

VII-I Silanechalcogenolato Complexes

Transition metal–chalcogenido clusters have attracted attention in light of their relevance to various active sites of metalloproteins, desulfurization catalysis, and inorganic functional materials. An important and challenging subject in this chemistry is to develop rational methods to synthesize desirable chalcogenido cluster complexes of high nuclearity, by assembling suitable metal–chalcogenido fragments. Compared with complexes containing alkyl(aryl) chalcogenolato ligands, the coordination chemistry of silanechalcogenolates has yet to be explored. However, the use of silanechalcogenolates has the following two advantages in developing rational synthetic routes to transition metal chalcogenido clusters. First, silicon–chalcogen (sulfur, selenium, and tellurium) bonds are expected to be more labile and more readily cleaved under a mild condition than corresponding carbon–chalcogen bonds. Secondly, the reactivity of silanechalcogenolato ligands can be controlled by steric and electronic properties of substituents in the silyl group. In this project, we are studying the chemistry of transition metal silanechalcogenolato complexes and their use as a precursor for cluster synthesis.

VII-I-1 Palladium Dimethylsilanedithiolato Complex: a Precursor for Ti–Pd and Ti–Pd–Ti Heterometallic Complexes

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The bis-silylated sulfides ($R_3Si)_2S$ have been widely used to prepare a variety of metal sulfide clusters, because these reagents exploit the strength of the Si–O and Si–Cl bond to replace a halide, alkoxide, acetate or oxide with a sulfido ligand under very mild and controlled conditions. Therefore, a metal-silanethiolato complex (e.g., $M-SSiR_3$) would be expected to serve as a synthetic precursor of homo- and hetero-metallic sulfido clusters. However, compounds containing the silanethiolato ligand are less common compared with alkylthiolato complexes. The silanedithiolato complex $Pd(S_2SiMe_2)(PEt_3)_2$ (**1**) reacted with $(C_5H_5)TiCl_3$ and $TiCl_4(thf)_2$ to produce the heterometallic clusters $(C_5H_5)TiCl(\mu-S)_2Pd(PEt_3)_2$ (**2**) and $TiCl_2(S)(\mu-S)_2Pd_2(PEt_3)_4$ (**3**) along with silicon–sulfur bond cleavage, respectively.

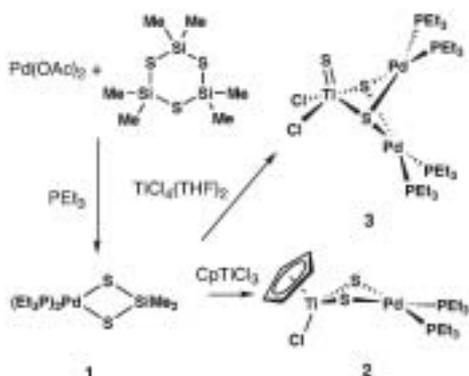


Figure 1.

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

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Reactions of $Fe[N(SiMe_3)_2]_2$ with 1 and 2 equiv of Ph_3SiSH in hexane afforded dinuclear silanethiolato complexes, $[Fe\{N(SiMe_3)_2\}(\mu-SSiPh_3)]_2$ (**1**) and $[Fe(SSiPh_3)(\mu-SSiPh_3)]_2$ (**2**), respectively. Various Lewis bases were readily added to **2**, generating mononuclear adducts, $Fe(SSiPh_3)_2(L)_2$ [$L = CH_3CN$ (**3a**), $4-tBuC_5H_4N$ (**3b**), PEt_3 (**3c**), $(L)_2 = tmeda$ (**3d**)]. From the analogous reactions of $M[N(SiMe_3)_2]_2$ ($M = Mn, Co$) and $[Ni(NPh_2)_2]_2$ with Ph_3SiSH in the presence of TMEDA, the corresponding silanethiolato complexes, $M(SSiPh_3)_2(tmeda)$ [$M = Mn$ (**4**), Co (**5**), Ni (**6**)], were isolated. Treatment of **3a** with $(PPh_4)_2[MoS_4]$ or $(NEt_4)_2[FeCl_4]$ resulted in formation of a linear trinuclear Fe–Mo–Fe cluster $(PPh_4)_2[MoS_4\{Fe(SSiPh_3)_2\}_2]$ (**7**) or a dinuclear complex $(NEt_4)_2[Fe_2(SSiPh_3)_2Cl_4]$ (**8**). On the other hand, the reaction of **3a** with $[Cu(CH_3CN)_4](PF_6)$ gave a cyclic tetranuclear copper cluster $Cu_4(SSiPh_3)_4$ (**9**), where silanethiolato ligands were transferred from iron to copper. Silicon–sulfur bond cleavage was found to occur when the cobalt complex **5** was treated with $(NBu_4)F$ in THF, and a cobalt-sulfido cluster $Co_6(\mu_3-S)_8(PPh_3)_6$ (**10**) was isolated upon addition of PPh_3 to the reaction system. The silanethiolato complexes reported here are expected to serve as convenient precursors for sulfido cluster synthesis.

VII-J Coordination Chemistry of New Multidentate Ligands and Activation of Small Molecules

This project is focused on the design and synthesis of new ligands that are capable of supporting novel structural features and reactivity. Currently, we are investigating multidentate ligands based on aryloxy, thiolate, and amidinate. Our recent efforts have been directed toward activation of small molecules.

VII-J-1 Binuclear Iron(II) Complex from a Linked-bis(amidinate) Ligand: Synthesis and its Reaction with Carbon Monoxide

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We synthesized and fully characterized binuclear iron(II) complexes supported by a linked bis(amidinate) ligand. As part of a program aimed at developing new ancillary ligands to support reactive binuclear metal centers, we chose to employ a *trans*-cyclohexane-linked bis(amidinate) ligand L^{2-} . The use of this linked bis(amidinate) ligand leads to isolation of double-stranded binuclear complexes of iron(II), in which metal centers are coordinatively unsaturated. According to X-ray analyses, the size of a cage created by the L^{2-} ligands is flexible. Furthermore, another interesting aspect of this system is the ligand self-recognition in the assembly process. Although the racemic L^{2-} ligand is used, the reaction of racemic $Li_2(L)$ with $FeCl_2$ exclusively affords two discrete homochiral metal complexes Λ, Λ - $Fe_2(L^{RR})_2$ and Δ, Δ - $Fe_2(L^{SS})_2$. The robustness of this homochiral binuclear frame is examined in the reaction with CO.

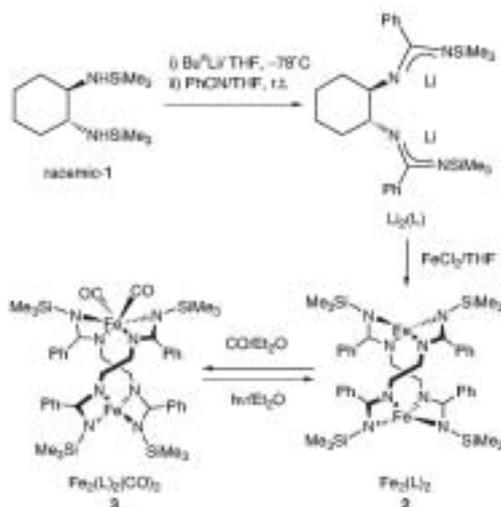


Figure 1.

VII-J-2 Synthesis and Structures of Ti(III) and Ti(IV) Complexes Supported by a Tridentate Aryloxy Ligand

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Titanium complexes of the tridentate aryloxy $Me-L^{3-}$ [$H_3(Me-L) = 2,6$ -bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol] have been prepared. Reaction of $TiCl_4$ with 1 equiv of $H_3(Me-L)$ gave $[Ti(Me-L)Cl]_2$ **1**. Recrystallization of **1** from THF resulted in formation of the THF adduct $Ti(Me-L)Cl(THF)_2$ **2**. Treatment of **1** with $[NEt_4]Cl$ in THF quantitatively gave $[NEt_4][Ti_2(Me-L)_2Cl_3]$ **3**. Complex **1** was reduced with 2 equiv of potassium to produce the Ti(III) complex $[Ti(Me-L)-(DME)]_2$ **4**. Structures of **1**, **2**, **3**, and **4** have been determined by X-ray analyses. For **1**, **2**, and **4**, the $Me-L$ ligand assumes a U-conformation. In the case of **3**, it is coordinated in an S-conformation.

VII-J-3 Dinitrogen-Bond Cleavage in a Niobium Complex Supported by a Tridentate Aryloxy Ligand

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The $N \equiv N$ triple bond cleavage took place in the reaction of $[Nb(tBu-L)Cl_2]_2$ (**1**) with $LiBHET_3$, resulting in the formation of $[Nb(tBu-L)(\mu-N)Li(THF)]_2$ (**3**) [$H_3(tBu-L) = 2,6$ -bis(4,6-methyl-*tert*-butyl-salicyl)-4-*tert*-butylphenol]. On the other hand, the analogous reaction of $[Nb(Me-L)Cl_2]_2$ (**2**) with $LiBHET_3$ yielded $[Nb_2(Me-L)_2(\mu-H)(\mu-Cl)(THF)_2]Li_4(THF)_4Cl_2$ (**4**) [$H_3(Me-L) = 2,6$ -bis(4,6-dimethylsalicyl)-4-*tert*-butylphenol] concomitant with reduction of the metal center from Nb^V to Nb^{III} . Structures of **3** and **4** have been determined by X-ray diffraction analyses. Repeating the experiment under an atmosphere of $^{15}N_2$ affords $[Nb(tBu-L)(\mu-^{15}N)Li(THF)]_2$ (**3-¹⁵N**). The ^{15}N NMR spectrum of **3-¹⁵N** shows a single peak at δ 312, thus unambiguously confirming the origin of the bridging ligands in **3** to be N_2 . This work clearly shows that each $R-L^{3-}$ ligand behaves in a very distinctive manner with respect to dinitrogen activation and metal-metal interaction.

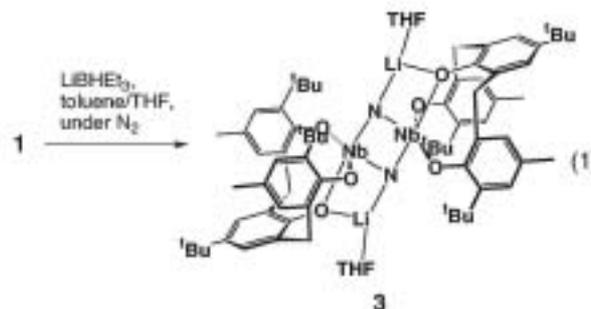


Figure 1.