Welcome to the Molecular Catalysis Research Team WEB Site

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Research Interests:

1. Cross-Dimerization of Alkenes: One of the major focuses in our lab is the selective cross-dimerization of substituted alkenes by zero-valent ruthenium complex. We have developed the first enantioselective cross-dimerization between substituted alkenes, that goes through an oxidative coupling mechanism. (Org. Lett., 2013, 15, 2486)

![Cross-Dimerization Reaction](image)

2. Bond Activation by Internal Electrophilic Substitution Mechanism: Internal Electrophilic Substitution (IES) mechanism, which is also named as Concerted Metallation Deprotonation (CMD) or Ambiphilic Metal-Ligand Activation (AMLA), is one of the current topics in bond activation processes. However, the understanding in the molecular level and the application is still limited. We have shown multiple C-H bond activation processes of alkyl group in the ortho position of the aryloxo group. (Organometallics, 2014, 33, 1235)

![Bond Activation Diagram](image)
3. Successive C-O/C-H Bond Activation of Esters: The C-H bond activation by the Internal Electrophilic Substitution (IES) mechanism normally starts from the oxidative addition of organic halide to the low valent metal compound followed by the anion exchange between the resulting halido and carboxylato (or carbonato) to give (carboxylate)(organo)metal species. If we can make this species directly from esters by the C-O bond activation, this process must be very attractive from the atom and step economy point of view. We have succeeded direct formation of fluorene by the C-O/C-H bond activation process by a Pd catalyst. (*Organometallics*, 2014, 33, 1921)

4. Highly Active Catalyst for Hydrometallation: We recently found the mono-phosphine Pd(0) compounds to be a highly active hydrometallation catalyst under mild conditions. Hydrometallations, particularly those using main group elements, are highly attractive for the synthetic point of view.
Research Interests:

The MOLCAT

The molcat is a research team headed by Masafumi Hirano at Tokyo University of A & T. The molcat is interested in Molecular Catalysis and Organometallic and Coordination Chemistries.

Interested in becoming a MOLCAT? Don’t hesitate to contact MH.

METAL CHICKS

The Metal chicks is an alumnae and alumni organization of molcats.

The Keyaki Party

The united alumni organization involving those of Prof. Emer. S. Komiya and Prof. A. Fukuoka (Hokkaido U) is named Keyaki Party (Zelkova).
DOI: 10.1246/bcsj.20210163

Nobuyuki Komine,* Tatsuo Mitsui, Shu Kikuchi, Masafumi Hirano, Ligand-Controlled Rgiodivergent Hydrosilylation of Conjugated Dienes Catalyzed by Mono(phosphine)palladium(0) Complexes, Organometalics, 2020, 39, 4510-4524.
DOI: 10.1021/acs.organomet.0c00597

DOI: 10.1021/acscatal.0c00918

Table of Contents Graphic


DOI: 10.1039/c9nj04880d

DOI: 10.1039/c9cc05930j

(butadiene)Ru(bidentate)(1,5-cod)] (10 mol%) + (iPrO)₂B
benzene, r.t., 3 h

83%
28 examples


DOI: 10.1016/j.tetlet.2019.07.015
DOI: 10.1021/acscatal.8b04676

**Catalytic Linear Cross-Dimerization**

DOI: 10.1021/acs.organomet.8b00645

A Homogeneous Catalyst Poison was Reborn as an Efficient Ligand by Ph Substitution.

Masafumi Hirano,* Kosuke Sano, Yuki Kanazawa, Nobuyuki Komine, Zen Maeno, Takato Mitsudome,* Hikaru Takaya,* Mechanistic Insights on Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate,
In industrial plants for the production of precursors for polyimides, this reaction requires harsh conditions. The total product yield is mostly less than 10%. Nevertheless, this process is operated directly use aromatic compounds as reactants with high atom presence of oxygen. This is a halogen-free process, and one can dehydrogenative coupling of arenes, which is from the reaction. The dehydrogenative coupling of arenes is compound in advance. The other problem is emission of wastes methods of biaryls involve Ullmann coupling, cross-coupling, and indispensable approaches to produce electronic materials.

**ABSTRACT:**

The first catalytic dehydrogenative coupling was reported by Itatani and Yoshimoto for the coupling of toluene catalyzed by \([\text{Pd(OAc)}_2]\) along with small amounts of the Wacker-type catalyst probably by an internal electrophilic substitution (IES) as shown in Scheme 1. According to an analogy to the Wacker-type catalysis, resulting \([\text{Pd(OAc)}\text{ArL}]\) reacts with a second arene, as observed by a detailed kinetic study using XAFS supports the formation of an (acetato)(dimethyl phthalyl)(phen)-...

DOI: 10.1021/acs.organomet.7b00593

![Chemical structure]

● Masafumi Hirano, Masahiro Moritake, Tasuku Murakami, Nobuyuki Komine, Ru(0)-Catalyzed C3-Selective Coupling Reactions of Unsaturated 5-Membered Heterocycles with Methyl Methacrylate and Methacryl Amide, *Chemistry Letters*, 46, 1522-1524 (2017). (Editor’s Choice)

DOI: 10.1246/cl.170683

Present method

![Chemical reaction]

Conventional method

![Chemical reaction]

● Sayori Kiyota, Seonyoung In, Nobuyuki Komine, and Masafumi Hirano*
Regioselectivity Control by Added MeCN in Ru(0)-Catalyzed Cross-Dimerization of Internal Alkynes with Methyl Methacrylate, *Chemistry Letters, 46*, 1040-1043 (2017).

DOI: 10.1246/cl.170224


DOI: 10.1016/j.molcata.2016.08.027

![Reaction Scheme]


DOI: 10.1016/j.ccr.2015.07.008

DOI: 10.1021/acs.organomet.6b00668


DOI: 10.1016/j.poly.2016.04.006

DOI: 10.1021/acs.organomet.5b00987


DOI: 10.1016/j.jorganchem.2015.08.022
DOI: 10.1016/j.jorganchem.2015.04.048

Nobuyuki Komine,* Makoto Abe, Ryoko Suda, Masafumi Hirano, Markovnikov-Selective Hydrosilylation of Electron-Deficient Alkenes with Arylsilanes Catalyzed by Mono(phosphine)palladium(0), Organometallics, 34, 432-437 (2015).
DOI: 10.1021/om500927z
Yuki Hiroi, Nobuyuki Komine, Sanshiro Komiya, Masafumi Hirano,* Regio- and Enantioselective Linear Cross-Dimerization between Conjugated Dienes and Acrylates Catalyzed by New Ru(0) Complexes, *Organometallics*, 33, 6604-6613 (2014).

DOI: 10.1021/om500927z


DOI: 10.1039/C4NJ01001A
DOI: 10.1021/om500341v

DOI: 10.1021/om500248
Nobuyuki Komine, Ayako Kuramoto, Kouhei Nakanishi, Masafumi Hirano, Sanshiro Komiya,*

Alkene and Alkyne Insertion into Hydrogen-Transition Metal Bonds Catalyzed by Palladium(0) Complex, Topics in Catalysis, 57, 960-966 (2014).

DOI: 10.1007/s11244-014-0258-8
Cross-dimerization between Different cisoid- and transoid-1,3-Dienes at a Ruthenium(0) Center. New J. Chem. 37, 3433-3439 (2013).

DOI: 10.1039/c3nj00429e

Asymmetric Cross-dimerization between Methyl Methacrylate and Substituted Alkenes by Ru(0)-Bicyclononadiene Complex, Org. Lett. 15, 2486-2489 (2013).

DOI: 10.1021/ol400963d
DOI: 10.1016/j.jorganchem.2013.04.003

Stoichiometric Carbon-Hydrogen Bond Cleavage Reaction in a Bis(carboxylato)ruthenium(II)

DOI: 10.1002/cctc.201200686

Masafumi Hirano,* Takuya Okamoto, Nobuyuki Komine, and Sanshiro Komiya

Stoichiometric Carbon-Carbon Bond Forming Reaction of 1,3-Diene with 1,2-Diene in a Ruthenium(0) Complex, *Organometallics* 31, 4639-4642 (2012).

DOI: 10.1021/om300326q

Masafumi Hirano,* Yasutomo Arai, Yuka Hamamura, Nobuyuki Komine, and Sanshiro Komiya


DOI: 10.1021/om300234d
DOI: 10.1016/j.jorgchem.2012.02.018

DOI: 10.1021/om200974c

DOI: 10.1021/om200345h
These reactions. Cinnamyl carbonate (7) was less reactive in comparison with crotyl derivative, but exclusively gave the branched allylation product (13) (Entry 7). Unusual effect of interfacial area on branch/linear ratio of the products by changing stirring speed was not observed in these reactions [2b]. On the other hand, trisubstituted allyl carbonate such as prenyl carbonate (8) showed no reactivity in this allylation reaction (Entry 10). Such a trend was also observed for allylic acetates (Entry 11). These reactivity differences are probably due to the large steric hindrance of the trisubstituted allylic moiety, discouraging prerequisite coordination of the C=C double bond to rhodium leading to a common allylrhodium intermediate to which nucleophilic reaction of acetylacetone takes place. Importance of prior coordination of C=C double bond has been proposed [11]. The low reactivity of acetates compared to that of carbonate may be attributed to the difficulty in oxidative addition.

We also examined some other water-soluble phosphorus ligands for comparison and the results are also shown in Table 2. Use of DAPTA as ligands gave a similar selectivity and reactivity in H2O/AcOEt biphasic system. Unfortunately the combinations with other well-known water-soluble phosphine ligands such as TPPTS, TPPMS, and tris(hydroxylmethyl)phosphine showed very low catalytic activity.

The ratio of PTA to Rh was also important. When using 2 equivs of PTA per mole of Rh, the yield of allylation products significantly decreased in comparison with the result using 3 equivs of PTA (Table 1, entry 8). On the other hand, addition of 6 equivs of PTA/Rh completely inhibited the reaction, suggesting the prior dissociation of PTA (Table 1, entry 9). The results suggest that active intermediate needs PTA as a ligand, but excess PTA compete with prior coordination of allyl carbonate.

By analogy of previously reported branch-selective allylation, following mechanism is proposed for this catalytic allylation (Scheme 1) [2b]. An allylrhodium(III) species initially formed by oxidative addition of allylic carbonate or acetate to Rh(I), followed by nucleophilic reaction of acetylacetone to give the corresponding allylation product. Exclusive formation of the branched product from both 1-methylallyl and crotyl carbonates suggests the involvement of a common allylrhodium intermediate. It is unlikely to suppose h3-allylrhodium(III) intermediate, since less-hindered side is generally allylated by the steric reason, though electronic effect of substituents and ligand effect are also important factors [6d,12]. Initially formed h3-allylrhodium(III) probably rearranges to the h1-allylrhodium(III) by coordination of three trimethylphosphine ligands, where methyl substituents in the allylmetal intermediate would stay in the remote position from Rh metal center to...

DOI: 10.1021/om100956f


DOI: 10.1016/j.jorganchem.2010.09.020

**DOI**: 10.1021/om100822n

![Chemical structure](image1)

● Masafumi Hirano, Yuki Hiroi, Nobuyuki Komine, and Sanshiro Komiya, **Catalytic Tail-to-tail Selective Dimerization of Methyl Methacrylate Promoted by Ruthenium(0) Complex**, *Organometallics*, 29, 3690-3693 (2010).

**DOI**: 10.1021/om100646q

![Chemical reaction](image2)

● Masafumi Hirano, Sayaka Togashi, Muneaki Ito, Yuko Sakaguchi, Nobuyuki Komine, and Sanshiro Komiya, **Carbon-Hydrogen Bond Cleavage Reaction in 5-Coordinate Bis(2,6-dimethylbenzenethiolato)ruthenium(II) Complexes**, *Organometallics*, 29, 3146-3159 (2010).

**DOI**: 10.1021/om100249s

![Chemical structures](image3)
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Chemical Communications (Cambridge) (1999), (6), 489-490.
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