

アカデミックプログラム [B講演] | 10. 有機化学—有機金属化合物：口頭B講演

📅 2025年3月27日(木) 13:00 ~ 15:10 🏢 [F]2102(第4学舎 2号館 [1階] 2102)

[[F]2102-2pm] 10. 有機化学—有機金属化合物

座長：近藤 梓、増田 侑亮

◆ 日本語

13:00 ~ 13:20

[[F]2102-2pm-01]

アンチ光レドックス白金触媒によるケトン及びイミンの還元的アリル化反応

○下里 絢平¹、西村 亘世¹、福世 文大¹、清水 洋平^{1,2}、増田 侑亮¹、澤村 正也^{1,2} (1. 北大理、2. WPI-ICReDD)

◆ 英語

13:20 ~ 13:40

[[F]2102-2pm-02]

The rare PNC pincer ligand, its Pt metalation, and reactivity of associated Pt complexes

○Eugene Khaskin¹, Mikhail Losev¹, Azamat Yessengazin¹ (1. Okinawa Institute of Science and Technology)

◆ 英語

13:40 ~ 14:00

[[F]2102-2pm-03]

銅触媒によるアリールプロパルギルエーテルのアニオン性1,3-プロパルギル基移動反応

○Aderian SETIAWAN¹、近藤 梓¹、寺田 眞浩¹ (1. 東北大学)

14:00 ~ 14:10

休憩

◆ 英語

14:10 ~ 14:30

[[F]2102-2pm-04]

ジフルオロアレンとアルデヒドの[2 + 2]/[3 + 2]付加環化: 選択的反応とその機構に関する研究

○宮崎 大輔¹、工藤 湖南¹、藤木 裕介¹、渡邊 夏実¹、松井 亨¹、市川 淳士²、淵辺 耕平¹ (1. 筑波大学、2. 相模中研)

◆ 英語

14:30 ~ 14:50

[[F]2102-2pm-05]

MOF-無機材料積層構造の開発とn-アルカン認識センサへの応用

○弘世 幹久¹、高橋 綱己¹、運 愛斗¹、細見 拓郎¹、田中 航¹、Jiangyang Liu¹、本田 陽翔¹、細野 暢彦¹、植村 卓史¹、柳田 剛^{1,2} (1. 東大、2. 九大)

◆ 日本語

14:50 ~ 15:10

[[F]2102-2pm-06]

データ駆動型触媒設計のための3次元分子画像解析ツール

○山口 滋¹ (1. 理研CSRS)

アンチ光レドックス白金触媒によるケトン及びイミンの還元的アリル化反応

(北大理¹・WPI-ICReDD²) ○下里 絢平¹・西村 亘世¹・福世 文大¹・清水 洋平^{1,2}・増田 侑亮¹・澤村 正也^{1,2}

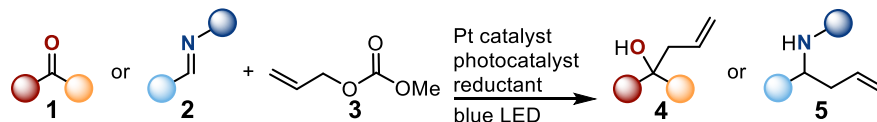
Anti-photoredox Platinum-catalyzed Reductive Allylation of Ketones and Imines (¹*Hokkaido University*, ²*WPI-ICReDD*) ○Junpei Shimosato,¹ Kousei Nishimura,¹ Bunta Fukuyo,¹ Yohei Shimizu,^{1,2} Yusuke Masuda,¹ Masaya Sawamura^{1,2}

Photoredox-catalyzed reductive allylation reactions of carbonyl compounds offer a practical way to synthesize homoallylic alcohols. However, these catalytic systems were only applied to allylation of aldehydes in most cases.¹⁾ We previously reported photoinduced platinum-catalyzed reductive allylation of α -diketones with allyl carbonates under blue LED irradiation.²⁾ Based on this finding, we developed a photoredox/platinum dual-catalytic system for reductive allylation of more general substrates, monoketones and imines. When a mixture of a ketone (**1**) or an imine (**2**) and allyl carbonate (**3**) was irradiated with blue LED light in the presence of a platinum catalyst, a photoredox catalyst, and the reducing agent, the corresponding homoallylic alcohol (**4**) or homoallylic amine (**5**) was obtained. The reaction proceeded specifically with platinum, while nickel and palladium were much less effective metals. Mechanistic studies suggested that "anti-photoredox property" of the platinum catalyst enables selective substrate reduction and efficient allylation.

Keywords : Platinum catalyst; Ketone; Imine; Photoredox catalyst; Reductive allylation

光酸化還元触媒を用いたカルボニル化合物の還元的アリル化反応は、ホモアリルアルコールを合成する実用的な手法であるが、主に基質がアルデヒドに制限されていた¹⁾。これに対し我々は、光と白金触媒を用いた α -ジケトンの還元的アリル化反応を見出した²⁾。しかし、反応には基質分子の直接励起が必要であり、依然として適用可能な基質に制限があった。

本研究では、白金触媒に加えて光酸化還元触媒を共存させることで、可視光領域に吸収を持たないモノケトンやイミンの還元的アリル化反応が進行することを見出した。基質であるケトン(**1**)もしくはイミン(**2**)と炭酸アリルエステル(**3**)の混合物に対して、青色 LED 光の照射下で白金触媒、光酸化還元触媒、および還元剤を作用させることで、ホモアリルアルコール(**4**)もしくはホモアリルアミン(**5**)が高収率で得られた。本反応は白金触媒で特異的に進行し、ニッケルやパラジウム触媒では収率が大幅に低下した。機構解析により、白金触媒が光酸化還元触媒による 1 電子還元を受けにくい「アンチ光レドックス特性」を持つことが明らかになり、これが基質の選択的還元と目的のアリル化反応を可能にしたと考えられる。

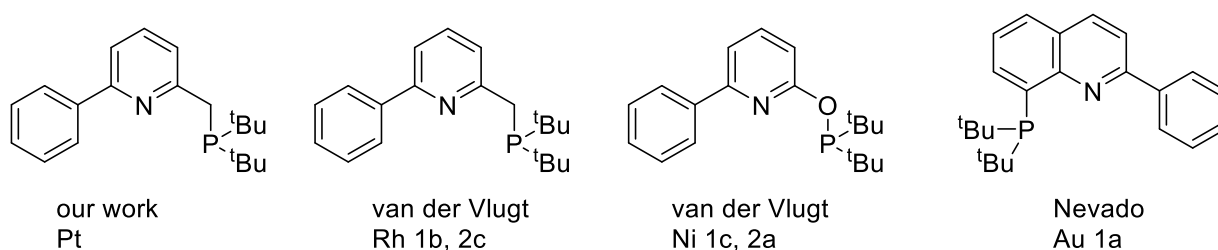


1) For selected examples, see: a) P. G. Cozzi *et al.* *ACS Catal.* **2020**, *10*, 3857. b) L. Shi *et al.* *ACS Catal.* **2021**, *11*, 2992. 2) J. Shimosato, M. Sawamura, Y. Masuda, *Org. Lett.* **2024**, *26*, 2023.

The rare PNC pincer ligand, its Pt metalation, and reactivity of associated Pt complexes

Eugene Khaskin, Mikhail Losev, Azamat Yessengazin

The 2phenyl-6bis-*t*-butylphosphinemethyl-pyridine (PNC) ligand and its close analogue, has only rarely been used in coordination chemistry¹ due to the difficulty of obtaining the desired pincer complexes cleanly, an inability to metalate the CH bond trans to the phosphine donor, and a tendency for facile cyclometallation of the pyridine ring instead of the pendant phenyl group. In addition, reductive elimination leading to a free phenyl moiety is a common decomposition pathway.²



In the referenced works, the ligand or its derivatives have been used for Au, Rh, and Ni complexation. However, the pincer ligand offers an opportunity to create highly reactive T-shaped Pt complexes by utilizing metal/ligand cooperation when dearomatizing the ligand with base. In the current presentation, we report on the synthesis of stable PNC-Pt pincer complexes and discuss our initial exploration of their reactivity. The initial PNC-Pt-Cl complex and its alkyl derivative are remarkably stable, even under air and at elevated temperatures. Attempts to deprotonate the ligand arm for metal/ligand cooperation reactivity in substrate activation will be discussed, as well as the reactivity and properties of the PNC-Pt-Me complex.

1. a) Martin, J.; Schoergenheimer, J.; Biedrzycki, M.; Nevado, C., **2024**, *Inorg. Chem.*, 63, 8390-8396. b) Jongbloed, L.S.; de Bruin, B.; Reek, J.N.H.; Lutz, M.; van der Vlugt, J.I., **2015**, *Chem. Eur. J.*, 21, 7297-7305. c) Joengbloed, L.S.; Vogt, N.; Sandleben, A.; de Bruin, B.; Klein, A.; van der Vlugt, J.I., *Eur. J. Inorg. Chem.*, **2018**, 2408-2418.

2. a) Jongbloed, J.S.; Garcia-Lopez, D.; van Heck, R.; Siegler, M.A.; Carbo, J.J.; van der Vlugt, J.I., **2016**, *Inorg. Chem.*, 55, 8041-8047. b) Jongbloed, L.S.; de Bruin, B.; Reek, J.N.H.; Lutz, M.; van der Vlugt, J.I., **2016**, *Catal. Sci. Technol.*, 6, 1320-1327.

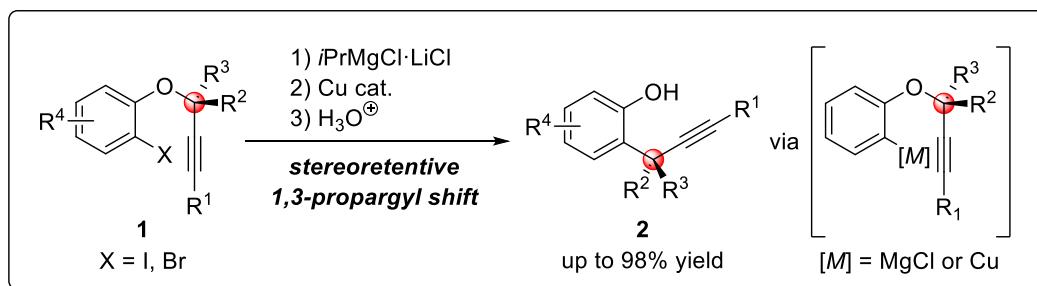
Copper-catalyzed 1,3-Propargyl Shift of *ortho*-Metalated Aryl Propargyl Ethers

(¹Graduate School of Science, Tohoku University) ○ Aderian SETIAWAN,¹ Azusa KONDOH,¹ Masahiro TERADA,¹

Keywords: Copper Catalysis; Rearrangement; Grignard Reagent; Propargyl Compounds; Stereospecificity

Propargyl compounds are versatile building blocks for the construction of complex molecular structures. Continuous studies on development of novel synthetic transformation of propargyl compounds would be highly beneficial to expand accessible chemical space. One of the characteristic properties of propargyl compounds is serving as a building block for the synthesis of allenes. Various types of propargyl compounds can be converted to the corresponding allenes through isomerization, rearrangement, and cross-coupling reaction under catalysis of transition metals, Brønsted bases and Brønsted acids. For example, propargyl vinyl ethers and aryl propargyl ethers are well-known to undergo the [3,3]-rearrangement in a stereoretentive manner, providing allenyl carbonyl compounds and allenyl phenols.¹ On the other hand, the [1,3]-type propargyl shift of propargyl ethers is unknown to the best of our knowledge.² This research shows the rare example of [1,3]-propargyl shift from *ortho*-metalated aryl propargyl ether under copper catalysis.

Generation of *ortho*-metalated aryl propargyl ether was achieved by treating *ortho*-haloaryl propargyl ether **1** with *i*PrMgCl·LiCl, which involved the halogen-magnesium exchange. After the halogen-magnesium exchange was completed, a copper catalyst was introduced to the reaction system followed by acidic work-up, furnishing *ortho*-propargyl phenol derivatives **2** in moderate to good yields. In the crude reaction mixture, *ortho*-allenyl phenol compound, which formed via the [3,3]-rearrangement, was not observed at all, suggesting that the propargyl shift proceeded in an exclusively [1,3]-selective manner. In addition, the control experiment using enantio-enriched *ortho*-haloaryl propargyl ether revealed that the [1,3]-propargyl shift proceed in a stereoretentive manner.



- 1) D. Tejedor, G. Méndez-Abt, L. Cotos, F. García-Tellado, *Chem. Soc. Rev.* **2013**, 42, 458.
- 2) J. Barluenga, R. Sanz, F. J. Fañanás, *Tetrahedron Lett.* **1997**, 38, 6103.

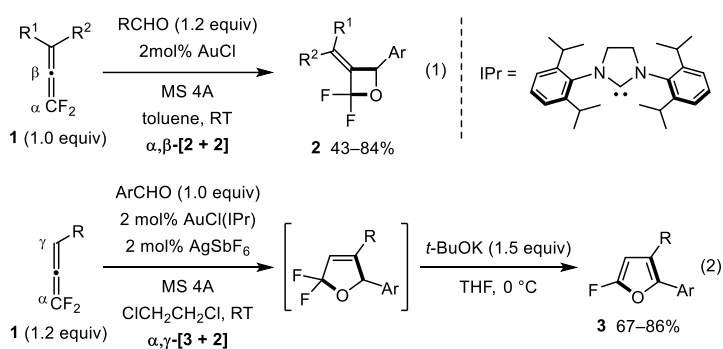
Gold(I)-Catalyzed [2 + 2]/[3 + 2] Cycloadditions of Difluoroallenes with Aldehydes: Selective Syntheses and Their Mechanistic Studies

(¹University of Tsukuba, ²Sagami Chemical Research Institute) ○Daisuke Miyazaki,¹ Konami Kudo,¹ Yusuke Fujiki,¹ Natsumi Watanebe,¹ Toru Matsui,¹ Junji Ichikawa,² Kohei Fuchibe¹

Keywords: Allene; Carbenoid; Cycloaddition; Fluorine; Gold catalyst

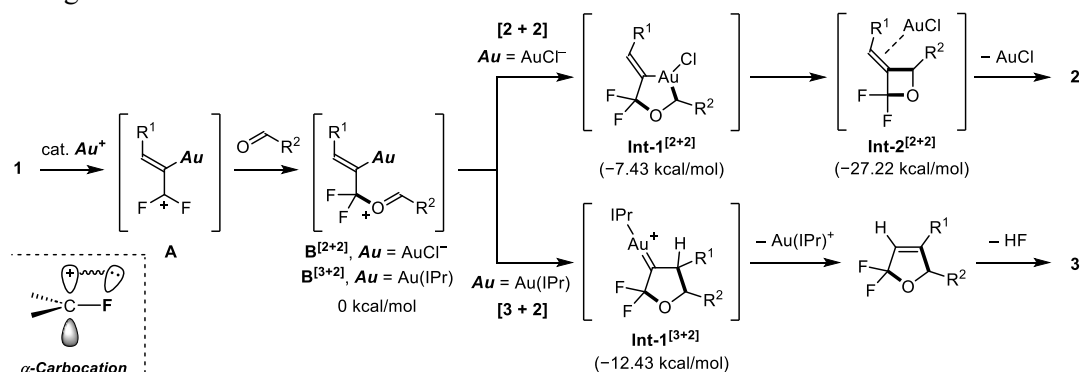
1,1-Difluoroallenes **1** [$R(R')C=C=CF_2$], characterized by two fluorine substituents on a 1,2-diene framework, have emerged as highly versatile synthetic intermediates for cyclic and acyclic organofluorine compounds. We have recently achieved the switchable syntheses of 2,2-difluorooxetanes and 2-fluorofurans by the regioselective cycloadditions of 1,1-difluoroallenes with aldehydes depending on the gold(I)-catalysts used.

In the presence of an AuCl catalyst, 1,1-difluoroallenes **1** underwent [2 + 2] cycloaddition with aldehydes on their α,β -position to afford (*E*)-3-alkylidene-2,2-difluorooxetanes **2** in 43–84% yields (eq 1). In contrast, an AuCl(IPr)–AgSbF₆ catalyst



enabled [3 + 2] cycloaddition of **1** with aldehydes on their α,γ -position, followed by dehydrofluorination to produce 2-fluorofurans **3** in 67–86% yields (eq 2).

1,1-Difluoroallenes **1** are activated by the Au(I) catalysts,¹ and the resulting allylic CF₂ cations **A** stabilized by two fluorines react with aldehydes at the position α to the fluorine substituents to generate intermediates **B**. DFT calculations suggest that the [2 + 2] cycloaddition proceeds via Au(III)-containing metallacycles **Int-1**^[2+2] generated from the intermediate **B**^[2+2], whereas the [3 + 2] cycloaddition proceeds via cyclic Au(I)-carbenoids **Int-1**^[3+2] generated from the intermediate **B**^[3+2].



DFT, B3LYP/6-31G** for C, H, Cl, F, N, O; Lan2dz for Au ($R^1 = R^2 = CH_3$).

[1] Fuchibe, K.; Abe, M.; Sasaki, M.; Ichikawa, J. *J. Fluorine Chem.* **2020**, *232*, 109452.

Fabrication of MOF-on-Inorganic Material Heterostructure Thin Film for n-Alkane Recognition Sensor

(¹Graduate School of Engineering, The University of Tokyo, ²Graduate School of Engineering, Kyushu University) ○Mikihisa Hirose¹, Tsunaki Takahashi¹, Manato Un¹, Takuro Hosomi¹, Wataru Tanaka¹, Jiangyang Liu¹, Haruka Honda¹, Nobuhiko Hosono¹, Takashi Uemura¹, Takeshi Yanagida^{1,2}

Keywords: Metal Organic Framework; Quartz Crystal Microbalance Gas Sensor; Surface Chemistry

Metal-organic Frameworks (MOFs) are characterized by their highly porous structures, which endow them with exceptional adsorption capabilities [1]. Therefore, integrating MOFs into sensors, such as quartz crystal microbalance (QCM) systems, presents significant potential for practical applications in molecular detection [2]. However, conventional fabrication techniques like drop-casting lead to poor interfacial adhesion, which limits the potential of adsorption properties. Here, we present a unique MOF-on-inorganic heterostructure layer directly grown on a QCM substrate. Aided by the inorganic adhesion layer, this structure allows the shear-mode vibration to propagate effectively through the sensing layer to encode MOF's molecular adsorption events accurately. As a proof-of-concept, this MOF-integrated QCM sensor was exposed to trace amounts of n-alkanes (hexane, heptane, octane). The sensor exhibits high signal-to-noise ratios, which are 80 times higher than drop-casted prepared sensors, and demonstrates a response to n-alkanes that outperforms previously reported sensors by several orders of magnitude.

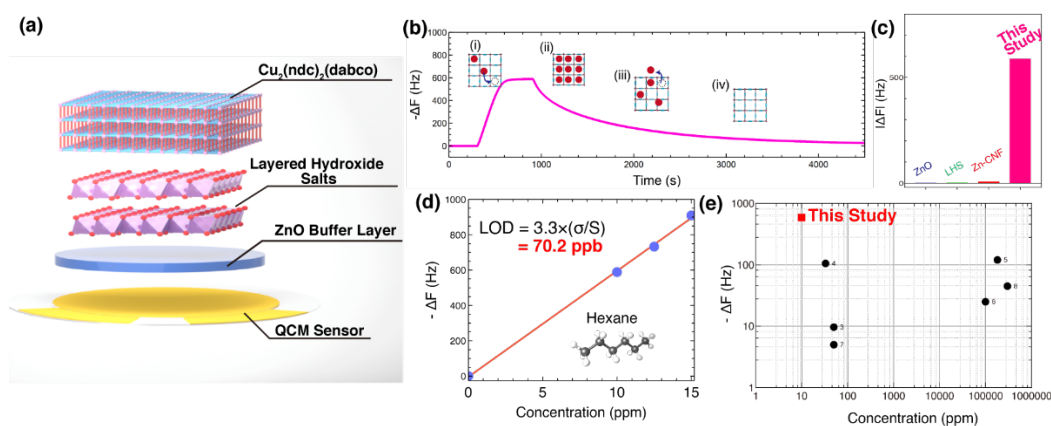


Figure. (a) Illustration of the overall structure of MOF-inorganic heterostructure-based QCM sensor. (b) Kinetics of the sensor response to 10 ppm hexane. (c) Comparison of the response of different sensing materials to 10 ppm hexane. (d) The limit of detection (LOD) for hexane was calculated to be less than 100 ppb. (e) Comparison with previously reported hexane sensors [3][4][5][6][7][8].

- [1] H.Wang, *Acc. Chem. Res.* **2019**, 52, 1968–1978. [2] H.Sorabi, *Mat.Chem.Phys.* **2023**, 299, 127512.
 [3] E Haghighi, *RSC. Adv.* **2019**, 9(42), 24460–24470. [4] C.Huang, *Env. Sci.*, **2011**, 45(10), 4490–4496.
 [5] S.Okur, *ACS.Sens.* **2024**, 9, 2, 622–630. [6] C.Yim, *RSC. Adv.* **2015**, 5(83), 67454–67458.
 [7] U.Latif, *Anal. Bio. Chem.* **2011**, 400(8), 2457–2462. [8] N.Speller, *Anal. Chem.*, 87(10), 5156–5166.

データ駆動型触媒設計のための 3 次元分子画像解析ツール

(理研 CSRS) ○山口 滋

Molecular 3D-Image Data Analysis Tool for Data-Driven Catalyst Design (*RIKEN CSRS*)

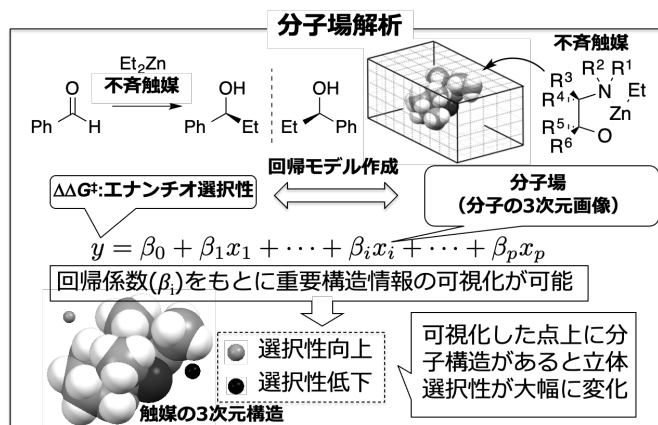
○Shigeru Yamaguchi

Machine learning of catalytic reactions in some cases enables the design of catalysts that are difficult to develop through human intuition alone. In particular, regression analysis using three-dimensional molecular image data (voxel data) as descriptors—commonly referred to as molecular field analysis (MFA)—can visualize which parts of a molecule are important for catalytic activities. Due to its high interpretability, this approach has facilitated data-driven catalyst design for controlling complicated reactions such as stereodivergent asymmetric synthesis and polymerization catalysis. However, despite its usefulness, this methodology has not been widely used in organic synthesis. One of the reasons is the lack of an interface enabling easy access to the MFA. To address this issue, we have developed a web application for MFA. In this presentation, we will provide an overview of the web application and demonstrate analysis of asymmetric catalysis using the tool.

Keywords : *Data-Driven Catalyst Design; Asymmetric Catalysis; Machine Learning*

機械学習による触媒反応の解析はときに人間の直感のみでは困難な触媒の設計を可能にする。とくに分子の 3 次元画像データ（ボクセルデータ）を記述子として用いた回帰分析（下図：分子場解析）は、触媒反応にとって分子のどこが重要かを可視化できる。高い解釈性のため立体分岐型不斉合成¹⁾や重合触媒反応²⁾といった複雑な反応のデータ駆動型触媒設計による制御を実現する³⁾。しかし、有機合成分野で一般的に使われるにいたっていない。

原因のひとつとして、分子場解析法を研究に活用するためのインターフェースの欠如が挙げられる。そこで本研究では、データ駆動型触媒設計のための分子場解析 web アプリ（3 次元分子画像解析ツール）を開発した。本講演では開発した web アプリを用いた不斉触媒反応の解析例を中心に、アプリの概要について述べる。



- 1) H. Chen, S. Yamaguchi, Y. Morita, H. Nakao, X. Zhai, Y. Shimizu, H. Mitsunuma, M. Kanai, *Cell Rep. Phys. Sci.* **2021**, 2, 100679.
- 2) S. Yamaguchi, T. Kikuchi, K. Tanaka, I. Takamiya, *Catal. Sci. Technol.* **2024**, 14, 2434.
- 3) S. Yamaguchi, *Org. Biomol. Chem.* **2022**, 20, 6057.