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 and silanechalcogenolato complexes as a precursor for cluster syntheses and their cluster-forming reactions.

VII-F-1 Synthesis of a Pentamethylcyclopentadienyl Complex of Tungsten with Three Different Chalcogenido (O^{2-}, S^{2-}, Se^{2-}) Ligands

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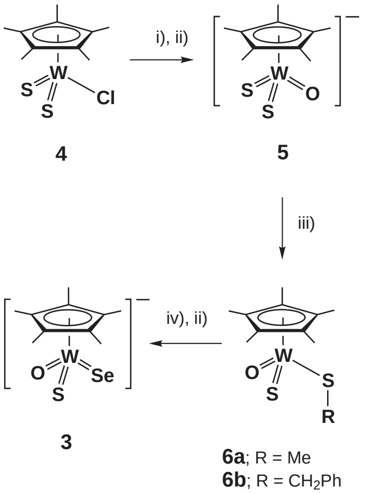
We have synthesized a pentamethylcyclopentadienyl complex of tungsten, $[PPh_4][Cp^*W(O)(S)(Se)]$ (**3**, Cp* = η^5-C_5Me_5), in which three different chalcogenide ligands (O^{2-}, S^{2-}, Se^{2-}) are bound to the metal center. This unique mixed-chalcogenide complex is thermodynamically stable, and does not exhibit chalcogen-exchange reactions in solution. The successful route to **3** begins with the high yield synthesis of $[Cp^*W(S)_2Cl]$ (**4**) attained by the reaction between $[Cp^*WCl_4]$ and 1 equiv of $Me_3SiSCH_2CH_2SSiMe_3$. Addition of a small amount of H_2O to a THF solution of **4** under the presence of NEt_3 produced $[Cp^*WS_2O]^-$ (**5**), which was then alkylated by CH_3I or $PhCH_2Br$ to give $[Cp^*W(O)(S)(SR)]$ (R = CH_3 (**6a**), CH_2Ph (**6b**)). Finally, a terminal selenide was introduced by the reaction of **6a** or **6b** with Li_2Se_2 and PPh_4Br leading to the desired oxo/thio/seleno complex $[PPh_4][Cp^*W(O)(S)(Se)]$ (**3**).



i) H_2O/Et_3N / THF, ii) PPh_4Br / CH_3CN
iii) $PhCH_2Br$ or CH_3I / THF
iv) Li_2Se_2 / THF

Figure 1.

VII-F-2 Synthesis and Reactions of Triphenylsilanethiolato Complexes of Manganese(II), Iron(II), Cobalt(II), and Nickel(II)

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Treatment of $Fe[N(SiMe_3)_2]_2$ with 1 and 2 equiv of Ph_3SiSH in hexane afforded $[Fe\{N(SiMe_3)_2\}(\mu\text{–}SSiPh_3)]_2$ **1** and $[Fe(SSiPh_3)(\mu\text{–}SSiPh_3)]_2$ **2**, respectively. Complex **2** reacted with Lewis bases to form the adducts $Fe(SSiPh_3)_2(L)_2$ [L = CH_3CN **3a**, 4-^{t}BuC_5H_4N **3b**, PEt_3 **3c**, $(L)_2$ = tmeda **3d**]. The reactions of $M[N(SiMe_3)_2]_2$ (M = Mn, Co) with Ph_3SiSH in the presence of TMEDA gave rise to the corresponding silanethiolato complexes $M(SSiPh_3)_2$(tmeda) (M = Mn **4**, Co **5**). The analogous reaction using $[Ni(NPh_2)_2]_2$ generated $Ni(SSiPh_3)_2$(tmeda) **6**. The reaction of **3a** with $(PPh_4)_2[MoS_4]$ produced the linear trinuclear complex $(PPh_4)_2[MoS_4\{Fe(SSiPh_3)_2\}_2]$ **7**, while **3a** reacted with $(NEt_4)_2[FeCl_4]$ to afford $(NEt_4)_2[Fe_2(SSiPh_3)_2Cl_4]$ **8**. The reaction of **3a** with $[Cu(CH_3CN)_4](PF_6)$ gave the cyclic tetranuclear complex $Cu_4(SSiPh_3)_4$ **9**, in which a ligand transfer reaction occurred. Finally, when **5** was treated with $(NBu_4)F$ in THF containing PPh_3, silicon-sulfur bond cleavage took place to produce the cobalt-sulfido cluster $Co_6(\mu_3\text{–}S)_8(PPh_3)_6$ **10**.

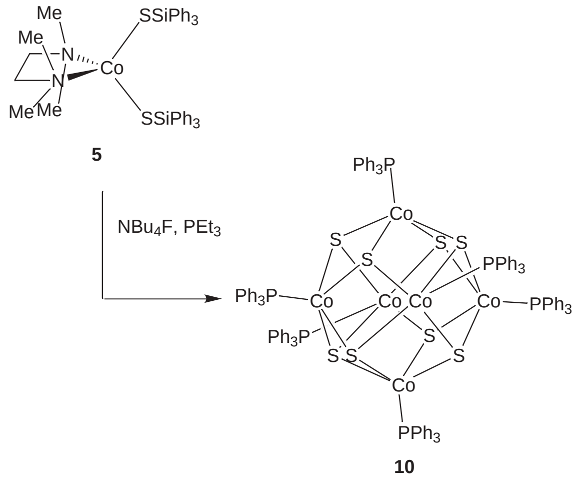

Figure 1.