

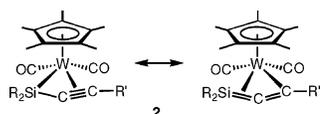
$\eta^1:\eta^2$ -Alkynyl-Bridged W–Si Complexes: Formation, Structure, and Reaction with Acetone

Hiroyuki Sakaba,* Mako Yoshida, Chizuko Kabuto, and Kuninobu Kabuto

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

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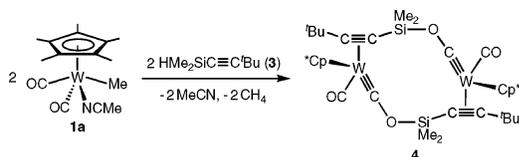
Activation of the Si–H bonds of hydrosilanes by transition-metal complexes is a versatile synthetic route to transition-metal silyl complexes.¹ Recently, we showed the formation of an η^3 -silaallyl complex by the reaction of the labile tungsten complex *cis*-Cp*(CO)₂(MeCN)WMe (**1a**; Cp* = η^5 -C₅Me₅) with alkenylhydrosilane HR₂SiCH=CR'₂ via Si–H bond activation.² As a further utilization of this methodology to synthesize a novel tungsten–silicon-bonded complex, we have studied the reaction of **1a** with alkynylhydrosilane HR₂SiC≡CR' in the expectation of the formation of η^3 -silapropargyl/silaallenyl complex **2**. Rosenthal



and co-workers have previously reported the formation of Cp₂Ti(η^2 -*trans*-HMe₂SiC≡C'Bu), having an agostic Si–H–Ti interaction, by the reaction of Cp₂Ti(η^2 -Me₃SiC≡CSiMe₃) with HMe₂SiC≡C'Bu (**3**).³ They made the interesting observation that a hydrido η^3 -silaallenyl structure contributed considerably at low temperatures and in the solid state. In our system using **1a** and **3**, a formal dimeric complex of the expected η^3 -silapropargyl/silaallenyl complex was isolated, and further studies using HPh₂SiC≡C'Bu led to the formation of a unique monomeric alkynyl-bridged W–Si complex. In this communication, we describe the formation and structures of these dimeric and monomeric complexes and the reaction of the latter with acetone.

The reaction of **1a** with **3** in toluene afforded the dinuclear complex **4** (46%), a dimer of the expected Cp*(CO)₂W–(SiMe₂CC'Bu) species, as a yellow solid after removal of the volatiles and recrystallization of the residue in pentane at –60 °C (Scheme 1).⁴ The molecular structure of **4** was determined by X-ray analysis and is depicted in Figure 1. The molecule has C₂ symmetry, and one carbonyl oxygen atom of each monomeric unit is bound to each silicon atom. The W1–C9 distance (1.826(3) Å) is considerably shorter than the W1–C10 distance (1.959(4) Å) of the terminal carbonyl ligand and is comparable to W–C triple bond distances (1.81–1.82 Å) in carbyne complexes of the type Cp(CO)₂W≡CR.⁵ The Si1–O1 bond (1.707(3) Å) is at the upper end of the range for Si–O single bonds (1.58–1.70 Å).⁶ These structural features indicate that **4** has a siloxycarbyne structure.

Scheme 1



The formation of **4** suggested that the dimerization was caused by nucleophilic attack of the carbonyl oxygen of the monomeric

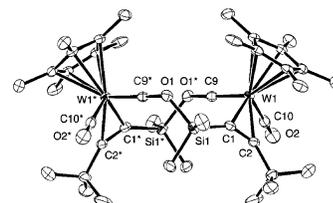
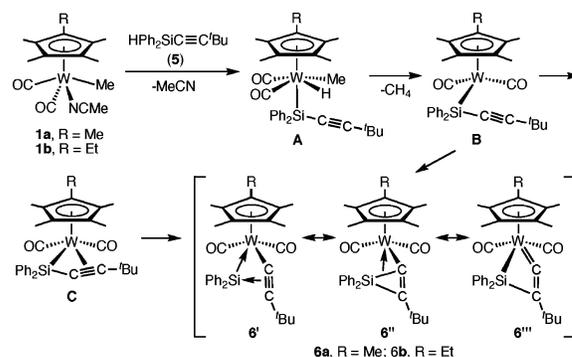


Figure 1. Molecular structure of **4**.

Scheme 2



species on the silicon of another molecule. We then carried out the reactions of **1a** and its Cp' derivative **1b** (Cp' = η^5 -C₅Me₄Et) with HPh₂SiC≡C'Bu (**5**) having bulkier phenyl groups on the silicon atom in order to prevent this dimerization. The reactions gave monomeric species; however, their structures were revealed to be the unprecedented alkynyl-bridged W–Si complexes **6a** and **6b**, which were isolated as air-sensitive orange–brown solids in 63 and 64% yields, respectively (Scheme 2).

X-ray quality crystals were obtained by recrystallization of **6b** from pentane, and the X-ray analysis showed a unique structure with an alkynyl ligand bridged between the tungsten and silicon atoms in an $\eta^1:\eta^2$ -coordination mode (Figure 2). The W1–C1 bond distance (2.050(7) Å) is comparable to W–C(alkynyl) bond distances (2.05–2.09 Å) in di- and polynuclear complexes containing a Cp*(CO)₂W(μ - $\eta^1:\eta^2$ -C≡CR) fragment.⁷ The Si1–C1 (1.937(7) Å) and Si1–C2 (2.009(7) Å) distances in the three-membered ring skeleton are significantly longer than the Si–C distances (1.80–1.86 Å) of silacyclopropenes,⁸ whereas the C1–C2 distance (1.270(9) Å) is shorter than their C=C distances (1.32–1.37 Å) and is intermediate between those of standard C=C and C≡C bonds. The W1–Si1 bond distance (2.567(2) Å) is in the range of the tungsten–silyl bonds (2.533–2.633 Å) in the structurally related silyltungsten complexes Cp*(CO)₂(L)WSiR₃ (L = PR'₃, pyridine) and is longer than the tungsten–silylene bond in a typical lone-pair-donor-stabilized silylene complex Cp*(CO)₂(H)W=SiPh₂·Py (2.445 Å).⁹ These observations suggest that a dative W←Si interaction between the 16e Cp*(CO)₂W(C≡C'Bu) fragment and the :SiPh₂ silylene ligand, which is stabilized by π -complexation of the alkynyl moiety to the silylene center, may be essential for

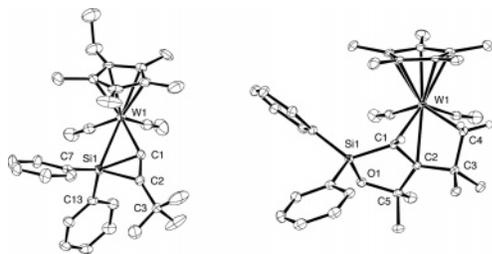


Figure 2. Molecular structures of **6b** (left) and **7** (right).

the W–Si bond, leading to a novel formulation: an intramolecularly π -bond-donor-stabilized silylene complex **6'** with a σ,π -bridging alkynyl ligand.¹⁰ The importance of the interaction between a silylene ligand and a C–C multiple bond has been shown in recent studies. Tilley proposed a new mechanism for hydrosilylation catalyzed by the ruthenium silylene complex $[\text{Cp}^*(\text{Pr}_3\text{P})(\text{H})_2\text{Ru}=\text{Si}(\text{H})\text{Ph}\cdot\text{Et}_2\text{O}][\text{B}(\text{C}_6\text{F}_5)_4]$, in which addition of the Si–H bond of the silylene ligand to alkene is a key step.¹¹ Hall subsequently reported a theoretical support for the mechanism and revealed that the initial step is the formation of a π -complex between the silylene center and alkene followed by insertion of the alkene into the Si–H bond.¹²

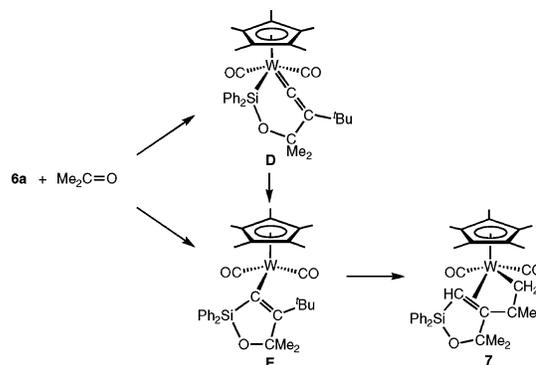
Consideration of the resonance contribution of **6** leads to additional interesting contributors **6''** and **6'''**. The former is a silacycloprenyl complex with an α -C–Si agostic interaction involving the strained C–Si bond, and the latter has a four-membered cyclic tungstaallene structure.¹³ The ²⁹Si resonances of δ –48.1 for **6a** and –47.8 for **6b** at –70 °C, which are relatively close to the very high field shifted ²⁹Si resonances (around δ –100) characteristic of silacycloprenes,¹⁴ suggest a bonding interaction between the silicon and two alkynyl carbon atoms; hence, the contribution from **6'''** is minor. We may view **6** as an intermediate state between complexation of the triple bond to the silylene center and coordination of the C–Si bond of the silacycloprenene ring to the metal center. To obtain information on the best formulation for **6**, theoretical studies are necessary.

A possible mechanism for the formation of **6** is shown in Scheme 2. Complex **1** dissociates the coordinated acetonitrile to form the coordinatively unsaturated species, which activates the Si–H bond of **5** to give intermediate **A**. Reductive elimination of methane forms unsaturated silyl complex **B**, from which two routes leading to **6** are conceivable: 1,2-alkynyl migration followed by the coordination of the alkynyl ligand to the resulting silylene center or the direct coordination of the alkynyl ligand to the metal center to form **C** followed by isomerization to **6** via σ – π interchange of the coordination mode. The σ – π interchange has often been proposed in dinuclear complexes with a μ - η^1 : η^2 -alkynyl ligand.¹⁵

When **6a** was treated with acetone (1.5 equiv) in toluene-*d*₈, the sole formation of chelate-type alkyl–alkene complex **7** (98%) was observed over the course of 2 days, with no intermediates detected by ¹H NMR spectroscopy (Scheme 3). The structure of **7** was determined by X-ray analysis (Figure 2). A plausible mechanism is shown in Scheme 3 and involves nucleophilic attack of the carbonyl oxygen of acetone at the silicon center and C–C bond formation between the carbonyl carbon and the β -carbon of the alkynyl ligand to give cyclic silyl vinylidene intermediate **D**. 1,2-Silyl migration in **D** to give **E** followed by C–H activation of the ^tBu group would lead to the formation of **7**. Alternatively, the direct formation of **E** by acetone insertion into the silacycloprenene-like framework of **6a** is also possible. Acetone insertion into the Si–C bond of a silacycloprenene has been demonstrated.¹⁶

In summary, a novel η^1 : η^2 -alkynyl-bridged W–Si complex was synthesized for the first time and was found to undergo the insertion

Scheme 3



of acetone into the silicon–alkynyl linkage. Future studies, including theoretical studies, will be directed toward elucidating the formation mechanism, isomerism, and bonding of this W–Si complex and toward exploring its reactivity.

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Supporting Information Available: Experimental details and spectroscopic data (PDF). X-ray crystallographic data for **4**, **6b**, and **7** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- When the reaction of **1a** with **3** was monitored by ¹H NMR spectroscopy, several species were observed prior to the formation of **4**. One such species may be ascribed to a monomeric species equilibrated with **4** on the basis of the observation that a higher complex concentration favors **4**. Because of this phenomenon, attempts at its spectroscopic characterization and isolation were unsuccessful.
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- Complex **6** can be viewed as a tungstapropargyl/tungstaallenyl silicon compound as suggested by a reviewer, showing an interesting structural comparison with $\text{Cp}_2\text{Ti}(\eta^2\text{-trans-HMe}_2\text{SiC}\equiv\text{C}^t\text{Bu})$. We thank the reviewer for insightful comments on its structure and the formation mechanism of **7**.
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