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Structure and Reactivity of Alkyne-Chelated Ruthenium Alkylidene Complexes

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Abstract

The isolation and structural characterization of alkyne-bound Ru-alkylidene complexes has been elusive. However, with a sequential enyne ring-closing metathesis of diyne moiety and metallotropic [1,3]-shift, followed by a second enyne ring-closing metathesis allowed the formation of a highly stable alkyne-chelated ruthenium complex. The full characterization of this complex was realized by NMR spectroscopy and X-ray crystallography.

The coordination of an alkene or an alkyne to the ruthenium metal center is one of the key steps in metathesis reactions catalyzed by Grubbs type complexes.¹ Snapper reported a crystal structure of alkene-chelated ruthenium complex **1** where the tricyclohexyl phosphine 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 *cis*-relationship between the NHC ligand and the bound alkene.³ Recently, Grubbs also reported crystal structures of both **3a** and **3b** where the coordinated alkene and *N*-heterocyclic carbene ligand have a *cis* relationship.⁴ In solution, **3a** and **3b** interconvert, providing a 2:3 equilibrium ratio at 25 °C.

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

In contrast, neither a crystal structure nor 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 to prepare Ru-complexes containing proper elements that stabilize the alkyne-coordinated structures. It is expected that the characterization of alkyne-coordinated ruthenium complexes would provide an important insight into the mechanism of enyne metathesis.⁵ Also this structural information would provide a clue for the unproductive metathesis reactions of substrates containing multiple alkyne moieties. Herein we report the structure and reactivity of the second-generation Grubbs-type ruthenium complexes containing an alkyne as the ligand.

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

(1)

Initial attempts to isolate the expected alkyne-coordinated complexes **6a/6b** generated from substrate **5a/5b** and a stoichiometric amount of the second-generation Grubbs complex⁸ were not successful (Scheme 1). Only the final metathesis products **7a/7b** were isolated.

Gratifyingly, however, the reaction of substrate **5c** containing *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 shows that the alkyne moiety is chelated to the ruthenium center trans to the *N*-heterocyclic carbene (Figure 1). The overall ligand array of **6c** around the ruthenium center is nearly similar to that of the Grubbs-Hoveyda complex,⁹ where an isopropoxide is chelated to the ruthenium instead of the alkyne moiety. 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 to form stable alkyne chelate is the *gem*-dimethyl group, because a similar substrate **5b** lacking this group provided only the metathesis product **7b**. To get further insight into stable alkyne-coordinated ruthenium complexes, we examined other substrates having variation at the propargylic substituents and the incipient ring size (Scheme 2). We expected that the propargylic substituents in alkylidene **6d,e** may

affect their stability. The 5-membered ring in **6f** and 7-membered ring in **6g** would change the strength of the interaction between the alkyne and the ruthenium center due to different bond angles. Indeed, under identical reaction conditions, substrates **5d–g** showed markedly dissimilar behaviors. Substrates **5d,e** provided metal complexes **6d,e** exclusively without forming **7d,e** whereas the reaction of **5f** gave a mixture of complex **6f** and metathesis product **7f**.¹¹ It is disappointing that the expected 7-membered ring closure did not happen in the reaction of **5g**, giving only a prematurely terminated product **7g**, which preempts the formation of **6g**.

To examine whether these alkyne-complexed ruthenium species are viable catalysts for metathesis reaction, **6c** and **6f** were treated with ethylene (Scheme 3). As expected, 6-membered ring-containing complex **6c** was recovered unchanged¹² but the 5-membered ring-containing complex **6f** was readily converted to **7f** and methyldiene complex **8**.¹³

In conclusion, we have demonstrated that certain structural elements on Ru-alkylidenes can effectively modulate their reactivity and stability such that alkyne-chelated ruthenium complexes could be isolated by introducing *gem*-dimethyl group near the metal center. For the first time, we have obtained X-ray crystal structure of a Ru-alkylidene containing an alkyne as the ligand. We believe that the observed alkyne-ruthenium chelate formation would not only provide an insight into the mechanism of enyne metathesis but also guide us to design more efficient and sophisticated tandem processes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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11. Complex **6f** was characterized by ^1H NMR monitoring without isolation due to 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 CDCl_3), both compounds were remained unchanged after 3 h at 40 °C.
13. Ethylene was introduced to the reaction after complete consumption of starting material **5f**. Therefore, PCy_3 in complex **8** is originated from the starting Grubbs II.

Figure 1.

Molecular structure of **6c** in the solid state with selected bond lengths (Å) and angles (°): Ru (1)–C(1) 1.851(3), Ru(1)–C(21) 2.049(3), Ru(1)–C(8) 2.370(4), Ru(1)–C(9) 2.402(4), Ru(1)–Cl(1) 2.3378(9), Ru(1)–Cl(2) 2.3128(10), C(1)–Ru(1)–C(21) 98.67(19), C(1)–Ru(1)–Cl(1) 99.07(11), C(1)–Ru(1)–Cl(2) 98.75(11), C(1)–Ru(1)–C(9) 102.60(19).

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

Scheme 2.
Formation of an Alkyne-Chelated Ru-Alkylidenes