



## Laboratory for Molecular Design: Inorganic Material Science of Coordination Compounds and Clusters

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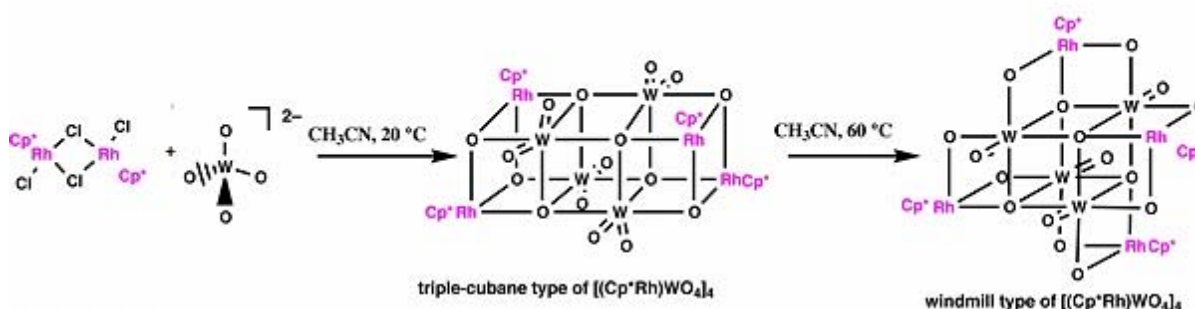
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#### 1. Current Research and Principal Research Interests

My research interest is in the area of synthetic chemistry of functional organometallic and coordination compounds. Research projects currently in progress involve the synthetic study of organometallic oxide clusters and photosensitive crystalline-state complexes and development of artificial sulfur cycle on M-M bonds.

*Organometallic oxide clusters* which have cubic, incomplete cubic and valley site frameworks are useful as homogeneous and heterogeneous catalysts in the oxidation and metathesis of unsaturated hydrocarbons. We have synthesized several organometallic oxide clusters with the latter frameworks, for example the triple cubic  $[(Cp^*Rh)_4Mo_4O_{16}]$  ( $Cp^* = \eta^5-C_5Me_5$ ), the incomplete double cubic  $[(Cp^*Rh)_2Mo_3O_9(OMe)_4]$ , the double bookshelf  $[(Cp^*Rh)_2Mo_6O_{20}(OMe)_2]^{2-}$  type oxide clusters and so on. These clusters are formed by the condensation of oxometalate anions on the Lewis acidic  $Cp^*Rh$  moiety, which is able to provide three coordination sites for the condensation.

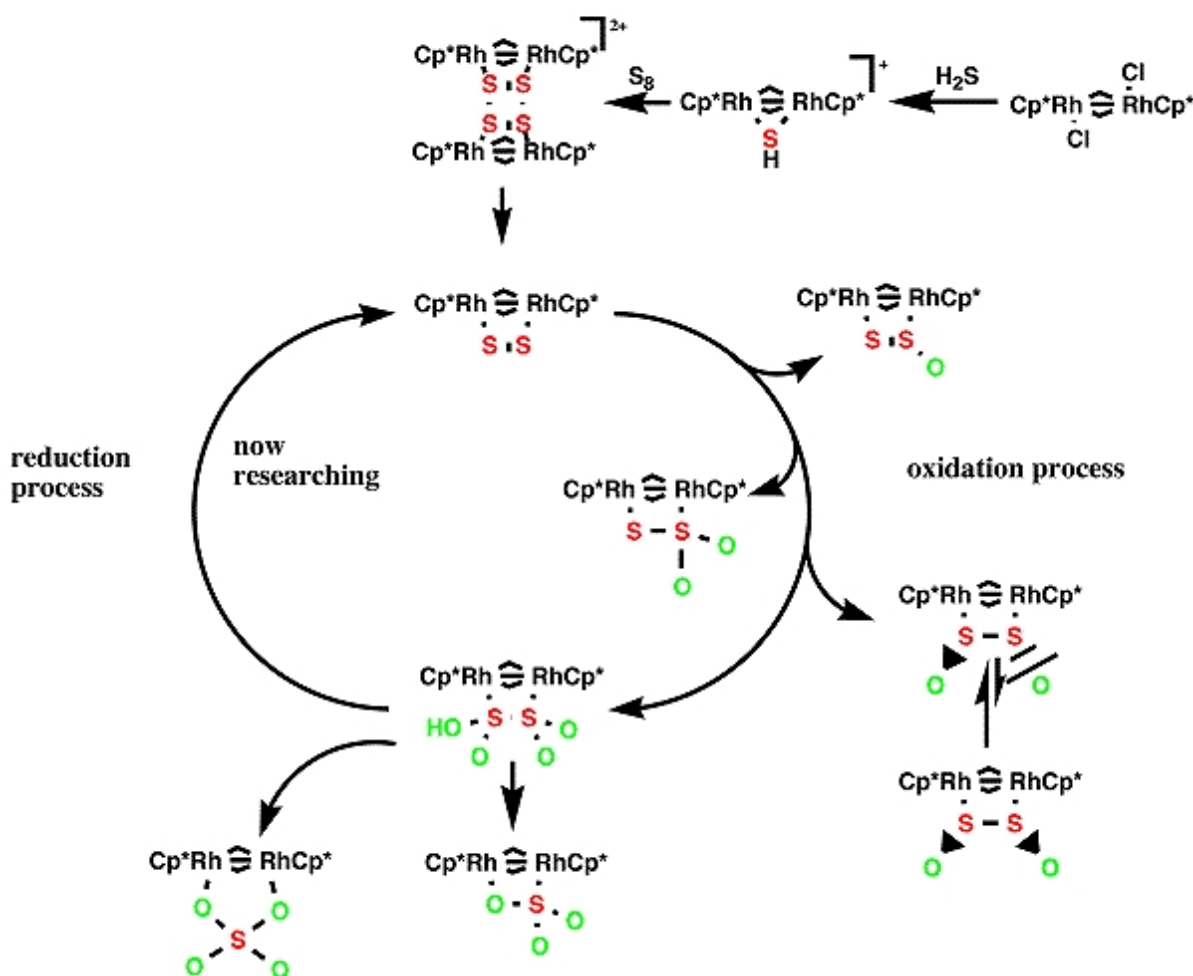
##### Design of Oxide Clusters



*Artificial sulfur cycle on M-M bonds.* Oxidation is an important part of most sulfur cycles and sulfur chemistry in general. In the oceanic thermal vents, it was reported that  $H_2S$  is released and then oxidized to  $SO_4^{2-}$ , which then settles back to the vent to be reduced back to  $H_2S$ . Also, some bacteria perform a stepwise conversion of organic disulfides into  $RSO_3H$ . Herein, we will report a strictly inorganic oxidation of an  $\mu-S_2$  rhodium complex  $[\{Cp^*Rh(\mu-CH_2)\}_2(\mu-S_2)]$  which is derived from several steps starting at the reaction of  $trans-[\{Cp^*Rh(\mu-CH_2)\}_2Cl_2]$  with  $H_2S$ . From the oxidation reaction, the mono- $[\mu-SS(O)]$ , bis- $[\mu-SS(O)_2]$  and  $\mu-S(O)S(O)$  and tetra- $[\mu-S(O)_2S(O)_2]$  oxygenated species have been isolated and characterized. Preliminary  $^1H$  NMR data suggests that the oxidation process, like the oxidation of organic disulfides, may

happen in a stepwise fashion. Tetra- $[\mu\text{-S}(\text{O})_2\text{S}(\text{O})_2]$  oxygenated species is oxidized further with  $\text{O}_2$  to give  $\text{SO}_3$  and  $\text{SO}_4$  complexes under irradiation of light. Mechanistic details of the oxidation reaction as well as attempts to reduce the oxide complexes are under progress.

### Sulfur Cycle on Rh-Rh Bond



## 2. Selected Publications

1. "Structure and Reactivity of a Novel Parallel Thiosulfite ( $\text{SSO}_2\text{-S,S'}$ ) Rhodium Dinuclear Complex", K. Shiomi, B. K. Breedlove, H. Kitayama, T. Nishioka, I. Kinoshita, N. Koga and K. Isobe, *Chem. Commun.*, **2002**, 1756-1757.
2. "Direct Observation by Electrospray Ionization Mass Spectrometry of  $[\text{Cp}^*\text{RhMo}_3\text{-O}_8(\text{OMe})_5]^-$ , a Key Intermediate in the Formation of the Double-Bookshelf-Type Oxide Cluster  $[(\text{Cp}^*\text{Rh})_2\text{Mo}_6\text{O}_{20}(\text{OMe})_2]^{2-}$ ", S. Takara, S. Ogo, Y. Watanabe, K. Nishikawa, I. Kinoshita and K. Isobe, *Angew. Chem. Int. Ed.*, **38**, 3051-3053 (1999).
3. "Tetranuclear  $\text{Mo}_2\text{Rh}_2$  Complexes Obtained from Reactions between Triple Cubane-type Oxide Cluster  $[(\text{Cp}^*\text{Rh})_4\text{Mo}_4\text{O}_{16}]$  ( $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$ ) and Methanethiol:  $[\{\text{Cp}^*\text{Rh}(\mu\text{-SCH}_3)_3\text{MoO}_2\}_2(\mu\text{-O})]$  and  $[\{\text{Cp}^*\text{Rh}(\mu\text{-SCH}_3)_3\text{MoO}\}_2(\mu\text{-X})(\mu\text{-Y})]$  ( $\text{X}, \text{Y} = \text{O}$  and  $\text{X} = \text{O}, \text{Y} = \text{S}$ ). Synthesis, X-ray Structures, and Dynamic Behavior in Nonaqueous Media", R. Xi, B. Wang, M. Abe, Y. Ozawa, I. Kinoshita and K. Isobe, *Bull. Chem. Soc. Jpn.*, **72**, 1985-1996 (1999).

4. "Reactions of Terminal and Bridging Thiol Di- $\mu$ -methylene Dirhodium Complexes with Alkynes to Afford the Corresponding Ethenethiolate Complexes. Remarkable C-C bond Formation between Two  $\mu$ -CH<sub>2</sub> and Alkynes on the Bridging Ethenethiolate Complexes", Y. Kaneko, N. Suzuki, A. Nishiyama, T. Suzuki and K. Isobe, *Organometallics*, **17**, 4875-4883 (1998).
5. "Structures, Bonding and Reactivity of M-S-M' (M and M' = Rh, W, and Cu) Groups in Higher-Nuclearity Heterometallic Sulfide Clusters", S. Ogo, T. Suzuki, Y. Ozawa and K. Isobe, *Inorg. Chem.*, **35**, 6093-6101 (1996).
6. "[{Rh<sub>2</sub>Cp\*<sub>2</sub>( $\mu$ -CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>( $\mu$ -S<sub>4</sub>)<sup>2+</sup>: A Novel Tetranuclear Cationic Complex with a Rectangular S<sub>4</sub> Unit", K. Isobe, Y. Ozawa, A. Vázquez de Miguel, T.-W. Zhu, K.-M. Zhao, T. Nishioka, T. Ogura and T. Kitagawa, *Angew. Chem. Int. Ed. Engl.*, **33**, 1882- 1883 (1994).
7. "Cubane-Type Clusters as Potential Models for Inorganic Solid Surfaces", K. Isobe and A. Yagasaki, *Acc. Chem. Res.*, **26**, 524-529 (1993).
8. "Site-selective Oxygen-exchange and Substitution of Organometallic Groups in an Amphiphilic Quadruple-Cubane-Type Cluster. Synthesis and Molecular Structure of [(MCp\*)<sub>4</sub>V<sub>6</sub>O<sub>19</sub>](M = Rh, Ir)", Y. Hayashi, Y. Ozawa and K. Isobe, *Inorg. Chem.*, **30**, 1025-1033 (1991).
9. "Novel Triple Cubane-Type Organometallic Oxide Clusters: [MCp\*MoO<sub>4</sub>]<sub>4</sub>•nH<sub>2</sub>O (M = Rh and Ir; Cp\* = C<sub>5</sub>Me<sub>5</sub>; n = 2 for Rh and 0 for Ir)", Y. Hayashi, K. Toriumi and K. Isobe, *J. Am. Chem. Soc.*, **110**, 3666-3668 (1988).
10. "trans-Bromo(2-, 3-, and 4-pyridyl)bis(triethylphosphine)palladium(II) Complexes", K. Isobe, E. Kai, Y. Nakamura, K. Nishimoto, T. Miwa, S. Kawaguchi, K. Kinoshita and K. Nakatsu, *J. Am. Chem. Soc.*, **102**, 2475-2476 (1980).

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専 攻 物質分子専攻

学 歴 昭和44年3月 高知大学文理学部 卒業  
昭和46年3月 大阪市立大学大学院修士課程 修了  
昭和49年3月 大阪市立大学大学院博士課程 修了

職 歴	昭和49年4月	から	日本学術振興会		奨励研究員
	昭和50年3月	まで			
	昭和50年4月	から	大阪市立大学	理学部	研究員
	昭和50年9月	まで			
	昭和50年10月	から	大阪市立大学	理学部	助手
	昭和61年3月	まで			
	昭和61年4月	から	大阪市立大学	理学部	講師
	昭和61年12月	まで			
	昭和62年1月	から	岡崎国立共同研究 機構分子科学研究 所		助教授
	平成6年9月	まで			
	平成6年10月	から	大阪市立大学	理学部	教授
	平成13年3月	まで			
	平成13年4月	から	大阪市立大学	理学部・大学院理学 研究科	教授
	平成14年3月	まで			
	平成14年4月	から	大阪市立大学	大学院理学研究科・ 理学部	教授
	平成15年3月	まで			
	平成15年4月	から	金沢大学	理工研究域	教授
	平成22年3月	まで			
	平成26年5月	から	大阪市立大学	研究支援課	特任教授
	平成27年3月	まで			

在 職 中 の  
主 な 役 職

学 位 理学博士 ( 昭和49年3月23日 大阪市立大学 )