VII-K 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 a metal-silicon unsaturated bonding and a metal-hydrogen-gallium 3c2e bonding. We also developed a versatile preparative method of anionic metal complexes $CpM(CO)_2^-$ (M = Fe, Ru).

VII-K-1 Synthesis of Self-Stabilized and Donor-Free Silyl(silylene)tungsten Complexes

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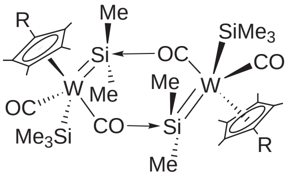
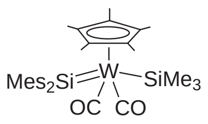
[*Organometallics* **21**, 1326–1328 (2002)]

Photolysis of Cp'W$(CO)_3$Me (**1a**: Cp' = η-C_5Me_5; **1b**: Cp' = η-C_5Me_4Et) in the presence of excess $HSiMe_2SiMe_3$ afforded a self-stabilized silyl(silylene)-tungsten complex with a dimeric structure, [Cp'W$(CO)_2(=SiMe_2)(SiMe_3)]_2$ (**2a**: Cp' = η-C_5Me_5; **2b**: Cp' = η-C_5Me_4Et), respectively. In contrast, photolysis of **1a** in the presence of $HSiMe_2SiMeMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$) resulted in the formation of the first donor-free silyl(silylene) complex with only alkyl and aryl substituents on the silicon atoms Cp'W$(CO)_2(=SiMes_2)(SiMe_3)$ (**3**).



2a: R = Me
2b: R = Et



3

VII-K-2 Synthesis of the First Gallane-Coordinated Transition Metal Complex

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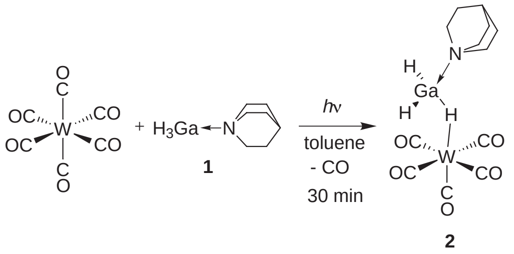
[*Organometallics* **21**, 2347–2349 (2002)]

The first gallane-coordinated metal complex $(OC)_5W(\eta^1\text{-}GaH_3\cdot$quinuclidine) (**2**) was synthesized by photolysis of a *ca.* 1:1 mixture of $W(CO)_6$ and quinuclidine-coordinated gallane $H_3Ga\cdot$quinuclidine (**1**) in toluene and by the reaction of $(OC)_5W$(THF) with 1 eq of gallane **1** in THF. X-ray crystal structure analysis of **2** revealed that gallane **1** is bound to the tungsten fragment *via* a W–H–Ga 3-center 2-electron bond.



VII-K-3 Convenient Preparation of Li[(η^5-C_5Me_5)M$(CO)_2$] (M = Ru, Fe) by the Reaction of (η^5-C_5Me_5)M$(CO)_2$H with *n*-BuLi

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[*J. Organomet. Chem.* **645**, 201–205 (2002)]

The anionic ruthenium and iron complexes Li[(η^5-C_5Me_5)M$(CO)_2$] (M = Ru (**1-Ru**), Fe (**1-Fe**)) were generated by deprotonation of the transition metal hydride (η^5-C_5Me_5)M$(CO)_2$H with *n*-BuLi in tetrahydrofuran (THF). The reaction proceeded at –45 °C immediately. Reactions of **1** with various electrophiles (Me_3SiCl, pTol$_2$HSiCl, Me_2SiCl_2, $MeSiCl_3$, $SiCl_4$, $Me_3SiSiMe_2Cl$, and Ph_2GeCl_2) afforded the corresponding nucleophilic substitution products (η^5-C_5Me_5)M$(CO)_2ER_3$ (E = Si, Ge) *via* salt-elimination.