Academic Program [Oral B] | 10. Organic Chemistry -Organometallic Compounds-：Oral B

Fri. Mar 20, 2026 9:00 AM - 11:10 AM JST | Fri. Mar 20, 2026 12:00 AM - 2:10 AM UTC | E1112 (1112, Bldg. 11 [1F])

[E1112-4am] Oral B

Chair: Yusuke Masuda, Eisuke Ota

Japanese
9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC

[E1112-4am-01] Cobalt-Catalyzed 1,4-Addition for the Synthesis of Silyl Enol Ethers bearing Skipped Diene

○Shuto Odagaki[1], takuya kurahashi[1] (1. Kwansei Gakuin University)

English
9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC

[E1112-4am-02] Ligand-Controlled (3+2) and (2+2) Cycloaddition of Arylalkynes with Norbornene by Palladium Catalysis

○Sakura Takahashi[1], Mamoru Tobisu[1,2], Yusuke Ano[3] (1. Graduate School of Engineering, The University of Osaka, 2. ICS-OTRI, The University of Osaka, 3. Faculty of Engineering, Kindai University)

English
9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC

[E1112-4am-03] Pt/Photoredox-Catalyzed C4-Selective Allylation of Quinolines through a Dearomatized Intermediate

○Junpei Shimosato[1], Yusuke Masuda[1], Masaya Sawamura[1,2] (1. Hokkaido University, 2. WPI-ICReDD)

10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
Break

English
10:10 AM - 10:30 AM JST | 1:10 AM - 1:30 AM UTC

[E1112-4am-04] Pd-Catalyzed Intermolecular Nitro Transfer

○Masayuki Kubo[1], Junichiro Yamaguchi[1] (1. Waseda University)

English
10:30 AM - 10:50 AM JST | 1:30 AM - 1:50 AM UTC

[E1112-4am-05] Nickel-Catalyzed Cross-Coupling of Allylic Alcohols with Organoboroxines Mediated by Pyrimidine

○Thakun Chen[1,2], Takanori Iwasaki[2], Kyoko Nozaki[1] (1. The University of Tokyo, 2. Kyushu University)

Japanese
10:50 AM - 11:10 AM JST | 1:50 AM - 2:10 AM UTC

[E1112-4am-06] Ligand Design for Photoexcited Palladium Catalysts via Computational Approach: Efficient Generation of Ketyl Radicals from Alkyl Ketones

○Kosaku Tanaka, III[1,2,3], Ren Yamada[4], Suvankar Debbarma[2,3], Wataru Kanna[4], Hiroki Hayashi[2,3], Wataru Matasuoka[2,3], Satoshi Maeda[2,3,4], Tsuyoshi Mita[2,3] (1. ITSUU Laboratory, 2. WPI-ICReDD, Hokkaido Univ., 3. JST-ERATO, 4. Fac. of Sci., Hokkaido Univ.)

コバルト触媒による1,4-付加反応によるスキップトジエン骨格を有するシリルエノールエーテルの合成

（関西学院大院理工）○小田垣柊人・倉橋拓也

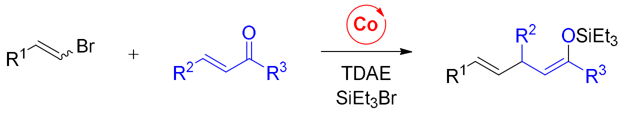
Nickel-Catalyzed Reductive Cross-Coupling Reaction of Aldehydes with Alkenyl Halides

(*Graduate School of Science and Engineering, Kwansei Gakuin University*) ○Shuto Odagaki, Takuya Kurahashi

Silyl enol ethers are versatile synthetic intermediates applicable to a wide range of bond-forming reactions and play an important role in modern organic synthesis, including the total synthesis of natural products. Accordingly, the development of efficient synthetic methods for silyl enol ethers continues to attract significant attention. Among them, silyl enol ethers bearing a skipped diene framework are useful reagents for the introduction of substituted homoallylic frameworks and skipped dienes. Several methods for the construction of silyl enol ethers possessing a skipped diene framework have been reported, including coupling reactions of enones with alkenes and reductive coupling of enones with alkynes via oxidative cyclization intermediates.[1,2] However, these approaches often suffer from limited substrate scope as well as insufficient control over regioselectivity and *E*/*Z* selectivity. Herein, we report a new method for the synthesis of silyl enol ethers bearing a skipped diene framework through a 1,4-addition of alkenyl Co(II) species in the presence of an organic reductant, a silylating reagent, and an enone, enabling controlled suppression of alkene isomerization.

Keywords : Cobalt; Silyl enol ethers; skipped diene; 1,4-addition

シリルエノールエーテルは、幅広い結合形成反応に利用可能な汎用性の高い合成中間体であり、現代有機合成化学および天然物全合成において重要な役割を担っている。そのため、効率的な合成手法の開発は依然として高い関心を集めている。なかでもスキップドジエン骨格を有するシリルエノールエーテルは、置換ホモアリル骨格やスキップトジエンを導入する有用な反応剤である。これまでに、エノンとアルケンとのカップリング反応、あるいは酸化的環化中間体を経由したエノンとアルキンとの還元的カップリング反応により、スキップドジエン骨格を有するシリルエノールエーテル合成法が報告されている[1,2]。しかし、これらの反応は基質適用範囲が限定的であることに加え、位置選択性および *E*/*Z* 選択性の制御に課題を残している。本研究では、有機還元剤、シリル化剤、エノンの存在下においてアルケニル Co(II)種の 1,4-付加反応により、アルケンの異性化を制御しながら、スキップドジエン骨格を有するシリルエノールエーテルの新規合成法を開発した。



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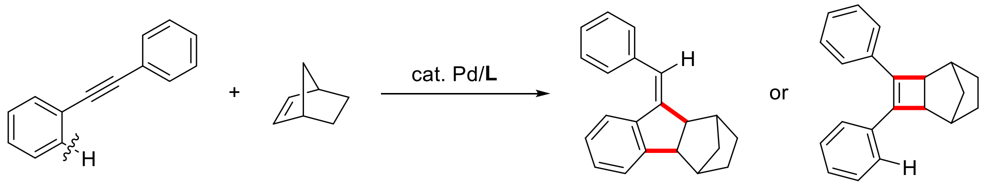
Ligand-Controlled (3+2) and (2+2) Cycloaddition of Arylalkynes with Norbornene by Palladium Catalysis

([1]*Graduate School of Engineering, The University of Osaka*, [2]*ICS-OTRI, The University of Osaka,* [3]*Faculty of Engineering, Kindai University*) ○Sakura Takahashi,[1] Mamoru Tobisu,[1,2] Yusuke Ano[3]

Keywords: *Palladium Catalyst; Alkyne; Cycloaddition; Norbornene; C−H Bond Activation*

Cycloaddition of phenylacetylene derivatives is a simple and useful method for constructing various sizes of cyclic compounds. The (4+2) cycloaddition of phenylacetylene *via* the cleavage of *ortho* C–H bond has been widely studied in the presence of a variety of metal catalysts, leading to the formation of naphthalene derivatives. However, to the best of our knowledge, the only reported example of a catalytic (3+2) cycloaddition using phenylacetylene derivatives is homodimerization of diphenylacetylenes,[1] and the catalytic (3+2) cycloaddition between phenylacetylene and another 2π component has not been achieved.

Herein, we present the Pd-catalyzed (3+2) cycloaddition reaction between phenylacetylene derivatives and norbornene via the C–H bond cleavage. Interestingly, changing the ligand switches the reaction pathway to the (2+2) cycloaddition, giving cyclobutene derivatives.



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脱芳香族中間体を介した白金/光酸化還元触媒によるキノリンのC4 位選択的アリル化反応

（北大理 [1]・WPI-ICReDD [2]）○下里 絢平 [1]・増田 侑亮 [1]・澤村 正也 [1,2]

Pt/Photoredox-Catalyzed C4-Selective Allylation of Quinolines through a Dearomatized Intermediate

([1]*Hokkaido University*, [2]*WPI-ICReDD*) ○Junpei Shimosato,[1] Yusuke Masuda,[1] Masaya Sawamura[1,2]

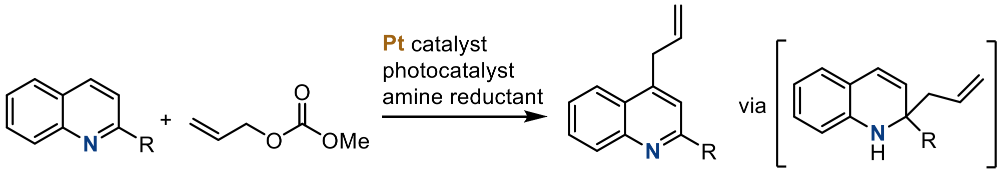
Metallaphotoredox catalysis, which merges photoredox and transition metal catalysis, has enabled a wide range of bond-forming reactions.1) While these reactions involve various transition metals such as Co, Ni, Cu, Rh and Pd, Pt/photoredox catalytic systems are largely unexplored.

In this study, we report C4-selective allylation of quinoline derivatives, enabled by a Pt/photoredox synergistic catalytic system. Upon irradiating a mixture of 2-ethoxycarbonylquinoline and allyl carbonate with visible light in the presence of Pt catalyst, photoredox catalyst and catalytic amount of amine reductant, a C4-allylated product was obtained. Mechanistic studies suggested that quinoline undergoes reductive allylation at the C2 position, generating a dearomatized intermediate. Subsequent allyl migration from the C2 to C4 position followed by oxidative rearomatization affords the C4-allylated product.

Keywords : Platinum catalyst, Quinoline, Dearomatization, Photoredox catalyst, Allylation

遷移金属触媒と光酸化還元触媒を協働して用いる反応はメタラフォトレドックス反応と呼ばれ、革新的な分子変換手法として発展の著しい分野である 1)。これまでに遷移金属触媒として Co, Ni, Cu, Rh, Pd などを用いた反応が数多く報告されているが、Pt を用いた反応の報告例は限られている。一方で、我々はπ-アリル Pt 錯体が還元条件下で安定であるという Pt 触媒特異的な反応性を見出し、Pt/光酸化還元協働触媒系によるケトンおよびイミン類の還元的アリル化反応を開発した。

本研究では、この Pt 触媒の特性を発展的に活用することで、キノリンの C4 位選択的アリル化反応を達成した。すなわち、2 位にエトキシカルボニル基を有するキノリンと炭酸アリルエステルを基質に用いて、Pt 触媒、光酸化還元触媒、触媒量のアミン還元剤存在下において可視光を照射することで、C4 位がアリル化された生成物を得た。機構解析の結果、キノリンの C2 位が還元的にアリル化されることで、脱芳香族中間体を生じたのち、続く C2 から C4 へのアリル基の転位、および酸化的再芳香族化を経て目的物へと至ることが分かった。



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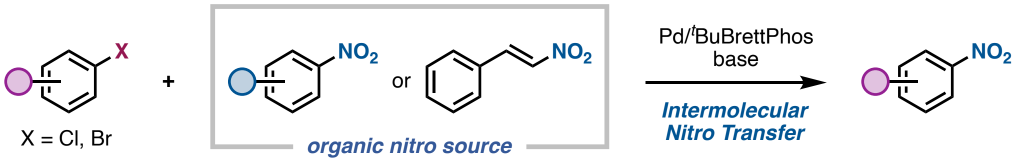
Pd-Catalyzed Intermolecular Nitro Transfer

(*Graduate School of Advanced Science and Engineering, Waseda University*)
○Masayuki Kubo, Junichiro Yamaguchi

Keywords: *Palladium, Transfer nitration, Nitroarene, β-Nitrostyrene, Haloarene*

Nitroarenes are essential structural motifs and versatile intermediates in organic synthesis, material science, and drug discovery. Conventional routes to nitroarenes are represented by electrophilic aromatic substitution via mixed-acid nitration or milder protocols employing electrophilic nitrating reagents, and by radical nitration, most often using *tert*-butyl nitrite as the major nitro source.[1] While these approaches remain valuable, the regioselectivity of electrophilic nitration is often governed by the intrinsic electronic properties of the aromatic ring, limiting site selectivity and substrate diversity. To address these limitations, transition-metal-catalyzed cross-coupling-type nitration of haloarenes has emerged as a powerful alternative. To date, Pd-, Cu-, and Fe-catalyzed nitrations employing inorganic nitrite salts as the nitro source have been developed.[2] However, these nitrite salts such as $NaNO_2$ raise safety concerns due to their oxidizing and toxic nature. Moreover, in Pd-catalyzed systems, the reaction efficiency is known be strongly halide-dependent; for example, Buchwald and co-workers reported effective nitration of chloroarenes, whereas bromoarenes gave significantly lower yields.[3] These drawbacks motivated us to identify a safer, more controllable nitro source capable of delivering nitrite under the reaction conditions.

Herein, we developed a Pd-catalyzed transfer nitration of haloarenes using nitroarenes or β-nitrostyrene as organic nitro sources.[4] The reaction proceeds via *in situ* generation of nitrite (NO_2^-) from nitroarenes and β-nitrostyrene, followed by palladium-catalyzed coupling with haloarenes. While both nitro sources were effective for the nitration of chloroarenes, β-nitrostyrene successfully expanded the substrate scope to (hetero)bromoarenes with good functional-group tolerance.



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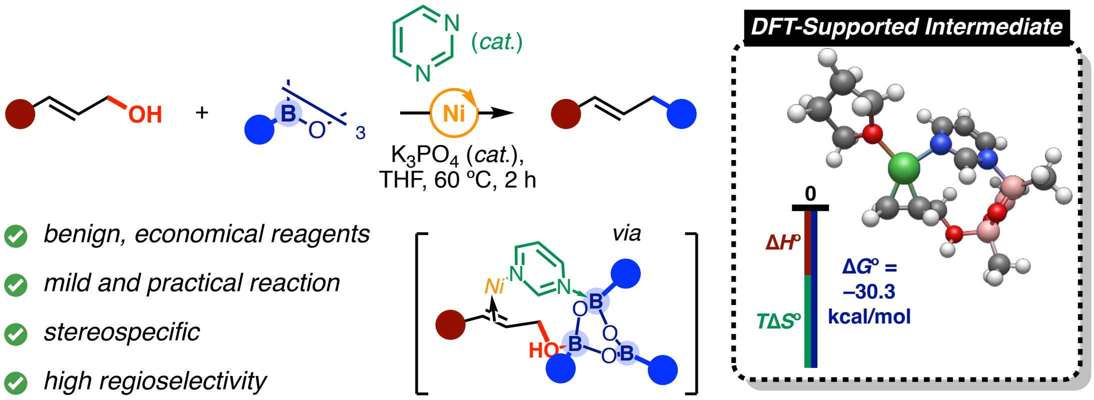
Nickel-Catalyzed Cross-Coupling of Allylic Alcohols with Organoboroxines Mediated by Pyrimidine

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Engineering, Kyushu University*) ○Thakun Chen,[1,2] Takanori Iwasaki,[2] Kyoko Nozaki[1]

Keywords: Allylic Substitution; Cross-Coupling; Alcohols; Organoboroxines; Pyrimidine

Alcohols are ideal feedstocks for allylic substitution due to their low toxicity and renewability, but their direct utilization in cross-coupling reactions remains challenging due to the intrinsic inertness of C–O bonds.[1] Building upon our previous work on the substitution of allylic ethers with organoboroxines in the presence of pyrimidine,[2] a Suzuki–Miyaura-type coupling of allylic alcohols has been developed that enables efficient deoxygenative substitution under mild conditions. The transformation proceeds with low loadings of a cheap nickel(II) catalyst and exhibits broad substrate scope, high regioselectivity, and complete stereospecificity.

Systematic evaluation of structurally related additives identified coordination geometry and basicity as the key parameters governing the catalytic efficiency of pyrimidine. Mechanistic studies support a cooperative activation mode in which pyrimidine, the Lewis acidic organoboroxine, the nickel catalyst, and the allylic alcohol assemble into a transient, conformationally constrained intermediate that lowers the energetic barrier for oxidative addition of otherwise unreactive C–O bonds. Evidence for this cooperative intermediate is provided by competition experiments and DFT calculations, which together indicate that both Lewis acid–mediated activation of the allylic C–O bond and conformational preorganization are essential to account for the high efficiency of the transformation.



- ✓ *benign, economical reagents*
- ✓ *mild and practical reaction*
- ✓ *stereospecific*
- ✓ *high regioselectivity*

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計算化学的アプローチによる光励起パラジウム触媒の配位子設計：アルキルケトン由来ケチルラジカルの効率的生成

(乙卯研究所[1]・北大 WPI-ICReDD[2]・JST-ERATO[3]・北大院理[4]) ○田中耕作三世[1,2,3]・山田 蓮[4]・Debbarma Suvankar[2,3]・神名 航[4]・林 裕樹[2,3]・松岡 和[2,3]・前田 理[2,3,4]・美多 剛[2,3]

Ligand Design for Photoexcited Palladium Catalysts via Computational Approach: Efficient Generation of Ketyl Radicals from Alkyl Ketones

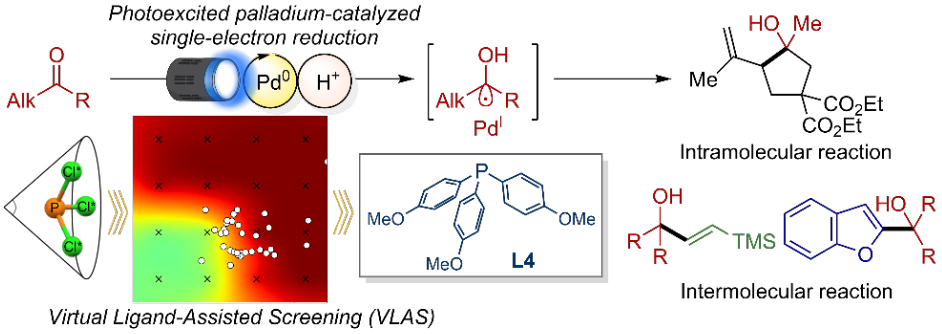
([1]ITSUU Laboratory, [2]WPI-ICReDD, Hokkaido Univ., [3]JST-ERATO, [4]Fac. of Sci., Hokkaido Univ) ○Kosaku Tanaka, III,[1,2,3] Ren Yamada,[4] Suvankar Debbarma,[2,3] Wataru Kanna,[4] Hiroki Hayashi,[2,3] Wataru Matsuoka,[2,3] Satoshi Maeda,[2,3,4] Tsuyoshi Mita[2,3]

Ketyl radicals are versatile intermediates that enable a wide range of carbon–carbon bond-forming reactions. However, the generation of ketyl radicals via single-electron reduction from substrates with low reduction potentials, such as alkyl ketones, remains challenging.
Previous study[1] have experimentally shown that the primary reason for inefficient reactivity is back-electron transfer (BET). In this study, to elucidate ligand features that contribute to BET suppression, ligand screening was performed using the Virtual Ligand-Assisted Screening (VLAS) method.[2] Based on the computational results, ligand optimization was carried out, and experimental validation leveraging the strong reducing power of photoexcited palladium species enabled the generation of ketyl radicals from alkyl ketones, achieving highly efficient reductive coupling and Heck-type reactions with unactivated alkenes and alkynes.[3]

Keywords : Photoexcited palladium; Computational chemistry; Back-electron transfer (BET); Virtual Ligand-Assisted Screening; Ketyl radicals

ケチルラジカルは、多様な炭素–炭素結合形成反応を可能にする有用な中間体である。しかし、アルキルケトンのように還元電位が低い基質から、一電子還元によってケチルラジカルを生成することは依然として困難である。

先行研究[1]により、反応が十分に進行しない主要因が逆電子移動（back-electron transfer, BET）であることが実験的に示されている。そこで本研究では、BET 抑制に寄与する配位子の特性を明らかにするため、計算化学に基づく Virtual Ligand-Assisted Screening（VLAS）法[2]を用いた配位子探索を行った。得られた計算結果に基づいて配位子を最適化し、光励起パラジウム種の高い還元力を活用した実験的検証により、アルキルケトンからケチルラジカルを生成し、不活性アルケンおよびアルキンを基質とする高効率な還元的カップリング反応および Heck 型反応を実現した[3]。



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