# SYNLETT **Spotlight 59**

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## **NHC Ruthenium Complexes as Second Generation Grubbs Catalysts**

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### Introduction

Developments in two seemingly unconnected fields have given rise to a new family of powerful catalysts with many applications in olefin metathesis. On the one hand, the progress made over the past decade in the synthesis of N-heterocyclic carbenes (NHCs) and their complexes, as well as the catalytic applications of these systems, has been impressive.<sup>1,2</sup> On the other hand, the achievements in the evolution of homogeneous catalysts for olefin metathesis have turned this reaction into a common C–C coupling process<sup>3</sup> with various possibilities including ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), acyclic diene metathesis polymerization (ADMET), ring-opening metathesis (ROM), and cross-metathesis (CM or XMET).

Herrmann et al.<sup>4</sup> were the first to synthesize a modified Grubbs catalyst that included N-heterocyclic carbene ligands. The bis(NHC)-substituted derivatives 2 showed a minor improvement in terms of catalytic activity compared to conventional Grubbs catalyst 1. Soon after, papers concurrently published by Nolans',<sup>5</sup> Grubbs',<sup>6</sup> and Herrmanns'<sup>7</sup> groups described the synthesis of mono(NHC)-substituted complexes such as those of type 3 and 4. This new family of compounds has been called the second generation Grubbs catalysts.

The strong  $\sigma$  donor character of NHC ligands facilitates the dissociation of the phosphine in compounds 3 and 4 due to the trans effect, although the key step for olefin metathesis consists of the coordination of the olefin to the unsaturated ruthenium complex.<sup>8</sup> These new compounds (3 and 4), which are reasonably air- and water-stable, are more active than 2 or 1 and can also tolerate the presence of different functional groups (with the ex-

#### Abstracts

Complex 4a is able to catalyse RCM to give di-, tri- or tetra-substituted cycloolefins while complex 1 failed in the case of tri- and tetrasubstituted ones. The stability and tolerance towards different functional groups of the second generation Grubbs' catalyst has also been demonstrated.<sup>6b</sup>

situ. Mes Mes CL. PCy<sub>3</sub> O<sup>t</sup>Bu H 0.01 M Ph-H/THF C Cy₃P Cy<sub>3</sub> 80 °C, 15-30 min

2



CI

R = alkyl, aryl; R' = CH<sub>3</sub>, Cy, Cp

ception of basic ones like nitriles and amines).<sup>3a</sup> The enhanced

activity of these compounds means that the reactions can be carried out under mild conditions. Three years after its synthesis,6b

complex 4a [R = Mes (mesityl), R' = Cy] has become commer-

Compound 4a was synthesized from 1 and the saturated 1,3-dimesityl-2,3,4,5-tetrahydro-1H-imidazol-2-ylidene, which was

protected as the alkoxide to generate the free carbene ligands in

cially available<sup>9</sup> owing to its wide-ranging applications.







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The syntheses of several macrocycles by ring expansion have recently been published.<sup>10</sup> Bis-(vinylketones) and bis-acrylate systems react with a set of cycloalkenes, giving rise to a variety of structures in an atom-economical process employing only one catalyst. Factors like concentration or stoichiometry are crucial in order to control the product distribution.

En-yne CM between ethylene and alkynes substituted with a heteroatom in the propargylic or homopropargylic position failed when **1** was employed – except in the case where the heteroatom was protected. Nevertheless, even when a protection protocol is employed alcohols, ethers or silyl ethers do not react or react very poorly.<sup>11</sup> Chelation at the Ru centre is thought to be responsible for decelerating or shutting down catalysis. Complex **4a** is successful in this reaction without resorting to a protection/ deprotection sequence and gives the desired products with good/ excellent yields.<sup>12,13</sup>

Catalyst **4a** also performs well in ROMP reactions, thus showing its ability to build polymeric structures while tolerating the presence of a huge variety of polar functional groups. Different low-strain cyclic olefins, like cyclooctene or norbornene [using 1,4-bis(acetoxy)-*cis*-2-butene as a chain transfer agent (CTA)], have also been studied.<sup>14,15</sup>

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