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

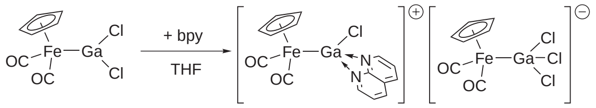
Synthesis of transition metal complexes with unprecedented bonds between a metal and a heavy main group element is one of current topics on inorganic chemistry. In this project, we have investigated the synthesis, structure, and reactivities of metal complexes containing metal-silicon and metal-gallium unsaturated bonding. We also investigated germylene-bridged diiron complexes having a triplet ground state.

VIII-J-1 Synthesis, Structure, and Reactivity of Cationic Base-Stabilized Gallyleneiron Complexes

UENO, Keiji[1]; WATANABE, Takahito[2]; OGINO, Hiroshi[3]
(*[1]IMS and Gunma Univ.; [2]Tohoku Univ.; [3]Univ. Air)*

[*Appl. Organomet. Chem.* **17**, 403–408 (2003)]

Addition of 2,2'-bipyridine (bpy) to an acetonitrile solution of dichlorogallyliron complex $FpGaCl_2$ (**1**: Fp = (η-C_5H_5)Fe$(CO)_2$) afforded almost quantitatively a salt consisting of a cationic base-stabilized gallylene complex $[FpGaCl \cdot bpy]^+$ ([**3a**]$^+$) and an anionic complex $[FpGaCl_3]^-$ ([**4**]$^-$). Reaction of Fp'$GaCl_2$ (Fp' = Fp (**1**), Fp* (**2**); Fp* = (η-C_5Me_5)Fe$(CO)_2$) with $NaBPh_4$ in the presence of a bidentate donor (Do_2) gave [Fp'GaCl·Do_2]BPh_4 where Do_2 was bpy or 1,10-phenanthroline (phen). These cationic complexes may be useful precursors for the synthesis of gallyleneiron complexes with various substituents on the gallium atom. Indeed, reaction of [Fp*GaCl·phen]BPh_4 ([**5b**]BPh_4) with NaS^{p}Tol or Me_3SiS^{p}Tol afforded the gallyleneiron complex [Fp*GaS^{p}Tol·phen]BPh_4 ([**6**]BPh_4), the first example of a gallium-transition metal complex having a thiolate group on the gallium atom. The molecular structures of [**5b**]BPh_4 and [**6**]BPh_4 were determined by single crystal X-ray diffraction.



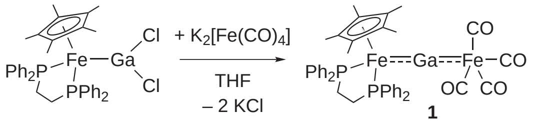
1 **3a** **4**

VIII-J-2 Synthesis and Structure of the First Dinuclear Complex Bridged by a Substituent-Free Gallium Atom

UENO, Keiji[1]; WATANABE, Takahito[2]; TOBITA, Hiromi[2]; OGINO, Hiroshi[3]
(*[1]IMS and Gunma Univ.; [2]Tohoku Univ.; [3]Univ. Air)*

[*Organometallics* **22**, 4375–4377 (2003)]

The first dinuclear complex bridged by a substituent-free gallium atom, Cp*Fe(dppe)(μ-Ga)Fe$(CO)_4$ (**1**, Cp* = η-C_5Me_5, dppe = $Ph_2PCH_2CH_2PPh_2$), was synthesized by the reaction of Cp*Fe(dppe)$GaCl_2$ with $K_2[Fe(CO)_4]$. Crystal structure analysis of complex **1** revealed that the geometry around the gallium atom is essentially linear and the Fe–Ga bonds are significantly shorter than that of usual single bonds. These structural features indicate that the Fe–Ga bonds bear significantly unsaturated character.



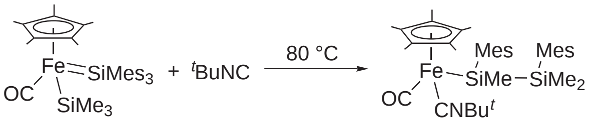
1

VIII-J-3 Direct Evidence for Extremely Facile 1,2- and 1,3-Group-Migrations on an $FeSi_2$ System

TOBITA, Hiromi[1]; MATSUDA, Akihisa[1]; HASHIMOTO, Hisako[1]; UENO, Keiji[2]; OGINO, Hiroshi[3]
(*[1]Tohoku Univ.; [2]IMS and Gunma Univ.; [3]Univ. Air)*

[*Angew. Chem., Int. Ed.* **43**, 221–224 (2004)]

Photolysis of [Cp'Fe$(CO)_2$Me] (**1a**: Cp' = η^5-C_5Me_5 (Cp*); **1b**: Cp' = η^5-C_5H_5 (Cp)) in the presence of $HSiMe_2SiMes_2Me$ (**2**; Mes = mesityl (2,4,6-trimethylphenyl)) produced the first donor-free silyl(silylene)iron complexes [Cp'Fe(CO)(=$SiMes_2$)$SiMe_3$] (**3a**: Cp' = Cp*, 60%; **3b**: Cp' = Cp, 38% yield, calculated by NMR spectroscopy). Complex **3a** was isolated as orange crystals in 40% yield, whereas isolation of **3b** was unsuccessful. When **3a** was heated to 80 °C for 6 h in the presence of ^{t}BuNC, a disilanyl complex [Cp*Fe(CO)(CN^{t}Bu)SiMesMeSiMesMe$_2$] (**4**) was isolated as a main product in 25% yield. These results provide the most straightforward evidence for extremely facile 1,2- and 1,3-group migrations of the substituents between two silicon atoms in silyl(silylene) complex systems.



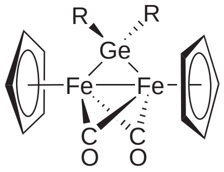
3a **4**

VIII-J-4 Synthesis and Characterization of Triplet Germylene-Bridged Diiron Complexes and Singlet Stannylene-Bridged Diiron Complexes

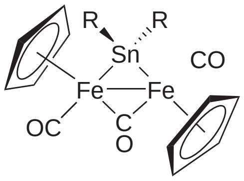
MOHAMED, Bahaa. A. S.[1]; KIKUCHI, Mami[1]; HASHIMOTO, Hisako[1]; UENO, Keiji[2]; TOBITA, Hiromi[1]; OGINO, Hiroshi[3]
(*[1]Tohoku Univ.; [2]IMS and Gunma Univ.; [3]Univ. Air)*

[*Chem. Lett.* **33**, 112–113 (2004)]

Photoreaction of CpFe(CO)$_2$Me with sterically congested R$_2$GeH$_2$ [R = 2,4,6-C$_6$H$_2$^{i}Pr$_3$ (Tip), 2,4,6-C$_6$H$_2$Me$_3$ (Mes)] afforded paramagnetic germylene-bridged diiron complexes having a triplet ground state, Cp$_2$Fe$_2$(μ-CO)$_2$(μ-GeR$_2$) (**3a**, R = Tip; **3b**, R = Mes), while the analogous reaction with R$_2$SnH$_2$ afforded diamagnetic complexes Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-SnR$_2$) (*trans*-**5a**, R = Tip; *trans*-**5b**, R = Mes). The structure of **3a** was determined by X-ray crystallography.



3: R = Tip, Mes



trans-**5**: R = Tip, Mes