η³-Silapropargyl/Alkynylsilyl and Silylene Acetylide Complexes of [Cp(CO)₂M]⁺ (M=W or Mo): Theoretical Study of their Interesting Bonding Nature and Stability

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Introduction

Silapropargyl, Si analogue of propargyl, is interesting because it is the simplest of all conjugate systems including Si; note conjugate system of Si has been rare. Although it would not be stable, interaction with the transition metal complex is expected to stabilize this species. Thus, bonding nature of the transition metal η³-silapropargyl complex is worthy of investigation. However, the transition metal η³-silapropargyl complex has not been synthesized so far, to our best knowledge. Recently, a tungsten η³-silapropargyl complex, Cp*(CO)₂W(η³-Ph₂SiCC^tBu) **A** (Scheme 1), was proposed for the first time as intermediate in the formation reaction of Cp*(CO)₂W(CC^tBu)(SiPh₂) **B**, but it was not isolated.[1] However, similar tungsten η³-silaallyl complex, Cp*(CO)₂W(η³-Me₂SiCHCMe₂) **C**, was synthesized recently.[2] Bonding nature of **B** is interesting because it is not clear from experimental study whether **B** is a tungsten acetylide silylene complex (Scheme 2A) or a tungsten complex involving silacyclopropenyl group (Scheme 2B). Also, we theoretically investigated **A**, **B**, and **C**.[3,4]

A   **B**

Scheme 1

(A)   **(B)**

Scheme 2

Here, we will present detailed theoretical study on the bonding nature and relative stability of Cp(CO)₂M(η³-R²₂SiCCR¹) **1** and Cp(CO)₂M(CCR¹)(SiR²₂) **2**, where M=W or Mo, R¹=H, Me, ^tBu, CF₃, or COOMe, and R²=H, Me, or F. **1** and **2** are models of **A** and **B**, respectively. Our purposes are to present a clear understanding of the bonding nature of **1** and **2** and how the stability and bonding nature of **1** and **2** depend on substituents and metal center.

Computational Details

Geometries were optimized by the DFT method with B3PW91 functional. Energy was evaluated with the DFT, MP4(SDTQ), and CCSD(T) methods. Because of large size of the system, energy was calculated by the DFT method for various substituents. Double zeta basis sets were used for metal and ligand atoms. Gaussian 03 program package was used.
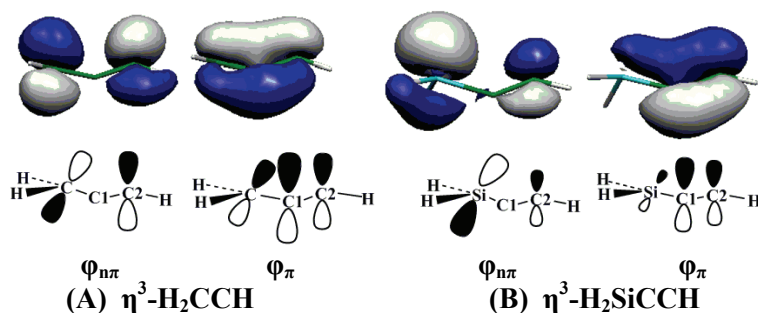
Results and Discussion

Frontier orbitals of the η³-H₂SiCCH group of **1** is much different from that of the η³-

(A) η³-H₂CCH   **(B) η³-H₂SiCCH**
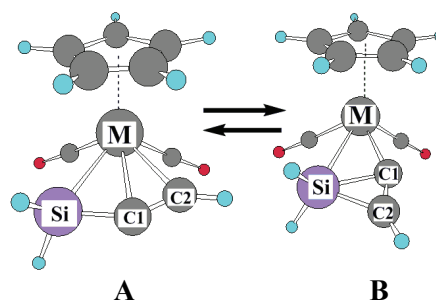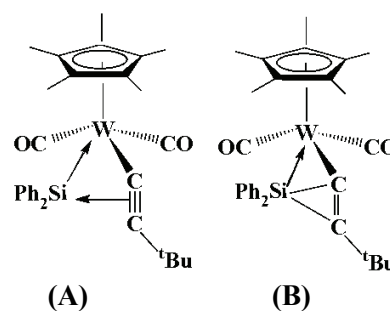
Scheme 3

propargyl group, as shown in Scheme 3A and B. For instance, Si p orbital more contributes in non-bonding π orbital ($\varphi_{n\pi}$) and less in π orbital (φ_π) of η^3-H$_2$SiCCH group than C p orbitals (Scheme 3B).[3] Thus, **1** is understood to be a species between tungsten η^3-silapropargyl and tungsten η^3-alkynylsilyl complex.

Complex **2** is understood to be a tungsten acetylide silylene complex in which strong charge transfer (CT) occurs from sp^2 lone pair orbital of silylene to π^* orbital of acetylide and from π orbital of acetylide to empty p orbital of silylene (see HOMO-2 and HOMO-6 in Scheme 4).[3] Despite this strong CT between silylene and acetylide moieties silacyclopropenyl group is not formed in **2** because of the bonding interaction between the sp^2 lone pair of silylene and the empty d orbital of tungsten center, as shown in Scheme 4.

HOMO-2   **HOMO-6**
Scheme 4

Our computations, as shown in Table 1, clearly show that the stability of η^3-silapropargyl/alkynylsilyl form **1** is larger in molybdenum complexes, while the stability of acetylide silylene form **2** is larger in tungsten complexes. The stability of **1** moderately increases by introduction of π electron-donating group such as F on Si (see Table 1). Introduction of electron-withdrawing group such as CF$_3$ on C2 and use of C$_5$F$_5$ in place of Cp also increase the stability of **1**. Largest stability of **1** is observed when F and CF$_3$ are introduced on Si and C2 atoms, respectively, in (C$_5$F$_5$)(CO)$_2$Mo complex, indicating the possibility that molybdenum η^3-silapropargyl/alkenylsilyl complex (C$_5$F$_5$)(CO)$_2$Mo(η^3-F$_2$SiCCCF$_3$) is isolated. Introduction of bulky electron-donating group such as ^{t}Bu on C2 increases the

Table 1. Relative stability ($\Delta E)^{a)}$ of Cp(CO)$_2$M(R$^2_2$SiCCR^1) to Cp(CO)$_2$M(CCR^1)(SiR$^2_2$).

R^1 on C2	R^2 on Si	Method	ΔE (kcal/mol)	
			M=W	**M=Mo**
H	H	DFT	-4.9	-1.9
		CCSD(T)	-0.7	+2.9
		DFT	(-2.6)	(+0.5)
^{t}Bu	H	DFT	-5.2	-2.3
COOMe	H	DFT	-5.0	-1.8
H	Me	DFT	-4.2	-0.7
CF$_3$	H	DFT	-4.1	-0.7
Me	F	DFT	-3.9	-1.8
Me	H	DFT	-3.5	-0.4
Me	Me	DFT	-2.6	+0.4
H	F	DFT	-2.0	+0.1
COOMe	F	DFT	-1.1	+0.6
CF$_3$	F	DFT	+1.1	+2.6
		DFT	(+1.3)	(+2.8)

$^{a)}$ ΔE is energy difference between acetylide silylene form and η^3-silapropargyl/alkenylsilyl form. In parentheses values are for Cp*=C$_5$F$_5$

stability of the acetylide silylene form **2**. Thus, ^{t}Bu on C2 and H on Si in (C$_5$H$_5$)(CO)$_2$W complex is the best to isolate the acetylide silylene form. The key factors for the larger stability of molybdenum η^3-silapropargyl/alkynylsilyl complex Cp(CO)$_2$Mo(η^3-F$_2$SiCCCF$_3$) are summarized as follows: Mo-acetylide bond is considerably weak in the acetylide silylene form. The CF$_3$ group on C2 moderately increases the Mo-(η^3-R$^2_2$SiCCR^1) interaction in the η^3-silapropargyl/alkynylsilyl form more than the M-CCR^1 interaction in the acetylide silylene form. The F substituent on Si considerably weakens the CT interaction from the sp^2 lone pair orbital of silylene to the π^* orbital of acetylide. Thus, the stability of the η^3-silapropargyl/alkynylsilyl form Cp(CO)$_2$Mo(η^3-F$_2$SiCCCF$_3$) is larger than the acetylide silylene form Cp(CO)$_2$Mo(CCCF$_3$)(F$_2$Si).

References

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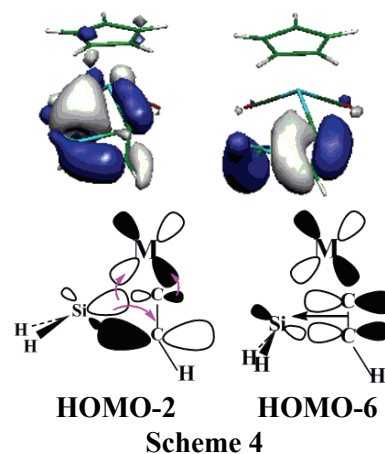(4) Ray, M.; Nakao, Y.; Sato, H.; Sakaki, S. *Organometallics*. in press.