1. Introduction and Aim

1.1 Introduction

Phosphine compounds are used with great success as ligands in the synthesis of a large variety of homogeneous catalyst systems.\(^1\) Hydroformylation,\(^2\)-4 hydrogenation\(^5\) and hydrocyanation\(^6\) are but a few examples where phosphine metal complexes are used as catalysts. The ability of phosphines to stabilise the low oxidation states of metal atoms makes them useful for homogeneous catalysis.\(^1\) Additionally, phosphines promote the solubility of metal complexes in a wide range of organic solvents.\(^1\) Changes in the properties of phosphorous ligands and their transition metal complexes are observed by changing the substituents on the ligands.\(^7\)

Alicyclic carbon compounds have a three-dimensional structure that can increase the steric volume of alicyclic phosphine ligands by extending the three-dimensional spatial structure of the molecule. Alicyclic carbon compounds are also very stable, which may enable alicyclic phosphine ligands to further stabilise the catalyst.\(^8\)-11

The commercially available Grubbs first generation precatalyst (Ru(=CHPh)Cl\(_2\)(PCy\(_3\))\(_2\), Grubbs 1) (A\(_1\), Figure 1.1) contains the strong electron donating group PCy\(_3\).\(^12\) The Ru-alkylidene fragment is not as nucleophillic as the alkylidene of the Schrock-type complexes.\(^12\) The five-coordinate, 16-electron metal centre is very stable towards water, acid and various functional groups. The Grubbs 1 precatalyst (A\(_1\)) is useful for ring-opening metathesis polymerisation (ROMP), and ring-closing metathesis (RCM).\(^12\) The thermal stability, lifetime and activity of Grubbs 1 was improved by replacing one of the PCy\(_3\) groups with an N-heterocyclic carbene (NHC) ligand to form the second generation Grubbs precatalyst, A\(_2\) (Grubbs 2).\(^13\),\(^14\)

In a 2004 publication, Forman et al.\(^15\) reported the new Phobcat precatalyst, A\(_3\), using the alicyclic phosphine 9-cyclohexyl-9-phospha-9H-bicyclononane as a new ligand for A\(_1\).\(^16\)-18 Precatalyst A\(_3\) was tested on various metathesis reactions and it was found that the precatalyst showed better stability at higher temperatures, higher activity and better selectivity.\(^15\) The success of the alicyclic phosphine in the A\(_3\) precatalyst system serves as motivation to investigate other alicyclic phosphine compounds that might serve as ligands for A\(_1\).
Figure 1.1  The precatalysts investigated in this study. A indicates the first step in the metathesis reaction; L indicates ligands 4 to 8 and 10 to 28. This AL numbering format will be used throughout the text to avoid having to renumber the structures and thus avoiding having multiple notations for the same structure in one text.
Compound 30 could be successfully synthesised from the work done by Katz *et al.*,19-21 Quin *et al.*,22 and Marx23 (Scheme 1.1). Unfortunately, compound 30 only offers limited options for the manipulation of the steric bulk and electronic properties of the ligand. One way to overcome this limitation is compounds 6 and 7 (Scheme 1.2).

Scheme 1.1  Ligand 30 offers limited options for the manipulation of the steric bulk and electronic properties of a Grubbs-type precatalyst.

In 1997, Zhu *et al.*24 and Chen *et al.*25 reported the multi-step synthesis of 6 and 7 from 31 and 32 through the addition of the dilithium salt of phenylphosphine, Li₂PPh (Scheme 1.2). Compounds 6 and 7 offer a potential easy and effective method to manipulate the steric bulk and electronic properties of the ligands. By manipulating the functional group R in the starting compound, various new phosphine ligands can be synthesised for A1. No evidence could be found in literature of these alicyclic phosphine compounds being used as ligands for A1.

Scheme 1.2  Ligands 6 and 7 offer more options for the manipulation of the steric bulk and electronic properties of a Grubbs-type precatalyst than ligand 30.

Organometallic chemists have been trying for more than 50 years to quantify the properties of transition-metal complexes in terms of the stereoelectronic properties of the ancillary ligands.26-29 Such quantification would in principle be useful as a probe into the mechanism and to predict and control the reactivity, stereochemistry, and regiochemistry of stoichiometric and catalytic reactions involving phosphines, phosphine complexes, and other related ligands.30 In order to investigate the electronic properties of ligands, a probe needs to be found that responds effectively and sensitively to changes in the electronic properties of the ligands.30
Over the last decade, molecular modelling has been successfully used in the study of chemical reactions catalysed by transition metals.\textsuperscript{31-33} Molecular modelling provides a powerful tool to study the catalytic reaction mechanism of alkene metathesis, where ruthenium carbenes are used, before arduous synthesis of these ligands is attempted. Complete studies of the Grubbs-type precatalyst systems are very limited.\textsuperscript{32,33}

1.2 Aim of the study

In literature, only limited attention has been paid to acyclic phosphine compounds that can be used as ligands for the Grubbs-type catalyst system.

The first aim of this study is to attempt to identify a phosphine-ligated Grubbs-type precatalyst for alkene metathesis with molecular modelling; to study the complete catalytic cycle of the precatalyst systems AL, Figure 1.1; and to determine whether phosphine compounds 4 to 8 and 10 to 28 will be suitable new ligands for the Grubbs-type precatalyst systems.

The second aim of this study is to attempt to identify the steric properties of the ligands and catalytic cycle steps with the Solid-G program as well as by means of the measurement of the various bond angles and lengths.

1.3 Literature references

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