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. Chemistry of Multinuclear 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).

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.

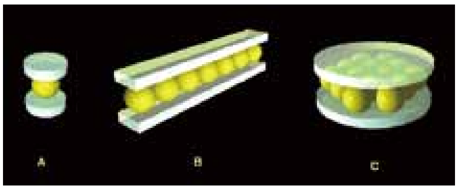
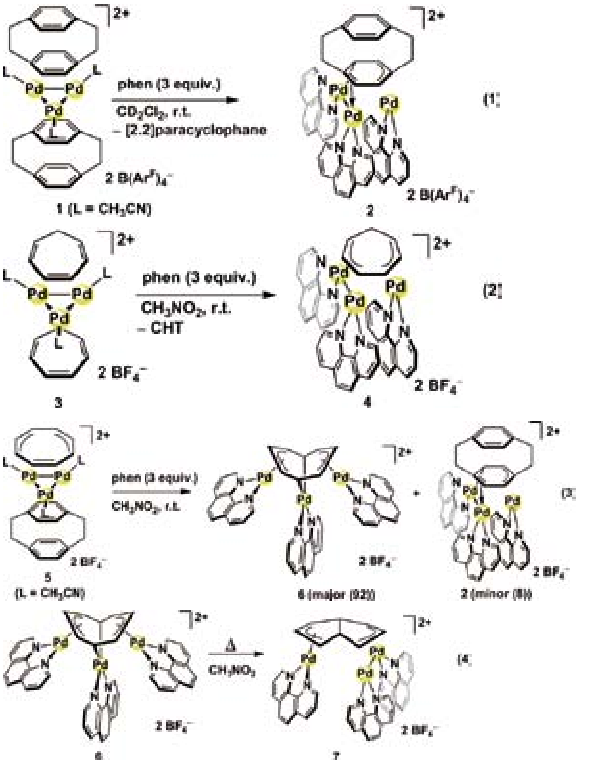


Figure 1. Schematic representation of sandwich compounds: (**A**) mononuclear metallocenes, (**B**) one-dimensional metal chain sandwich complexes, (**C**) two-dimensional metal sheet sandwich complexes. Our group revealed the existence of categories **B** and **C**.

Conversion of Trinuclear Sandwich Complexes to Trinuclear Half-Sandwich Complexes[5)]

Our group recently showed that triangular trimetal sandwich complexes are isolable. It is now known that a variety of cyclic unsaturated hydrocarbons such as arene, cycloheptatrienyl, cycloheptatriene, and cyclooctatetraene work as excellent μ_3-face-capping binder for a Pd_3 moiety.[2–4)] We found that the tripalladium sandwich complexes of [2.2]paracyclophane, cycloheptatriene, and cyclooctatetraene can be converted to trinuclear half-sandwich complexes upon treatment with 1,10-phenanthroline (phen). During the reaction, one of the facially-capping ligands is replaced with three phen ligands. Interestingly, the Pd_3 moiety underwent trinuclear addition to the remaining carbocyclic ligand to form unusual coordination modes. For the [2.2]paracyclophane ligand, a $Pd^0 \rightarrow Pd^{II}$ dative bonded moiety and a Pd^{II} moiety coordinated to an arene ring synfacially in a η^3:η^3 manner (eq. 1). The cycloheptatriene ligand was added by a Pd_3 moiety, where a Pd^I–Pd^I moiety and a Pd^{II} moiety is bound synfacially to the triene face (eq. 2). On the other hand, the Pd_3 moiety added to a cyclooctatetraene to form a cyclooctatetraenetetrayl tripalladium complex, where formally tetraanionic cyclooctatetraene ligand coordinates to three Pd^{II} centers through a μ_3:η^1:η^3:η^1:η^3 coordination mode (eq. 3). The tripalladium addition product of cyclooctatetraene further converted to a dihydropentalenediyl complex via intramolecular reductive C–C coupling (eq. 4).

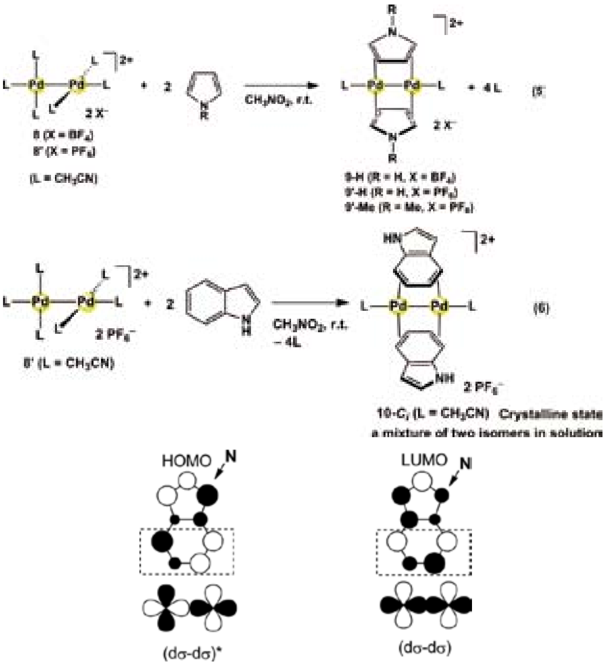


2. Reaction Mechanism of Highly Reactive Pd–Pd Complexes

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.[6)] 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 including arenes in a syn addition manner.[7)]

π-Coordination Pyrrole and Indole on a Pd–Pd Bond[8)]

We found that pyrrole and indole form stable π-complexes. Thus, the reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ with pyrrole or indole gave the dinuclear sandwich complexes (eqs 5 and 6). These results provided the first evidence of the π-coordination of azoles having no chelating functionality to a Pd center. Particularly interesting is the coordination mode of indole which used its six-membered ring in the μ-η^2:η^2-coordination. Usually, the carbons at 2- and 3-positions are reactive sites in indole transformations. The bridging coordination mode of indole using six-membered ring carbons at 4-, 5-, 6-, and 7-positions is understood by a qualitative MO consideration: The π-orbital array at 4-, 5-, 6-, and 7-positions is isolobal with that of the 1,3-butadiene, which becomes an excellent bridging ligand on a Pd–Pd bond due to the efficient orbital overlap of diene-type HOMO or LUMO with (dσ–dσ)* or (dσ–dσ).



Scheme 1. Schematic representation of the HOMO and the LUMO of indole, and (dσ–dσ)* and (dσ–dσ) of a Pd−Pd moiety.

References

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