VII-E Silanechalcogenolato Complexes

The development of synthetic routes to mixed-metal chalcogenido clusters is a critical prerequisite for study of these important materials. It is well known that $(Me_3Si)_2E$ (E = S, Se, Te) is a good chalcogen transfer reagent, which can replace a halide, alkoxide, acetate, and oxide with a chalcogen ligand by taking advantage of formation of Si–Cl and Si–O bonds. Therefore the corresponding $M{-}ESiMe_3$ species hold great promise for synthetic precursors of chalcogenido clusters. However, because of the high lability of Si–E bond, there is a strong tendency to restrict the use of these complexes. Thus, their stabilization is required to develop cluster synthesis based on silanechalcogenolato complexes.

In this work, we have chosen to stabilize silanethiolato complexes by the chelating effect of the ligands. The chelating effect in coordination chemistry has most pronounced kinetic and thermodynamic consequences. This strategy could suppress the undesired degradation process of silanethiolato complexes *via* aggregation and/or ligand redistribution.

VII-E-1 Coordination Chemistry of Silanedithiolato Ligands Derived from Cyclotrisilathiane: Synthesis and Structures of Complexes of Iron(II), Cobalt(II), Palladium(II), Copper(I), and Silver(I)

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[*Inrog. Chem.* **42**, 5340 (2003)]

The coordination chemistry of chelating silanedithiolato ligands has been investigated on Fe(II), Co(II), Pd(II), Cu(I), and Ag(I). Treatment of $M(OAc)_2$ (M = Fe, Co, Pd) with cyclotrisilathiane $(SSiMe_2)_3$ in the presence of Lewis bases resulted in formation of $Fe(S_2SiMe_2)$(pmdeta) (**1**), $Fe(S_2SiMe_2)(Me_3tacn)$ (**2**), $Co(S_2SiMe_2)$(pmdeta) (**3**), and $Pd(S_2SiMe_2)(PEt_3)_2$ (**4**). The analogous reactions of M(OAc) (M = Cu, Ag) in the presence of PEt_3 gave rise to the dinuclear complexes $M\{(SSiMe_2)_2S\}(PEt_3)_3$ [M = Cu (**5**), Ag (**6**)]. Complexes were characterized in solution by ^1H, $^{31}P\{^1H\}$, and $^{29}Si\{^1H\}$ NMR and in the solid state by single-crystal X-ray diffraction. Mononuclear complexes **1**, **2**, and **3** have a four-membered MS_2SiMe_2 ring, and these five-coordinate complexes adopt trigonal-bipyramidal (for the pmdeta adducts) or square-pyramidal (for the Me_3tacn adduct) geometries. In dimer **6**, the $(SSiMe_2)_2S^{2-}$ silanedithiolato ligand bridges two metal centers, one of which is three-coordinate and the other four-coordinate. The chelating effect of silanedithiolato ligands leads to an increase in the stability of silylated thiolato complexes.

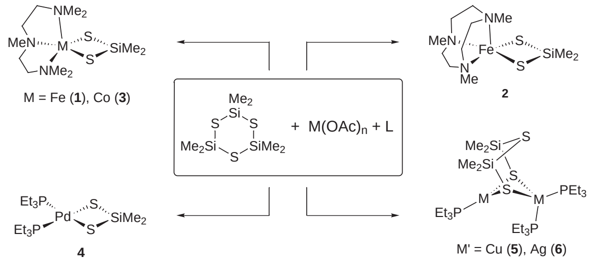

Figure 1.

VII-E-2 Copper and Silver Complexes Containing the $S(SiMe_2S)_2{}^{2-}$ Ligand: Efficient Entries into Heterometallic Sulfido Clusters

KOMURO, Takashi[1]; MATSUO, Tsukasa; KAWAGUCHI, Hiroyuki; TATSUMI, Kazuyuki[1]
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[*Angew. Chem., Int. Ed.* **42**, 465 (2003)]

Reactions of copper and silver acetates with cyclotrisilathane in the presence of PEt_3 afforded the silanedithiolate-bridged dinuclear complexes $[M_2\{(SSiMe_2)_2S\}(PEt_3)_3]$ (M = Cu (**1a**), Ag (**1b**)) in high yields. Although these complexes are thermally stable in solution, they are found to react smoothly under mild conditions with metal halides, giving mixed-sulfido clusters. Treatment of **1a** with $[CpTiCl_3]$ and $[TiCl_4(thf)_2]$ produced copper-titanium sulfido clusters $[Cp_2Ti_2Cu_6S_6(PEt_3)_6]$ (**2**) and $[ClTiCu_3S_3(PEt_3)_4]$ (**3**), respectively. Addition of [CpLi] to **3** resulted in the formation of **2**. Structures of **1a**, **2**, and **3** have been determined by X-ray analysis.

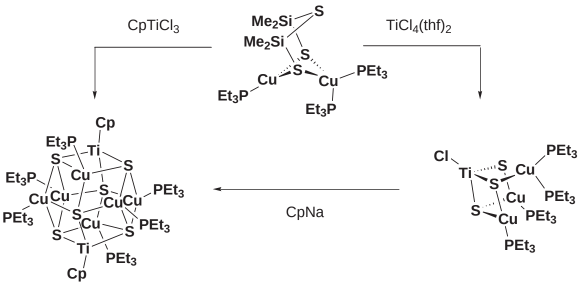

Figure 1.

VII-F Coordination Chemistry of Sterically Hindered Ligands and 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 aryloxide, thiolate, and amidinate. In addition, we set out to study metal complexes with sterically hindered arylthiolate ligands. Our recent efforts have been directed toward activation of small molecules.

VII-F-1 Titanium N-Hetrocyclic Carbene Complexes Incorporating an Imidazolium-Linked Bis(phenol)

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[*Chem. Commun.* 2204 (2003)]

We synthesized and fully characterized titanium(II) complexes supported by a bis(aryloxido) ligand with an N-heterocyclic carbene (NHC) function. The use of NHC as ligands has attracted considerable attention, because their complexes are highly active and very stable catalysts for various organic reactions. However, the vast majority of NHC systems contain late transition metals. This is due to the lack of NHC derivatives suitable for studies of early transition metal chemistry. Thus we designed the aryloxido-functionalized NHC hybrid ligand, in which the carbene unit is flanked by two aryloxide groups. The aryloxido group acts as an anchor and reduces the tendency for NHC dissociation. This enables us to explore the effect of NHC on the properties of early transition metal complexes. In this context, we use this ligand (**L**) to prepare titanium complexes, which were fully characterized. Furthermore, another interesting aspect of this system is that these aryloxido-carbene complexes of titanium showed a high activity for ethylene polymerization. This is a first example of ethylene polymerization promoted by NHC complexes.

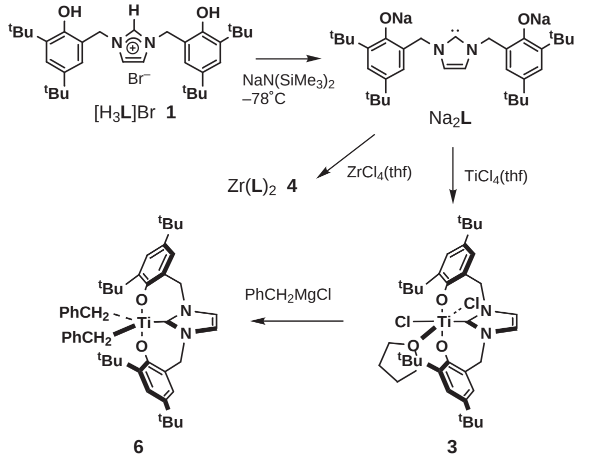

Figure 1.

VII-F-2 Unusual Coordination Modes of Arylthiolates in Mo{η^5-SC_6H_3-2,6-$(SiMe_3)_2$}{η^7-SC_6H_3-2,6-$(SiMe_3)_2$}

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[*J. Am. Chem. Soc.* **125**, 2070 (2003)]

Although arylthiolate ligands are ubiquitous in transition metal coordination chemistry, they are invariably S-bonded for either terminal or bridging coordination. This is probably because the affinity of transition metal elements to thiolate sulfurs is strong relative to the metal-aryl π interactions. In contrast, analogous aryloxide complexes have occasionally been found to assume π coordination geometries at the aryl substituents, in an η^5-pentadienyl or an η^3-allyl bonding manner, leaving the C=O portion intact. As a part of our ongoing study on activation of small molecules by means of coordinatively unsaturated transition metal complexes, we were interested in preparation of molybdenum complexes of the 2,6-disubstituted arylthiolates, SC_6H_3-2-Ph-6-$SiMe_3$ and SC_6H_3-2,6-$(SiMe_3)_2$. This work describes the reactions of $MoCl_3(thf)_3$ with the lithium salts of these arylthiolates, which resulted in isolation of the unexpected π-sandwiched bis-arylthiolato complex, Mo{η^5-SC_6H_3-2,6-$(SiMe_3)_2$}{η^7-SC_6H_3-2,6-$(SiMe_3)_2$} (**1**). We also report here that the π-bonding in **1** is labile and the treatment with acetonitrile gave rise to the S-bonded bis-arylthiolato complex carrying three acetonitrile molecules, one of which is coordinated in an η^2-mode, Mo{SC_6H_3-2,6-$(SiMe_3)_2$}$_2$(η^1-CH_3CN)$_2$(η^2-CH_3CN) (**2**).

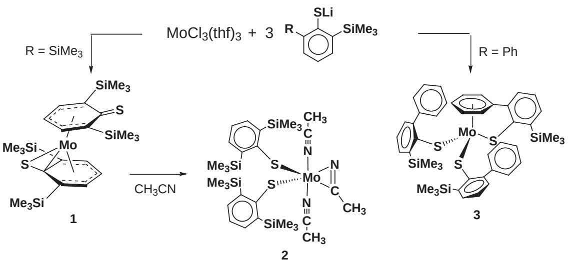

Figure 1.