

## 論文内容の要旨

論文題目 Extension of Metalladithiolene Multinuclear Systems  
with  $\pi$ -Conjugation and Intermetallic Interaction

( $\pi$ 共役と金属間相互作用によるメタラジチオレン多核系の拡張)

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### Introduction

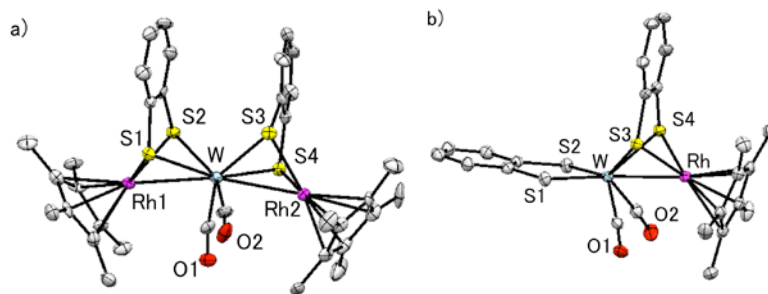
Transition metal cluster complexes can be regarded as intermediate materials between nanoparticles and mononuclear metal complexes. They exhibit interesting properties attributable to the delocalization of electrons on metal atoms, and thereby they are possible to undergo multistep electron transfer. Because of these features, transition metal cluster complexes have formed an important research field relating to biological systems and catalytic chemistry. However, to synthesize metal cluster complexes at will by condensation or self-assembly of metals and ligands has been still difficult; hence more strategic methods are highly desired. The aim of my research in the Ph.D. course is to develop a new strategy to design and synthesize metal cluster complexes, in which the kind, number and location of metals are precisely controlled, based on integration of metal atoms two- and three-dimensionally starting from a metalladithiolene complex as a building block. I developed three types of new metalladithiolene cluster complexes; (1) cluster complexes including metal-metal bonds, (2)  $\pi$ -conjugated triangular trinuclear complexes, (3) a nonanuclear cluster complex formed by integration of metal atoms on a  $\pi$ -conjugated triangular trinuclear complex.

### Dithiolato-bridged Rh-W-Rh and Rh-W Cluster Complexes

Metal-metal bond formation reactions of metalladithiolenes have been found and developed in our laboratory. So far, mixed-metal dithiolato-bridged trinuclear cluster complexes with Co-Mo, Co-W, and Rh-Mo bonds have been synthesized. The present study aimed at the synthesis of new

cluster complexes with Rh-W bonds.

Trinuclear complex **1** was synthesized by a reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhS}_2\text{C}_6\text{H}_4]$  with  $\text{W}(\text{CO})_3(\text{py})_3$  in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  in toluene. Surprisingly, mixed-metal dinuclear complex **2** was also obtained as a by-product. The



**Figure 1.** ORTEP drawing of **1** (a) and **2** (b).

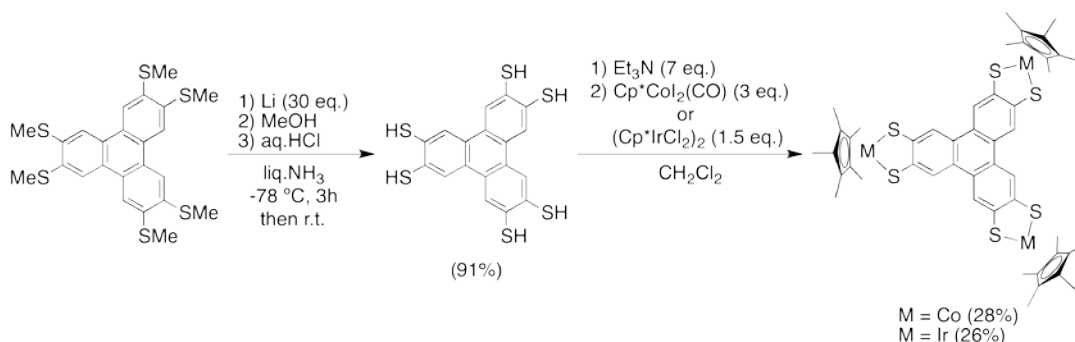
structural feature of **1** is similar to that of a previously reported Rh-Mo-Rh complex,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{S}_2\text{C}_6\text{H}_4)]_2\text{Mo}(\text{CO})_2$  (Figure 1). On the other hand, **2** have a unique structure. The  $\text{Rh}_2\text{S}_2\text{C}_2$  ring loses planarity due to the formation of bridging structure between Rh and W. On the other hand, the  $\text{WS}_2\text{C}_2$  ring is planar, indicative of the retainment of the quasi-aromaticity:  $^1\text{H-NMR}$  spectrum in dichloromethane- $d_2$  also confirmed its quasi-aromaticity.

To gain insight into the formation mechanism of **2**, a conversion from **1** to **2** was pursued by  $^1\text{H-NMR}$ . **1** is stable even under refluxing benzene- $d_6$  without additives or against addition of Lewis base such as 2,2'-bipyridine, 1,2-bis(diphenylphosphino)ethane, or 1,5-cyclooctadiene. However, **1** reacts with an excess amount of  $\text{BF}_3 \cdot \text{OEt}_2$  to give rise to **2**, indicating that Lewis acid assist the demetallation reaction.

## $\pi$ -Conjugated Cyclic Trinuclear Dithiolato Complexes of Group 9 Metals Using Triphenylenehexathiol

Triangular trinuclear complexes of transition metals exhibit interesting properties such as spin frustration and mixed-valent (MV) stabilization derived from intramolecular metal-metal interaction. We previously reported the synthesis and properties of  $\pi$ -conjugated cyclic trinuclear dithiolene complexes  $[(\text{C}_6\text{S}_6)(\text{M}(\eta^5\text{-C}_5\text{Me}_5))_3]$  ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ ) with benzenehexathiol as a triangular scaffold,

### **Scheme 1.** Synthesis of triphenylenehexathiol complexes

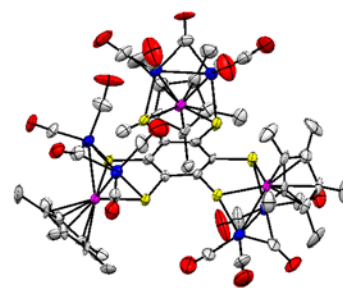
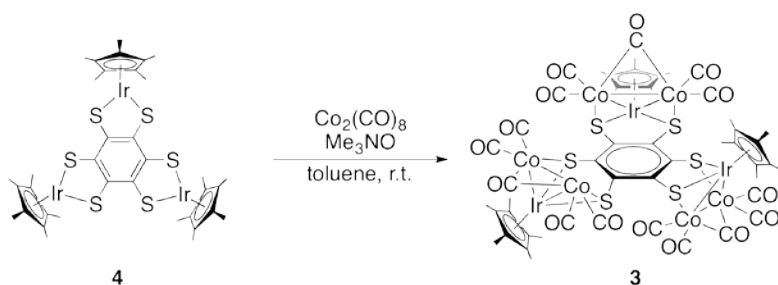


and demonstrated MV interaction and cation-induced spin state manipulation. In the present study, I examined an extension of the central arene unit from benzene to triphenylene,  $[(C_6(C_4H_2S_2M(\eta^5-C_5Me_5)))_3]$  ( $M = Co, Rh, Ir$ ) (Scheme 1).

The synthetic procedure is shown in Scheme 1. The Co and Ir complexes were successfully isolated and identified with  $^1H$  NMR, MALDI-TOF-MS and elemental analysis. On the other hand, the Rh complex has been hard to isolate. This is presumably attributed to the fact that Rh dithiolene complexes are easy to dimerize. Metal-metal interaction of triphenylenehexathiols complexes was evaluated by means of electrochemical measurements. This interaction was weak compared to the phenylene complexes due to the longer distances among the metal centers.

### Nonanuclear $Ir_3Co_6$ Dithiolene Cluster Complex

**Scheme 2.** Synthesis of **3**

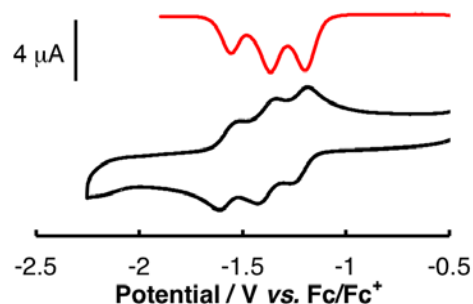


**Figure 2.** ORTEP drawing of **3**.

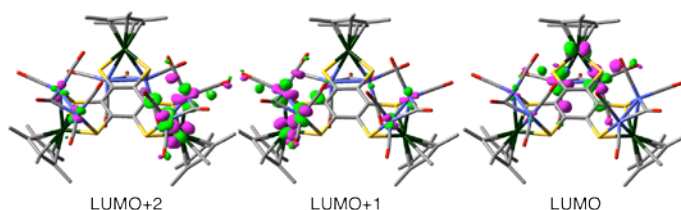
Exploiting the two strategies described in the above sections, fabrication of metalladithiolene cluster complexes with metal-metal bond formations and cyclic triangular trinuclear metalladithiolenes, here I intended to synthesize gigantic nonanuclear dithiolene cluster complex. **3** was prepared by a reaction of  $[(C_6S_6)(Ir(\eta^5-C_5Me_5))]_3$  **4** with  $Co_2(CO)_8$  in the presence of  $Me_3NO$  in toluene at room temperature, and obtained as brown crystals (Scheme 2). The crystal structure of **3** is shown in Figure 2. **3** has two potential structural isomers with  $(syn, syn, syn)$  and  $(syn, syn, anti)$  configurations, where the three  $[Co_2]$  units ( $[Co_2] = Co_2(CO)_5$ ) all trend in the same direction, and one of them faces away from the rests, respectively. **3** exclusively showed the  $(syn, syn, anti)$  structure. The absence of the  $(syn, syn, syn)$  isomer might be attributed to steric hindrance among the bulky  $[Co_2]$  units. The plane comprising the three iridadithiolene rings and the central phenylene bridge was slightly bent to form a bowl-like framework, but the extent of the bending was insignificant (the average S-C-C-S torsion angle was  $5.72^\circ$ ). The shorter C-C bonds of the central phenylene belonged to the metalladithiolene five-membered rings, whereas the longer ones linked the rings together. The maximum difference among the C-C bond lengths was less than  $0.06 \text{ \AA}$ . This difference was smaller than that of **4** ( $0.12 \text{ \AA}$ ), indicating that the central phenylene of **3** was more

strongly aromatic than that of **4**. In total,  $\pi$ -conjugation in **3**, which spanned the three iridadithiolene rings and the phenylene bridge, was expected to remain, even upon attachment of the [Co<sub>2</sub>] units.

Figure 3 shows differential pulse voltammogram and cyclic voltammogram of **3**. **3** underwent three reversible one-electron reductions. Judging from the DFT calculation, these redox waves could be assigned to electron donation to the three [Co<sub>2</sub>] units (Figure 4). Here three reductions occurred stepwisely, which was assigned to electronic communication in the MV state. **3** exhibits strong



**Figure 3.** A differential pulse voltammogram (above) and a cyclic voltammogram (bottom) of **3** in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>-PhCN.



**Figure 4.** Frontier orbitals of **3** estimated by DFT calculations (B3LYP/Lanl2DZ for Ir, 6-31g(d,p) for other atoms).

electronic communication than that of **4**, indicating that multiple metal-metal bond formation manages strong internuclear electronic communication in the reduced MV states among the three [Co<sub>2</sub>] units.

## Conclusions

I achieved extension of metalladithiolene systems; a novel metal-metal bond formation reaction, two-dimensionally metal integrated triphenylene complexes, and a nonanuclear cluster complex by means of integration of metals on dithiolene complex. In cluster complex **3**, owing to this planar configuration and resultant  $\pi$ -conjugated electronic structure, the three [Co<sub>2</sub>] units show strong electronic communication in the reduced mixed-valent states. Novel tri- and dinuclear cluster and triphenylene complexes are useful components for the integration method. Therefore, these study results have a huge potential for growth of cluster complex chemistry.