VIII-E Synthesis of Transition Metal Complexes Containing a Novel Metal-Silicon and Metal-Gallium Bonding

Synthesis of transition metal complexes with unprecedented bonds between a metal and a heavy main group element is one of current topics on inorganic chemistry. In this project, we have investigated the synthesis, structure, and reactivities of metal complexes containing organosilicon and -gallium ligands. We also synthesized a cofacial dimanganese complex, which shows catalytic activity for asymmetric oxidation of sulfides.

VIII-E-1 Synthesis of a Cofacial Schiff-Base Dimanganese(III) Complex for Asymmetric Catalytic Oxidation of Sulfides

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Asymmetric oxidation of sulfides is a key reaction for synthesis of biologically active compounds with chiral sulfoxide centers. It has been reported that optically active salen-type Schiff base manganese(III) complexes are efficient catalysts for the asymmetric oxidation of sulfides. However, the enantioselectivity is not high enough for synthetic applications. Design of chiral macrocyclic dinuclear complexes would be a good approach to efficient asymmetric catalysts, because two metal centers are expected to behave cooperatively as an enantioselective Lewis acid center to catch a sulfide and an active oxidation site upon sulfoxidation, respectively. Among macrocyclic Schiff base complexes, face-to-face salen-type complex dimers have been limited to a few systems. In this work, we report a new catalyst, optically active Schiff base manganese(III) complex dimer **1** (Figure 1). The two Schiff base manganese(III) units in **1** are doubly bridged by two 9,9-dimethylxanthenediyl spacers to form a cofacial structure. The dimanganese complex catalyzed the asymmetric oxidation of methyl phenyl sulfide by iodosobenzene.

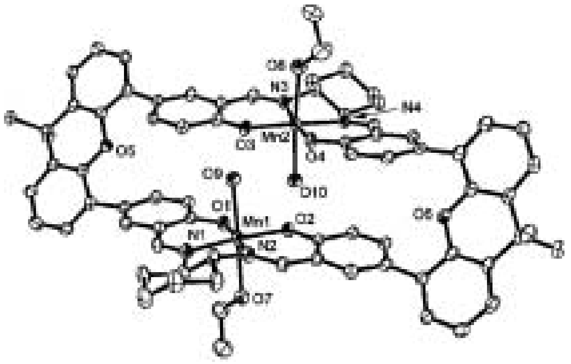

Figure 1. Molecular Structure of Dimanganese Complex **1**.

VIII-E-2 Synthesis and Structure of a Base-Stabilized Silyl(silylene)tantalum Complex

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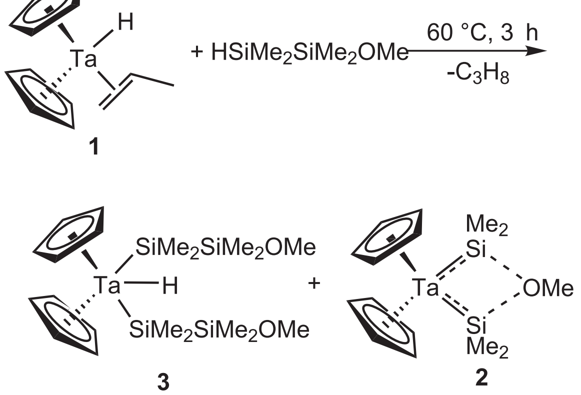
Over the past few decades, transition-metal silylene complexes with metal–silicon double bonds have attracted much interest as silicon analogues of carbene complexes, and as possible intermediates in various transformation reactions of organosilicon compounds. Until now, a wide variety of silylene complexes has been synthesized as not only a base-stabilized form but also a base-free form. To our best knowledge, all these examples are Fischer-type ones, in which the metal–silicon bond is polarized in a $M^{\delta-}$–$Si^{\delta+}$ manner. Theoretical studies on early transition metal–silylene complexes revealed that the Schrock-type metal–silylene complex $L_nNb=SiR_2$ is more stable than the Fischer-type $L_nM=SiR_2$ (M = Fe, Cr), although silylene complexes of group 5 transition metals have not been prepared yet. We herein report the synthesis and structure of methoxy-bridged silyl(silylene)tantalum complex. Thermal reaction of $Cp_2Ta(\eta^2\text{-}C_3H_6)$ (**1**) with $HSiMe_2SiMe_2OMe$ in toluene at 60 °C gave $Cp_2Ta\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (**2**) (7%) and $Cp_2TaH(SiMe_2SiMe_2OMe)_2$ (**3**) (8%). The former methoxy-stabilized silyl (silylene) complex was characterized by X-ray diffraction study.



VIII-E-3 Synthesis and Structures of the First Titanium(IV) Complexes with Cyclic Tetrasiloxide Ligands: Incomplete and Complete Cage Titanosiloxanes

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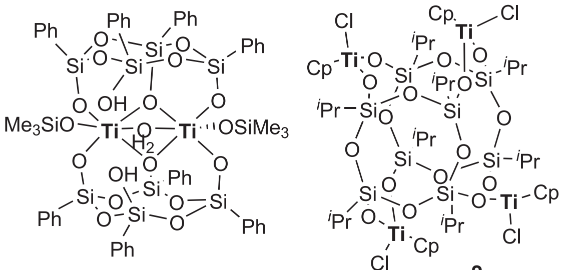
Group 4 metal complexes immobilized on silica surfaces are industrially and commercially important catalysts. However, the improvement of the catalysts is hindered by the complicated surface structures, making the reaction processes unclear. Several types of siloxido complexes have been synthesized using mono-, di-, and trisiloxide ligands, which can be considered as model compounds for the heterogeneous catalysts. Cyclic tetrasiloxide ligands are also potentially useful as a silica surface model but few complexes with such ligands have been reported so far. Here we report the first titanium(IV) complexes with cyclic tetrasiloxide ligands, $[Ti(L^1H)(OSiMe_3)]_2(H_2O)$ (**1**) and $(CpTiCl)_4(L^2)_2$ (**2**), which were synthesized using the all-*cis* isomer of cyclotetrasiloxanetetraols $R_4(SiO)_4(OH)_4$ (L^1H_4: R = Ph, L^2H_4: R = ^{i}Pr) as ligand precursors. X-ray analysis revealed that **1** is a binuclear complex with bridging siloxy and aqua ligands while **2** has a tetranuclear cage structure capped by two L^2 ligands.



1 **2**

Figure 1. Molecular Structure of Titanium Complexes with Cyclic Tetrasiloxide Ligands.