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Review

Ruthenium vinyl carbene intermediates in enyne metathesis

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Contents

Abstract

This review provides an overview of ruthenium vinyl carbene reactivity as it relates to enyne metathesis. Methods for the synthesis of metathesis-active and metathesis-inactive complexes are also summarized. Some of the early hypotheses about vinyl carbene intermediates in enyne metatheses were tested in the arena of synthetic chemistry and subsequently led to mechanistic studies. In these two areas, studies from the author's labs are described. There are still many unresolved questions in enyne metathesis that trace back to vinyl carbene reactivity. Hopefully this review will stimulate further investigation into vinyl carbene reactivity which should further refine our understanding of catalytic enyne metathesis.

Keywords: Enyne metathesis; Vinyl carbene

1. Introduction

Enyne metathesis has emerged as an important synthetic method to construct conjugated dienes. The enyne metathesis joins an alkene and alkyne reactant together to produce

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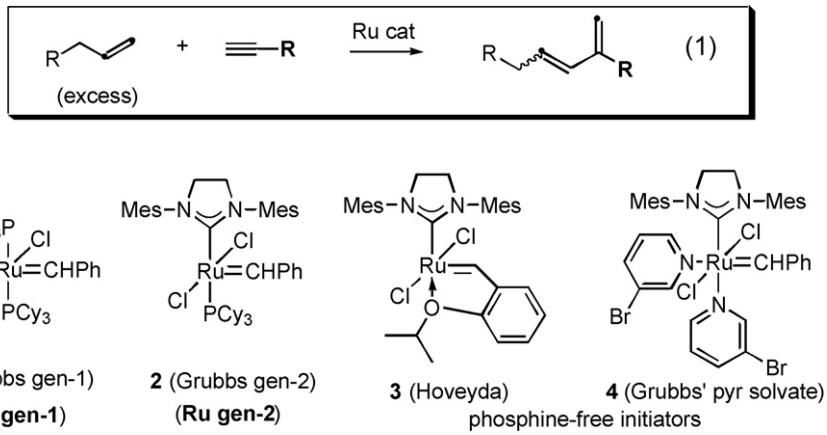
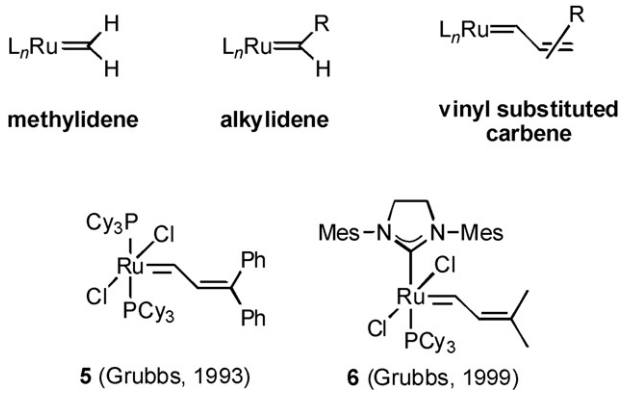


Scheme 1. Enyne metathesis and Grubbs' ruthenium carbene catalysts.

a conjugated 1,3-diene by pi bond reorganization (Eq. (1)). The intermolecular enyne metathesis, or 'cross-metathesis', is depicted in Eq. (1). This catalytic reaction is promoted by Grubbs' ruthenium carbenes, complexes **1**–**4** (Scheme 1). Though other late transition metal cycloisomerizations are known, the Grubbs' carbene-promoted reaction is mechanistically distinct. The high degree of chemoselectivity displayed by carbenes **1**–**4** explains their widespread use in metathesis. The chemoselectivity for alkenes is known as functional group tolerance, a paramount concern for controlling reactivity as needed in complex molecule synthesis. Though many metal complexes will promote intramolecular enyne bond reorganization, the Grubbs carbenes are by far the most useful carbene catalysts in enyne metathesis because they are functional group tolerant and because they promote intermolecular enyne metathesis. Several reviews are available [2–5].

Alkynes react with metal carbenes to produce vinyl carbene intermediates. A major difference between enyne and alkene metathesis is the presence of the alkyne in enyne metathesis. Alkene metathesis involves two types of carbene intermediate: the alkylidene and the methylidene. The alkylidene has the generic structure $L_nRu{=}CHR$. The methylidene has the general structure $L_nRu{=}CH_2$. Reaction of either of these ruthenium carbenes with alkynes produces vinyl carbene complexes of ruthenium (Scheme 2).



Scheme 2. Vinyl carbenes.

In fact, there are two stable 16-electron ruthenium vinyl carbenes known from Grubbs' group. The neophylidene complex **5** was the first group 8 carbene developed by Grubbs' group [6] and displayed characteristic high functional group tolerance suitable for applications in organic synthesis. This vinyl carbene was employed as a carbene initiator for early applications in alkene and enyne metathesis. The second vinyl carbene complex **6** features the *N*-heterocyclic carbene supporting ligand, which is typical of the 'second generation' Grubbs carbenes [7,8]. When the latter two stable ruthenium vinyl carbene complexes are employed as initiators, they produce alkylidene intermediates. The derived ruthenium alkylidenes are involved in catalysis. A fundamental question relates to the relative reactivity of ruthenium vinyl carbenes as compared to ruthenium alkylidenes. In addition, the substitution on the vinyl group can influence reactivity by steric or electronic effects, and this substitution is not present in an alkylidene.

Vinyl carbenes are unique *intermediates* in enyne metathesis. The presence of these ruthenium carbenes distinguishes enyne metathesis as a catalytic process uniquely different from alkene metathesis. Accordingly, the mechanism of catalysis involves alkene coordination complexes of vinyl carbenes, and vinyl carbene reactivity will influence the rate of catalysis. Though mechanistic details of catalysis are slowly emerging (*vide infra*) fundamental reactivity studies on vinyl carbenes are lacking. The purpose of this review is to survey ruthenium vinyl carbene complexes and relate our understanding of their reactivity to our emerging mechanistic view of catalytic enyne metathesis. It is significant to note that most of the known reactivity of ruthenium vinyl carbenes comes from inferences based on their intermediacy in catalysis. For organic chemists, this means that reactivity is deduced from phenomenology when studying the scope of reaction or influence of reaction parameters. Typically this judgment is focused on product yield rather than reaction rates. For organometallic chemists, the structure of vinyl carbenes has been studied. However, the structural study is often not linked to catalytic activity. It is therefore useful to blend both viewpoints of ruthenium vinyl carbene reactivity from these two bodies of literature to generate a cogent view of their structure and reactivity.