New Tungsten η^3-Silaallyl/Vinylsilyl, η^3-Silapropargyl/Alkynylsilyl, and Silylene Complexes. Theoretical Understanding of Bonding Nature

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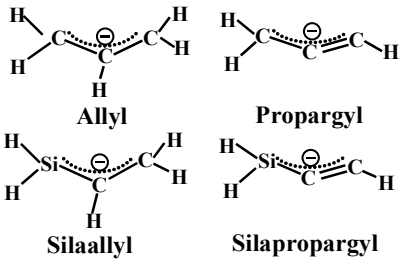
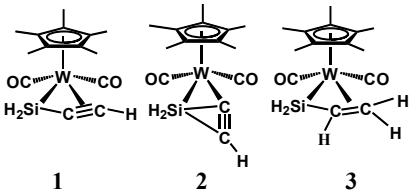
Silaallyl and silapropargyl species are silicon analogues of allyl and propargyl, respectively (Scheme 1). Recently, research on the transition metal (TM) silaallyl, silapropargyl, and silylene complexes gets momentum because of their importance as intermediates in the conversion process of various silicon materials, such as silicon-containing functional materials, polymers, and so on. They are also attractive research subject in theoretical/computational chemistry, because TM complexes of silaallyl and silapropargyl would have interesting bonding nature and electronic structure.



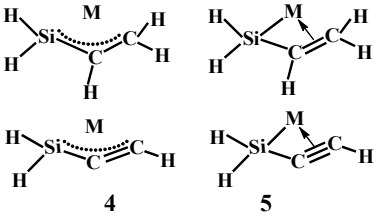
Scheme 1

We theoretically investigated the bonding nature and stability of tungsten η^3-silapropargyl complex $Cp(CO)_2W(\eta^3\text{-}H_2SiCCH)$ **1**, tungsten acetylide silylene complex $Cp(CO)_2W(CCH)(SiH_2)$ **2**, and tungsten η^3-silaallyl complex $Cp(CO)_2W(\eta^3\text{-}H_2SiCHCH_2)$ **3** (Scheme 2) using the DFT, MP4, and CCSD(T) methods with double zeta quality basis sets. Complexes **1** and **3** were proposed in experiments and expected to be intermediates in synthesis of various organosilicon compounds, and **2** was isolated.[1,2]



Scheme 2

Our theoretical work reveals fundamental understanding of the electronic structures of **1**, **2**, and **3**, and the interaction between the TM complex and silicon containing species, such as silaallyl and silapropargyl, as follows: Though the non-bonding π orbital (HOMO) of TM-silaallyl and silapropargyl complexes are similar to those of TM-allyl and propargyl complexes, the π orbital (next HOMO) is much different from those of the TM-allyl and propargyl complexes, indicating that the electronic structures of the TM-silaallyl and silapropargyl complexes are intermediate between completely conjugated system **4** and non-conjugated system **5** (Scheme 3).[3,4] Complex **2** exhibits also interesting CT interactions.[3] These new bonding interaction arises from the characteristic features of silicon conjugated system. Detailed discussion will be presented in poster.



Scheme 3

References

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2. H. Sakaba, M. Yoshida, C. Kabuto, K. Kabuto, *J. Am. Chem. Soc*. **127**, 7276 (2005).
3. M. Ray, Y. Nakao, H. Sato, H. Sakaba, S. Sakaki, *J. Am. Chem. Soc*. **128**, 11927 (2006).
4. M. Ray, Y. Nakao, H. Sato, S. Sakaki, *Organometallics* **26**, 4413 (2007).