

# Synthetic Inorganic and Organometallic Chemistry of Transition Metals

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### Education

1995 B.S. Osaka University  
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### Professional Employment

1999 Assistant Professor, Osaka University  
2003 JSPS Fellow for Research Abroad, Massachusetts Institute of Technology  
2005 JST-PRESTO Researcher  
2007 Associate Professor, Osaka University  
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2012 Professor, Institute for Molecular Science  
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### Awards

2007 The Chemical Society of Japan (CSJ) Award for Young Chemists  
2007 The Japan Society of Coordination Chemistry (JSCC) Award for Young Chemists  
2008 The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, and Technology, Japan  
2010 Dalton Lectureship Award, Royal Society of Chemistry

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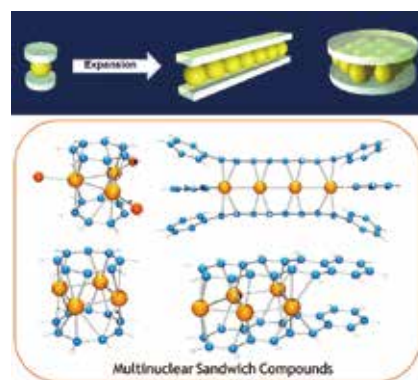
### Keywords

Coordination Chemistry, Organometallic Chemistry, Mechanism of Catalysis

Our research focuses mainly on two topics in inorganic and organometallic chemistry: i) Synthesis and structural elucidation of a new class of transition metal complexes; ii) elucidation of reaction patterns and mechanism of reactive transition metal complexes. Novel synthetic methods are developed to realize a new class of transition metal complexes. Some transition metal complexes are converted to more reactive forms, and their reaction mechanisms are elucidated. The research leads to development of fundamental concepts of transition metal chemistry.

The “sandwich” structure is one of the fundamental structural motifs for transition metal complexes. Most of sandwich complexes contain a mononuclear metal moiety between parallel cyclic unsaturated hydrocarbon ligands. On the other hand, it had been difficult to synthesize a stable sandwich complex in which a metal assembly is sandwiched between two cyclic unsaturated hydrocarbons. Recently, our group discovered that multinuclear sandwich complexes exist as the stable and isolable molecules (Figure 1). These findings expand the structural concept of sandwich compounds from

zero-dimension to one- and two dimensions, and provide a new opportunity to develop a novel class of organo-metal cluster compounds. Multinuclear sandwich complexes showed unique chemical properties stemming from their ( $\pi$ -conjugated unsaturated hydrocarbon)-(multinuclear metal) hybrid structures.



**Figure 1.** The concept of dimensionally extended sandwich structures and some examples of the multinuclear sandwich complexes.

### Selected Publications

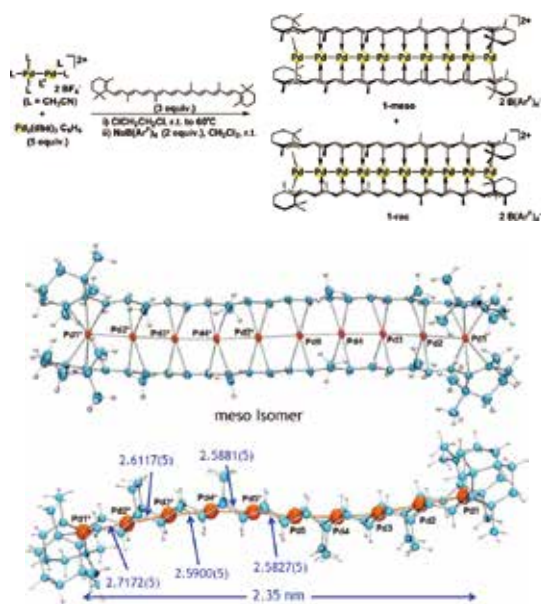
- T. Murahashi, T. Uemura and H. Kurosawa, “Perylene Tetrapalladium Sandwich Complexes,” *J. Am. Chem. Soc.* **125**, 8436–8437 (2003).
- T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki and H. Kurosawa “Discrete Sandwich Compounds of Monolayer Palladium Sheets,” *Science* **313**, 1104–1107 (2006).
- T. Murahashi, R. Inoue, K. Usui and S. Ogoshi, “Square Tetrapalladium Sheet Sandwich Complexes: Cyclononatetraenyl as a Versatile Face-Capping Ligand,” *J. Am. Chem. Soc.* **131**, 9888–9889 (2009).
- T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi and H. Kurosawa, “Redox-Induced Reversible Metal Assembly through Translocation and Reversible Ligand Coupling in Tetranuclear Metal Sandwich Frameworks,” *Nat. Chem.* **4**, 52–58 (2012).

## 1. Chemistry of Multinuclear Sandwich Complexes

### Synthesis and Structural Elucidation of the Carotene Metal Chain Sandwich Complexes: $[\text{Pd}_{10}(\beta\text{-carotene})_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$ (**1**)

Carotenoids are naturally abundant pigments containing extended  $\pi$ -conjugated C=C double bond arrays. While the fascinating physical and chemical properties of carotenoids have been explored, their metal binding ability has been undeveloped. We found the remarkable multinuclear metal binding ability of  $\beta$ -carotene, through synthesis and characterization of bis-( $\beta$ -carotene) decanuclear metal chain complexes.

It has been proven that bis- $\beta$ -carotene  $\pi$ -framework can accommodate ten-Pd-atoms-array through remarkable multi-dentate bridging  $\pi$ -coordination. The decanuclear palladium complex  $[\text{Pd}_{10}(\mu_{10}\text{-}\beta\text{-carotene})_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$  (**1**,  $\text{B}(\text{Ar}^{\text{F}})_4 = \text{B}(\text{3,5-(CF}_3)_2\text{C}_6\text{H}_3)_4$ ) was synthesized by the redox-condensation reaction of  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$  and excess  $\text{Pd}_2(\text{dba})_3 \cdot \text{C}_6\text{H}_6$  in the presence of  $\beta$ -carotene at 60 °C (Figure 2). The molecular structures of the two isomers **1-meso** and **1-rac** were determined by X-ray crystallographic analysis (Figure 2). The decanuclear complexes **1-meso** and **1-rac** are the soluble and isolable organometallic clusters having a long metal chain.

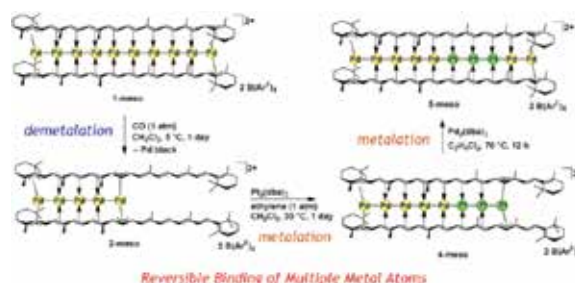


**Figure 2.** Synthesis of bis-carotene  $\text{Pd}_{10}$  chain complexes, and X-ray structure of the meso-isomer.

The metallo-carotene framework showed interesting multinuclear metalation-demetalation reactivity, allowing us to construct heterobimetallic decanuclear chain. The metal-deficient sandwich complex,  $[\text{Pd}_5(\beta\text{-carotene})_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$  (**2-meso**) or  $[\text{Pd}_7(\beta\text{-carotene})_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$  (**3-meso**), was obtained as a single product by demetalation from **1-meso** with CO in certain reaction conditions. Then metal-refilling with  $\text{Pt}^0$  afforded the bimetallic  $\text{Pd}_5\text{Pt}_3$  chain complex  $[\text{Pd}_5\text{Pt}_3(\beta\text{-carotene})_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$  (**4-meso**). Subsequent metalation of **4-meso** with  $\text{Pd}^0$  gave decanuclear bimetallic chain complex

$[\text{Pd}_5\text{Pt}_3\text{Pd}_2(\beta\text{-carotene})_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$  (**5-meso**) having alternative metal arrangement (Figure 3).

This work showed that natural extended  $\pi$ -conjugated unsaturated hydrocarbons can be utilized as the multi-dentate  $\pi$ -scaffolds for the construction of giant metal clusters.

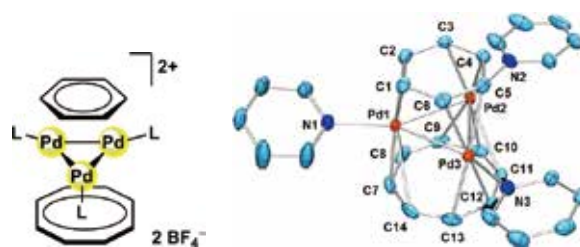


**Figure 3.** Demetalation-metalation sequence of metallo-carotene framework.

## 2. Reaction Mechanism of Highly Reactive Metal Complexes

### Modulation of Cluster Binding Sites by the Backside-Ligand Effect<sup>2)</sup>

One of our main interests is in the elucidation of the reaction patterns and mechanisms of highly reactive transition metal complexes in relevance to catalysis. We developed a method to modulate the trinuclear cluster binding site by the backside-ligand effect. We found that the backside cyclo-octatetraene (COT) ligand of the  $\text{Pd}_3$  clusters significantly enhances the benzene binding ability at the  $\text{Pd}_3$  cluster site, leading to the first  $\mu_3$ -benzene- $\text{Pd}_3$  clusters which are stable in solution (Figure 4). Theoretical analysis supported the electronic stabilization effect of the backside COT ligand. The naphthalene binding by  $\text{Pd}_4$  clusters was also attained by using a  $\text{Pd}_4$  sheet bearing the backside COT ligand. These new aspects might represent a promising backside-ligand-modulation strategy to control the reactivity of metal clusters.



**Figure 4.** The first solution-stable  $\mu_3$ -benzene  $\text{Pd}_3$  cluster and its X-ray structure.

## References

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