

Transition metal complexes of Si analogue of π -allyl: Interesting Geometry, Bonding Nature, and Stability

(Kyoto University) O Mausumi Ray, Yoshihide Nakao, Hirofumi Sato, and Shigeyoshi Sakaki*

ray@qmst.mbox.media.kyoto-u.ac.jp

Silaallyl and silapropargyl, which are Si analogue of π -allyl and propargyl, respectively, are interesting species because they are the simplest of all conjugate systems including Si. Though silaallyl and silapropargyl would not be stable, the interaction with transition metal complex is expected to stabilize these species. Thus, the bonding nature of transition metal silaallyl and silapropargyl complexes is interesting. Recently, a tungsten η^3 -silaallyl complex $\text{Cp}^*(\text{CO})_2\text{W}(\eta^3\text{-Me}_2\text{SiCHCMe}_2)$ **A1** was isolated,¹ while similar tungsten η^3 -silapropargyl complex, $\text{Cp}^*(\text{CO})_2\text{W}(\eta^3\text{-Ph}_2\text{SiCC}^t\text{Bu})$ **B1**, was not. Complex **B1** was proposed as intermediate in the formation of $\text{Cp}^*(\text{CO})_2\text{W}(\text{CC}^t\text{Bu})(\text{SiPh}_2)$ **B2**.² Though **B2** was isolated, its similar vinyl analogue $\text{Cp}^*(\text{CO})_2\text{W}(\text{CHCMe}_2)(\text{SiMe}_2)$ **A2** was not.

We theoretically investigated bonding nature of $\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-H}_2\text{SiCHCH}_2)$ **1** in comparison to its carbon analogue, tungsten η^3 -allyl complex $\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-H}_2\text{CCHCH}_2)$ **1C** and the reason why **1** was isolated but similar $\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-H}_2\text{SiCCH})$ **3** was not.³ We also investigated conversion reaction of **1** to $\text{Cp}(\text{CO})_2\text{W}(\text{CHCH}_2)(\text{SiH}_2)$ **2** and that of **3** to $\text{Cp}(\text{CO})_2\text{W}(\text{CCH})(\text{SiH}_2)$ **4**,⁴ to make comparison between **1** and **3** and between **2** and **4**, where **1**, **2**, **3**, and **4** are models of **A1**, **A2**, **B1**, and **B2**, respectively. DFT, MP2 to MP4(SDTQ), and CCSD(T) methods were employed here.

By comparing the geometries and frontier orbitals of **1** and **1C**, we found that **1** is much different from **1C**; for instance, Si p orbital more participates in HOMO-2 and less in HOMO-5 than C p orbitals in **1**. Thus, **1** is understood to be between tungsten η^3 -vinylsilyl and η^3 -silaallyl complexes. Complex **1** is calculated to be much more stable than **2** by 21.0 kcal/mol, while **3** is less stable than **4** by 0.7 kcal/mol. These results are consistent with experimental results. These differences are interpreted, as follows: W-(η^3 -H₂SiCHCH₂) interaction is considerably strong in **1**. Moreover, W-vinyl and silylene-vinyl interactions are very weak in **2**. On the other hand, W-(η^3 -H₂SiCCH) interaction is weak in **3**. Moreover, W-acetylide and silylene-acetylide interactions are very strong in **4**. Thus, **1** is isolated but **2** is not, while **4** is isolated but **3** is not.

References:

- (1) Sakaba, H.; Watanabe, S.; Kabuto, C.; Kabuto, K. *J. Am. Chem. Soc.* **2003**, *125*, 2842.
- (2) Sakaba, H.; Yoshida, M.; Kabuto, C.; Kabuto, K. *J. Am. Chem. Soc.* **2005**, *127*, 7276.
- (3) Ray, M.; Nakao, Y.; Sato, H.; Sakaki, S. Submitted.
- (4) Ray, M.; Nakao, Y.; Sato, H.; Sakaba, H.; Sakaki, S. *J. Am. Chem. Soc.* **2006**, *128*, 11927.

