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 研究課題名（和文）高周期 14 族元素環状ポリイン配位子をもつ遷移金属錯体に関する研究
 研究課題名（英文）Transition Metal Complexes with the Cyclic Polyene Ligands of the Heavy Group 14 Elements
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研究成果の概要（和文）：

近年、炭素 π 電子系の高周期元素類縁体が知られるようになった。そこで高周期元素からなる環状 π 配位子もつ有機金属錯体の構造や性質の解明を行った。本研究ではケイ素、ゲルマニウム等の高周期 14 族元素からなるシクロブタジエンジアニオンやシクロペンタジエニドを合成し、その構造や電子状態を比較検討した。テトラゲルマシクロブタジエンジアニオンは現在知られている 6 π 電子配位子の中では最も重い高周期元素からなる化合物である。

研究成果の概要（英文）：

Using tetragermacyclobutadiene dianion derivatives, we synthesized novel coordination compounds with the unprecedented tetragermacyclobutadiene ligand, including iron and cobalt complexes. It was found that the ligand is much stronger pi-donor.

交付決定額

(金額単位：円)

	直接経費	間接経費	合計
2009 年度	1,900,000	570,000	2,470,000
2010 年度	900,000	270,000	1,170,000
2011 年度	900,000	270,000	1,170,000
年度			
年度			
総計	3,700,000	1,110,000	4,810,000

研究分野：化学

科研費の分科・細目：基礎化学・有機化学

キーワード：有機元素化学

1. 研究開始当初の背景

The field of the low-coordinate compounds of the heavy group 14 elements is one of the most important and fundamental areas of the contemporary organometallic chemistry with many world-leading research groups being involved in such studies. The synthesis of the tri- and dicoordinate derivatives,

featuring double or triple bonds between the group 14 elements, is one of most attractive synthetic targets for organometallic chemists during several decades. On the other hand, utilization of the cyclic polyene ligands with the skeletal heavy group 14 elements for the synthesis of the novel transition metal complexes became recently a new great synthetic

challenge, bridging together the research areas of both main group and transition metals chemistry. However, this field was very poorly explored until now. Therefore, the main purpose of our project proposals is the breakthrough in such highly promising novel area, associated with the systematic synthesis, study and search for practical application of the transition metal complexes of the new generation featuring heavy group 14 elements in their cyclic polyene ligands.

(1) Heavy Analogues of Alkenes

The field of the doubly-bonded derivatives of the heavy group 14 elements ("heavy alkenes") was developed since the synthesis of the first stable disilene $\text{Mes}_2\text{Si}=\text{SiMes}_2$ by R. West (USA) in 1981. Our contribution to this field includes the first heteronuclear "heavy alkenes, dienes and allenes": $>\text{Si}=\text{Ge}<$ (*J. Am. Chem. Soc.* **2000**, *122*, 9034, 12604, highlighted in *ACS C&E News*, **2000**, issue 39, p. 39), $>\text{Si}=\text{Sn}<$ (*J. Am. Chem. Soc.* **2002**, *124*, 14822, highlighted in *ACS C&E News*, **2002**, issue 50, p. 24), $>\text{Ge}=\text{Sn}<$ (*Organometallics* **2003**, *22*, 1483), $[\text{E}-\text{M}-\text{E}] \cdot \text{Li}^+$ ($\text{E} = \text{Si}, \text{Ge}$; $\text{M} = \text{Ga}, \text{In}$) (*J. Am. Chem. Soc.* **2004**, *126*, 5058; *Chem. Lett.* **2008**, *37*, 1146).

(2) Heavy Analogues of Cyclic Polyenes

We also synthesized the first examples of the new class of compounds – cyclic polyenes and their anionic derivatives: **heavy cyclopropenes** (*J. Am. Chem. Soc.* **2000**, *122*, 9034; *Angew. Chem. Int. Ed.* **2005**, *44*, 6378; *J. Am. Chem. Soc.* **2007**, *129*, 2436), **heavy cyclobutenes** (*J. Am. Chem. Soc.* **2003**, *125*, 6012; *J. Am. Chem. Soc.* **2004**, *126*, 4758; *Angew. Chem. Int. Ed.* **2004**, *43*, 6703; *J. Am. Chem. Soc.* **2008**, *130*, 2758), **heavy cyclopentadienes** (*J. Am. Chem. Soc.* **2000**, *122*, 12604; *J. Am. Chem. Soc.* **2005**, *127*, 13142; *J. Am. Chem. Soc.* **2007**, *129*, 10340).

(3) Heavy Analogues of Carbocations, Free Radicals, Carboanions

Another important class of low-coordinate organometallics, tricoordinate cations, radicals and anions of the heavy group 14 elements, was a long-standing problem and highly desirable target for organometallic chemists. Our group prepared the first isolable Si-, Ge- and Sn-cations, radicals and anions and established their reversible redox interconversion (*J. Am. Chem. Soc.* **2002**, *124*, 9865; *J. Am. Chem. Soc.* **2003**, *125*, 9250; *Angew. Chem. Int. Ed.* **2003**, *42*, 1143; *J. Am. Chem. Soc.* **2004**, *126*, 11758; *Acc. Chem. Res.* **2007**, *40*, 410).

(4) Heavy Analogues of Cage Compounds

The chemistry of the polyhedral cage compounds with a "non-classical" hybridization of the skeletal atoms, first of all, bicyclo[1.1.0]butanes and tricyclo[2.1.0.0^{2,5}]pentanes, is one of the milestone discoveries in organic chemistry. We prepared the first heavy group 14 element analogues of the cage compounds with either extremely long, **tricyclo[2.1.0.0^{2,5}]pentanes** (*J. Am. Chem. Soc.* **2002**, *124*, 9962), or extremely short, **bicyclo[1.1.0]butanes** (*J. Am. Chem. Soc.* **2007**, *129*, 2436; *J. Am. Chem. Soc.* **2008**, *130*, 2758), bridging E–E bonds.

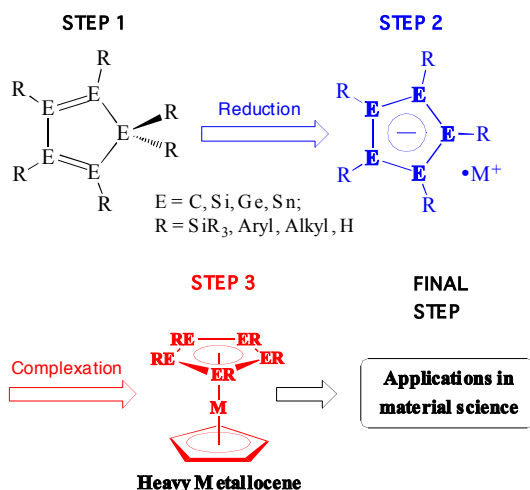
2. 研究の目的

Based on our experience and previous achievements in the field of low-coordinate derivatives of heavy group 14 elements (particularly, cyclic polyenes), we decide to start up a new project bridging the fields of the main group elements and transition metals. The major goal of this project is the design, study and search for the practical applications of the totally new class of hybrid main group element–transition metal complexes. The project consists of three major steps: 1) synthesis of the cyclic polyenes, 2) generation of the aromatic ($4n + 2$) p-electron species from them, 3)

synthesis of the transition metal complexes with the heavy cyclic polyene ligands. Finally, we plan to find the possible utilization of new complexes: catalysis, supramolecular chemistry, nonlinear optics, molecular magnets, etc.

3. 研究の方法

Abstract: During the period of the proposed project we plan to develop the synthesis and study of the transition metal complexes with the cyclic polyene ligands of the heavy group 14 elements. Such complexes are expected to possess novel, technologically attractive, highly promising properties, which would allow their successful practical utilization for production of advanced easily processable materials of the new generation for various branches of our life.



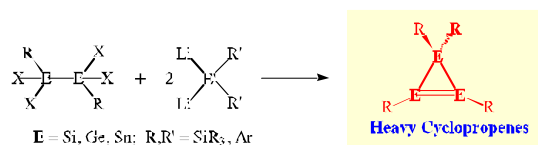
(1) The first year of the project (2009.4 – 2010.3):

During the first year of the project we will synthesize precursors of the 2π - and 6π -electron charged derivatives (cyclopropenylum ion $R_3E_3^+$, cyclobutadiene dianion $R_4E_4^{2-}$ and cyclopentadienide ion $R_5E_5^-$; E = Si, Ge, Sn, Pb). The chemistry of such compounds is still largely unexplored, therefore the novel synthetic strategies based on the specific properties of the heavy group 14 elements will be developed.

The heavy cyclopropenes R_4E_3 (precursors for the heavy cyclopropenylum

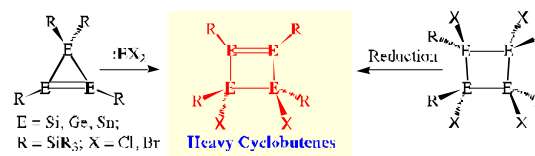
ions $R_3E_3^+$) are planned to be prepared by the recently discovered by us coupling reaction of tetrahalodimetalanes RX_2E-EX_2R and 1,1-dilithio derivatives R'_2ELi_2 in aromatic solvents (Scheme 1).

Scheme 1: Synthesis of the Heavy Cyclopropene Derivatives



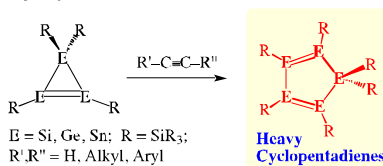
The heavy cyclobutenes $R_4X_2E_4$ (precursors for the heavy cyclobutadiene dianions $R_4E_4^{2-}$) will be prepared by either cycloaddition–ring expansion of the heavy cyclopropenes R_4E_3 or reduction of the corresponding halocyclo-tetrametalanes $R_4X_4E_4$ (Scheme 2).

Scheme 2: Synthesis of the Heavy Cyclobutene Derivatives



The heavy cyclopentadienes R_6E_5 (precursors for the heavy cyclopentadienide ions $R_5E_5^-$) will be synthesized by the cycloaddition–ring expansion reaction of the heavy cyclopropenes R_4E_3 and alkynes (Scheme 3).

Scheme 3: Synthesis of the Heavy Cyclopentadiene Derivatives



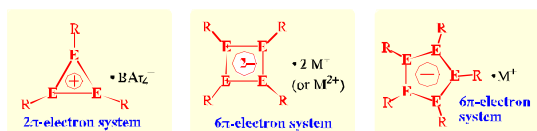
All above-described precursors will be synthesized in necessary amounts (gram-order scales) to for their further transformation to the 2π - and 6π -electron species, and finally – to transition metal complexes.

(2) The second and third years of the project (2010.4 –2012.3):

During the second year of the project

we plan to generate stable charged $2\pi^-$ and $6\pi^-$ -electron heavy analogues of the cyclopropenylum ion, cyclobutadiene dianion and cyclopentadienide ion derivatives (Scheme 4).

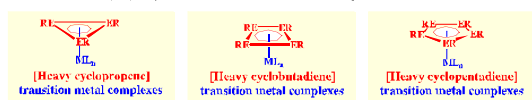
Scheme 4: Heavy Cyclopropenylum Ions, Heavy Cyclobutadiene Dianions, Heavy Cyclopentadienide Ions



Thus, the heavy cyclopropenylum ions are planned to be prepared by the oxidation of heavy cyclopropenes (Scheme 1) with the powerful Lewis acids, such as $\text{Ph}_3\text{C}^+\cdot\text{BAR}_4^-$, $\text{Et}_3\text{Si}^+\cdot\text{BAR}_4^-$, etc. The heavy cyclobutadiene dianions will be prepared by the dehalogenative reduction of the heavy cyclobutenes (Scheme 2) with either alkali or alkaline earth metals. The heavy cyclopentadienide ions are planned to be prepared by the desilylative reduction of the heavy cyclopentadienes (Scheme 3) with alkali metals. The synthesis of target $2\pi^-$ and $6\pi^-$ -electron species will be accompanied by their comprehensive investigation: estimation of their aromaticity, study of their structures and bonding, synthetic application of these species in organometallic chemistry.

Finally, during the third year of the project we will utilize such $2\pi^-$ and $6\pi^-$ -electron species as ligands for the synthesis of the novel transition metal complexes (first of all, metallocenes) for their possible technological use. The reactions of the above-described $2\pi^-$ and $6\pi^-$ -electron derivatives with a variety of transition metal complexes (first of all, of the groups 6–9) will be performed to prepare the desired novel complexes (Scheme 5). After the preparation of such complexes, their particular structures and

Scheme 5: Heavy Cyclopropene, Heavy Cyclobutadiene and Heavy Cyclopentadiene Transition Metal Complexes



bonding interactions will be studied in details. As a final part of the work, the newly synthesized complexes will be tested for their possible practical utilization as precursors for OMCVD and conducting materials, coatings, ceramics, polymers, nanocrystals for electronic devices, etc.

In the case of problems to realize our original plan for the synthesis of appropriate precursors for the cyclic polyene ligands for novel transition metal complexes, we will then examine other synthetic routes for their preparation, for example: for the synthesis of heavy cyclopropenes – direct coupling of REX_3 and $\text{R}_2\text{E}'\text{X}_2$ with metallic Na, for the synthesis of heavy cyclobutenes – reduction of REX_3 with LiNp or KC_8 , for the synthesis of heavy cyclopentadienes – coupling reaction of the heavy cyclobutadiene dianions $\text{R}_4\text{E}_4^{2-}\cdot 2\text{M}^+$ with dihalometallanes R_2EX_2 , etc.

To realize the specific goals of the project, we have a team of undergraduate, graduate and post-graduate students, supervised by the staff members. In the framework of the project we plan to collaborate with the world-famous groups of both theoreticians (Profs. Y. Apeloig (Israel) and G. Frenking (Germany)) for comprehensive computational studies and experimentalists (Profs. J. Escudie (France) and M. Driess (Germany)) for the joint synthetic work.

4. 研究成果

The precursor for the “heavy” cyclobutadiene dianion derivative, dichlorotetragermacyclobutene, was successfully prepared and fully characterized. By the reduction of this precursor with potassium graphite, the heaviest analogue of the $6\pi^-$ -electron cyclobutadiene dianion, namely, tetragermacyclobutadiene dianion dipotassium salt derivative, was synthesized and structurally characterized for the first time, and its preparation method was optimized. The degree of

aromaticity of this compounds was evaluated from both experimental and computational points of view, systematic structural comparison of the tetragermacyclobutadiene cyclobutadiene dianion to its lighter analogues, silicon and carbon counterparts, has been made. From the structural and magnetic (computational) properties of this new compound, it was classified as a non-aromatic organometallic. The reactivity of both neutral precursor, 3,4-dichlorotetragermene, and the dipotassium salt of the tetragermacyclobutadiene dianion derivative was studied with the particular attention paid for their utilization as the novel ligands for transition metal complexes of the new generation. Both compounds appeared to be very useful for the preparation of novel coordination compounds with the tetragermacyclobutadiene ligand. Thus, several novel coordination compounds with the unprecedented tetragermacyclobutadiene ligand, including (tetragermacyclobutadiene)tricarbonyl iron and (tetragermacyclobutadiene)cobalt cyclopentadienyl complexes, were successfully synthesized. The solution and solid-state structures and particular bonding situations of the newly prepared complexes were determined by the spectroscopic, structural and computational methods. On the basis of X-ray crystallography, ¹³C NMR spectroscopy and IR spectroscopy, it was found that the tetragermacyclobutadiene ligand is much stronger π -donor towards the transition metal than the corresponding carbon and even silicon analogues. Such enhanced π -donating ability of the tetragermacyclobutadiene ligand was attributed to its higher HOMO energy level compared with those of the tetrasilacyclobutadiene and cyclobutadiene ligands.

5. 主な発表論文等

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[その他]

ホームページ等

<http://nao.chem.tsukuba.ac.jp/sekiguch/index.htm>
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