

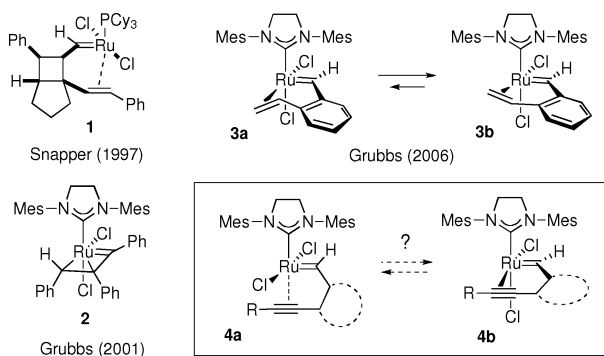
Structure and Reactivity of Alkyne-Chelated Ruthenium Alkylidene Complexes

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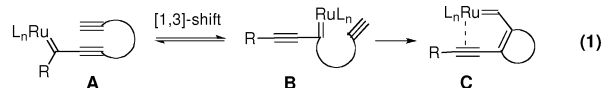
The coordination of an alkene or alkyne to the ruthenium metal center is one of the key steps in metathesis reactions catalyzed by Grubbs-type complexes.¹ Snapper and co-workers reported a crystal structure of alkene-chelated ruthenium complex **1** in which the tricyclohexylphosphine ligand and an alkene are bound to the ruthenium in trans fashion.² On the other hand, vinyl alkylidene complex **2**, an N-heterocyclic carbene (NHC)-containing ruthenium complex reported by Grubbs, shows a cis relationship between the NHC ligand and the bound alkene.³ Recently, Grubbs also reported crystal structures of both **3a** and **3b** in which the coordinated alkene and the NHC ligand have a cis relationship.⁴ In solution, **3a** and **3b** interconvert, providing a 2:3 equilibrium ratio at 25 °C.



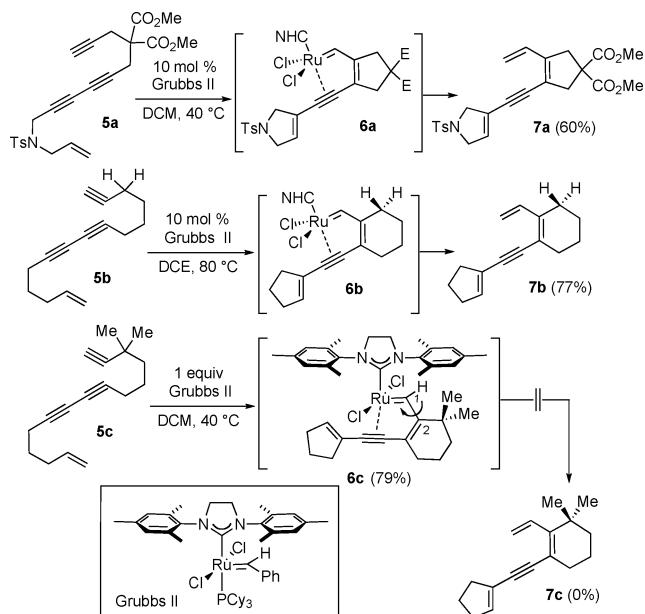
In contrast, neither a crystal structure nor a spectroscopy-based structural characterization of alkyne-coordinated Grubbs-type ruthenium complexes such as **4a** and **4b** has been reported to date. This discrepancy may be due to the lack of efficient methods for preparing Ru complexes containing proper elements that stabilize the alkyne-coordinated structures. It is expected that the characterization of alkyne-coordinated ruthenium complexes would provide important insight into the mechanism of enyne metathesis.⁵ This structural information would also provide a clue concerning the unproductive metathesis reactions of substrates containing multiple alkyne moieties. Herein we report the structure and reactivity of second-generation Grubbs-type ruthenium complexes containing an alkyne as a ligand.

On the basis of the reactivity of Grubbs-type Ru alkylidenes in enyne metathesis and the facile metallotropic [1,3]-shift,⁶ we envisioned that an alkynyl Ru alkylidene **A**, formed via an initial enyne ring-closing metathesis (RCM) or cross-metathesis (CM), would induce a metallotropic [1,3]-shift to provide a new alkylidene **B** (eq 1).⁷ Subsequent RCM of **B** would be expected to provide a new vinyl alkylidene **C**, which, because of the proximity of the cis-oriented alkyne moiety and the metal center, would form a chelated ruthenium complex stable enough to be isolated if appropriate stabilizing elements are present.

Initial attempts to isolate the expected alkyne-coordinated complexes **6a** and **6b** generated from substrates **5a** and **5b** and a



Scheme 1. Ring-Closing Metathesis of 1,3-Diynes and the Formation of an Alkyne-Chelated Ru Alkylidene Complex



stoichiometric amount of the second-generation Grubbs complex⁸ were not successful (Scheme 1). Only the final metathesis products **7a** and **7b** were isolated. Gratifyingly, however, the reaction of substrate **5c** containing a *gem*-dimethyl group at the propargylic carbon provided a deep-green crystalline material **6c** without the formation of metathesis product **7c**. X-ray diffraction analysis of **6c** clearly showed that the alkyne moiety is chelated to the ruthenium center trans to the NHC (Figure 1). The overall ligand array of **6c** around the ruthenium center is similar to that in the Grubbs–Hoveyda complex,⁹ in which an isopropoxide instead of an alkyne moiety is chelated to the ruthenium. To the best of our knowledge, **6c** is the first alkyne-bound Grubbs-type complex ever isolated and fully characterized.¹⁰

We surmised that one of the key structural features for formation of a stable alkyne chelate is the *gem*-dimethyl group, because a similar substrate **5b** lacking this group provided only the metathesis product **7b**. To gain further insight into stable alkyne-coordinated ruthenium complexes, we examined other substrates with variation of the propargylic substituents and the incipient ring size (Scheme 2). We expected that the propargylic substituents in alkylidenes **6d** and **6e** may affect their stability. The five-membered ring in **6f** and the seven-membered ring in **6g** would change the strength of the interaction between the alkyne and the ruthenium center because

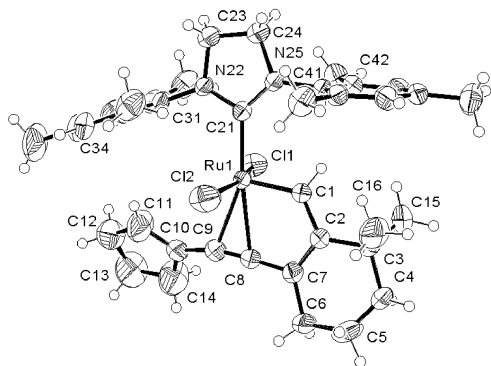
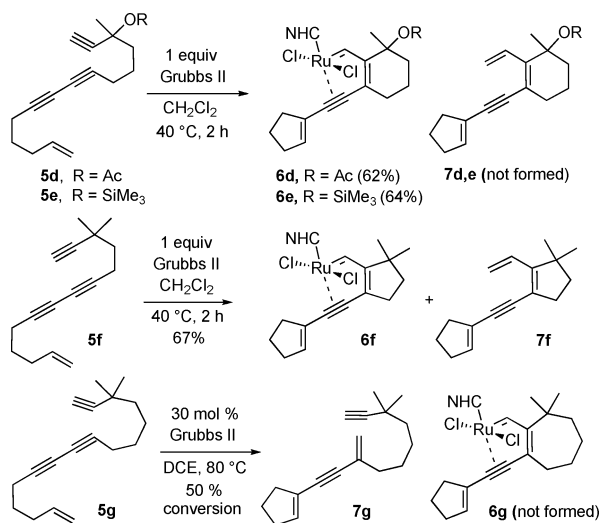


Figure 1. Molecular structure of **6c** in the solid state. Selected bond lengths (Å) and angles (deg): Ru1–C1, 1.851(3); Ru1–C21, 2.049(3); Ru1–C8, 2.370(4); Ru1–C9, 2.402(4); Ru1–Cl1, 2.3378(9); Ru1–Cl2, 2.3128(10); C1–Ru1–C21, 98.67(19); C1–Ru1–Cl1, 99.07(11); C1–Ru1–Cl2, 98.75(11); C1–Ru1–C9, 102.60(19).

of the different bond angles. Indeed, under identical reaction conditions, substrates **5d–g** showed markedly dissimilar behaviors. Substrates **5d** and **5e** provided metal complexes **6d** and **6e** exclusively without forming **7d** and **7e**, whereas the reaction of **5f** gave a mixture of complex **6f** and metathesis product **7f**.¹¹ It is disappointing that the expected seven-membered-ring closure did not happen in the reaction of **5g**, which gave only the prematurely terminated product **7g**, preempting the formation of **6g**.

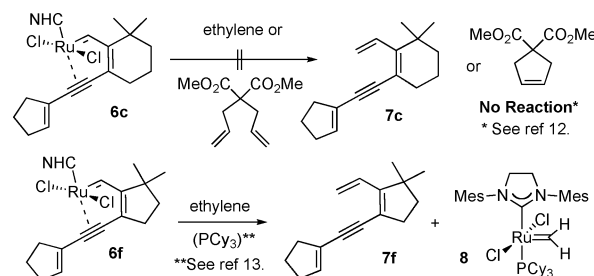
Scheme 2. Formation of Alkyne-Chelated Ru Alkylidenes



To examine whether these alkyne-complexed ruthenium species are viable catalysts for metathesis reactions, **6c** and **6f** were treated with ethylene (Scheme 3). As expected, complex **6c** containing the six-membered ring was recovered unchanged,¹² but complex **6f** containing the five-membered ring was readily converted to **7f** and methyldiene complex **8**.¹³

In conclusion, we have demonstrated that certain structural elements of Ru alkylidenes can effectively modulate their reactivity and stability by showing that alkyne-chelated ruthenium complexes can be isolated by introducing a *gem*-dimethyl group near the metal center. For the first time, we have obtained the X-ray crystal structure of a Ru alkylidene complex containing an alkyne as a

Scheme 3. Reactivity of Alkyne-Chelated Ru Alkylidenes



ligand. We believe that the observed alkyne–ruthenium chelate formation will not only provide insight into the mechanism of enyne metathesis but also guide us in the design of more efficient and sophisticated tandem processes.

Acknowledgment. We thank UIC and NIH (CA106673) for financial support of this work.

Supporting Information Available: An acknowledgment for the mass spectrometry facility at UIUC, general procedures, a CIF for **6c**, and characterization data for representative compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Complex **6f** was characterized by ¹H NMR monitoring without isolation (because of its instability) and by its conversion to **7f**. The reported yield is based on an internal standard (1,2,4,5-tetrabromobenzene).
- (12) In the reaction of dimethyl-2,2-diallyl malonate with **6c** (10 mol % in CDCl₃), both compounds remained unchanged after 3 h at 40 °C.
- (13) Ethylene was introduced into the reaction mixture after complete consumption of the starting material **5f**. Therefore, PCy₃ in complex **8** originated from the starting Grubbs II complex.

JA907155R