

VIII-G Silanechalcogenolato Complexes

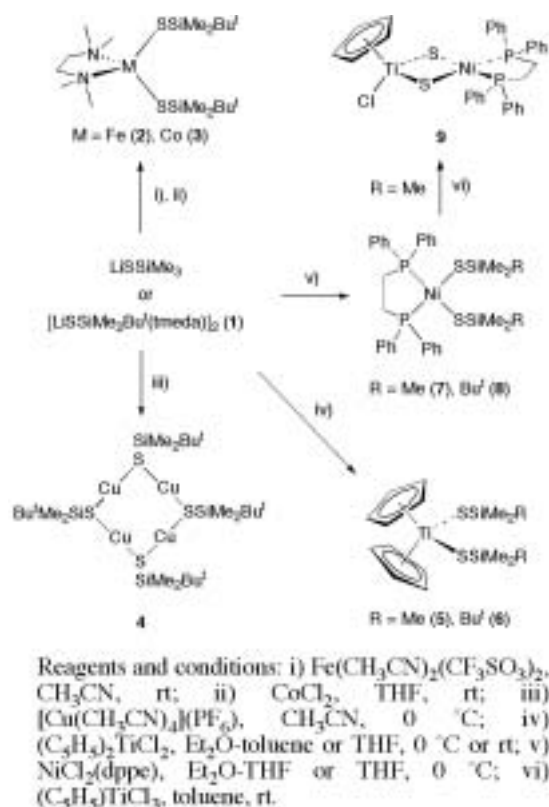
The development of synthetic routes to mixed-metal chalcogenido clusters is a critical prerequisite for study of these important materials. It is well known that $(\text{Me}_3\text{Si})_2\text{E}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) is a good chalcogen transfer reagent, which can replace a 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–ESiMe₃ species hold great promise for synthetic precursors of chalcogenido clusters. One of the important advantages of using this system is the possibility of controlling cluster-forming reactions by the choice of steric and electronic properties of the substituents on silicon. This approach has been widely used in organic syntheses, where silyl groups have proven to be useful as protecting agents of functional groups under various conditions. However, because of the high lability of Si–E bond, there is a strong tendency to restrict the use of silanechalcogenolato complexes. In this project, we have studied chemistry of silanechalcogenolato complexes, aiming at developing the rational synthesis of chalcogenido clusters.

VIII-G-1 Synthesis and Structural Characterization of Silanethiolato Complexes Having *tert*-Butyldimethylsilyl and Trimethylsilyl Groups

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Treatment of cyclotrisilathiane $(\text{Me}_2\text{SiS})_3$ with 3 equiv of RLi ($\text{R} = \text{Me}, \text{Bu}^t$) in hexane–Et₂O afforded the lithium silanethiolates LiSSiMe₂R, and the tmeda adduct $[(\text{tmeda})\text{LiSSiMe}_2\text{Bu}^t]_2$ **1** ($\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine) was isolated in the case of $\text{R} = \text{Bu}^t$. Reaction of $\text{Fe}(\text{CH}_3\text{CN})_2(\text{CF}_3\text{SO}_3)_2$, CoCl_2 , and $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ with **1** gave rise to the silanethiolato complexes $\text{M}(\text{SSiMe}_2\text{Bu}^t)_2(\text{tmeda})$ ($\text{M} = \text{Fe}$ **2**, Co **3**), and $[\text{Cu}(\text{SSiMe}_2\text{Bu}^t)]_4$ **4**, respectively. Complexes $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{SSiMe}_2\text{R})_2$ ($\text{R} = \text{Me}$ **5**, Bu^t **6**) and $\text{Ni}(\text{SSiMe}_2\text{R})_2(\text{dppe})$ [$\text{R} = \text{Me}$ **7**, Bu^t **8**; $\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane] were prepared from treatments of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ and $\text{NiCl}_2(\text{dppe})$ with the corresponding lithium silanethiolates. Complex **7** readily reacted with $(\text{C}_5\text{H}_5)_2\text{TiCl}_3$ to produce the Ti–Ni heterobimetallic compound $(\text{C}_5\text{H}_5)_2\text{TiCl}(\mu\text{-S})_2\text{Ni}(\text{dppe})$ **9**, in which silicon–sulfur bond cleavage took place.



VIII-H 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 aryloxy, 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.

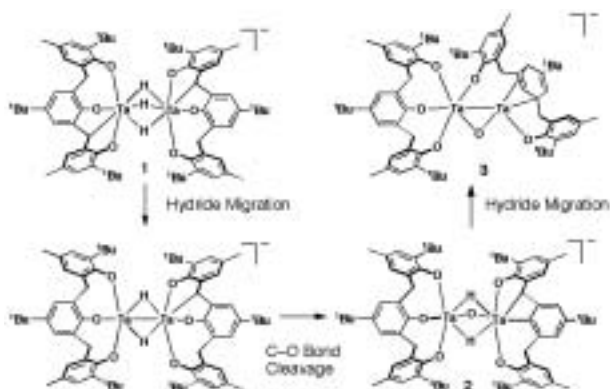
VIII-H-1 Aryl-Oxygen Bond Cleavage by a Trihydride-Bridging Ditantalum Complex

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

[J. Am. Chem. Soc. **125**, 14254–14255 (2003)]

Treatment of $[\text{Ta}^t\text{Bu-L}]_2$ with LiBHET_3 gave $[\text{Ta}^t\text{Bu-L}]_2(\text{H})_3\text{Li}(\text{thf})_2$ (**1**). Complex **1** is a Ta(V) dimer, in which two metal center are bridged by three hydride ligands. The formation of **1** is believed to proceed *via* a Ta(III)–Ta(III) intermediate which undergoes intramolecular addition of a methylene CH bond of the

ligand. Complex **1** is thermally unstable and gradually undergoes rearrangement. The first step is likely the migration of one hydride to the methine carbon of the *bit*-^tBu-L ligand to form a dihydride Ta(IV)–Ta(IV) intermediate. Subsequent C–O scission occurs across the metal–metal bond, in which two electrons stored in metal–metal bonding is used to yield an oxo-dihydride dimer **2**. The final formation of **3** requires the migration of two hydrides to a methine and an aryl carbon, respectively. The overall transformation implies an internal redox process and does not require electrons to be added to or removed from **1**.

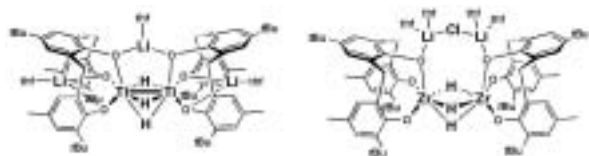


VIII-H-2 Triple Hydrogen Bridged Ditungsten(III) and Dizirconium(IV) Aryloxy Complexes

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[*Organometallics* **22**, 5379–5381 (2003)]

The first example of triple hydrogen bridged ditungsten(III) system, $[\text{Li}_3(\text{thf})_3][\text{Ti}(\text{tBu-L})_2(\mu\text{-H})_3]$ (**2**) supported by the tridentate aryloxy ligand was synthesized by the reaction of $[\text{Ti}(\text{tBu-L})\text{Cl}]_2$ (**1**) with LiBHET_3 [$\text{H}_3(\text{tBu-L}) = 2,6\text{-bis}(4,6\text{-methyl-}t\text{-butyl-salicyl})\text{-4-}t\text{-butylphenol}$]. On the other hand, the analogous reaction of $\text{Zr}(\text{tBu-L})\text{Cl}(\text{thf})_2$ (**3**) yielded the triple hydrogen bridged dizirconium(IV), $[\text{Li}_2\text{Cl}(\text{thf})_4][\text{Zr}(\text{tBu-L})_2(\mu\text{-H})_3]$ (**4**). Structures of **2** and **4** were determined by X-ray crystallography. The titanium dimer adopts a face-sharing bioctahedral geometry with a very short Ti–Ti distance (2.621(1) Å). The diamagnetic nature and the dynamic behavior of **2** in solution were revealed by NMR studies.



VIII-H-3 Formation of an Iron(II) Carbene Thiolato Complex via Insertion of Carbon Monoxide into Si–C Bond

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[*Angew. Chem., Int. Ed.* **43**, 1404–1407 (2004)]

The reaction of $\text{Fe}(\text{CF}_3\text{SO}_3)_2(\text{CH}_3\text{CN})_2$ with $\text{Li}_3[\text{TMS}_3\text{Si}]$ ($\text{H}_3[\text{TMS}_3\text{Si}] = \text{tris}(3\text{-trimethylsilyl-2-mercaptophenyl)methylsilane}$) followed by addition of PPh_4Br afforded $(\text{PPh}_4)[\text{Fe}(\text{TMS}_3\text{Si})(\text{thf})]$ (**1**). Complex **1** reacted with CO to produce $(\text{PPh}_4)[\text{Fe}(\text{TMS}_3\text{Si})(\text{CO})_3]$ (**2**). The carbonyl compound **2** is thermally unstable in solution. Stirring the solution of **2** at room temperature resulted in formation of the carbene-thiolato complex **3**, in which the insertion of CO into Si–C bond took place. A kinetic study of this reaction showed that this was first order in **2** with the appreciable positive entropy of activation. The crystal structures of **1** and **3** were determined by the X-ray analysis. The most remarkable feature in **3** is that the crystal structure exhibits substantial bonding interaction between the carbene carbon and the thiolato sulfur.

