

令和 3 年 6 月 9 日現在

機関番号：12102
研究種目：基盤研究(C) (一般)
研究期間：2018～2020
課題番号：18K05137
研究課題名(和文) Binuclear Sandwiches of the Main Group Elements

研究課題名(英文) Binuclear Sandwiches of the Main Group Elements

研究代表者
Lee Vladimir (Lee, Vladimir)

筑波大学・数理物質系・講師

研究者番号：90375410
交付決定額(研究期間全体)：(直接経費) 3,400,000円

研究成果の概要(和文)：主要族元素を含む多層式多核サンドイッチ化合物は、新しい多面体クラスターであり、光素子や光データストレージ、データ伝送への利用の可能性から、最近大きな関心を集めている。しかし、これらの錯体はどれも単離、同定されていなかった。本プロジェクトでは、シクロブタジエンジアニオンと主要族元素のハロゲン化物との反応により、多くのハウゼン類やピラミダン類のようなサンドイッチ型クラスター化合物の新しい合成戦略を見出した。ハウゼン類の二量化により、極めて特異な構造と反応性を有するビス(ハウゼン)類の初めての合成に成功した。

研究成果の学術的意義や社会的意義

We developed a synthetic route to unprecedented class of the main group clusters, bis(housenes) and their derivatives. Based on the magnetic and transport properties of these complexes, they can be used in molecular spintronics for quantum computing and high-performance nonlinear optics materials.

研究成果の概要(英文)：The multidecker polynuclear sandwiches with the main group elements represent a novel class of polyhedral clusters which recently attracted a great interest due to their potential use in photonic devices, optical data storage and data transmission. However, none of these complexes were isolated and characterized. In the current project, we developed a new synthetic strategy towards such sandwich clusters based on the reaction of the cyclobutadiene dianions with the main group element halides forming a wide range of housenes or pyramidanes. By dimerization of housenes we succeeded in the preparation of the first representatives of bis(housenes) which exhibited very unusual structural and reactivity features.

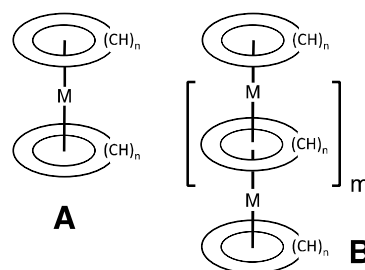
研究分野：有機化学

キーワード：cluster cyclobutadiene dianion housene pyramidane bis(housene) group 14 element group 15 element multidecker sandwich

科研費による研究は、研究者の自覚と責任において実施するものです。そのため、研究の実施や研究成果の公表等については、国の要請等に基づくものではなく、その研究成果に関する見解や責任は、研究者個人に帰属します。

1. 研究開始当初の背景

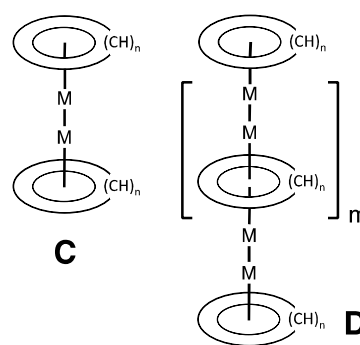
Double-decker sandwich complexes (Scheme 1, **A**), such as ferrocene, found widespread applications in both synthetic organic chemistry and material science. Since then a variety of other metallocenes, including extended sandwich complexes (triple-decker, quadruple-decker, etc.), were prepared. However, if the multidecker complexes of the *d*-block elements are widely known, their *s*- and *p*-block element counterparts, that is multidecker sandwiches of the Main Group elements, are very rarely encountered being almost exclusively represented by those featuring cyclopentadienyl ligands (Cp–E–Cp–E–Cp).



Scheme 1

Multidecker sandwiches (Scheme 1, **B**) are better electron donors than conventional metallocenes, which makes them useful for the design of next generation advanced materials for nonlinear optics, information storage, data processing, and quantum computing devices.

A further development of multidecker complexes are binuclear sandwich compounds, in which a pair of the central atoms M is sandwiched between two cyclic polyene ligands [Scheme 2, **C** (double-decker) and **D** (multi-decker)]. The first representative of the complexes **C** [Cp*–Zn–Zn–Cp* (Cp* = C₅Me₅)] was reported only in 2004 [Carmona, *Science* **2004**, 305, 1136]. However, if a few binuclear sandwiches of the type **C** with the *d*-block elements M were reported to date, none of them featuring Main Group elements M as the central atoms are currently known. Likewise, multidecker sandwiches of the type **D** are unknown for any elements M, both transition metals and Main Group elements.



Scheme 2

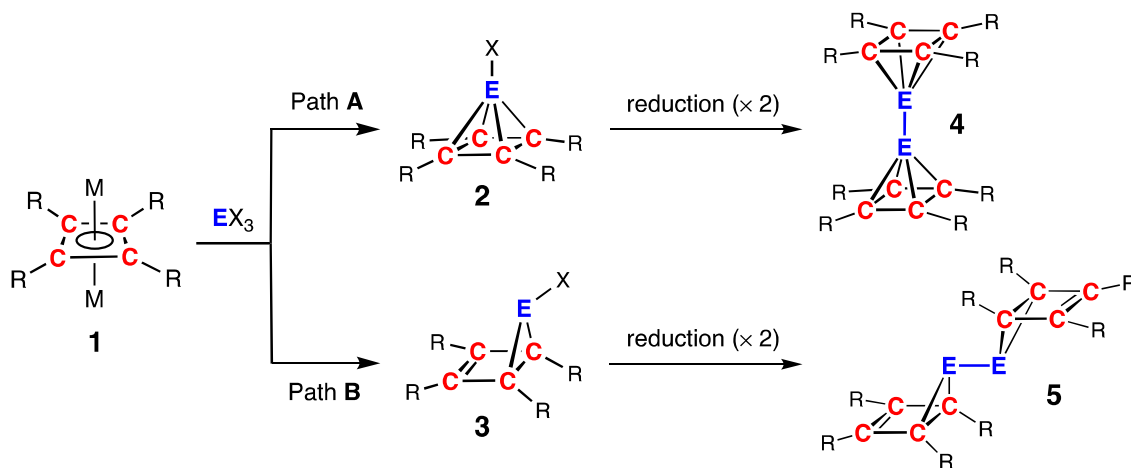
2. 研究の目的

Based on the above-described scientific background in the field, the purpose and the goal of our project was design of unique binuclear sandwiches of the Main Group elements with potentially advanced chemical and physico-chemical properties, as the response to increasing technological demand for the next generation electronic devices with enhanced functionality. Thus, the objective of this research project is the synthesis of unprecedented binuclear sandwiches of the Main Group elements of the type **C** and binuclear multidecker sandwiches of the type **D** (Scheme 2). Both types of sandwich complexes are of particular importance from fundamental and applied points of view. Thus, from the academic viewpoint, these compounds possess unique molecular architecture that the classical bonding theory fails to adequately describe. From the viewpoint of practical importance, such binuclear sandwiches are promising due to their enhanced electroconductive, magnetic and transport properties enabled by their unique structures with extended chain of electronic communication between the M–M fragments and cyclic polyene ligands. Moreover, given the theoretically predicted weakness of the bond between the apex and base in pyramidanes, such metal-rich clusters may serve as suitable thermal/photochemical precursors for ceramic composites and nanomaterials (nanoparticles, nanocrystals, nanowires). And even more so, binuclear sandwiches may also serve as useful chemical reagents, for example, as catalysts or hydrogen storage materials.

3. 研究の方法

Our proposed synthetic strategy is based on the use of the readily available cyclobutadiene dianion salt derivatives **1** (Scheme 3), which were recently developed in our group [Lee et al.: *J. Am. Chem. Soc.* **2004**, 126, 4758; *J. Am. Chem. Soc.* **2011**, 133, 5103] and which have already been proven as an indispensable tool for preparation of a variety of sandwich and half-sandwich complexes of transition metals [reviews by Lee et al.: *Angew. Chem. Int. Ed.* **2007**, 46, 6596; *Chem. Soc. Rev.* **2008**, 37, 1652]. By the reaction of such cyclobutadiene dianion derivatives with

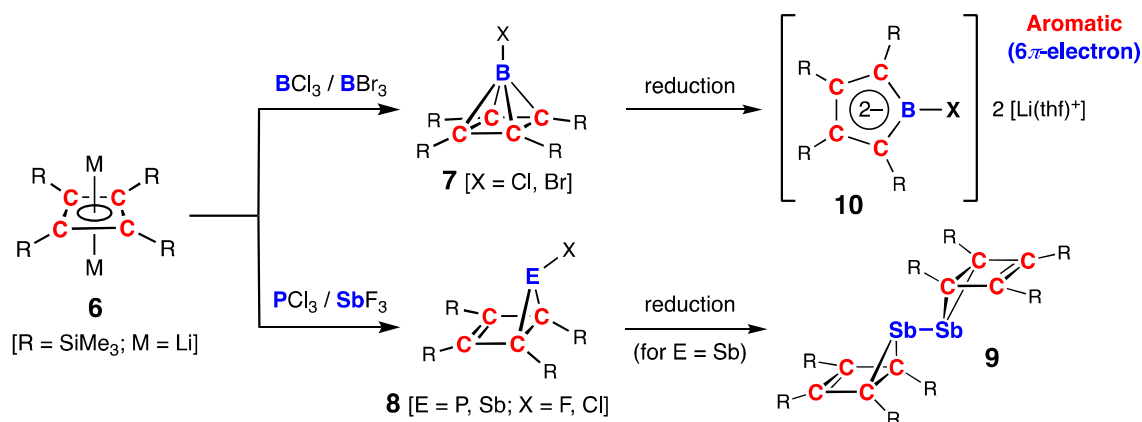
the Main Group element halides EX_3 , a wide range of pyramidanes **2** and housenes (bicyclo[2.1.0]pentenes) **3** with the element E of the Groups 13 and 15 as the core atom can be prepared (Scheme 3). The subsequent dimerization of the latter cage compounds **2** and **3** under the reductive dehalogenation conditions may then result in the formation of either bis(pyramidanes) **4** or bis(housenes) **5** (Scheme 3). As bis(housenes) **5** are valence isomers of the target bis(pyramidanes) **4**, the thermal or photochemical isomerization of the former may produce the desired binuclear sandwich complexes of the type **4**. Moreover, repetition of the path B for bis(pyramidanes) **5** may produce the poly(housene)-type structures, which may also exist in the form of isomeric binuclear multidecker poly(pyramidanes).



4. 研究成果

During the course of the current project studies, we found that the outcome of the reaction of the cyclobutadiene dianion derivative **6** (Scheme 4) with the Main Group element halides EX_3 is totally governed by the nature of the element E. Thus, when E is the group 13 element (for example, B) the product is pyramidane **7**, whereas when E is group 15 element (such as P or Sb) the product is housene **8** (Scheme 4). The reason for such a sharp distinction between the group 13 and group 15 elements was thoroughly elaborated by the DFT computations.

Reduction of housene **8** (E = Sb) resulted in the formation of the target bis(stibahousene) **9**, which was isolated and fully characterized including X-ray structure determination (Scheme 4). This cluster **9** is a first representative of a new type of Main Group element cluster compounds. It has unique structural and reactivity features, for example, it readily undergoes cycloelimination of the cyclobutadiene moieties, thus potentially serving as a hypothetical $[:Sb-Sb:]$ -fragment transfer reagent. On the other hand, reduction of (halobora)pyramidanes **7** [which was expected to produce bis(pyramidane) of the type **4**, see Scheme 3] quite unexpectedly formed derivative of



the borole dianion **10** (Scheme 4) [Lee et al.: *J. Am. Chem. Soc.* **2018**, *140*, 6053]. The reason why reduction of **7** proceeded not at the B–X bond (as was initially expected) but at the C₄-base instead was clearly explained by calculations: LUMO of **7** is mostly located at the carbon base whereas σ^* -orbital of the B–Cl bond lies much higher (LUMO+8). According to our experimental (⁷Li NMR, X-Ray) and computational (NICS) data, borole dianion derivative **10** is 6 π -electron aromatic species, and as such it may serve as a novel type ligand for transition metal complexes of the sandwich and half-sandwich types.

All novel compounds were isolated in pure form and were fully characterized, spectroscopically and crystallographically. The mechanisms of their formation, as well as their peculiar structural features and bonding situations were thoroughly studied by the high-level computations.

5. 主な発表論文等

〔雑誌論文〕 計11件（うち査読付論文 11件/うち国際共著 11件/うちオープンアクセス 2件）

1. 著者名 V. Ya. Lee,* R. Sakai, K. Takanashi, O. A. Gapurenko, R. M. Minyaev, H. Gornitzka, A. Sekiguchi	4. 巻 60
2. 論文標題 Titanium Germylidenes	5. 発行年 2021年
3. 雑誌名 Angew. Chem. Int. Ed.	6. 最初と最後の頁 3951-3955
掲載論文のDOI (デジタルオブジェクト識別子) 10.1002/anie.202015704	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する
1. 著者名 V. Ya. Lee,* Y. Ito, O. A. Gapurenko, R. M. Minyaev, H. Gornitzka, A. Sekiguchi	4. 巻 142
2. 論文標題 From a (Silatrigerma)cyclobutenylium Ion to a (Silatrigerma)cyclobutenyl Radical and Back	5. 発行年 2020年
3. 雑誌名 J. Am. Chem. Soc.	6. 最初と最後の頁 16455-16460
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/jacs.0c08052	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する
1. 著者名 W. S. Putro, A. Ikeda, S. Shigeyasu, S. Hamura, S. Matsumoto, V. Ya. Lee, J.-C. Choi, N. Fukaya	4. 巻 14
2. 論文標題 Sustainable Catalytic Synthesis of Diethyl Carbonate	5. 発行年 2020年
3. 雑誌名 ChemSusChem	6. 最初と最後の頁 842-846
掲載論文のDOI (デジタルオブジェクト識別子) 10.1002/cssc.202002471	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する
1. 著者名 R. R. Aysin, S. S. Bukalov, L. A. Leites, V. Ya. Lee, A. Sekiguchi	4. 巻 892
2. 論文標題 Electronic structure and conformational isomerism of the digermene (tBu ₂ MeSi) ₂ Ge=Ge(SiMe ₂ tBu) ₂ as studied by temperature-dependent Raman and UV-Vis spectra and quantum-chemistry calculations.	5. 発行年 2019年
3. 雑誌名 J. Organomet. Chem.	6. 最初と最後の頁 18-23
掲載論文のDOI (デジタルオブジェクト識別子) 10.1016/j.jorganchem.2019.04.014	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1. 著者名 O. A. Gapurenko, V. Ya. Lee, R. M. Minyaev, V. I. Minkin	4. 巻 -
2. 論文標題 Theoretical Prediction for Synthetic Realization: Pyramidal Systems for Synthetic Realization CIE[E4R4] (E = B-Ga, E = C-Ge, R = SiMe3, SiMetBu2): A DFT Study	5. 発行年 2019年
3. 雑誌名 Heteroatom Chem.	6. 最初と最後の頁 3659287
掲載論文のDOI (デジタルオブジェクト識別子) 10.1155/2019/3659287	査読の有無 有
オープンアクセス オープンアクセスとしている (また、その予定である)	国際共著 該当する

1. 著者名 V. Ya. Lee, S. Horiguchi, O. A. Gapurenko, R. M. Minyaev, V. I. Minkin, H. Gornitzka, A. Sekiguchi	4. 巻 -
2. 論文標題 [2 + 2] Cycloadduct of Titanium Silylidene and Benzonitrile	5. 発行年 2019年
3. 雑誌名 Eur. J. Inorg. Chem.	6. 最初と最後の頁 4224-4227
掲載論文のDOI (デジタルオブジェクト識別子) 10.1002/ejic.201900601	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1. 著者名 V. Ya. Lee	4. 巻 88
2. 論文標題 Tricoordinate Silicon Cations (Silylium Ions) (invited)	5. 発行年 2019年
3. 雑誌名 Russ. Chem. Rev.	6. 最初と最後の頁 351-369
掲載論文のDOI (デジタルオブジェクト識別子) 10.1070/RCR4868	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1. 著者名 N. Fukaya, T. Mizusaki, K. Hatakeyama, Y. Seo, Y. Inaba, K. Matsumoto, V. Ya. Lee,* Y. Takagi, J. Kuwabara, T. Kanbara, Y.-K. Choe, J.-C. Choi	4. 巻 38
2. 論文標題 [Pd(4-R3Si-IPr)(allyl)Cl], a Family of Silyl-Substituted Pd - NHC Complexes: Catalytic Systems for the Buchwald - Hartwig Amination	5. 発行年 2019年
3. 雑誌名 Organometallics	6. 最初と最後の頁 376-384
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/acs.organomet.8b00757	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1. 著者名 V. Ya. Lee,* S. Horiguchi, A. Sekiguchi, O. A. Gapurenko, T. N. Gribanova, V. I. Minkin, H. Gornitzka	4. 巻 4
2. 論文標題 Tuning Philicity of Dichlorosilylene: Nucleophilic Behavior of the Dichlorosilylene - NHC Complex Cl ₂ Si - IPr	5. 発行年 2019年
3. 雑誌名 ACS Omega	6. 最初と最後の頁 2902-2906
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/acsomega.8b03429	査読の有無 有
オープンアクセス オープンアクセスとしている (また、その予定である)	国際共著 該当する

1. 著者名 V. Ya. Lee,* M. Kawai, O. A. Gapurenko, V. I. Minkin, H. Gornitzka, A. Sekiguchi	4. 巻 54
2. 論文標題 Arsagermene, a compound with an As=Ge double bond	5. 発行年 2018年
3. 雑誌名 Chem. Commun.	6. 最初と最後の頁 10947-10949
掲載論文のDOI (デジタルオブジェクト識別子) 10.1039/c8cc05630g	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1. 著者名 V. Ya. Lee,* H. Sugawara, O. A. Gapurenko, R. M. Minyaev, V. I. Minkin, H. Gornitzka, A. Sekiguchi	4. 巻 140
2. 論文標題 From Borapyramidane to Borole Dianion	5. 発行年 2018年
3. 雑誌名 J. Am. Chem. Soc.	6. 最初と最後の頁 6053-6056
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/jacs.8b03473	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕 計17件 (うち招待講演 6件 / うち国際学会 0件)

1. 発表者名 Y. Seo, T. Mizusaki, Y. Takagi, K. Hatakeyama, V. Ya. Lee, Y.-K. Choe, K. Matsumoto, J.-C. Choi, N. Fukaya
2. 発表標題 Catalytic Performance of Silyl Group-Substituted N-Heterocyclic Carbene Complexes
3. 学会等名 00th Annual Meeting of The Chemical Society of Japan, Noda, Tokyo University of Science, 22-25 March
4. 発表年 2020年

1. 発表者名 J. Fujiwara, Y. Ozaki, V. Ya. Lee, T. Matsui, K. Morihashi
2. 発表標題 Computational Chemical Verification of Activation of [R3Si-IPr]Pd Catalyst Precursor in Suzuki-Miyaura Cross-Coupling Reaction
3. 学会等名 00th Annual Meeting of The Chemical Society of Japan, Noda, Tokyo University of Science, 22-25 March
4. 発表年 2020年

1. 発表者名 V. Ya. Lee
2. 発表標題 Schrock-Type Silylidenes and Germylidenes
3. 学会等名 2nd International Conference of Hyper- and Hypocoordinated Compounds of the Group 14 Elements, France, Rennes, June 19-21 (招待講演)
4. 発表年 2019年

1. 発表者名 V. Ya. Lee, O. A. Gapurenko, A. Sekiguchi, R. M. Minyaev, V. I. Minkin
2. 発表標題 Pyramidane: The Smallest Member of the Fenestranes Family
3. 学会等名 5th EuChemS Inorganic Chemistry Conference (EICC-5), Russia, Moscow, June 24-28 (招待講演)
4. 発表年 2019年

1. 発表者名 V. Ya. Lee
2. 発表標題 Cyclobutadiene Complexes of the s-, p-, and d-Block Elements
3. 学会等名 13th International Conference on Heteroatom Chemistry (ICHAC 2019), Czech Republic, Prague, June 30-July 5 (招待講演)
4. 発表年 2019年

1. 発表者名 V. Ya. Lee, R. Sakai, T. Yokoyama, S. Aoki, K. Takanashi, A. Sekiguchi
2. 発表標題 Group 4 Metal Germlyidenes (and Related Complexes)
3. 学会等名 16th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead (GTL-2019), Japan, Saitama, September 1-6
4. 発表年 2019年

1. 発表者名 V. Ya. Lee
2. 発表標題 Alkene Metathesis: Silicon and Germanium Versions
3. 学会等名 XXIth Mendeleev Congress on General and Applied Chemistry, Saint-Petersburg, Russia, September 9-13 (招待講演)
4. 発表年 2019年

1. 発表者名 V. Ya. Lee
2. 発表標題 Pyramidanes
3. 学会等名 Visiting Professor at the Graz University of Technology, Graz, Austria, 18-28 October (招待講演)
4. 発表年 2019年

1. 発表者名 F. Takemura, V. Ya. Lee,* K. Morihashi
2. 発表標題 Pyramidanes: Study of the Electronic Structures of Pyramidal Compounds and Their NMR Properties
3. 学会等名 99th Annual Meeting of The Chemical Society of Japan, Japan, Kobe, Konan University, Japan
4. 発表年 2019年

1. 発表者名 Y. Seo, T. Mizusaki, Y. Takagi, K. Hatakeyama, V. Ya. Lee, K. Matsumoto, J.-C. Choi, N. Fukaya
2. 発表標題 Catalytic Performance of Novel Silyl Group-Substituted N-Heterocyclic Carbene Complexes
3. 学会等名 8th JACI/GSC Symposium 2019(Japan Association for Chemical Innovation/Green and Sustainable Chemistry), Tokyo, Tokyo International Forum, 24-25 June
4. 発表年 2019年

1. 発表者名 Y. Seo, T. Mizusaki, Y. Takagi, K. Hatakeyama, V. Ya. Lee, K. Matsumoto, J.-C. Choi, N. Fukaya
2. 発表標題 Catalytic Performance of Novel Silyl Group-Substituted N-Heterocyclic Carbene Complexes
3. 学会等名 66th Symposium on Organometallic Chemistry, Tokyo, Tokyo Metropolitan University, 14-16 September
4. 発表年 2019年

1. 発表者名 V. Ya. Lee*
2. 発表標題 Cyclobutadiene Complexes of the s-, p-, and d-Block Elements
3. 学会等名 XIV Andrianov Conference "Organosilicon Compounds. Synthesis, Properties, Applications", Moscow, Russia (招待講演)
4. 発表年 2018年

1. 発表者名 O. A. Gapurenko, V. Ya. Lee,* R. M. Minyaev, V. I. Minkin
2. 発表標題 Group 13 Element Silicon Pyramidanes
3. 学会等名 XIV Andrianov Conference "Organosilicon Compounds. Synthesis, Properties, Applications", Moscow, Russia
4. 発表年 2018年

1. 発表者名 V. Ya. Lee,* H. Sugasawa, K. Ota, Y. Ito, A. Sekiguchi, O. A. Gapurenko, R. M. Minyaev, V. I. Minkin
2. 発表標題 R E [C4R4] (E = Group 15 or 13 Element) Cages and Clusters
3. 学会等名 15 International Symposium on Inorganic Ring Systems (IRIS-15), Kyoto, Japan
4. 発表年 2018年

1. 発表者名 V. Ya. Lee,* O. A. Gapurenko, A. Sekiguchi, R. M. Minyaev, V. I. Minkin
2. 発表標題 Pyramidanes: New Class of Cluster Compounds
3. 学会等名 28 International Conference on Organometallic Chemistry (ICOMC 2018), Florence, Italy
4. 発表年 2018年

1. 発表者名 V. Ya. Lee,* O. A. Gapurenko, A. Sekiguchi, R. M. Minyaev, V. I. Minkin
2. 発表標題 Pyramidanes
3. 学会等名 The 14th International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-14), Kyoto, Japan
4. 発表年 2018年

1. 発表者名 Y. Seo, T. Mizusaki, Y. Takagi, K. Hatakeyama, N. Fukaya, V. Ya. Lee,* J.-C. Choi
2. 発表標題 The Study of Catalytic Performance of Novel Silyl Group-Substituted N-Heterocyclic Carbene Complexes
3. 学会等名 48th Petroleum-Petrochemicals Symposium of JPI, Tokyo, Japan
4. 発表年 2018年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

-

6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
--	---------------------------	-----------------------	----

7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
---------	---------