アカデミックプログラム［Ｂ講演］ | 14. 有機化学—芳香族・複素環・ヘテロ原子化合物：口頭Ｂ講演

2025年3月28日(金) 10:00 ~ 11:40 [F]2304(第4学舎 2号館 [3階] 2304)

[[F]2304-3am] 14. 有機化学—芳香族・複素環・ヘテロ原子化合物

座長：荒巻 吉孝、菅又 功

英語

10:00 ~ 10:20

[[F]2304-3am-01]

ホウ素架橋ヘキサゼンの誘導体化

〇山本 真洋[1]、山下 誠[1] (1. 東京科学大学)

英語

10:20 ~ 10:40

[[F]2304-3am-02]

Highly Efficient Excimer Emission Properties of Multi-Bladed Benzenes Featuring Adjacent Boryl Units

〇Yunyi Song[1]、庄子 良晃[1]、酒井 隼人[2]、羽曾部 卓[2]、福島 孝典[1] (1. 科学大化生研、2. 慶應理工)

英語

10:40 ~ 11:00

[[F]2304-3am-03]

求核的アルミニウムアニオンを用いた$\mathrm{Al_3}$および$\mathrm{Al_4}$分子の合成

〇山梨 遼太朗[1]、山下 誠[2] (1. 名古屋大学、2. 東京科学大)

英語

11:00 ~ 11:20

[[F]2304-3am-04]

Al架橋反転Ge間二重結合化合物の合成とその性質

〇任 喆[1]、時任 宣博[1]、山田 容子[1]、水畑 吉行[1] (1. 京大化研)

英語

11:20 ~ 11:40

[[F]2304-3am-05]

N-シリルイミノエステルを用いた不斉環化縮合反応によるキラル4-イミダゾロンの合成研究

〇小倉 和樹[1]、安藤 翔太[1]、中村 修一[1] (1. 名工大院工)

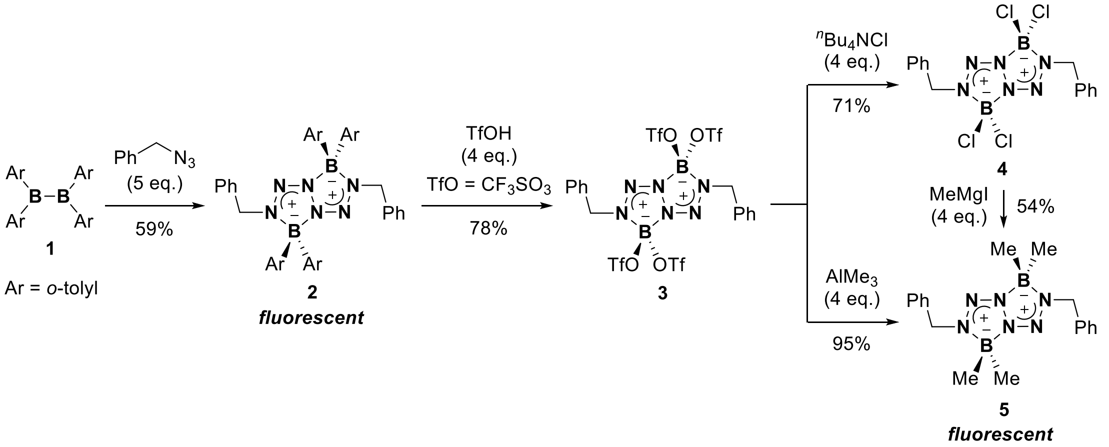
ホウ素架橋ヘキサゼンの誘導体化

（科学大理）○山本真洋・山下誠
Derivatization of Boron-Bridged Hexazenes (*School of Science, Institute of Science Tokyo*) ○Masahiro Yamamoto, Makoto Yamashita

We recently reported characteristic reactivities of tetra(*o*-tolyl)diborane **1** toward H_2, CO, nitrile, and isocyanide.[1)–3)] The reaction of **1** with various organic azides resulted in the formation of three different compounds depending on the organic substituent. Especially, the reaction of **1** with an excess amount of benzyl azide afforded boron-bridged hexazene B_2N_6 compounds **2** to exhibit fluorescence in solution or solid state.[4)] Herein, we report the derivatization of these B_2N_6 molecules **3**, **4**, **5**, as new heterocyclic compounds by replacing tolyl group with triflate, chloro, and methyl groups. In this presentation, synthesis, structures, properties, and further derivatization of them will be discussed.

Keywords : Diborane(4); Organic Azide; Fluorescent Compound; Boron-Bridged Hexazene

我々は最近、テトラ(*o*-トリル)ジボラン **1** の H_2・CO・ニトリル・イソシアニドへの特徴的な反応性を報告している[1)–3)]。また、ジボラン **1** と有機アジド（$R–N_3$）との反応において､アジドの置換基により異なる 3 種類の分子が生成することを発見した[4)]。特に、**1** と過剰量のベンジルアジドとの反応では、溶液中・固体状態で蛍光を示すホウ素架橋ヘキサゼン B_2N_6 分子 **2** が生成することを明らかとしている。本研究では、**2** のホウ素上の置換基変換による光電子物性の変調や B_2N_6 骨格を持つ新奇平面分子の創出に向けて、ホウ素上のトリル基をトリフラート、クロロ、メチル基へ変換した誘導体 **3**、**4**、**5** の合成を行った。発表では得られた分子の構造・性質およびさらなる誘導化の検討についても述べる。



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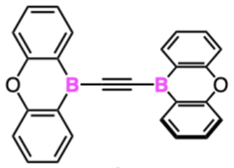
2) Katsuma, Y.; Tsukahara, N.; Wu, L.; Lin, Z.; Yamashita, M., *Angew. Chem. Int. Ed*. **2018**, *57*, 6109.
3) Katsuma, Y.; Wu, L.; Lin, Z.; Akiyama, S.; Yamashita, M., *Angew. Chem. Int. Ed*. **2019**, *58*, 317.
4) Yamamoto, M.; Chan, W. C.; Lin, Z.; Yamashita, M., *Chem. Eur. J.* **2023**, e202302027.

Highly Efficient Excimer Emission Properties of Multi-Bladed Benzenes Featuring Adjacent Boryl Units

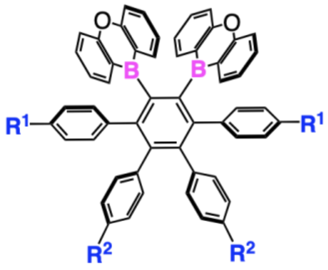
([1]*CLS, Science Tokyo*, [2]*Sch. Mater. Chem. Tech., Science Tokyo*, [3]*ASMat, Science Tokyo*, [4]*Facul. Sci. Tech., Keio Univ.*) ○Yunyi Song,[1,2] Yoshiaki Shoji,[1,2,3] Hayato Sakai,[4] Taku Hasobe,[4] Takanori Fukushima[1,2,3]

Keywords: Boron; D-π-A system; Dual emission; Transient absorption spectroscopy; Excimer

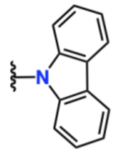
We recently reported a chemically stable diborylacetylene (**1**) composed of 9-oxaboraanthracene, which exhibits reactivities typical of alkyne species and thus is useful as a synthetic building block to construct boron-rich molecules.[1] Upon heating with tetraarylcyclopentadienones, Diels-Alder reaction followed by elimination of carbon monooxide take place, giving the corresponding multi-bladed benzene derivatives with the boraanthracene units at the 1,2-positions.[1] Interestingly, we found that carbazole-appended derivatives (**2**) show excimer emission in solution even at very low concentration conditions (*e.g.*, 10^{-7} M).[2] In this presentation, we will discuss the mechanism of this emission based on nanosecond transient absorption spectroscopy measurements and target analysis.



1



2a: $R^1 = R^2 = H$
2b: R^1 = carbazole, $R^2 = H$
2c: $R^1 = H$, R^2 = carbazole
2d: $R^1 = R^2$ = carbazole



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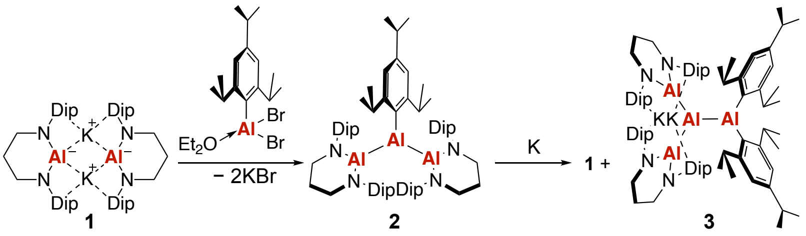
Syntheses of Al_3 and Al_4 molecules by Reaction of Nucleophilic Alumanyl Anion

([1]*Graduate School of Engineering, Nagoya University*, [2]*School of Science, Institute of Science Tokyo*) ○Ryotaro Yamanashi,[1] Makoto Yamashita[2]

Keywords: Aluminum; Trialumane; Catenation; XPS analysis

Catenation is a term that refers to the ability of elements to form linear chain structures through 2c-2e (2-center-2-electron) bonds.[1] This property is commonly observed in group 14 elements to form polyolefins used as commodity plastics and polysilanes used in optical materials and semiconductors. In contrast, linear chain structures of group 13 elements are rare due to their electron-deficient nature leading to a formation of clusters possessing multicenter-multielectron bond.[2] In the field of Al chemistry, the synthesis of such molecules is extremely rare. The first example of the Al_3 linear chain molecule connected through covalent bonds was just recently reported through stabilization by the coordination of N-heterocyclic carbene,[3] however, a base-free Al_3 molecule has never been reported.

We performed the reaction of our reported nucleophilic alumanyl anion **1**[4] with $TipAlBr_2(Et_2O)$ (Tip = 2,4,6-triisopropylphenyl) to synthesize a base-free trilaumane **2** through a double salt-elimination reaction. In the obtained structure, two Al–Al bond lengths are about 2.6 Å, which is consistent with reported Al–Al single bonds.[5] The oxidation states of the aluminum centers in **2** were evaluated using XPS measurements, and its electron-accepting properties were assessed through cyclic voltammetry. These findings will be presented in detail. Furthermore, the chemical reduction of **2** with potassium regenerated the alumanly anion **1** with a concomitant formation of dianionic species **3**, which contains a core of four aluminum atoms and two potassium cations. The structure, absorption properties, and electronic characteristics of **3** will be also discussed in this presentation.



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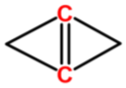
Synthesis and Properties of an Inverted Ge–Ge Double-bond Compound Bridged by Aluminum Atoms

(*Institute for Chemical Research, Kyoto University*) ○Zhe Ren, Norihiro Tokitoh, Hiroko Yamada, Yoshiyuki Mizuhata

Keywords: Heavy Analogue; Germanium; Aluminum; Inverted Double Bond.

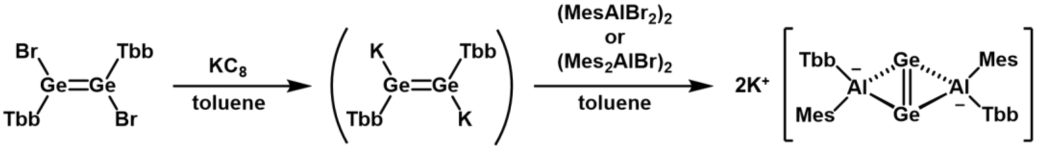
Bondings having geometries in which all bonds on a tetravalent atom exist only on the hemispherical side of the atom are termed "inverted bonds", which have been studied experimentally and theoretically over a long period of time in view of interest in the electronic states produced by these unusual bonds. As for an inverted single-bond compound, [1.1.1]propellane was synthesized in 1982, and its heavy-element analogues have also been reported. On the other hand, the synthesis of inverted double-bond compounds is still challenging. Bicyclo[1.1.1]but-1(3)-ene, a typical example, has been studied theoretically for several decades and only been proposed experimentally as a reaction intermediate.[1] In 2019, Iwamoto and co-workers succeeded in the synthesis and isolation of its tetrasilicon analogue, which made the experimental study of inverted double bonds possible.[2]

[1.1.1] propellane



bicyclo[1.1.1]but-1(3)-ene

However, the isolated examples of inverted double-bond compounds are still limited, and there are still many unsolved issues. In this study, we report the synthesis and isolation of $Ge_2Al_2R_4$ (R: substituent) dianion having a four-membered-ring structure. According to the result of X-ray diffraction analysis, the bond length between the two bridgehead Ge atoms was found to be 2.54 Å, which is slightly longer than those of typical digermenes. However, the results of DFT calculations showed σ- and π-type orbitals between the bridgehead Ge atoms, similarly to the orbitals of the reported tetrasilicon analogue. The WBI value of the Ge–Ge bond was calculated as 1.51. These results clearly indicate that $Ge_2Al_2R_4K_2$ can be regarded as an inverted double-bond compound.



Tbb = 4-(*t*-butyl)-2,6-bis[bis(trimethylsilyl)methyl]phenyl
Mes = 2,4,6-trimethylphenyl

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N-シリルイミノエステルを用いた不斉環化縮合反応によるキラル 4-イミダゾロンの合成研究

（名工大院工）○小倉 和樹・安藤 翔太・中村 修一

Enantioselective synthesis of 4-imidazolones via cyclocondensation of *N*-silyl iminoesters

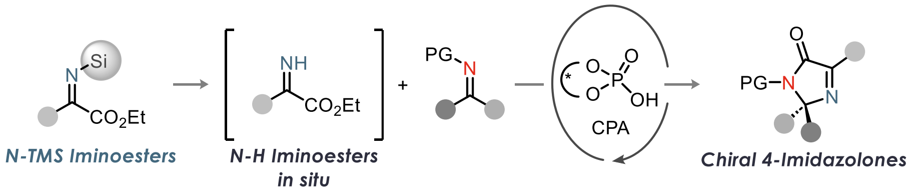
(*Graduate School of Nagoya Institute of Technology*) ○Kazuki Ogura, Shota Ando, Shuichi Nakamura

Chiral imidazolones are components of several natural products and are known as precursors for various structural modifications. They have been synthesized via optical resolution using amino acids or chiral amines. We have developed a catalytic enantioselective cyclocondensation using ketimines and *N*-unprotected iminoesters. However, the synthesis and use of *N*-unprotected iminoesters is challenging due to their instability. Herein, we focused on *N*-silyl iminoesters as precursors of unstable iminoesters for use in the asymmetric synthesis of chiral imidazolones. We examined their reaction with *N*-unprotected ketimines derived from isatins and *N*-TMS iminoesters under chiral phosphoric acid catalysis, giving the desired products with high enantioselectivity. This catalytic system is also applicable to the homo-cyclocondensation of *N*-TMS iminoesters. Finally, we investigated the synthetic transformation of the products and provided mechanistic insights through DFT calculations.

Keywords : Chiral Imidazolones; N-TMS iminoesters; Enantioselective Reaction

イミダゾロンは天然物にしばしば見られる骨格であり、また、様々な含窒素複素環式化合物のビルディングブロックとしても有用である。従来、アミノ酸やキラルアミンを出発物質とした光学分割による合成法が報告されてきた[1]が、触媒的不斉合成法は未だ達成されていない。そこで、ケチミンと無保護イミノエステルを用いた環化縮合反応を設計したが、無保護イミノエステルが不安定性から反応への利用が困難であった。本研究では、安定に取り扱うことが可能なシリルイミノエステルを用いることで、エナンチオ選択的な環化縮合反応による合成を達成した。

イサチン由来の無保護ケチミンと *N*-TMS イミノエステルとの反応をジエチルエーテル中、キラルリン酸触媒下で行ったところ、良好なエナンチオ選択性で目的化合物が得られた。更にプロトン源としてイソプロピルアルコールを共溶媒として用いることで収率が大幅に向上した。また、シリルイミノエステル同士のホモ環化縮合反応への適用や、生成物の合成的変換反応を行った。更に、コントロール実験や分子軌道計算を用いることで本反応の立体選択性の発現機構を解明した。[2]



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