シンポジウム | アジア国際シンポジウム：アジア国際シンポジウム—錯体化学・有機金属化学ディビジョン—

📅 2024年3月19日(火) 9:15 ~ 11:40 🏛 A1423(14号館 [2階] 1423)

[A1423-2am] アジア国際シンポジウム—錯体化学・有機金属化学ディビジョン—

座長、シンポジウム関係者：橋本 久子、松田 亮太郎、正岡 重行、西林 仁昭、大木 靖弘、中島 裕美子、二瓶 雅之、嶌越 恒

9:15 ~ 9:20

開会挨拶

🏷 英語 🏷 Invited Lecture
9:20 ~ 9:40
[A1423-2am-01]

協働金属触媒による有機合成

〇仙波 一彦[1] (1. 京都大学大学院工学研究科)

🏷 英語 🏷 Invited Lecture
9:40 ~ 10:00
[A1423-2am-02]

Photocatalytic CO_2 Reduction Using Mononuclear Metal Complexes as Self-photosensitized Catalysts

〇Jieun Jung[1] (1. Graduate School of Science, Nagoya University)

🏷 英語 🏷 Invited Lecture
10:00 ~ 10:20
[A1423-2am-03]

水からの水素生成を超高速駆動するコバルトNHC錯体触媒に関する研究

〇山内 幸正[1] (1. 九大)

10:20 ~ 10:30

休憩

🏷 英語 🏷 Asia Special Lecture
10:30 ~ 10:50
[A1423-2am-04]

金属キレート部位の環状多量体の超分子化学

〇中村 貴志[1] (1. 筑波大)

🏷 英語 🏷 Invited Lecture
10:50 ~ 11:10
[A1423-2am-05]

N-ヘテロサイクリックカルベン配位子修飾による遷移金属添加セリア系複合酸化物の触媒活性誘起

〇邨次 智[1] (1. 名古屋大学)

🏷 英語 🏷 Keynote Lecture
11:10 ~ 11:40
[A1423-2am-06]

Exploring the Influence of Structure and Chemical Properties in Metal-Organic Framework for Photocatalysis

〇Sareeya Bureekaew[1]、Ladawan Pukdeejorhor[1]、Kanyaporn Adpakpang[1]、Yollada Inchongkol[1]、Taya Saothayanun[1] (1. Vidyasirimedhi Institute of Science and Technology (VISTEC))

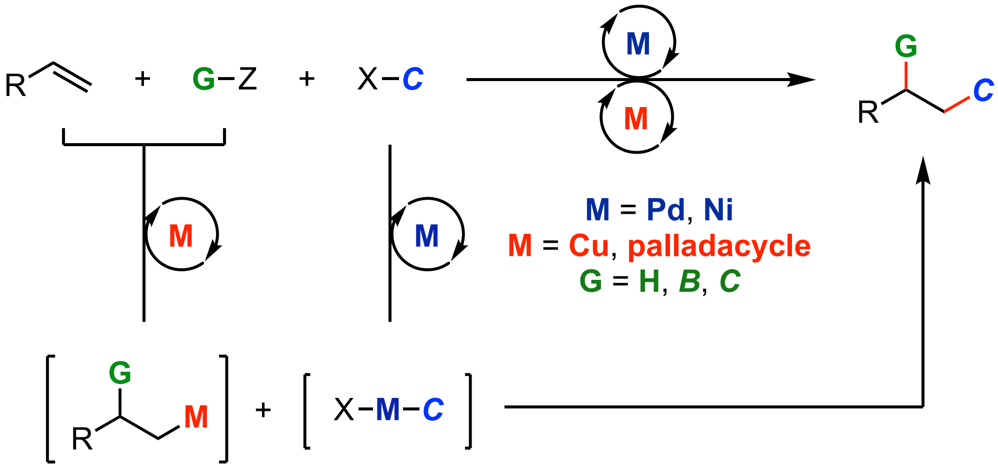
Organic Synthesis by Cooperative Metal Catalysis

(*Graduate School of Engineering, Kyoto University*) ○Kazuhiko Semba

Keywords: *Cooperative Catalysis*, *Transition-Metal Catalyst, Synthetic Organic Chemistry*

Csp^3-enriched molecules are increasing their importance in drug discovery due to their target specificity.[1] Cross-coupling reactions with alkylmetal reagents enable rapid access to Csp^3-enriched molecules in a modular fashion.[2] Typically, these reactions require pre-synthesized alkylmetal reagents. However, common alkylmetals such as alkylmagnesium, alkylzinc, and trialkylboron reagents are sensitive toward moisture and O_2, leading to laborious operations in handling them. In contrast to the typical method, a method based on catalytically generated alkylmetals from alkenes offers several advantages: 1) Laborious operation for the reactive alkylmetals is not required. 2) Stable and abundant alkenes serve as alkylmetal surrogates. 3) Decorated alkylmetals, which are rarely used under the typical cross-coupling conditions, can be utilized.

Our group has contributed to developing the cross-coupling with alkenes by taking advantage of cooperative transition-metal catalysis (Scheme 1).[3] In this line, we have successfully developed hydroarylation, carboboration, dicarbofunctionalization of alkenes that are unattainable by single metal catalysis. In this presentation, we will share recent progress on the cross-coupling with alkenes as alkylmetal surrogates by cooperative transition-metal catalysis.



1) F. Lovering, *Med. Chem. Commun.* **2013**, *4*, 515.
2) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417.
3) K. Semba, Y. Nakao, *J. Synth. Org. Chem., Jpn.* **2017**, *75*, 1133.

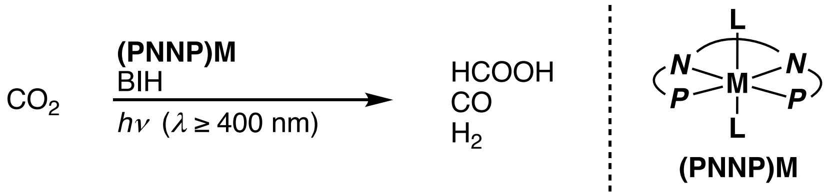
Photocatalytic CO_2 Reduction Using Mononuclear Metal Complexes as Self-photosensitized Catalysts

([1]*Graduate School of Science, Nagoya University*) ○Jieun Jung[1]

Keywords: Molecular Complexes; Carbon Dioxide; Photoreduction; Laser Flash Photolysis; Mechanism

Photocatalytic reduction of carbon dioxide (CO_2) is recognized as an important research area owing to problems related to the depletion of fossil fuels and environmental problems. Typical examples of CO_2 photoreduction by transition metal complexes were achieved by a combination of a photosensitizer (PS) and a catalyst (Cat). On the other hand, development of self-photosensitized metal complexes acting as both PS and Cat is advantageous in terms of lowering the activation energy of the catalytic reaction and controlling its selectivity. However, the development of robust homogeneous photocatalysts has remained challenging, as most exhibit low turnover numbers (TONs).

Herein, I introduce structurally robust tetradentate PNNP-type metal complexes, (PNNP)M (M = Ir, Ru, and Os), as efficient homogeneous self-photosensitized catalysts for photocatalytic CO_2 reduction. The (PNNP)Ir and (PNNP)Ru complexes[1,2] are able to reduce CO_2 to mainly formic acid (HCOOH) and carbon dioxide (CO) under photoirradiation ($\lambda \geq$ 400 nm) in the presence of a sacrificial electron donor, giving the products continuously for over 1 week. Especially, (PNNP)Ir complex furnished HCOOH with 87% selectivity together with CO to achieve the highest TON of > 10400. Meanwhile, (PNNP)Os complex acts as a panchromatic self-photosensitized catalyst for CO_2 reduction that allows the use of a broader range of visible light. CO_2 photoreduction proceeded under irradiation with blue (λ_0 = 405 nm), green (λ_0 = 525 nm), or red (λ_0 = 630 nm) light to give CO with >90% selectivity. It is worth noting here that the major product changed from HCOOH to CO upon replacing the metal center coordinated to the PNNP-type ligand from Ir (group 9, 5d) to the adjacent element Os (group 8, 5d).



1) a) K. Kamada, J. Jung*, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, S. Fukuzumi, S. Saito*, *J. Am. Chem. Soc.* **2020**, *142*, 10261. b) K. Kamada, J. Jung*, Y. Kametani, T. Wakabayashi, Y. Shiota, K. Yoshizawa, S. H. Bae, M. Muraki, M. Naruto, K. Sekizawa, S. Sato, T. Morikawa, S. Saito*, *Chem. Commun.* **2022**, *58*, 9218.

2) K. Kamada, H. Okuwa, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, J. Jung*, S. Saito*, *Synlett* **2022**, *33*, 1137.

Co-NHC Catalysts Promoting Hydrogen Evolution from Water with High Turnover Number and Frequency

(*Kyushu University*) ○Kosei Yamauchi

Keywords: Artificial Photosynthesis; Alkaline Hydrogen Evolution; N-heterocyclic Carbene Cobalt Complexes; Turnover Frequency; Turnover Number

Artificial photosynthesis based on splitting water into H_2 and O_2 with solar energy has attracted recent years. In order to realize overall water-splitting reaction ($2H_2O + 4h\nu \rightarrow 2H_2 + O_2$) on the basis of molecular systems, it is crucial to ensure sufficient driving force for both H_2 and O_2 evolution reactions (HER and OER). We have previously studied on molecular photosystems in which HER is driven by oxidative quenching of $[Ru^*(bpy)_3]^{2+}$, but the reaction rates and turnover numbers were relatively low when **Co-NHC1** and other molecular catalysts were employed [1,2]. On the other hand, the reductive quenching of $[Ru^*(bpy)_3]^{2+}$ [3,4] provides large driving force for HER but insufficient driving force for OER in the acidic to neutral pH range. In this study, we focus on a new strategy to maintain the driving force for both HER and OER by carrying out the reductive quenching process of $[Ru^*(bpy)_3]^{2+}$ under highly alkaline conditions.

A large amount of H_2 (turnover number = 40000 at pH = 12.8) evolved when using a $[Ru(bpy)_3]^{2+}$/ascorbate photochemical system in the presence of a newly synthesized new Co-NHC catalyst for HER even under highly alkaline conditions (Figure 1). Furthermore, it was found that the new catalyst is more durable than **Co-NHC1**. More interestingly, as the pH is increased, sustained evolution of H_2 takes place in larger amounts (pH < 12.8).

On the other hand, the turnover frequency (TOF) of **Co-NHC1** has been also determined by conducting the electrochemical studies. Importantly, the TOF in the aqueous phosphate buffer solution (pH = 7) was estimated as tens of million s^{-1}, which will be also discussed in the presentation.

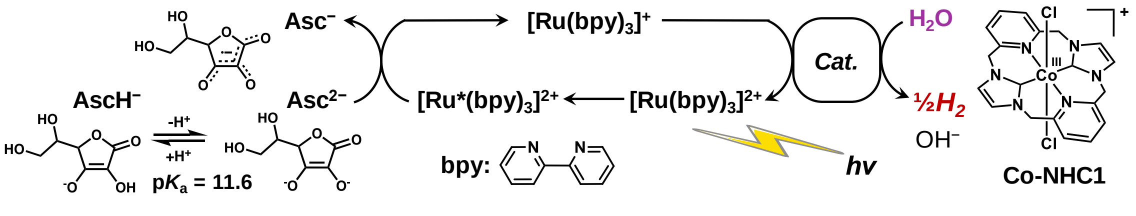


Figure 1. Photochemical hydrogen evolution from alkaline water.

[1] Kawano, K.; Yamauchi, K.*; Sakai, K.*, *Chem. Commun.* **2014**, *50*, 9872-9875.

[2] Yatsuzuka, K.; Yamauchi, K.*; Kawano, K.; Ozawa. H.*; Sakai, K.*, *Sustainable Energy Fuels* **2021**, *5*, 740-749.

[3] Zhang, X.; Yamauchi, K.; Sakai, K.*, *ACS Catal.* **2021**, *11*, 10436-10449.

[4] Sueyoshi F.; Zhang, X.; Yamauchi, K.; Sakai, K.*, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217807.

Supramolecular Chemistry of Macrocyclic Oligomers of Metal Chelating Units

(*Institute of Pure and Applied Sciences, University of Tsukuba*) ○Takashi Nakamura

Keywords: Supramolecular Chemistry; Macrocycles; Coordination Bonds; Molecular Recognition; Dynamic Covalent Bonds

Macrocyclic oligomers of metal chelating units serve as unique ligands to synthesize multinuclear complexes that assemble coordination sites in the cavity (**Fig. 1a**).[1–4] Such metallomacrocycles can realize precise molecular binding by utilizing multi-point coordination and rigidity of the metal complex units. Desymmetrization of macrocycles is another approach to create functional molecules, because they can employ their unsymmetrically arranged interaction moieties (**Fig. 1b**).[1–3,5]

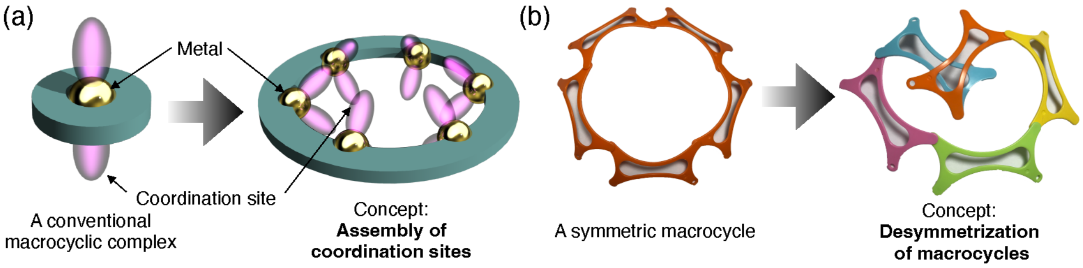


Figure 1. (a) Assembly of coordination sites. (b) Desymmetrization of macrocycles.

Pyridylmethylene-aminophenol (pap) hexamer and its Pd complexes as a metallohost[2d)]

We have developed multinuclear complexes of hexapap, macrocyclic ligands with six pyridylmethylene-aminophenol (pap) units.[2)] A hexanuclear Pd^{II} complex of hexapap [**1**Pd$_6$L$_6$](OTf)$_6$ (L: exchangeable ligand) has six inward coordination sites. Because of the planarity of one monomeric [Pd(pap)L] unit, [**1**Pd$_6$L$_6$](OTf)$_6$ can take two conformations. One is an *Alternate* conformation, in which six coordination sites of pap alternatively point to *Up-Down-Up-Down-Up-Down*. The other is a *Twisted* conformation, in which the coordination sites direct *Up-Middle-Down-Up-Middle-Down* (**Fig. 2**).

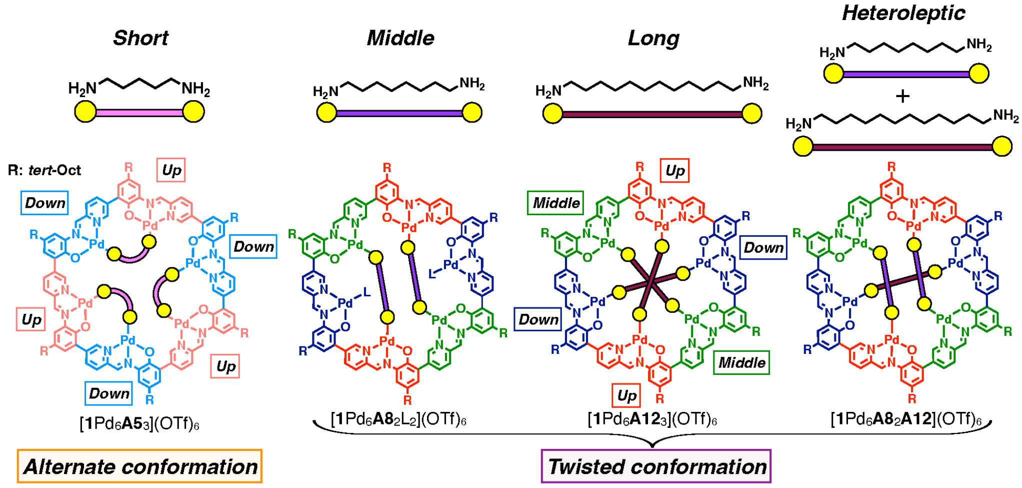
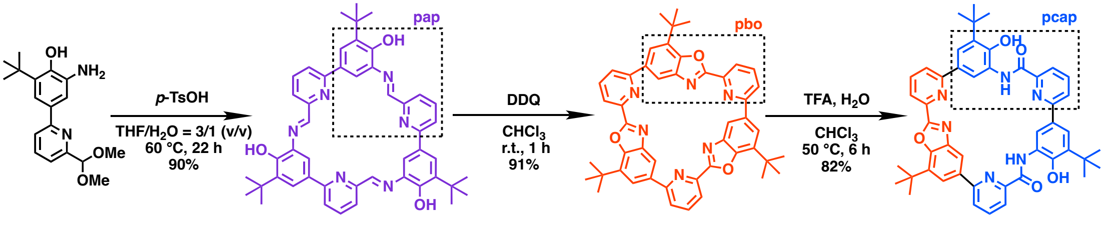


Figure 2. Site-selective ligand bridging of [**1**Pd$_6$L$_6$](OTf)$_6$ and its conformational regulation.

It was found that α,ω-diaminoalkanes $H_2N(CH_2)_nNH_2$ (**A*n***) bridged the inner coordination sites of [**1**Pd_6L_6]$(OTf)_6$ in different binding modes according to the number of methylene groups (*n*). **A4**–**A7** linked adjacent pap units to form [**1**Pd_6**A*n***$_3$]$(OTf)_6$ (n = 4–7) with *Alternate* conformation. **A8** connected 2 next pap units to yield [**1**Pd_6**A8**$_2L_2$]$(OTf)_6$ with *Twisted* conformation. **A12** connected diagonal Pd centers to result in [**1**Pd_6**A12**$_3$]$(OTf)_6$, again with *Twisted* conformation. Furthermore, in the case of **A8**:**A12** = 2:1, heteroleptic bridging was achieved to give [**1**Pd_6**A8**$_2$**A12**]$(OTf)_6$ (**Fig. 2**).

Pyridylbenzoxazole (pbo) trimer and its unsymmetric conversion[3)]

Synthesis of macrocycles with unsymmetric frameworks often suffers from multi-step reactions and low yields to sequentially connect different units. The use of dynamic covalent bonds is usually not effective for the synthesis of an unsymmetric macrocycle as a single product. We have achieved a high-yield 3-step synthesis of an unsymmetric macrocycle composed only of irreversible bonds (**Fig. 3**).



2 3 4 5

Figure 3. Synthesis of pcap-pbo mixed macrocycle **5** utilizing dynamic covalent bond

The three steps are comprised of macrocyclization, oxidation, and unsymmetric conversion. The first step is the macrocyclic oligomerization of the bifunctional monomer **2**, which has *o*-aminophenol and 2-formylpyridine subunits, utilizing imine bonds formation to yield the pap macrocycle **3**. The second step is the oxidation of the pap units of **3** to benzoxazole (pbo) units to yield the macrocycle **4** composed only of irreversible bonds. The last step is the unsymmetric conversion, that is, the selective addition reaction of water to only two of three pbo units of **3** to convert them into pyridylcarboxamidephenol (pcap) units, to obtain the unsymmetric macrocyclic ligand **5**. Moreover, the unsymmetric macrocycle **5** forms an interesting 2:1 complex with Zn^{II}, which holds the metal ion like a pearl in bivalve shells (**Fig. 4**).

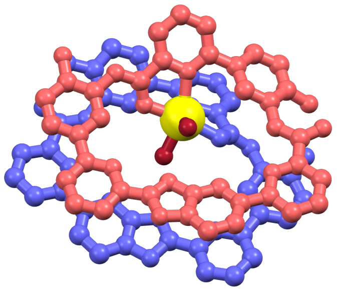


Figure 4. Structure of [$\mathbf{5}_2Zn(H_2O)_2$]$^{2+}$ determined by X-ray crystallography

1) T. Nakamura, *Chem. Lett.* **2021**, *50*, 1822. (*Highlight Review*)
2) a) T. Nakamura, Y. Kaneko, E. Nishibori, T. Nabeshima, *Nat. Commun.* **2017**, *8*, 129. b) A. Nagai, T. Nakamura, T. Nabeshima, *Chem. Commun.* **2019**, *55*, 2421. c) T. Nakamura, R. Y. Feng, T. Nabeshima, *Eur. J. Inorg. Chem.* **2021**, 308. d) T. Nakamura, S. Watanabe, *Inorg. Chem.* **2023**, *62*, 12886.
3) Y. Hokimoto, T. Nakamura, *Chem. Commun.* DOI: 10.1039/D3CC06216C
4) a) T. Nakamura, Y. Kawashima, E. Nishibori, T. Nabeshima, *Inorg. Chem.* **2019**, *58*, 7863. b) T. Nakamura, S. Tsukuda, T. Nabeshima, *J. Am. Chem. Soc.* **2019**, *141*, 6462.
5) a) T. Nakamura, S. Yonemura, T. Nabeshima, *Chem. Commun*. **2019**, *55*, 3872. b) S. Yonemura, T. Nakamura, T. Nabeshima, *Chem. Lett.* **2020**, *49,* 493. c) T. Nakamura, S. Yonemura, S. Akatsuka, T. Nabeshima, *Angew. Chem. Int. Ed.* **2021**, *60*, 3080.

Triggering Catalytic Activity by the Decoration of N-Heterocyclic Carbenes on Transition Metal Incorporated Cerium Oxides

([1]*Department of Chemistry, Graduate School of Science, Nagoya University*)
○Satoshi Muratsugu[1]

Keywords: Mixed Metal Oxide; NHC Ligand; Rhodium; Ceria; 1,4-Arylation

Cerium dioxide (CeO_2) is a class of metal oxides with a redox property of Ce ions (Ce^{4+} - Ce^{3+}); however, it is still difficult to achieve reversible redox performances with the reduction of Ce^{4+} below 373 K. The incorporation of additional transition metal ions to CeO_2 is one of the promising methods not only to reduce the redox reaction temperature of CeO_2, but also to generate/construct unique metal structures (ex. very small metal nanoclusters) directly on the surface of CeO_2, and the combination of additional metal ions are important.

We prepared a ceria-based oxide incorporated with Cr and a trace amount of Rh ions (denoted as $Cr_{0.19}Rh_{0.06}CeO_z$), and achieved reversible redox activity at low temperature below 373 K, together with the formation of very small Rh nanoclusters on its surface.[1] The surface structures and redox mechanisms of $Cr_{0.19}Rh_{0.06}CeO_z$ were fully characterized by *in situ* spectroscopic techniques; the formed very small Rh nanoclusters facilitated the reduction of Cr and surface Ce species at the very close temperature.[1]

Attachment of N-heterocyclic carbene (NHC) ligands to Rh nanoclusters prepared by the H_2 reduction of $Cr_{0.19}Rh_{0.06}CeO_z$ (denoted as r-$Cr_{0.19}Rh_{0.06}CeO_z$) newly emerged catalytic activity for 1,4-arylation of α,β-unsaturated ketones, which did not appear without NHC attachment (**Figure 1**).[2] Surface characterization clarified the existence of the interaction between NHC and Rh nanoclusters, which played a key role for this catalytic activity emergence. DFT calculations suggested the possible origin of this catalytic activity emergence; the coordination of NHC on the Rh nanocluster would switch the adsorption site of aryl group from arylboronic acid, facilitating the C-C bond formation.[2]

1) S. Ikemoto, et al., *Phys. Chem., Chem. Phys.* **2019**, *21*, 20868-20877. 2) S. Ikemoto, et al., *J. Am. Chem. Soc.* **2023**, *145*, 1497-1504.

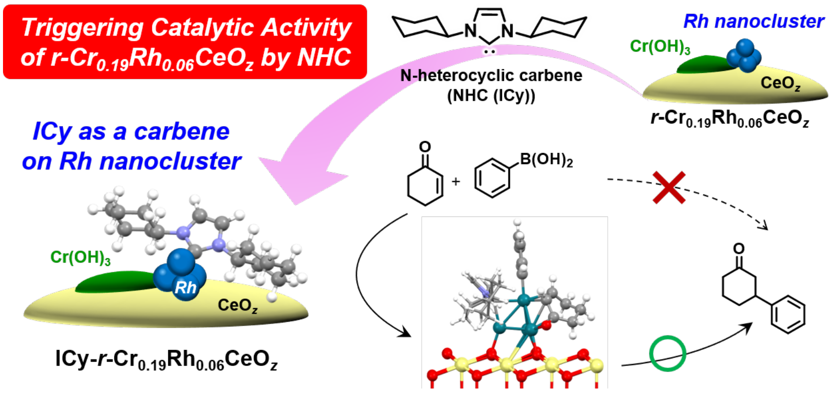


Figure 1. A schematic image of the attachment of a NHC ligand on r-$Cr_{0.19}Rh_{0.06}CeO_z$ and the emergence of catalytic 1,4-arylation.[2]