

Synthetic Inorganic and Organometallic Chemistry of Transition Metals

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Our research focuses on synthesis and structural elucidation of a new class of transition metal complexes. This research leads to development of fundamental concepts of transition metal chemistry as well as applications to catalysis and materials science. Novel synthetic methods are developed to realize transition metal complexes having unique bonding nature. The newly synthesized transition metal complexes are further converted to more reactive forms, and their reaction mechanisms are elucidated. The aspects gained by this research are applied to the understanding and development of molecular catalysis. Furthermore, unique properties of low-dimensional metal-organic hybrid molecules are investigated and developed in our group.

1. Synthesis and Chemical Properties of Metal Chain Sandwich Complexes

The molecular sandwich framework is one of the fundamental structures in transition metal chemistry. It had been believed that the structural concept can be applied only to mono- and dinuclear complexes. Our group revealed that the multinuclear sandwich complexes containing a one-dimensional metal chain or a two-dimensional metal sheet exist stably.^{1,2)} These findings expand the scope of the structural concept of sandwich compounds (Figure 1).

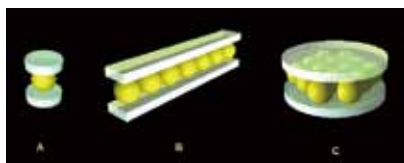


Figure 1. Schematic representation of sandwich compounds: (A) mononuclear metallocenes, (B) one-dimensional metal chain sandwich complexes, (C) two-dimensional metal sheet sandwich complexes. Our group revealed the existence of categories B and C.

For the one-dimensional metal chain sandwich complexes, we successfully developed a synthetic method that enables the size-selective construction of a metal chain sandwich frame-

work. Furthermore, our laboratory revealed that metal chain sandwich complexes show unique chemical properties such as i) dynamic sliding behavior of polyene ligands on a metal chain and ii) photo-induced flipping of polyene ligands on a metal chain.

Redox-Switchable Metal Assembling and Ligand Coupling in Sandwich Frameworks³⁾

In view of the widely developed redox chemistry of metallocenes and other mononuclear sandwich compounds, it is intriguing to elucidate the redox properties of the multinuclear sandwich compounds. Here we disclosed two novel modes of redox-induced reversible structural changes: i) redox-switchable reversible splitting of a Pd₄ chain via translocation, and ii) redox-switchable reversible C–C coupling of π -conjugated ligands in tetrapalladium sandwich complexes (Figure 2). These results provide new aspects for the redox function of (sp²-carbon)–(multinuclear metal)–(sp²-carbon) sandwich frameworks.

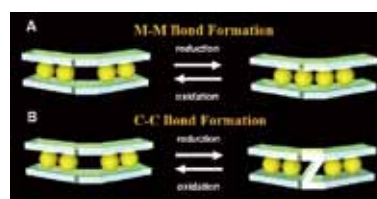
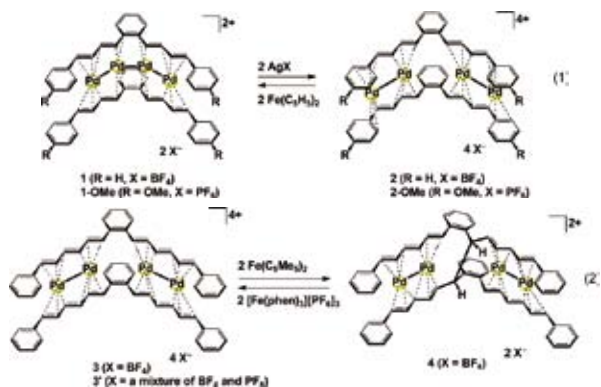


Figure 2. Schematic representations of (A) the reversible assembling of dimetal moieties and (B) the reversible coupling of ligands.

Oxidation of **1** or **1-OMe** with AgBF₄ or AgPF₆ (2 equiv.) resulted in the formation of **2** or **2-OMe** (bpbb = 1,2-bis(4-phenyl-1,3-butadienyl)benzene). Reduction of **2** or **2-OMe** with Fe(C₅H₅)₂ (2 equiv.) yielded **1** or **1-OMe** (eq. 1). During the two-electron oxidation, the Pd–Pd–Pd–Pd chain is cleaved, and the two Pd₂ units undergo translocation to the outer position during the oxidation process. In the reduction process, the two separate Pd₂ units migrate to the inside position to form the Pd–Pd–Pd–Pd chain. The observed redox behavior is highlighted by the coupling of two events, metal–metal bond formation/cleavage and metal translocation, under the redox control, and provides evidence of redox-switchable movement of multiple metal atoms associated with assembling/disas-

sembling behavior in the space between sp^2 -carbon planes.

We also found another mode of the redox-induced structural change featured by the intramolecular reversible C–C bond formation between the two sandwich ligands, by employing **3** (eq. 2).

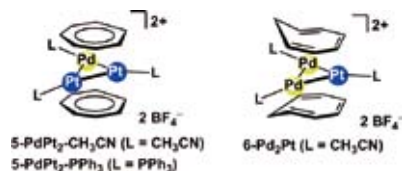


2. Synthesis and Reactivity of Metal Sheet Sandwich Complexes

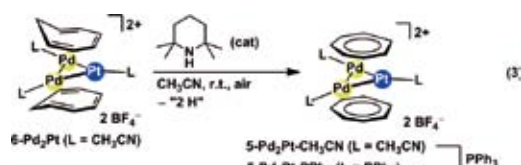
For the two-dimensional metal sheet sandwich complexes, our group has shown that six-, seven-, eight-, and nine-membered carbocycles, as well as polycyclic arenes behave as the excellent binders for metal sheets. These metal sheet sandwich complexes are stable even in solution. Thus, a reactive form of such metal sheet sandwich complexes may provide a new opportunity to develop sandwich type late transition metal catalysts.

Selective Synthesis of Mixed Metal Pd_2Pt and $PdPt_2$ Complexes of Tropylium⁴

Our group has reported a series of homonuclear metal sheet sandwich complexes, which have a metal sheet of a single metal element. Here, we reported selective construction of the triangular $PdPt_2$ and Pd_2Pt cores in a common sandwich framework, where a key is to use different carbocyclic ligands for the different composite sandwich; *i.e.*, cycloheptatrienyl for $PdPt_2$, and cycloheptatriene for Pd_2Pt (complexes **5- $PdPt_2$** and **6- Pd_2Pt**).



After construction of the Pd_2Pt core, the cycloheptatriene ligands can be converted to cycloheptatrienyl ligands where a (carbocyclic ligand)–(metal triangle)–(carbocyclic ligand) sandwich structure is retained (eq. 3). It was confirmed that the



mixed metal core once formed in a cycloheptatrienyl sandwich framework is robust against the intermolecular metal scrambling.

Thus, it has been proven that the mixed-metal triangular trimetal sandwich complexes are synthesizable in a selective manner. The present results expand the scope of the structural variability of multinuclear sandwich complexes from homonuclear to heteronuclear series.

3. Reaction Mechanism of Highly Reactive Pd–Pd Complexes

Our group has shown that a homoleptic dinuclear Pd–Pd complexes of nitriles such as $[Pd_2(CH_3CN)_6][BF_4]_2$ are isolable.⁵ These homoleptic solvento- Pd_2 complexes are highly substitutionally labile, and allow us to investigate reaction mechanism of the Pd–Pd complexes in details. For example, our group has shown that a Pd–Pd moiety adds to various unsaturated hydrocarbons in a syn addition manner.

Dinuclear Addition of a Pd–Pd Moiety to Arenes⁶

We found that a Pd–Pd moiety undergoes addition reaction to arenes to afford the bi- π -allyl type dipalladium complexes. Previously simple μ - η^2 : η^2 -(arene)- Pd_2 complexes have been isolated, but now we found that a Pd–Pd moiety undergoes dinuclear addition to several arenes to afford a novel binding mode of arene- Pd_2 , namely μ - η^3 : η^3 -(arene)- Pd_2^H (Figure 3), through isolation and characterization of **8'**, **9**, and **10**. The fact that bi- η^3 -allyl type structure is accessible via dinuclear syn-addition of a Pd–Pd moiety suggest possible involvement of a new activation mode of arenes by a Pd–Pd species in some palladium-catalyzed transformations.

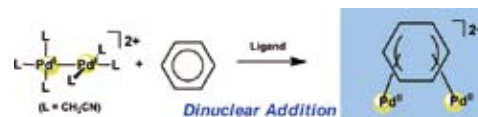
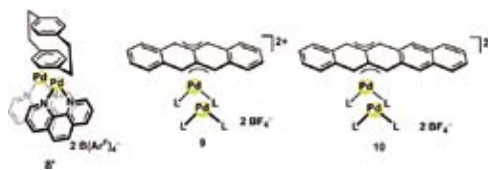


Figure 3. Dinuclear addition of a Pd–Pd moiety to arenes.



References

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