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Structure and Reactivity of Alkynyl Ruthenium Alkylidenes

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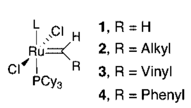
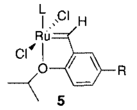
The stability and reactivity of Grubbs-type ruthenium complexes have been shown to be critically dependent on the nature of ligands on the metal and the substituents on the carbenic carbon.[1] The reactivity of Ru−methylidene (**1**)[1a,b] and its alkyl- (**2**),[1a,b] vinyl- (**3**),[1c] and phenyl-substituted (**4**)[1a,b,d] versions as well as the Hoveyda-type chelate (**5**) and its variants[2] are extensively studied and utilized in organic synthesis and polymer chemistry.[3]



1, R = H
2, R = Alkyl
3, R = Vinyl
4, R = Phenyl



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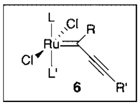

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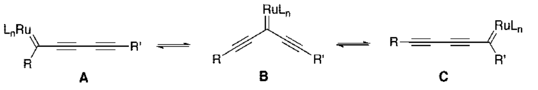
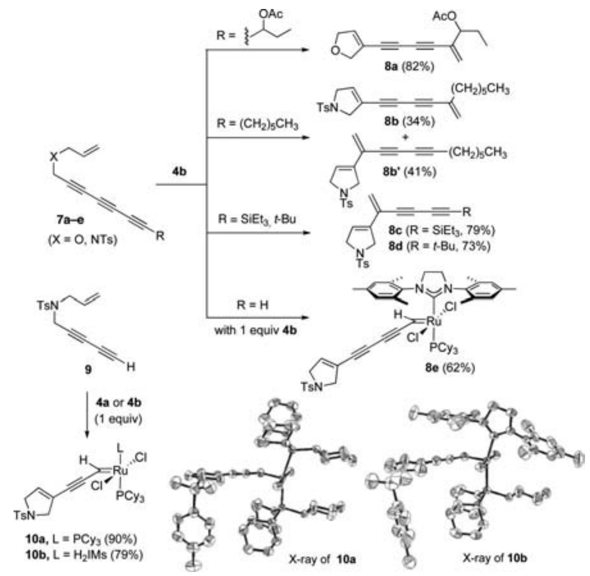
a: L = PCy$_3$
b: L = H$_2$IMs

However, to the best of our knowledge, little is known about the structure and reactivity of alkyne-substituted Ru−alkylidenes (**6**).[4] A part of this discrepancy could be due to the lack of efficient methods for their preparation, although several reported metathesis processes may involve the alkynyl Ru−alkylidene species as an intermediate.[5] In the enyne ring-closing metathesis of diyne- or triyne-containing substrates, putative alkynyl Ru−alkylidene species have been formed; however, because of their rapid metallotropic [1,3]-shift[6] and subsequent turnover, the isolation and structural characterization of these intermediates has been elusive. At this juncture, we surmised that the equilibrating alkylidenes **A**−**C** could be selectively trapped and fully characterized if suitable electronic and steric constraints of R and R′ substituents are met (eq 1). In this Communication we report the reactivity features of equilibrating Ru−alkynyl alkylidenes and their first X-ray structure-based characterization in the form of Grubbs-type and Hoveyda-type complexes.



(1)

Scheme 1. Regioselective Trapping of Alkynyl Ru−Alkylidenes



First, the substituent effect was examined with triynes **7a**−**e**,[7] which showed that both steric and electronic factors at the terminating end have a profound impact on the product distribution (Scheme 1). With Grubbs second-generation catalyst **4b**, substrate **7a** with an acetoxy-substituted alkyl group gave diyne **8a** (82%), whereas simple alkyl-substituted triyne **7b** gave a mixture of **8b** (34%) and **8b′** (41%). Triethyl silyl and *t*ert-butyl-substituted triynes **7c**[6] and **7d** provided exclusively **8c** (79%) and **8d** (73%). Surprisingly, terminal triyne **7e** (R = H) did not undergo catalytic turnover but afforded **8e** in 62% yield when a stochiometric amount of **4b** was used.[8] Similarly, diyne **9**[9] provided complexes **10a** (93%) and **10b** (79%) with stoichiometric amounts of **4a** and **4b**, respectively. The X-ray structures of **10a** and **10b** show a typical arrangement of ligands around the metal center without having any extra interaction of the attached alkyne moiety to the metal.[8,10] These results clearly indicate the important role of steric hindrance at the terminal position in generating alkylidene **A** and **C**. The lack of formation of products derived from Ru−alkylidene **B** in these reactions is less likely due to the steric hindrance of dialkynyl groups but more due to its less favorable electronic environment: cross-conjugation and the presence of two electron-withdrawing alkynyl substituents on the carbenic carbon. On the other hand, the particular stability (low reactivity) of alkynyl alkylidenes **8e** and **10a**,**b** is assumed to be the consequence of a low steric pressure exerted by the alkyne moiety in combination with that of the hydrogen on the carbenic carbon. Thus, once rebound to form a catalyst resting state, the dissociation of tricyclohexyl phosphine ligand from **8e** and **10a**,**b** would become more difficult compared to that of the corresponding alkyl-substituted alkylidenes.[11]

To gain more insight into the influence of substituents on the metallotropic shift versus turnover of the intermediate alkylidenes, probes **11a**−**c** and **15a**−**c** were examined (Scheme 2). The formation of stable complex **12** from **11a** (R = H) in the presence of a stoichiometric amount of **4b** indicates that the metallotropic shift could not be initiated from **12** once it is formed. On the other hand, rapid formation of metathesis products **13** (R = Me) and **14** (R = CH$_2$OPMB) from similar substrates **11b** (R = Me) and **11c** under catalytic conditions implies an efficient initiation of metallotropic shift followed by its termination by the tethered alkene. In comparison, despite an effective initiation of metallotropic shift, the termination behaviors of **15a**−**c** are markedly different. Substrate **15a** afforded only **16**, which is consistent with the termination mode of silylated alkyne **7c** producing only **8c**.[12] On the other hand, **15b** a *tert*-butyl surrogate of **7d**, afforded both **17a** (30%) and **17b** (41%). The exclusive formation of **18** from **15c**,

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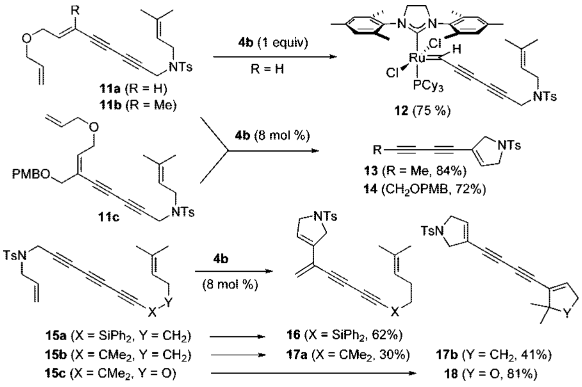
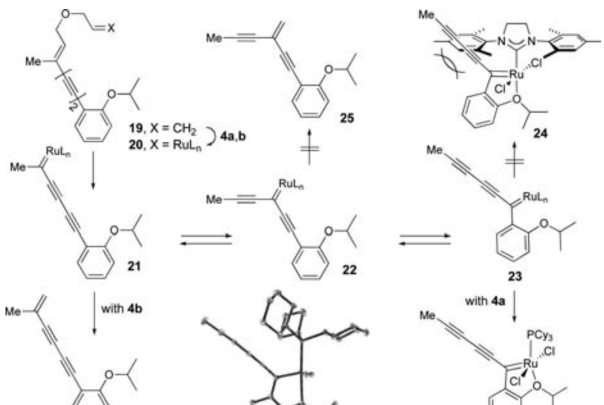
where a methylene unit of the tether in **15b** is replaced by and oxygen atom, further demonstrates that even a subtle difference in steric and electronic factors of substituents profoundly affects the metallotropic shift and turnover behavior of the equilibrating alkylidenes.

Scheme 2. Reactivity Difference of Alkynyl Ru−Alkylidenes



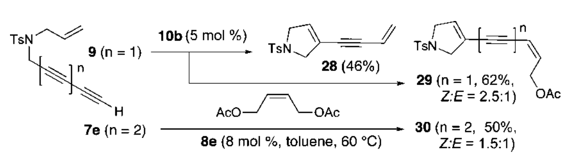
Next, chelation-induced trapping of equilibrating alkylidenes was explored with diyne **19** (Scheme 3). We predicted that the initial relay metathesis-based catalyst delivery[5a,13] to the trisubstituted double bond from **20** would generate alkylidenes **21**−**23**. Once the metal center is proximal to the isopropoxide moiety, the chelate formation[2,10] would ensue, which will shift the equilibrium toward **24**. However, a stoichiometric reaction between **19** and **4b** provided **26** as a sole product without the formation of **24** or **25**. Probably, the unavoidable interaction between one of the mesityl groups and the diyne moiety on **24** is energetically too unfavorable, rendering the rapidly equilibrating alkylidenes **21**−**23** to be trapped at the electronically most favorable or sterically least hindered site to deliver **26** selectively. On the other hand, the reaction between **19** and a stoichiometric amount of first-generation catalyst **4a** gave a new complex **27** quantitatively. We inferred that contrary to **24** complex **27** can avoid the severe steric clash by positioning the diyne moiety between the two cyclohexyl group of tricyclohexylphsophine ligand, which is unambiguously shown by the X-ray structure.

Scheme 3. Formation of a Chelated Alkynyl Ru−Alkylidene



Although stable enough to be isolated, some alkynyl Ru−alkylidenes retain metathesis activity. With a catalytic amount of **10b** (5 mol %), diyne **9** gave metathesis product **28** in 46% yield. Also, in the presence of added alkene, substrate **9** and **7e** gave RCM-CM product **29** and **30** in 62% and 50% yield, respectively. However, complex **27** did not show metathesis activity under the same conditions.

Scheme 4. Reactivity of Isolated Alkynyl Ru−Alkylidene **10b**



In conclusion, we have demonstrated that substituent on alkynyl Ru−alkylidenes can effectively modulate their reactivity and metallotropic [1,3]-shift behavior. For the first time, we have obtained X-ray crystal structures of alkynyl Ru−alkylidenes and the reactivity of these complexes was briefly examined. The behaviors of these unprecedented ruthenium complexes provide further insights into the reactivity of Grubbs-type complexes. Studies on the higher homologues of alkynyl Ru−alkylidenes and their metallotropic shift behavior will be reported in due course.

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Supporting Information Available: General procedures, CIF's for **10a**,**b**, **27**, characterization for representative compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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