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

This project focuses on the development of the new, relilable synthetic pathways affording 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 hetero-metallic site in these clusters to exploit the new catalytic reactions that are inaccessible by the mononuclear complex catalyst.

VII-D-1 Syntheses of a Dinuclear Ir Complex Containing Bridging Tetraselenide Ligands $[(C_5Me_5)Ir(\mu\text{–}Se_4)_2Ir(C_5Me_5)]$ and its Conversion into $Ir_2Pd_2Se_3$ and $Ir_2Pd_3Se_5$ Clusters

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[*Chem. Commun.* 207 (2000)]

Treatment of $[Cp^*IrCl(\mu\text{–}Cl)_2IrCp^*Cl]$ ($Cp^* = \eta^5\text{–}C_5Me_5$) with Li_2Se_4 gave a tetraselenide-bridged diiridium complex $[Cp^*Ir(\mu\text{–}Se_4)_2IrCp^*]$, which reacted further with two equivalents of $[Pd(PPh_3)_4]$ to afford a mixture of bimetallic tetra- and penta-nuclear selenido clusters $[(Cp^*Ir)_2\{Pd(PPh_3)\}_2(\mu_3\text{–}Se)_2(\mu_2\text{–}Se)]$ and $[(Cp^*Ir)_2\{Pd(PPh_3)\}_3(\mu_3\text{–}Se)_3(\mu_3\text{–}Se_2)]$.

VII-D-2 Preparation of Sulfido-Bridged Di- or Trinuclear Pyrrolylimido and Diazoalkane Complexes Derived from a Tungsten Dinitrogen Complex

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[*Bull. Chem. Soc. Jpn.* **s**, 631 (2000)]

Tungsten pyrrolylimido and diazoalkane complexes, *cis*,*mer*-$[WCl_2(NNC_4H_4)(PMe_2Ph)_3]$ and *cis*,*mer*-$[WCl_2(NN{=}CRR')(PMe_2Ph)_3]$, which are readily derived from the dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$, reacted with $[PPh_4][WS_4]$ to give the sulfide-bridged di- or trinuclear pyrrolylimido and diazoalkane complexes, $[PPh_4][WCl(NNC_4H_4)(PMe_2Ph)_2(\mu\text{–}S)_2WS_2]$ (**1**) and $[PPh_4][WCl(NN{=}CRR')(PMe_2Ph)_2(\mu\text{–}S)_2WS_2]$ (**2**; R = R' = Me (**2a**); R = Me, R' = Ph), or $[\{WCl(NNC_4H_4)(PMe_2Ph)_2(\mu\text{–}S)_2\}_2W]$ (**3**) and $[\{WCl(NN{=}CMePh)(PMe_2Ph)_2(\mu\text{–}S)_2\}_2W]$. Treatment of **1** or **2a** with tetraalkylthiuram disulfide resulted in the formation of sulfide-dithiocarbamate complexes: $[W(NNC_4H_4)(PMe_2Ph)(S_2CNR_2)(\mu\text{–}S)_2WS(S_2CNR_2)]$ (R = Et, Pr) and $[W(NN{=}CMe_2)(PMe_2Ph)(S_2CNEt_2)(\mu\text{–}S)_2WS(S_2CNEt_2)]$. On the other hand, replacement of two PMe_2Ph ligands in **1** and **2** by $Ph_2PCH_2CH_2PPh_2$ (dppe) afforded $[PPh_4][WCl(NNC_4H_4)(dppe)(\mu\text{–}S)_2WS_2]$ and $[PPh_4][WCl(NN{=}CRR')(dppe)(\mu\text{–}S)_2WS_2]$ (R = R' = Me; R = Me, R' = Ph (**3**)), where **3** has been shown to react further with $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) to give a bimetallic trinuclear complex $[WCl(NN{=}CMePh)(dppe)(\mu\text{–}S)_2W(\mu\text{–}S)_2Rh(cod)]$.