**, is that it is unclear when most of the catalyst starts to deactivate or whether there are multiple deactivation mechanisms.

One way to study this would be to synthesise the precatalyst **A134** (**Scheme 5.1**). Although precatalyst **A134** has already been synthesised by Lehman *et al.*,⁷ they did not test the catalytic activity with 1-octene. The diazo compound **132** can be prepared from the aldehyde **130** according to literature methods;^{8,9} where after the one-pot synthesis of Schwab *et al.*² can be used to synthesise **A134**. The advantage of metathesis with **A134** is the absence of activation steps **B** to **E** (**Scheme 3.4**). This means that, immediately after the phosphine dissociates, primary metathesis can take place. The measured kinetic data can then be compared with that of **A1** to

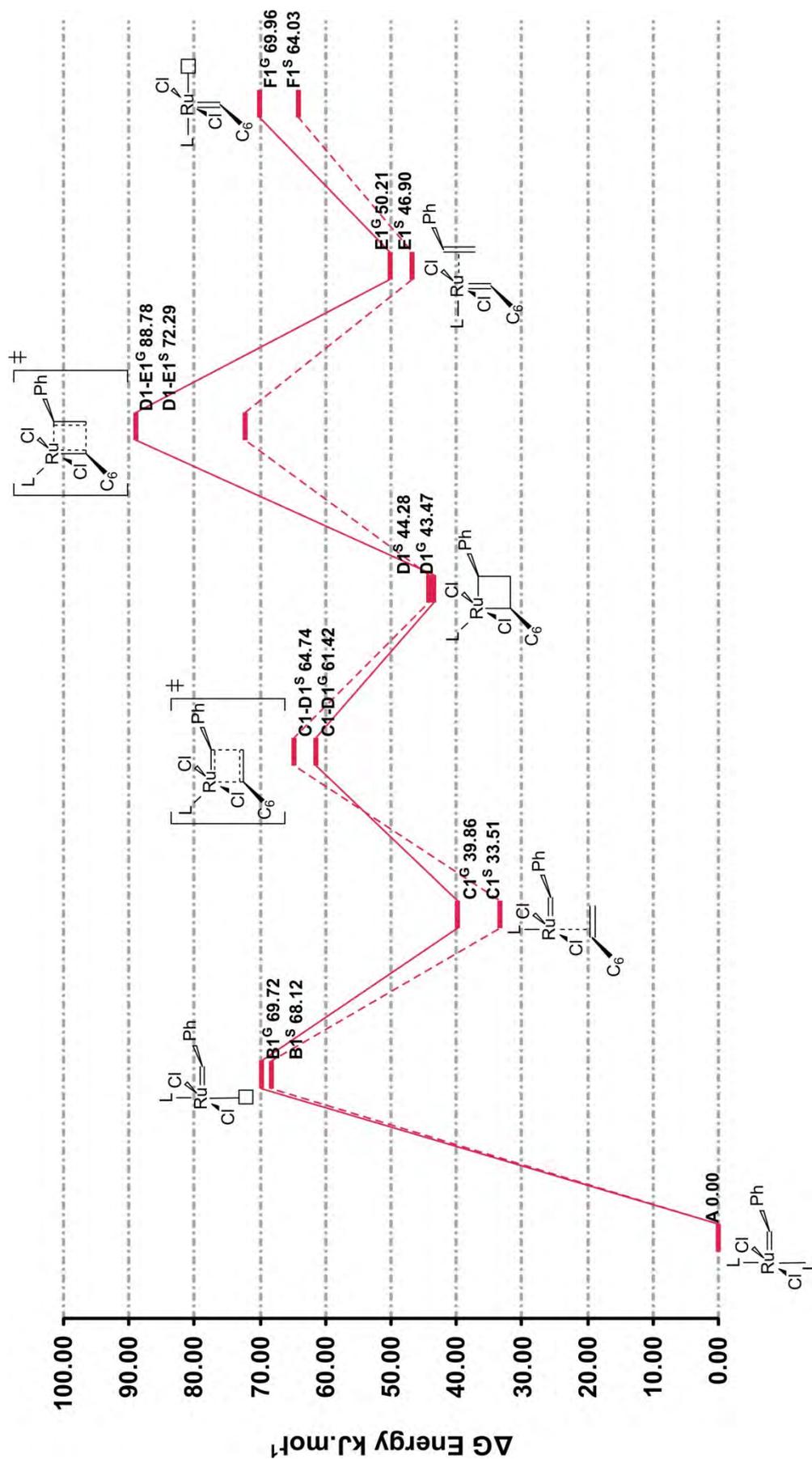
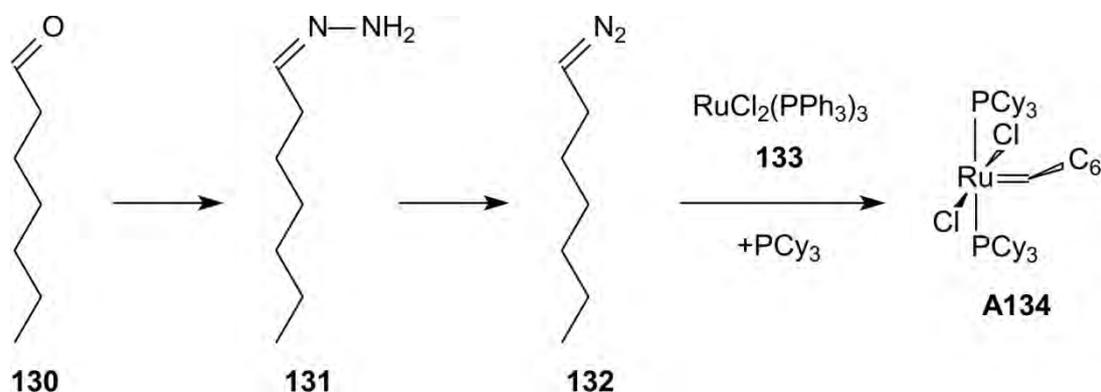


Figure 5.2 Comparison between the calculated ΔG energy values of **A1** in the gas phase (solid line) and in the solvent 1-octene (dashed line).

determine how the activation steps affect the overall catalytic activity. The lifetime of the catalyst can also be determined and could potentially shed some light on where in the metathesis reaction the most deactivation takes place. Comparing the amount and rate of PMPs and SMPs formed might also shed some light on when isomerisation of the 1-octene starts. Eliminating some steps from the metathesis reaction might also help to remove some clutter from the NMR spectra and thereby help with the elucidation of the various products.



Scheme 5.1 Synthesis of **A134** from **130**.

While it might initially look as if this thesis highlights some very severe shortcomings in theoretical approaches and paints a bleak picture of the understanding of the overall metathesis reaction, it is not the case. The results challenged the initially expected outcome and some valuable insights were gained that raise questions about the current way of thinking about alkene metathesis. It is also clear that to oversimplify a very complex reaction and using limited data will lead to false assumptions being made. It is therefore essential when theoretical data is compared to experimental data to always question whether observed trends and similarities are truly what they seem to be. The recommendation is therefore that before a new study into the metathesis reaction is started, serious consideration has to be given to determining the characteristics that will contribute to a better understanding of the complete reaction. Merely generating a bigger library of more precatalysts and approaching theoretical studies in the same way will in the long run in all likelihood not lead to the desired deeper understanding of the mechanism.

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