

Synthetic Inorganic and Organometallic Chemistry of Transition Metals

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Education

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Professional Employment

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2003 JSPS Fellow for Research Abroad, Massachusetts Institute of Technology
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2007 Associate Professor, Osaka University
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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
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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 are 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 new class of organo-metal cluster compounds. Multinuclear sandwich complexes showed unique chemical properties stemming from their (π -conjugated unsaturated hydrocarbon)-(multinuclear metal) hybrid structures.

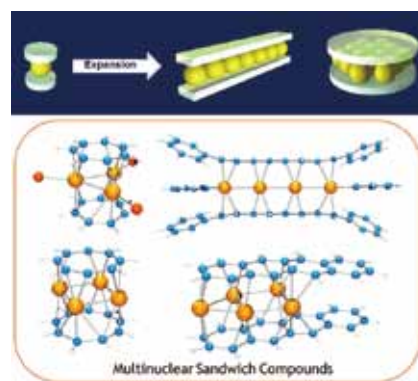


Figure 1. The concept of dimensionally extended sandwich structures and some examples of the multinuclear sandwich complexes.

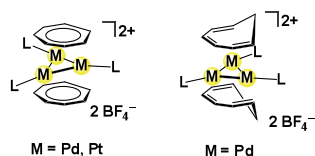
Selected Publications

- 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 Bis-Cyclooctatetraene Trimetal Sandwich Complexes

Our group has made research efforts to establish the generality of the metal sheet sandwich compounds. We have shown that several unsaturated hydrocarbon ligands such as [2.2]paracyclophane, cycloheptatriene, cycloheptatrienyl, and some polycyclic arenes behave as the excellent binders for triangular trimetal sheets.^{2–6} Particularly, it has been shown that seven-membered unsaturated hydrocarbons, *i.e.*, tropylium and cycloheptatriene, serve as an excellent facial μ_3 -binder for the triangular M_3L_3 core ($M = Pd, Pt$) (Scheme 1). However, it has not been verified whether larger π -conjugated carbocycles are able to form a simple triangular trimetal sandwich complex.

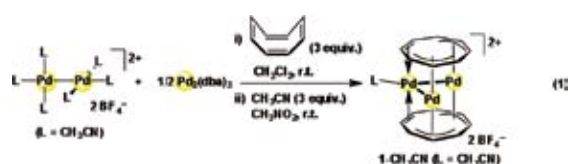


Scheme 1. The tropylium- and cycloheptatriene sandwich complexes.

1,3,5,7-Cyclooctatetraene (COT) is a potentially useful eight-membered carbocyclic ligand for metal sheet sandwich complexes, in view of its greater number of C=C bonds and a flexible electron-donating/back-donating nature. A recent finding by Grubbs *et al.* represents the versatility of the COT ligand, *i.e.*, a homoleptic trimetal tris-COT complex, $Fe_3(\mu-COT)_3$, was isolated through a catalytic method.⁷ Here, we successfully synthesized the first discrete bis-COT trimetal sandwich complexes.⁸

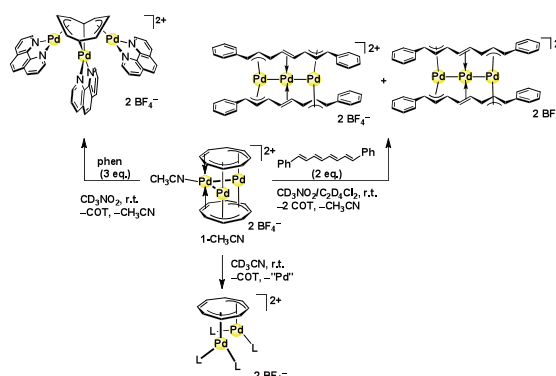
The bis-cyclooctatetraene Pd_3 sandwich complex $[Pd_3(\mu_3-C_8H_8)_2][BF_4]_2$ (**1-CH₃CN**) was obtained by the reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ and $Pd_2(dba)_3$ in the presence of cyclooctatetraene (COT), followed by treatment with CH_3CN (eq. 1). Recrystallization in an aerobic condition gave a single crystal of **1-H₂O**. The structure of **1-H₂O** was determined by X-ray diffraction analysis. The cyclooctatetraene ligands coordinate to an isosceles Pd_3 triangle ($Pd1-Pd2 = 2.7321(8)$ Å; $Pd2-Pd3 = 2.7359(8)$ Å; $Pd1 \cdots Pd3 = 3.0604(8)$ Å) through a $\mu_3-\eta^3:\eta^2:\eta^3$ mode. The sandwich structure seems to be related with that of a diphenyloctatetraene Pd_3 chain sandwich complex $[Pd_3\{Ph(CH=CH)_4Ph\}_2]^{2+}$ which exhibits the same $\mu_3-\eta^3:\eta^2:\eta^3$ coordination mode.⁹

A deep purple PPh_3 complex $[Pd_3(\mu_3-COT)_2(PPh_3)][BF_4]_2$ (**1-PPh₃**) or a PCy_3 complex $[Pd_3(\mu_3-COT)_2(PCy_3)][BF_4]_2$



(**1-PCy₃**) was obtained by treatment of **1-CH₃CN** with PPh_3 or PCy_3 (1 equiv.). In solution, **1-CH₃CN** and **1-PPh₃** showed a sharp singlet NMR signal for C_8H_8 protons or carbons at 25 °C. Lowering the temperature down to -90 °C of the related compound resulted in significant broadening of the resonance for the C_8H_8 protons, suggesting the dynamic fluxional rotation of the cyclooctatetraene ligands on the Pd_3 core.

The reactivity of **1-CH₃CN** with several coordinating substrates were investigated, and the results were summarized in Scheme 2, showing the substitutionally labile nature of the μ_3 -COT ligands in the bis-COT Pd_3 sandwich complex.



Scheme 2. Facile dissociation of the COT ligand in $[Pd_3(\mu_3-C_8H_8)_2(CH_3CN)][BF_4]_2$ (**1-CH₃CN**).

2. Reaction Mechanism of Highly Reactive Metal Complexes

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. Synthetic and structural chemistry of the arenes and hetero-arenes transition metal complexes are now ongoing in our laboratory, and several new aspects have been gained recently.^{10,11}

References

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- 11) T. Murahashi *et al.*, *Chem. Commun.* **49**, 4310–4312 (2013).

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