VII-F Synthesis of Transition-Metal Chalcogenido Complexes and Their Cluster-Forming Reactions

Transition-metal chalcogenido aggregates are of well-documented importance in biological systems and industrial processes such as hydrodesulfurization. A wide variety of metal chalcogenido clusters have been synthesized, in which the tetrathiometalato anions have been widely used as a building block. In this project, we are focusing on preparation of chalcogenido/chalcogenolato complexes as a precursor for cluster syntheses and their cluster-forming reactions.

VII-F-1 Synthesis of Bis{(2-dimthylphenylphosphino)ethane-1-thiolato}bis(tert-butylthiolato)molybdenum(IV) and Its Cluster-Forming Reactions with $FeCl_2$ and CuBr

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The Mo(IV) complex Mo(dmsp)$(S^tBu)_2$ (**1**) was readily prepared by the reaction of $Mo(S^tBu)_4$ with 2 equiv of $HSCH_2CH_2PMe_2$ (Hdmsp). The X-ray analysis of **1** reveals a distorted octahedral geometry with a *cis*-disposition of two ^{t}BuS ligands. Treatment of **1** with $FeCl_2$ and CuBr led to the formation of heterometallic clusters, $[Mo(O)(dmsp)_2]_2FeCl_2$ (**2**) and $[MoBr(dmsp)_2(\mu_3\text{-}S)Cu_2]_2(\mu_2\text{-}S^tBu)_2$ (**3**), respectively. The oxo ligand in **2** is most probably derived from adventitious H_2O contained in hygroscopic $FeCl_2$. In the structure of **2**, an $FeCl_2$ unit bridges two square-pyramidal $Mo(O)(dmsp)_2$ fragments through interactions between iron and sulfur atoms of dmsp. The formation of **3** involves C–S bond cleavage of one ^{t}BuS ligand of **1** and rearrangement of ligands between the Mo and Cu sites, resulting in the structure consisting of two $MoCu_2BrS(dmsp)_2$ units and two ^{t}BuS bridges.

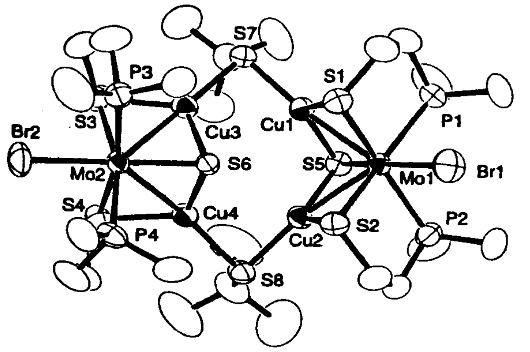

Figure 1. Structure of **3**.

VII-F-2 Synthesis and Structure of a Triply-Fused Incomplete-Cubane Cluster $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9](PF_6)_4$ and a 2D Polymer $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(MeCN)(pz)]PF_6$ (pz = pyrazine)

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The reaction of $(PPh_4)[Cp^*W(S)_3]$ with 3 equiv of $[Cu(MeCN)_4](PF_6)$ in MeCN yielded a triply-fused incomplete-cubane cluster $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9](PF_6)_4$ (**1**). Furthermore, we constructed a 2D polymeric structure $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(MeCN)(pz)]PF_6$ (**2**) by treating **1** with pyrazine in the presence of LiCl. The $W_3S_9Cu_7$ framework of **1** is broken during the reaction with LiCl and pyrazine, providing a WS_3Cu_3 incomplete-cubane cluster as a building block of the stacked sheet structure of **2**.

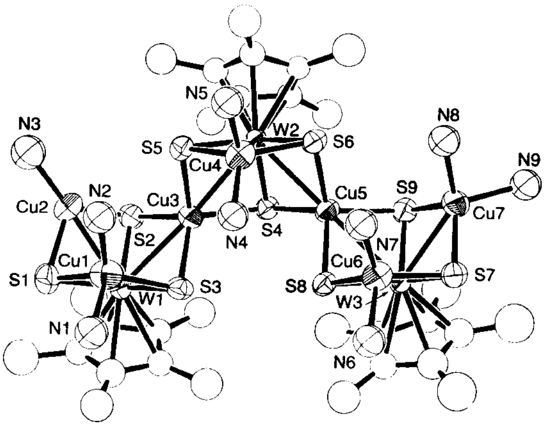

Figure 1. Structure of **1**.

VII-F-3 Synthesis and Structures of the Halfsandwich W(VI) Triselenido and W(II) Selenolato Complexes

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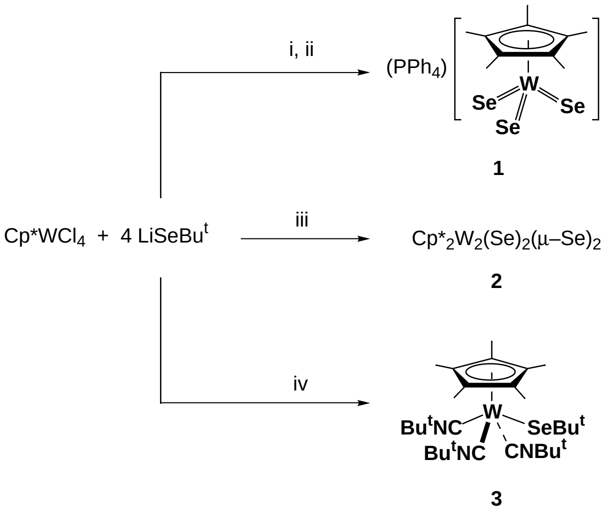
The reaction of Cp^*WCl_4 with $LiSe^tBu$ at room temperature gave rise to a mixture of *syn*- and *anti*-$Cp^*_2W_2(\mu\text{-}Se)_2(Se)_2$ (**1**), in which C–Se bond cleavage took place. When the similar reaction was carried out in the presence of ^{t}BuNC, the W(II) selenolato complex $Cp^*W(Se^tBu)(CN^tBu)_3$ (**2**) was formed. The structure of **2** was confirmed by X-ray analysis. While two of the isocyanides are nearly linear [C–N–C = 175.8(8)°, 164.3(7)°], the other contains essentially an sp^2-type nitrogen atom [N–C–N, 128.7(6)°] amongst the smallest of the known bent isocyanides (122–156°). In another experiment, a freshly prepared $Cp^*WCl_4/LiSe^tBu$ mixture was quickly transferred into Li_2Se_2 in THF. Cation exchange with PPh_4Br in CH_3CN provided $(PPh_4)[Cp^*W(Se)_3]$ (**3**) concomitant with a mixture of *syn*- and *anti*-**1**. The anion part of **3** has a three-legged piano-stool structure. The average W–Se distance

(2.322 Å) of **3** is similar to that of $(PPh_4)_2[WSe_4]$.



Scheme 1. *Reagents and condititons*: i, Li_2Se_2, THF; ii, PPh_4Br, CH_3CN; iii, 30 min, –78 °C, THF; iv, Bu^tNC, THF.