VII-H Synthesis and Reactivity of Complexes Containing Peculiar Bonds between Transition Elements and Main Group Elements

The bonds between transition elements and main group elements are attracting increasing attention in recent years. This is attributable not only to the great variety of the combination of elements but also to the peculiarity of their physical and chemical properties. We are currently focusing on transition metal complexes containing novel and peculiar bonds between transition elements and some main group elements, particularly single and multiple bonds to silyl, silene, and sulfido ligands. We are examining the synthesis, structures, fluxional behaviors, and reactivity of these complexes to gain a better understanding on the characters of these bonds.

VII-H-1 Fluxional Behavior of Alkoxy-Bridged Bis(silylene)ruthenium Complexes Cp*(Me$_3$P)-Ru{SiMe$_2$··O(R)··SiMe$_2$} (R = Me, ^{t}Bu) Caused by Rotation of the Silylene Ligands

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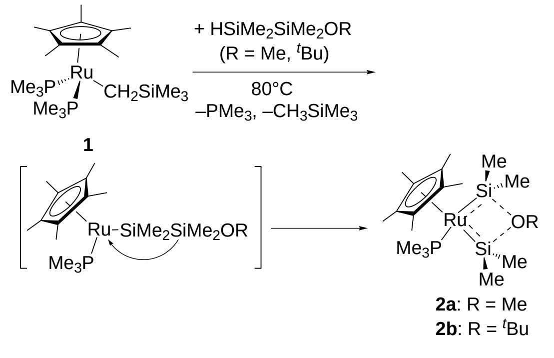
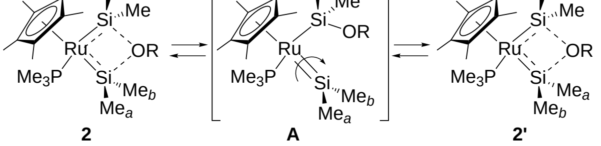
Heating a hexane solution of Cp*(Me$_3$P)$_2$RuCH$_2$-SiMe$_3$ (**1**; Cp* = η^5-C$_5$Me$_5$) and HSiMe$_2$SiMe$_2$OR (R = Me, ^{t}Bu) at 80 °C overnight in a sealed tube gave alkoxy-bridged bis(silylene)ruthenium complexes Cp*-(Me$_3$P)Ru{SiMe$_2$··O(R)··SiMe$_2$} (**2a**: R = Me; **2b**: R = ^{t}Bu) in 77 and 39% yields, respectively. The exchange of Si-Me groups in **2a** and **2b** through silylene ligand rotation on the intermediate **A** was observed by variable temperature ^{1}H NMR spectroscopy. Such a fluxionality was not observed in CpLRu{SiMe$_2$··O(Me)··SiMe$_2$} (L = PPh$_3$, CO) nor in the iron analogues. Thus, this fluxionality is considered to be due to the weakened Si··O partial bonds caused by the strong electron-releasing effect of Cp* and PMe$_3$ ligands.





VII-H-2 Preparation of Silanediyl-Bridged Fe-Fe and Fe-W Dinuclear Complexes. X-Ray Structures of [Cp*Fe(CO)(μ-CO){μ-Si(H)CHPh$_2$}-(CO)$_n$MCp] (Cp* = C$_5$Me$_5$, Cp = C$_5$H$_5$, M = Fe, n = 1; M = W, n = 2)

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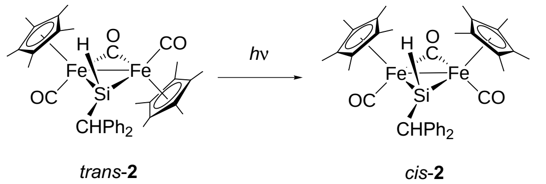
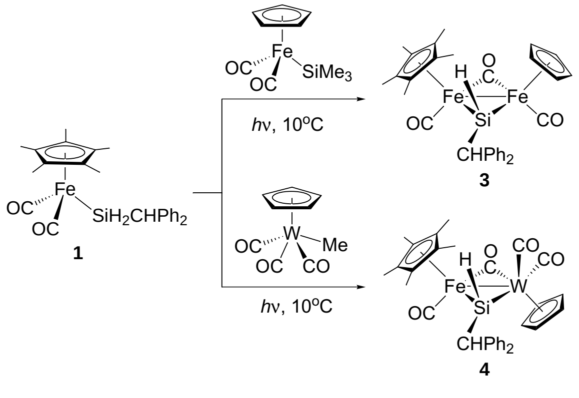
Photolysis of a 2:1 mixture of [Cp*Fe(CO)$_2$Me] and Ph$_2$CHSiH$_3$ produces the mononuclear silyl complex [Cp*Fe(CO)$_2${Si(H)$_2$CHPh$_2$}] (**1**) as a main product in 41% yield together with two silanediyl-bridged diiron complexes, *cis*- and *trans*-[Cp*$_2$(CO)$_2$Fe$_2$(μ-CO){μ-Si(H)CHPh$_2$}] (**2**), and [{Cp*Fe(CO)$_2$}$_2$]. The *trans*-**2** complex isomerizes to *cis*-**2** photochemically, but no *cis-trans* isomerization occurs thermally below 100 °C. Photolysis of [CpFe(CO)$_2$SiMe$_3$] or [CpW(CO)$_3$Me] in the presence of **1** produces novel unsymmetrical silanediyl-bridged complexes [Cp*Fe(CO)(μ-CO){μ-Si(H)CHPh$_2$}(CO)$_n$MCp] (**3**: M = Fe, n = 1; **4**: M = W, n = 2) in moderate yields. Complexes **3** and **4** have been characterized by X-ray diffraction analysis. To the best of our knowledge, complex **4** is the first example of silanediyl-bridged Fe-W complex. The Cp and Cp* rings are mutually *cis* with the dihedral angle of 78.7(2)° in complex **3** but they are *trans* with the dihedral angle of 13.1(6)° in complex **4**.





VII-H-3 Extremely Facile Arene Exchange on a Ruthenium(II) Complex Having a Novel Bis(silyl) Chelate Ligand (9,9-Dimethylxanthene-4,5-diyl)bis(dimethylsilyl) (Xantsil)

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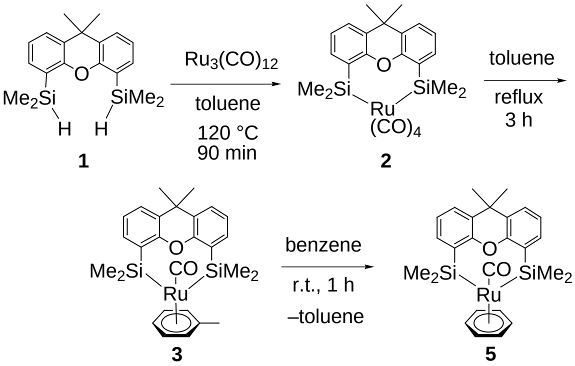
[*Organometallics* **18**, 2058 (1999)]

Heating a solution of 4,5-bis(dimethylsilyl)-9,9-dimethylxanthene (xantsilH_2) (**1**) and 0.4 molar equivalent of $Ru_3(CO)_{12}$ in toluene at 120 °C for 90 min afforded a ruthenium complex having a novel bis(silyl) chelate ligand (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl) (xantsil), *cis*-Ru(CO)$_4$(xantsil) (**2**), as a main product. The X-ray crystal structure analysis showed that the Ru-Si bonds in **2** (2.562(2) and 2.564(2) Å) represent the longest known Ru-Si bonds ever reported probably because of the intramolecular steric repulsion. Isolated **2** reacted with toluene on refluxing for 3 h to give *cis*-Ru(CO)(xantsil)(η^6-$C_6H_5CH_3$) (**3**) in 95% yield. When **3** was dissolved in benzene, the η^6-toluene ligand was cleanly substituted by the solvent at room temperature within 1 h to afford *cis*-Ru(CO)(xantsil)(η^6-C_6H_6) (**5**) quantitatively.



VII-H-4 Synthesis and Structures of Heterometallic Trinuclear Clusters [CpFe(CO)$_2$]$_2$(μ_3-S_2)W(CO)$_5$ and Cp_2Fe_2(CO)$_2$(μ-CO)(μ_3-S)W(CO)$_5$ and Kinetic Study of Migration of the W(CO)$_5$ Moiety in the Disulfido Complex

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Reaction of CpFe(CO)$_2$Br with an excess of NaSH in THF at room temperature resulted in formation of a brown solution. Addition of W(CO)$_5$(THF) after 2 h to the reaction mixture gave two heterometallic trinuclear clusters [CpFe(CO)$_2$]$_2$(μ_3-S_2)W(CO)$_5$ (**1**) and Cp_2Fe_2(CO)$_2$(μ-CO)(μ_3-S)W(CO)$_5$ (**2**) in 30 and 11% yields, respectively. X-ray crystal structures of both **1** and **2** were determined. Complex **1** is the first example of a trinuclear cluster connected by only one disulfido ligand in an η^1:η^1:η^1 fashion. Variable-temperature ^{1}H NMR spectroscopy of **1** clearly showed that the W(CO)$_5$ moiety is migrating between two sulfur atoms faster than the NMR time scale to make the two Cp ligands equivalent. A mechanism involving oxidative addition-reductive elimination of the S-S bond was proposed for this fluxional behavior.