VII-E Syntheses of Transition Metal-Sulfur Clusters and Development of Their Catalysis

This project focuses on the development of the new, reliable synthetic routes towards the transition metal-sulfur clusters with the tailored core structures in high yield, and also on the determination of the detailed structures of the novel clusters prepared in this study by the X-ray crystallography. Activation of the small molecules will be attempted by the use of polynuclear homo- or heterometallic site in these clusters to exploit the new catalytic reactions that are inaccessible by the mononuclear complex catalyst.

VII-E-1 Syntheses and Structures of Mixed-Metal Sulfido Clusters Containing Incomplete Cubane-Type $M_2M'S_4$ and Cubane-Type $M_2M'_2$-S_4 Cores (M = Mo, W; M' = Rh, Ir)

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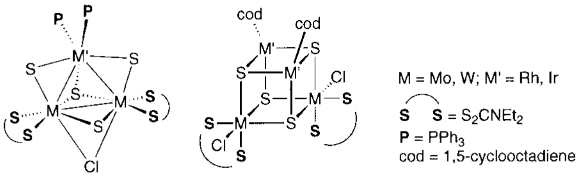
The reactions of sulfido-bridged dimolybdenum and ditungsten complexes $[M_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (**1**; M = Mo, W) with an equimolar amount of $[M'Cl(PPh_3)_3]$ (M' = Rh, Ir) gave a series of mixed-metal incomplete cubane-type sulfido clusters $[M'(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{M(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$. On the other hand, mixed-metal cubane-type sulfido clusters $[\{M'(cod)\}_2\{MCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (M' = Rh, Ir; cod = 1,5-cyclooctadiene) were obtained by the reactions of **1** with an equimolar amount of $[M'Cl(cod)]_2$. Detailed structures of $[Ir(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{W(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ and $[\{Rh(cod)\}_2\{MoCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ have been determined by X-ray crystallography.



VII-E-2 Synthesis and Reactivities of Ir_2Ru Heterobimetallic Sulfido Clusters Derived from a Hydrogensulfido-Bridged Diiridium Complex

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The hydrogensulfido-bridged diiridium complex $[ClCp^*Ir(\mu\text{-}SH)_2IrCp^*Cl]$ reacted with $[RuH_2(PPh_3)_4]$ to give a mixed-metal trinuclear cluster $[(Cp^*Ir)_2(\mu_3\text{-}S)_2RuCl_2(PPh_3)]$ **1**. which was further converted into the cationic diphosphine derivatives $[(Cp^*Ir)_2(\mu_3\text{-}S)_2\text{-}RuCl(L)]Cl$ (L = dppe = $Ph_2PCH_2CH_2PPh_2$ **2** or depe = $Et_2PCH_2CH_2PEt_2$ **3**). The reaction of **2** with Me_2CuLi followed by anion metathesis with KPF_6 afforded the methyl cluster $[(Cp^*Ir)_2(\mu_3\text{-}S)_2RuMe(dppe)][PF_6]$, while treatment of **2** with $CHCl_2Li$ led to formation of $[(Cp^*Ir)\{\eta^4\text{-}C_5Me_5CHCl_2)Ir\}(\mu_3\text{-}S)_2RuCl(dppe)]$, in which one of the Cp* ligands was alkylated by $CHCl_2Li$ to form an η^4-diene. Clusters **2** and **3** were also transformed into the dihydrido clusters $[(Cp^*Ir)_2(\mu_3\text{-}S)_2\text{-}(\mu\text{-}H)_2Ru(L)]$ (L = dppe or depe) by the reaction with $NaBH_4$. On the other hand, **1** was converted into the carbonyl cluster $[(Cp^*Ir)_2(\mu_3\text{-}S)_2RuCl(CO)(PPh_3)]Cl$, the isocyanide clusters $[(Cp^*Ir)_2(\mu_3\text{-}S)_2RuCl(CNXy)\text{-}(PPh_3)]Cl$ (Xy = 2,6-$C_6H_3Me_2$) and $[(Cp^*Ir)_2(\mu_3\text{-}S)_2Ru\text{-}Cl(CNXy)_2(PPh_3)][BPh_4]_2$ and the co-ordinatively unsaturated thiolato clusters $[(Cp^*Ir)_2(\mu_3\text{-}S)_2Ru(SAr)_2]$ (Ar = 2,4,6-$C_6H_2Pr^i_3$ **12** or Xy) on treatment with CO, XyNC and LiSAr, respectively.

VII-E-3 Formation of Linear Tetradentate Phosphine Ligand *o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$ by Coupling of Two Diphosphine Ligands Bound to Low-Valent Mo or W Center. Synthesis and Structure of [M{*o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$}-($Ph_2PCH_2CH_2PPh_2$)] (M = Mo, W)

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A mixture of *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) and dppe was heated to reflux in benzene or toluene to give the M(0) complex [M(**P**$_4$)(dppe)], which contains the novel tetradentate phosphine *o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$ (**P**$_4$) arising from the coupling of two dppe ligands. The reaction of [Mo(**P**$_4$)(dppe)] with CO afforded the carbonyl complex [Mo(CO)$_2$(**P**$_4$)].