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研究課題名（英文）Schrock-Type Silylene/Germylene Complexes of Transition Metals: On the Way to the Si or Ge Versions of Metathesis Process

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研究成果の概要（和文）：不飽和炭化水素化合物のメタセシス反応は、合成化学的に極めて有用な反応である。しかし、ケイ素やゲルマニウムからなる不飽和結合化合物のメタセシス反応は、これまで全く例がなく、もし高周期元素多重結合化合物のメタセシス反応が可能になれば、その技術の応用範囲は計り知れない。本基盤研究期間中に、Schrock型アルキリデン錯体のケイ素およびゲルマニウム類縁体の合成に成功した。４族遷移金属のシリレンあるいはゲルミレン錯体の構造解析を行い、また反応性に関しても理論、実験の両面より検討し、初めてのSchrock型シリレンおよびゲルミレン錯体であることを明らかにした。

研究成果の概要（英文）：Metathesis of unsaturated hydrocarbons is among the most technologically useful alkene transformations. The Si and Ge variations of the metathesis represent a new promising route for the synthesis of the highly reactive multiply-bonded organosilicon and organogermanium compounds as precursors for the advanced materials of the new generation. In this project we developed the first examples of the Schrock-type alkylidene complexes of Si and Ge, namely, silylidenes and germylidenes, of the early transition metals. Thus, stable silylene and germylene complexes of the group 4 metals were prepared, isolated, structurally characterized, and computationally studied. All data support classification of such complexes as Schrock-type silylidenes and germylidenes, which react with unsaturated substrates (alkynes, alkenes, nitriles) forming the corresponding [2 + 2] cycloadducts, whose particular structures and cycloreversion were studied both experimentally and computationally.

研究分野：有機化学

キーワード：cycloaddition　germylene　metathesis　Schrock complex　silylene

１．研究開始当初の背景

Alkene metathesis involves a redistribution of alkylidene fragments by the cleavage of the C=C bonds in alkenes, catalyzed by the transition metal carbene complexes. Metathesis of alkenes, alkynes, mixed metathesis of alkenes and alkynes, as well as their numerous variations (cross-metathesis, ring-closing metathesis, ring-opening metathesis, ring-opening-metathesis polymerization) are among the most technologically useful and ecologically friendly alkene transformations. As a sign of recognition of the importance of the metathesis process, a Nobel Prize was awarded to Y. Chauvin, R. H. Grubbs and R. R. Schrock in 2005.

The silicon and germanium versions of the metathesis process represent a totally unprecedented and very promising route for the synthesis of multiply-bonded organosilicon and organogermanium compounds, which may serve as the precursors for the advanced materials of the new generation. However, to date, there were no reports about any success in the field of silicon and germanium metathesis. To achieve this goal, at first we developed novel synthetic routes to the Schrock-type silylene and germylene compexes of the early transition metals (**Scheme 1**), based on the previously reported by us tetrasila- and tetragermacyclobutadiene dianion derivatives [*J. Am. Chem. Soc.* **2004**, *126*, 4758; *J. Am. Chem. Soc.* **2011**, *133*, 5103]

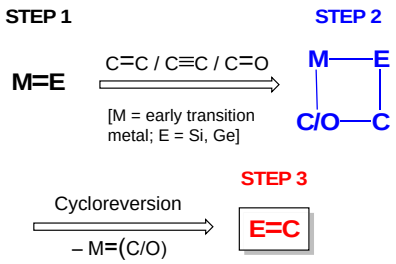
$Cp_2M{=}Si(SiR_3)_2$　　$Cp_2M{=}Ge(SiR_3)_2$

[M = Ti, Zr, Hf; R = alkyl group]

Scheme 1

２．研究の目的

The final goal of our project was the development of the totally unprecedented silicon and germanium versions of the commercially very important metathesis process as the principally novel route to a variety of multiply-bonded organosilicon and organogermanium derivatives. Accordingly, the project consisted of three major steps: 1) First step: synthesis of the novel Schrock-type silylene and germylene complexes of the early transition metals (TM), first of all - group 4 metals, possessing coordinatively unsaturated TM centers; 2) Second step: development of the [2 + 2] cycloaddition reactions of the above-mentioned silylene/germylene complexes and a variety of unsaturated hydrocarbons (alkenes, alkynes, 1,3-dienes, enynes, etc.) as well as carbonyl compounds (aldehydes and ketones); 3) Third step: optimization of the above-described cycloaddition reactions and search for the best reaction conditions allowing for the subsequent cycloreversion and generation of the novel silicon and germanium multiply-bonded derivatives as the target compounds of this project (**Scheme 2**). Successful realization of the specific goals of our project was expected to have an important impact on academic and industrial organometallic chemistry, both main group elements and transition metal chemistry fields. The unsaturated organometallic compounds, prepared by this method, are very prospective models to study their structural, bonding and reactivity aspects. Moreover, depending on their structural environment, such compounds can serve as the precursors for novel materials possessing unique electronic properties. From the synthetic point of view, development of the silicon and germanium versions of metathesis could open totally new ways for the highly reactive unsaturated organometallic species that are inaccessible in any other known synthetic method.



Scheme 2

３．研究の方法

(1) At first, for the preparation of the Schrock-type silylidene and germylidene complexes, we will use 1,1-dianionic derivatives of the type $(R_3Si)_2ELi_2$ [E = Si, Ge], which are very useful in the synthesis of a great variety of doubly-bonded derivatives. Their reaction with the dihalides of the early transition metal complexes (first of all, group 4 metals) X_2ML_n [X = Cl, Br] is expected to provide an access to the Schrock-type complexes of the type $L_nM{=}E(SiR_3)_2$.

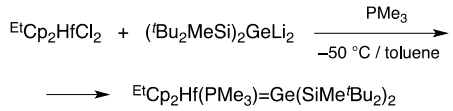
(2) Next, we will utilize alkali and alkaline earth metal derivatives of the “heavy” cyclobutadienedianion $[(R_3Si)_4E_4]^{2-}{\bullet}[K^+(thf)_2]_2$ [E = Si, Ge] and “heavy” bicyclo[1.1.0]butane dianion $[(R_3Si)_4E_4]^{2-}{\bullet}[Ca^{2+}(thf)_4]$ [E = Si, Ge] as precursors for the Schrock-type complexes. It is expected that their reaction with the metallocene dihalides Cp_2MX_2 in the presence of Lewis base (LB) would produce the Schrock-type silylene (and germylene) complexes $Cp_2(LB)M{=}E$, based on our preliminary results on the reaction of such

dianionic derivatives with the group 6 metallocene dichlorides.

(3) Above described Schrock-type silylene (and germylene) compexes will be reacted with the unsaturated substrates, such as alkenes and alkynes, to form the desired four-membered ring [2 + 2] cycloadducts. A wide range of alkyl-, aryl- and silyl-substituted alkenes, alkynes, dienes, as well as carbonyl compounds, such as formaldehyde, benzaldehyde, benzophenone, etc. will be tested for this reaction. The novel [2 + 2] cycloadducts, metallacyclobutanes (or metallacyclobutenes), are expected to undergo the subsequent cycloreversion and generation of the novel silicon and germanium multiply-bonded derivatives E=C as the final goal of this project.

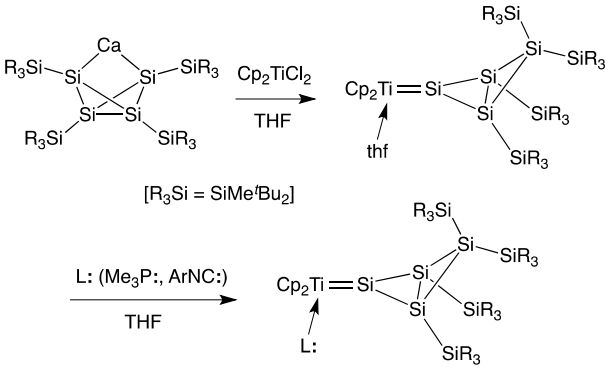
4．研究成果

(1) By the reaction of 1,1-dilithiogermane $(^{t}Bu_2MeSi)_2GeLi_2$ with the hafnocene dichloride $(\eta^5\text{-}C_5H_4Et)_2HfCl_2$ we successfully prepared rare example of the hafnium germylene complex, that was classified as the Schrock-type germylidene, $(\eta^5\text{-}C_5H_4Et)_2Hf{=}Ge(SiMe^{t}Bu_2)_2$ (**Scheme 3**) [*Organometallics*, **2015**, *34*, in press; DOI: 10.1021/om501134a].



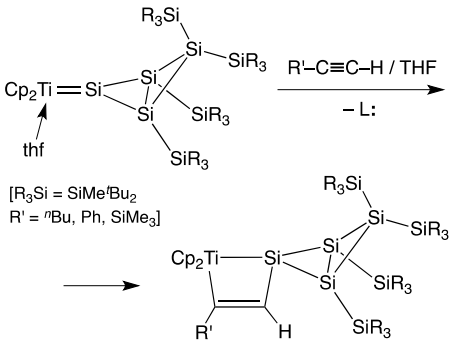
Scheme 3

(2) At first, in addition to the previously prepared tetrasilacyclobutadiene dianion derivative, we synthesized its germanium analogue, namely, tetragermacyclobutadiene dianion dipotassium salt $[(^{t}Bu_2MeSi)_4Ge_4]^{2-}\bullet[K^{+}(thf)_2]_2$ [*J. Am. Chem. Soc.* **2011**, *133*, 5103]. Both silicon and germanium cyclobutadiene dianion derivatives were used to generate alkaline earth metal salts of the tetrasila- and tetragermabicyclo-[1.1.0]butane-2,4-diide, from which Schrock-type complexes were prepared. Thus, reaction of the calcium salt of the tetrasilabicyclo[1.1.0]butane-2,4-diide with titanocene dichloride smoothly formed the desired Schrock-type titanium silylidenes with the different Lewis base ligands [thf, Me_3P, $(2,6\text{-}Me_2\text{-}C_6H_3)NC$] at the Ti center [*J. Am. Chem. Soc.* **2013**, *135*, 2987] (**Scheme 4**). This reaction is quite common for all group 4 metals and smoothly proceeds also with zirconocene and hafnocene dihalides, forming the corresponding zirconium and hafnium silylidenes. The Cp- and Lewis base ligands at TM center can also be varied.



Scheme 4

(3) Above described Schrock-type silylene (and germylene) compexes were reacted with the variety of unsaturated substrates, including terminal alkynes R–C≡C–H, nitriles R–C≡N, etc. [*J. Am. Chem. Soc.* **2013**, *135*, 2987], representing unprecedented [2 + 2] cycloaddition between the silylene TM complexes and unsaturated substrates (**Scheme 5**). The structures of the four-membered ring cycloadducts were verified by X-ray crystallography and NMR spectroscopy. According to our preliminary studies, whereas metallacyclobutenes ([2 + 2] cycloadducts with triply-bonded substrates) were thermally stable, their saturated analogues, metallacyclobutanes ([2 + 2] cycloadducts with doubly-bonded substrates), may undergo cycloreversion, which paves the way for the synthesis of novel metallaalkenes >E=C<.



Scheme 5

5．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

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〔産業財産権〕

○出願状況（計０件）

○取得状況（計０件）

〔その他〕

ホームページ等

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