ORGANOMETALLICS

Synthesis, Structure, and Bonding Nature of Ethynediyl-Bridged Bis(silylene) Dinuclear Complexes of Tungsten and Molybdenum

Hiroyuki Sakaba,^{*,†} Hiroyuki Oike,[†] Masaaki Kawai,[†] Masato Takami,[†] Chizuko Kabuto,[†] Mausumi Ray,^{‡,#} Yoshihide Nakao,[‡] Hirofumi Sato,[‡] and Shigeyoshi Sakaki^{*,§}

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

[‡]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

[§]Fukui Institute for Fundamental Chemistry, Kyoto University, Nishihiraki-cho, Takano, Sakyo-ku, Kyoto 606-8103, Japan

Supporting Information

ABSTRACT: Reactions of Ph₂HSiC \equiv CSiHPh₂ with 2 equiv of the labile complexes $Cp^*(CO)_2M(NCMe)Me$ (1a, M = W; 2, M = Mo; $Cp^* = \eta^5 - C_5Me_5$) gave the novel CC-bridged dinuclear complexes $Cp^{*}(CO)_{2}M(SiPh_{2})(\mu-CC)(SiPh_{2})M(CO)_{2}Cp^{*}(5,$ M = W; 6, M = Mo), whose molecular structures were determined by X-ray crystallography. The CC bridge interacts with both the metal and silylene centers of two Cp*(CO)₂M(SiPh₂) fragments to form two M-Si-C three-membered-ring skeletons which are linked nearly perpendicularly to each other. The W-Si bond distances of 5 are comparable to those of typical base-stabilized tungsten silylene complexes. The C-C bond distance is much longer than a typical C=C triple-bond distance and is similar to a typical C=C double-bond distance. The bonding nature and electronic structure of 5 were disclosed by a DFT study of the model complex $Cp(CO)_2W(SiH_2)(\mu$ -CC)(SiH_2)W(CO)_2Cp (5M; Cp = η^5 -C₅H₅). This study demonstrates that 5M is an ethynediyl-bridged bis(silylene) dinuclear tungsten



complex which contains various charge transfer (CT) interactions between the tungsten (W), silylene (SiH₂), and ethynediyl (CC), as follows. (1) CTs occur from the lone pairs (φ^{CC}_{lp}) and π orbital (φ^{CC}_{π}) of the ethynediyl to the unoccupied d orbital (d^{W}_{unoc}) of the W and from the occupied d orbital (d^{W}_{occ}) of the W to the π^* orbital ($\varphi^{CC}_{\pi^*}$) of the ethynediyl. (2) CTs occur from the lone pair orbital (φ^{Si}_{lp}) of the silylene to d^{W}_{unoc} and from d^W_{occ} to the empty p orbital (φ^{Si}_{p}) of the silylene. (3) CT occurs from the lone pair orbital (φ^{Si}_{lp}) of the silylene to d^W_{unoc} and from d^W_{occ} to the empty p orbital (φ^{Si}_{p}) of the silylene. (3) CT occurs from φ_{μ}^{CC} to φ_{p}^{Si} , which leads to considerably strong Si–C bonding interactions and a considerably large elongation of the C–C distance. The mixing of φ_{π}^{CC} into $\varphi_{\pi^*}^{CC}$ induces π orbital polarization of the CC moiety in one plane and a reverse π orbital polarization in the perpendicular plane. These polarizations in addition to the CT from d^{W}_{occ} to $\varphi^{CC}_{\pi^*}$ also participate in the C–C bond weakening of the ethynediyl. Reaction of 1a with 1 equiv of Ph₂HSiC≡CSiHPh₂ afforded a mixture of the mononuclear acetylide – silylene complex $Cp^{*}(CO)_{2}W(CCSiHPh_{2})(SiPh_{2})$ (7) and dinuclear complex 5. Addition of 1a to the mixture resulted in the conversion of 7 to 5, indicating the intermediacy of 7 in the formation of 5 in the 1:2 reaction of the bis(silyl)acetylene and 1a. A similar 1:1 reaction using molybdenum complex 2 strongly suggests the formation of an equilibrium mixture of the acetylide-silylene complex $Cp^{*}(CO)_{2}Mo(CCSiHPh_{2})(SiPh_{2})$ (8) and silapropargyl/alkynylsilyl complex $Cp^{*}(CO)_{2}Mo$ - $(\eta^3$ -Ph₂SiCCSiHPh₂) (9) in addition to dinuclear complex 6. Mononuclear complexes 8 and 9 were converted to 6 upon reaction with 2. The fluxional behavior of dinuclear complexes 5 and 6 in solution is also described.

INTRODUCTION

The Si-H bond activation of hydrosilanes by transition-metal complexes is a versatile method for producing complexes with transition-metal-silicon bonds.¹ Recently, this method has been widely applied for synthesizing a variety of base-stabilized²⁻⁶ and base-free⁷⁻¹³ transition-metal silylene complexes. Silylene complexes¹⁴ are interesting research targets in coordination chemistry, organometallic chemistry, synthetic chemistry, and theoretical chemistry because of their interesting bonding natures, electronic structures, and important roles as intermediates in various metalcatalyzed transformation reactions of organosilicon compounds. In this regard, silvlene complexes have been investigated in many experimental $^{2-16}$ and theoretical works 17,18 to understand their structural features, bonding natures, electronic structures, and reaction behavior.

In the course of our synthetic studies of tungsten and molybdenum complexes with novel silicon-containing ligands using the labile complexes $(\eta^5 - C_5 Me_4 R)(CO)_2 M(NCMe) Me$ (1a, M = W, R = Me; 1b, M = W, R = Et; 2, M = Mo, R = Me) and hydrosilanes, ¹⁹ the unique tungsten silylene complexes (η^{5} -C₅- Me_4R)(CO)₂W(CC^tBu)(SiPh₂) (3a, R = Me; 3b, R = Et) were recently obtained via Si-H bond activation of $Ph_2HSiC \equiv C^tBu$ by 1a,b (Scheme 1).^{19b} The novel bonding nature of these complexes

Received: February 2, 2011 Published: August 10, 2011



was revealed by a theoretical study of the model complex Cp-(CO)₂W(CCH)(SiH₂) (**3M**, Cp = η^{5} -C₅H₅), as follows. It is an acetylide–silylene complex which involves two kinds of charge transfer (CT) interactions between the silylene and acetylide moieties; one is the CT from the lone pair orbital of the silylene to the π^* orbital of the acetylide, and the other is the CT from the π orbital of the acetylide to the empty p orbital of the silylene (Scheme 1).^{18a} These interactions demonstrate an intriguing relationship to the reaction of silylene with acetylene to form silacyclopropene, and the (SiH₂)(CCH) moiety of **3M** can be viewed as an intermediate species trapped by the W center in the silacyclopropene formation reaction.²⁰

A subsequent theoretical study on the relative stability of the acetylide-silylene complex $Cp(CO)_2M(CCH)(SiH_2)$ (M=W, Mo) and its structural isomer, the silapropargyl/alkynylsilyl complex $Cp(CO)_2M(\eta^3-H_2SiCCH)$, showed that the tungsten center favors the acetylide-silylene complex, whereas the molybdenum center favors the silapropargyl/alkynylsilyl complex.^{18c} This theoretical prediction about the molybdenum system was recently realized by the successful synthesis of $Cp^*(CO)_2Mo$ - $(\eta^3 - Ph_2SiCC^tBu)$ (4) by reacting 2 with $Ph_2HSiC \equiv C^tBu$ (Scheme 1).^{19c} In the acetylide-silylene and silapropargyl/ alkynylsilyl complexes, one of the two π systems in the acetylide and alkynyl moieties is involved in bonding interactions. In considering the availability of two π systems in the acetylide, we were interested in a μ -ethynediyl ligand. This electronically flexible C₂ ligand can bridge two metal fragments using two π systems in several ways, as shown below, and may be used to form a novel dinuclear framework composed of metal, silicon, and carbon atoms in combination with two metal and two silicon centers.

Ethynediyl-bridged dinuclear complexes exhibit characteristic geometries, bonding natures, electronic structures, and physicochemical properties.²¹⁻⁴² Also, they are building blocks for the synthesis of bare carbon chains stabilized by transition-metal complexes.^{21a,b,41} In this regard, various ethynediyl-bridged dinuclear complexes have been synthesized and investigated in many experimental²¹⁻⁴⁰ and theoretical works.^{22b,38,41,42} Three possible bonding modes have been proposed so far: namely, the acetylenic form $L_nM-C\equiv C-ML_n$ the cumulenic form $L_nM\equiv C-C\equiv ML_n$ and the dimetalla-1,3-butadiyne form $L_nM\equiv C-C\equiv ML_n$.^{21b,38,41} Among these three valence bond descriptions, most of the synthesized complexes contain the acetylenic structure.²²⁻³² The cumulenic structure has been found in a few titanium, ^{31,33} tantalum, ³⁴ ruthenium, ³² and manganese³⁵ complexes, and the dimetalla-1,3-butadiyne structure is limited to tungsten, ^{36–39} molybdenum, ⁴⁰ and manganese³⁵ complexes.

Here, we examined the reaction of Ph₂HSiC \equiv CSiHPh₂ with 2 equiv of **1a** or **2** and found the formation of the ethynediylbridged dinuclear bis(silylene) complexes Cp^{*}(CO)₂M(SiPh₂)-(μ -CC)(SiPh₂)M(CO)₂Cp^{*} (**5**, M = W; **6**, M = Mo). Our present study provides a unique opportunity to investigate the interactions of two π systems of the ethynediyl with two metal and two silylene centers. We report their synthesis, solid-state structure, dynamic behavior in solution, and formation mechanism. A detailed theoretical study on the bonding nature and electronic structure of Cp(CO)₂W(SiH₂)(μ -CC)(SiH₂)W(CO)₂-Cp (**5M**), a model complex of **5**, is also described.

RESULTS AND DISCUSSION

1. Synthesis and Structure of $Cp^*(CO)_2M(SiPh_2)(\mu$ -CC)-(SiPh₂)M(CO)₂Cp* (5, M = W; 6, M = Mo). The reaction of Ph₂HSiC=CSiHPh₂ with 2 equiv of the acetonitrile complex $Cp^*(CO)_2W(NCMe)Me$ (1a) in toluene occurred at room temperature to give the dinuclear complex $Cp^*(CO)_2W(SiPh_2)$ - $(\mu$ -CC)(SiPh₂)W(CO)₂Cp* (5) as an air-sensitive orange solid in 55% isolated yield (Scheme 2).⁴³ The liberation of methane and acetonitrile was confirmed by ¹H NMR comparison with their authentic samples in an NMR tube reaction. A similar reaction using the molybdenum complex $Cp^*(CO)_2Mo(NCMe)$ -Me (2) afforded the corresponding dimolybdenum complex 6 in 51% yield.

Single crystals of **5** and **6** were grown from toluene/hexane and toluene/pentane solutions, respectively, and subjected to X-ray crystal analysis. In the tungsten complex **5** (Figure 1), two Cp*(CO)₂W(SiPh₂) fragments are linked by the ethynediyl bridge, which interacts with both of the tungsten and silicon centers, and two W–Si–C three-membered-ring skeletons are arranged almost perpendicularly to each other, as shown by the dihedral angle Si1–C1–C2–Si2 = 88.0(3)°. Each tungsten center adopts a highly distorted four-legged piano-stool geometry with acute Si–W–C angles of Si1–W1–C1 (47.55(12)°), Si1–W1–C3 (63.77(15)°), Si2–W2–C2 (48.35(13)°), and Si2–W2–C6 (61.94(14)°). The W–Si bond distances (W1–Si1 = 2.4801(14) Å, W2–Si2 = 2.4773(13) Å) in **5** are considerably shorter than that (2.567(2) Å) in the mononuclear acetylide–silylene complex **3b**^{19b} and are in the range of Scheme 2



W-Si bond distances (2.45-2.51 Å) in base-stabilized silylene tungsten complexes, 2c,3a,15a suggesting the increased partial double-bond character of the W-Si bond in 5 compared with that in 3b. The increased silylene character is also demonstrated by the sum of the three X-Si-Y angles (X, Y = W and C(ipso) of the two phenyl groups on Si): 356.1° about Si1 and 356.7° about Si2. These values are larger than the corresponding angle (348.3°) in 3b and close to the expected value (360°) for sp² hybridization. The W-C(ethynediyl) bond distances (W1-C1 = 2.089(5) Å, W2-C2 = 2.068(4) Å) are in the range of W-C (alkynyl) bond distances (2.05-2.09 Å) in di- and polynuclear complexes containing a Cp*(CO)₂W(μ - η ¹: η ²-CCR) fragment^{44,45} and are somewhat longer than the W-CC^tBu bond distance (2.050(7) Å) in 3b. Notably, the C1-C2 bond distance of 1.343(6) Å is significantly elongated from the C–C triple-bond distance of 1.208(5) Å in $Ph_2HSiC \equiv CSiHPh_2^{46}$ to a typical C-C double-bond distance.

The overall structural features of the molybdenum analogue 6 (Figure 2) resembles well those of 5, as shown by its characteristic angles: the dihedral angle $Si1-C1-C2-Si2 = 87.6(5)^\circ$, the sum of the three X-Si-Y angles (X, Y = Mo and C(ipso) of the two phenyl groups on Si) of 356.2° about Si1 and 356.9° about Si2, and acute Si-Mo-C angles of Si1-Mo1-C1 $(47.86(17)^{\circ})$, Si1-Mo1-C3 (63.2(3)°), Si2-Mo2-C2 (48.29(16)°), and Si2-Mo2-C6 (61.8(2)°). A comparison of the bond distances of the M-Si-C three-membered-ring skeletons between 5 and 6 revealed a contrasting difference in the M-Si and M-C bond distances. The Mo–Si bond distances (Mo1–Si1 = 2.4646(19)Å, Mo2–Si2 = 2.4562(19) Å) in 6, which are comparable to the Mo-Si bond distances (2.4439(14)-2.5008(9) Å) of basestabilized silylene molybdenum complexes with a Cp^(*)- $(CO)_2$ Mo fragment,^{2a,8é} are 0.015–0.02 Å shorter than the W-Si bond distances (W1-Si1 = 2.4801(14) Å, W2-Si2 = 2.4773(13) Å) in 5, whereas the Mo-C(ethynediyl) bond distances (Mo1-C1 = 2.120(6) Å, Mo2-C2 = 2.089(6) Å) in 6 are 0.03-0.02 Å longer than the W-C(ethynediyl) bond distances (W1-C1 = 2.089(5) Å, W2-C2 = 2.068(4) Å) in 5. Though no such clear differences are found in the bond distances of Si1–C1 (1.876(5) Å for 5 vs 1.886(7) Å for 6) and Si2–C2 (1.898(5) Å for 5 vs 1.889(6) Å for 6) considering the standard deviations, these Si-C bond distances are elongated considerably compared with the Si-C(sp) bond distance (1.833(3) Å) in $Ph_2HSiC \equiv CSiHPh_2^{46}$ and are longer than or comparable to the Si-C(phenyl) bond distances (1.863(7)-1.877(5) Å) in **5** and **6**. Given the small difference between the bond distances of W=Si $(2.3850(12) \text{ Å})^{8a}$ and Mo=Si $(2.3872(7) \text{ Å})^{8e}$ in the base-free

silylene complexes $Cp^{*}(CO)_{2}M(SiMe_{2})(SiMe_{3})$ (M = W, Mo), it is interesting to note the somewhat large differences between the W-Si and Mo-Si bond distances and the opposite tendency in the variation of the M-Si and M-C(ethynediyl)bond distances described above. These observations suggest that the M-C(ethynediyl) interaction seems to be balanced with the strength of the metal-silvlene interaction. For dinuclear complexes 5 and 6, the possible contribution of several resonance structures is conceivable: bis(silylene)-type structure A, bis-(carbene)-type structure B, 1,4-disilabutadienyl-bridged structure C,⁴⁷ and 1,4-disilabutatriene-bridged structure D^{48,49} (Scheme 2). Considering the relatively high silylene character of 5 and 6, A is suggested to be a major contributor. However, the double-bond-like distance of the C1-C2 bond in 5 and 6 may imply some interesting contributions of B-D. A detailed discussion on the bonding nature and electronic structure of a model complex of 5 based on the DFT calculations is described below.

2. Mechanistic Investigation of the Formation of Dinuclear Complexes 5 and 6. To obtain mechanistic information on the formation of dinuclear complex 5, the 1:1 reaction of 1a with $Ph_2HSiC \equiv CSiHPh_2$ was investigated. Toluene- d_8 was vacuumtransferred into an NMR tube containing an equimolar mixture of **1a** and the bis(silyl)acetylene at -196 °C, and the mixture was warmed to room temperature. When the ¹H NMR spectrum was measured after 5 min, a new set of Cp* and SiH signals ascribed to the mononuclear complex $Cp^{*}(CO)_{2}W(CCSiHPh_{2})(SiPh_{2})$ (7) were observed at 1.69 and 5.41 ppm, respectively, in addition to the signals of 5 (7:5 = 76:24) (Scheme 3). On a preparative scale, a relatively pure, orange solid of 7 was isolated, and the structure was characterized on the basis of variable-temperature NMR spectra in THF- d_8 . The ²⁹Si{¹H} NMR spectrum at room temperature showed a single signal at -39.2 ppm due to the SiHPh₂ group, while the spectrum at -70 °C exhibited two signals at -39.0 and -46.7 (¹ $J_{WSi} = 41$ Hz) ppm. Assignment of the former signal to $SiHPh_2$ is supported by its ${}^{1}H-{}^{29}Si$ correlation with a SiH signal at 4.97 ppm in the ¹H-²⁹Si HMQC spectrum, and the latter signal was assigned to WSiPh2. This temperature-dependent observation is probably due to the interconversion between 7 and a trace amount of its silapropargyl/ alkynylsilyl isomer; see below for the corresponding molybdenum system. In the ${}^{1}\text{H}-{}^{13}\text{C}$ HMBC spectrum at -70 °C, two signals showing correlations with the SiH signal were observed at 186.5 and 137.7 ppm and assigned to acetylide carbon atoms. These characteristic ²⁹Si and ¹³C signals of 7 (²⁹Si, -46.7 (¹ $J_{WSi} =$ 41 Hz) ppm; ¹³C, 186.5 and 137.7 ppm) are close to those of the SiCC framework (²⁹Si, -40.9 (¹ $J_{WSi} = 41$ Hz) ppm; ¹³C, 178.9





Figure 1. ORTEP drawings of (A) the whole structure and (B) the two $Cp^*(CO)_2W(SiPh_2)C$ fragments of 5. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W1-Si1 = 2.4801(14), W1-C1 = 2.089(5), W2-Si2 = 2.4773(13), W2-C2 = 2.068(4), Si1-C1 = 1.876(5), Si1-C7 = 1.864(5), Si1-C13 = 1.877(5), Si2-C2 = 1.898(5), Si2-C19 = 1.865(5), Si2-C25 = 1.867(5), C1-C2 = 1.343(6); Si1-W1-C1 = 47.55(12), Si2-W2-C2 = 48.35(13), W1-Si1-C1 = 55.23(15), W1-Si1-C7 = 122.36(16), W1-Si1-C13 = 124.17(18), C7-Si1-C13 = 109.6(2), W2-Si2-C2 = 54.49(13), W2-Si2-C19 = 125.84(16), W2-Si2-C25 = 121.44(14), C19-Si2-C25 = 109.4(2), W1-C1-Si1 = 77.22(18), W1-C1-C2 = 151.1(3), W2-C2-Si2 = 77.16(17), W2-C2-C1 = 165.1(4).

and 147.3 ppm) in the acetylide—silylene tungsten complex $Cp^*(CO)_2W(CCSiMe_3)(SiPh_2)$.^{19d} When the 76:24 mixture of 7 and 5 was treated with an amount of 1a equimolar with the amount of 7 in toluene- d_8 , 7 was consumed to give 5 in 79% yield based on 7, thereby demonstrating the intermediacy of 7 in the formation of 5 from the bis(silyl)acetylene and 2 equiv of 1a.

The 1:1 reaction using the molybdenum analogue 2 led to intriguing observations (Scheme 3). Similar to the case for the reaction with 1a described above, the room-temperature ¹H NMR spectrum of the reaction mixture in toluene- d_8 contained a set of Cp^{*} and SiH signals at 1.64 and 5.44 ppm in addition to signals attributed to dinuclear complex 6 in a composition ratio of 82:18. From a preparative reaction, a yellow solid was isolated, and its room-temperature ¹H NMR spectrum showed the same Cp^{*} and SiH signals as above. When variable-temperature ¹H NMR spectra were recorded in THF- d_8 , the Cp^{*} and SiH signals (1.73 and 5.20 ppm at room temperature) decoalesced into two sets of signals upon



(B)

Figure 2. ORTEP drawings of (A) the whole structure and (B) the two $Cp^*(CO)_2Mo(SiPh_2)C$ fragments of **6**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–Si1 = 2.4646(19), Mo1–C1 = 2.120(6), Mo2–Si2 = 2.4562(19), Mo2–C2 = 2.089(6), Si1–C1 = 1.886(7), Si1–C7 = 1.864(7), Si1–C13 = 1.863(7), Si2–C2 = 1.889(6), Si2–C19 = 1.872(7), Si2–C25 = 1.872(7), C1–C2 = 1.322(9); Si1–Mo1–C1 = 47.86(17), Si2–Mo2–C2 = 48.29(16), Mo1–Si1–C1 = 56.46(19), Mo1–Si1–C7 = 122.1(2), Mo1–Si1–C13 = 124.7(3), C7–Si1–C13 = 109.4(3), Mo2–Si2–C2 = 55.63(19), Mo2–Si2–C19 = 126.1(3), Mo2–Si2–C25 = 121.5(2), C19–Si2–C25 = 109.3(3), Mo1–C1–Si1 = 75.7(3), Mo1–C1–C2 = 151.2(5), Mo2–C2–Si2 = 76.1(3), Mo2–C2–C1 = 164.6(5).

cooling to -80 °C: 1.76 and 4.90 ppm for the major component and 1.62 and 5.80 ppm for the minor component in a ratio of 55:45. The SiH region of the variable-temperature spectra is shown in Figure 3. In the ${}^{29}Si{}^{1}H$ NMR spectrum, only a single signal appeared at -38.0 ppm at room temperature, whereas two sets of signals were observed at -90 °C: -39.0 (SiHPh₂) and -14.4 (MoSiPh₂) ppm for the major component and -24.0 $(SiHPh_2)$ and 55.2 $(MoSiPh_2)$ ppm for the minor component. The assignment of the SiHPh₂ signals was based on ¹H-²⁹Si correlations in the ¹H-²⁹Si HMQC spectrum. Additional structural information was obtained by the ¹H-¹³C HMBC spectrum at -90 °C, which showed signals at 190.5 and 143.7 ppm that correlated with the major SiH signal and those at 90.9 and 103.0 ppm that correlated with the minor SiH signal. The characteristic ¹H, ²⁹Si, and ¹³C signals of the major component (¹H, 4.90 ppm; ²⁹Si, -14.4 ppm; ¹³C, 190.5 and 143.7 ppm) were similar to those of 7 (¹H, 4.97 ppm; ²⁹Si, -46.7 ppm; ¹³C, 186.5

(A)

Scheme 3



Figure 3. SiH region of the variable-temperature ¹H NMR spectra of 8 and 9 in THF- d_8 .

and 137.7 ppm), taking into account the difference in metal centers. The ²⁹Si and ¹³C signals of the minor component (²⁹Si, 55.2 ppm; ¹³C, 90.9 and 103.0 ppm) were relatively close to those of the silapropargyl/alkynylsilyl complex Cp*(CO)₂Mo- $(\eta^3$ -Ph₂SiCCⁱPr) (²⁹Si, 46.2 ppm; ¹³C, 51.4 and 129.0 ppm).^{19c} Relatively large differences in the ¹³C chemical shifts were ascribed to the different substituents (SiHPh2 and 'Pr) at the alkynyl carbon atom. These observations strongly suggest the interconversion between the acetylide-silylene complex Cp*(CO)₂Mo-(CCSiHPh₂)(SiPh₂) (8, major) and silapropargyl/alkynylsilyl complex $Cp^*(CO)_2Mo(\eta^3-Ph_2SiCCSiHPh_2)$ (9, minor) for the dynamic behavior, and it is consistent with the aforementioned theoretical finding that the molybdenum center favors the silapropargyl/alkynylsilyl complex more than does the tungsten center.^{18c} The observation of a single ²⁹Si resonance at room temperature is explained by the chemical shift differences between the SiHPh₂ and SiPh₂ signals. In fast interconversion on the NMR time scale, a small chemical shift difference between the SiHPh₂ signals (-39.0 ppm for 8 and -24.0 ppm for 9) leads to a sharp, coalesced signal. In contrast, a large difference between the SiPh₂ signals (-14.4 ppm for 8 and 55.2 ppm for 9) causes significant signal broadening and results in no detectable signals. The reaction of the mixture of 8 and 9 with 2 afforded the dinuclear complex 6 in quantitative yield (Scheme 3). Although the differences in reactivity between 8 and 9 toward 2 are not clear, the formation of 6 is suggested to occur via Si-H bond activation of 8, which would require less steric hindrance around the SiHPh₂ group and a smaller structural change in the conversion to 6 than would be expected in 9.



3. Dynamic Behavior of Dinuclear Complexes 5 and 6. Despite the asymmetric solid-state structures of 5 and 6, when their ¹H NMR spectra were measured at room temperature, a single Cp* signal was observed in each spectrum, suggesting the existence of dynamic processes. The variable-temperature ¹H NMR spectra of **6** in CD_2Cl_2 showed interesting spectral changes (Figure 4). When the temperature was lowered to -90 °C, the sharp Cp* signal broadened and decoalesced into two signals at 1.69 and 1.58 ppm, and broad aromatic signals became sharp and well-resolved. Similar behavior was observed in the ${}^{13}C{}^{1}H{}$ NMR spectra (Figure 5A,B); a single C_5Me_5 signal was split into two signals at 10.3 and 9.9 ppm at -90 °C. In accord with the decoalescence of the Cp* signals in the ¹H and ¹³C NMR spectra, two ²⁹Si signals were observed at 5.3 and -5.0 ppm at -90 °C, whereas no signals were detected at room temperature, probably due to their significant broadening. For the aromatic carbon signals, only one set of broad signals was observed at 136.7, 135.4 (v br), 130.4, and 127.8 ppm in the room-temperature ${}^{13}C{}^{1}H{}$ NMR spectrum (Figure 5A), whereas approximately 13 signals appeared at -90 °C (Figure 5B). In addition, the room-temperature spectrum showed two broad signals at 240.1 and 230.2 ppm, which were assigned to the ethynediyl and CO ligands, respectively (Figure 5A). At -90 °C, the former decoalesced into two signals at 241.2 and 239.8 ppm and the latter split into four signals at 231.5, 230.6, 228.8, and 226.6 ppm (Figure 5B). Assignment of the four signals to the CO ligands was confirmed by the observation of their increased intensities compared to those of the signals at 241.2 and 239.8 ppm in the ${}^{13}C{}^{1}H$ NMR spectrum of



Figure 5. ¹³C{¹H} NMR spectra of **6** in CD₂Cl₂ (A) at 27 °C and (B) -90 °C and (C) the low-field region of **6*** at -90 °C. The asterisks mark the signals of toluene contained as a crystal solvent.



Figure 6. ${}^{13}C{}^{1}H$ NMR spectra of 5 in CD_2Cl_2 (A) at 27 °C and (B) at -90 °C. The asterisks mark the signals of toluene contained as a crystal solvent.

¹³CO-enriched **6**^{*} (Figure 5C). Complex **6**^{*} was prepared by the reaction of ¹³CO-enriched **2**^{*} with $Ph_2HSiC \equiv CSiHPh_2$. Thus, the NMR spectra corresponding to the solid-state structure of **6** were obtained by low-temperature measurements.

In the variable-temperature ¹H NMR spectra of 5, considerable broadening of the Cp* signal occurred upon cooling to -90 °C, although decoalescence was not observed (see the Supporting Information, Figures S1 and S2). On the other hand, the variable-temperature ${}^{13}C{}^{1}H$ NMR spectra showed decoalescence of the C₅Me₅ and ethynediyl signals (Figure 6); two decoalesced signals were observed at 10.2 and 10.0 ppm for the former and 235.2 and 231.6 ppm for the latter at -90 °C (Figure 6B), similar to the spectrum of 6 (Figure 5B). Three CO signals were observed at 223.6, 221.5, and 220.7 ppm with a relative intensity of 2:1:1, and the first signal was attributable to the coincidental overlap of two signals. The number of aromatic carbon signals was increased, and they were considerably broad compared to those at room temperature. The low-temperature $^{13}C\{^{1}H\}$ NMR spectrum of 5 resembled that of 6, although differences in the signal widths were observed; the sharper, decoalesced signals for 6 suggest a slower dynamic process at -90 °C. However, the room-temperature spectrum of 5 showed



two CO signals at 223.5 and 222.0 ppm and two sets of phenyl carbon signals at 137.9, 137.2, 136.3, 134.3, 130.7, 129.8, 128.2, and 127.4 ppm (Figure 6A), in contrast to the single CO signal and one set of phenyl carbon signals in the corresponding spectrum of 6 (Figure 5A). This observation indicates the possibility of another dynamic process that operates faster in 6 at room temperature. Cis-cis interconversion by pseudorotation⁵² around the metal centers is a likely dynamic process in 5 and 6, which are composed of two four-legged piano-stool type fragments. This process may cause stereochemical inversion (site exchange of the silylene and ethynediyl ligands) at the metal centers to lead to their similar dynamic behavior, and another process would be required to explain the difference observed in their room-temperature ${}^{13}C{}^{1}H$ NMR spectra. Although some changes in their coordination mode might be related to this difference, as suggested from the contrasting variable-temperature observations for mononuclear tungsten complex 7 and molybdenum complexes 8 and 9, more detailed studies are necessary to elucidate the entire mechanism, including investigation of intramolecular dynamic processes of closely related mononuclear acetylidesilylene and silapropargyl/alkynylsilyl complexes.

4. Bonding Nature and Electronic Structure of the Ethynediyl-Bridged Bis(silylene) Dinuclear Tungsten Complex Cp(CO)₂W(SiH₂)(µ-CC)(SiH₂)W(CO)₂Cp (5M). 4.1. Optimized Geometries of **5M**, Its Isomer $Cp(CO)_2(SiH_2)W - C = C - W(SiH_2)$ -(CO)₂Cp (10) without the Si---C Interaction, the Dicarbido-Bridged Dinuclear Tungsten Complex $(MeO)_3W \equiv C - C \equiv W(OMe)_3$ (**11**), and the Tungsten Carbyne Complex $Cp(CO)_2W \equiv CH$ (12). The geometries of the CC and SiPh₂ moieties of 5 are considerably different from those of 3b, as described above. Thus, it is worth investigating the bonding nature of 5. (i) Which bonding mode of the acetylenic form $W-C \equiv C-W$, the cumulenic form W=C=C=W, and the dimetalla-1,3-butadiyne form W=C-C=W is involved in 5? (ii) Can the Si-C-C-Si moiety of 5 be characterized as the deprotonated 1,4-disilabutadiene [Ph₂Si=C- $C=SiPh_2]^{2-}$ or the 1,4-disilabutatriene $Ph_2Si=C=C=SiPh_2$ (C or D in Scheme 2)? (iii) Is a bonding interaction formed between the Si and C atoms? In this section, we theoretically investigated $Cp(CO)_2W(SiH_2)(\mu$ -CC)(SiH_2)W(CO)_2Cp (5M, Cp = η^{5} -C₅- H_5) with the DFT method, where **5M** was employed as a model of **5**.

For a clear understanding of the bonding nature of **5M**, we also theoretically investigated the model ethynediyl-bridged bis-(silylene) dinuclear tungsten complex $Cp(CO)_2(SiH_2)W-C \equiv C-W(SiH_2)(CO)_2Cp$ (**10**), in which the CC and SiH₂ groups take positions opposite to each other; in other words, no interaction exists between them (Scheme 4). The typical dicarbido-bridged



Figure 7. Optimized geometries (determined by the DFT(B3PW91)/BS-I method) of (A) $Cp(CO)_2W(SiH_2)(\mu$ -CC)(SiH_2)W(CO)_2Cp (5M), (B) $Cp(CO)_2(SiH_2)W-C\equiv C-W(SiH_2)(CO)_2Cp$ (10), (C) (MeO)₃W $\equiv C-C\equiv W(OMe)_3$ (11), (D) $Cp(CO)_2W\equiv CH$ (12), and (E) $Cp(CO)_2W-(CCH)(SiH_2)$ (3M). Bond lengths are given in Å, along with the Wiberg bond indices in parentheses (from DFT(B3PW91)/BS-II NBO calculations). 3M was reported in ref 18a.

dinuclear tungsten complex $(MeO)_3W\equiv C-C\equiv W(OMe)_3$ (11) and the mononuclear tungsten carbyne complex $Cp(CO)_2W=CH$ (12) were also investigated here for comparison of **5M** with 11 and 12 (Scheme 4). Complex 10 is not unusual, because the similar ethynediyl-bridged dinuclear tungsten complex $Cp-(CO)_3W-C\equiv C-W(CO)_3Cp$ was experimentally isolated;²⁶ note that the silylene may be viewed as being similar to a CO ligand, since the silylene has a lone pair and an empty p orbital as does the CO. Complexes 11 and 12 are models of experimentally isolated (^tBuO)_3W\equiv C-C\equiv W(O^tBu)_3^{36-38} and $CpL_2W\equiv CR$ $(L = CO, P(OMe)_3$ and R = Ph, Me),⁵³respectively.

The optimized geometry of 5M (Figure 7) agrees well with the experimental geometry of 5, as shown in Table 1. The W-Si distance in 5M is somewhat shorter than that of the mononuclear tungsten acetylide-silylene complex $Cp(CO)_2W(CCH)(SiH_2)$ $(3M)^{18a}$ (Figure 7 and Table 1). The angle α between the lone pair of the SiH₂ group and the W–Si bond is 11° in 5M, which is much smaller than that (35°) of 3M (see Scheme 5 for the definition of the angle α). This small angle indicates the lone pair of the SiH₂ does not deviate very much from the W-Si axis. Also, the W-Si bond index is moderately larger in 5M than in 3M; see Figure 7 for the Wiberg bond indices. In 10, the interaction between the SiH₂ and CC moieties is absent because the SiH₂ moiety takes a position trans to the CC moiety (Figure 7). The W—Si distance of 10 is somewhat shorter than that of 5M by 0.10 Å, and the W–Si bond index is about 2 times larger than that of 5M. All these results indicate that the W–Si bonding interaction is moderately stronger in 5M than in 3M but considerably weaker than in 10 and that the SiH₂ moiety interacts with both of the W and the CC moieties in 5M. The weaker W-Si bond in 5M in comparison to that in 10 is an indication of the presence of a bonding interaction between the SiH₂ and CC moieties in 5M, as will be discussed below in more detail.

Table 1. Selected Optimized Parameters^{*a*} of Cp(CO)₂W(SiH₂)-(μ -CC)(SiH₂)W(CO)₂Cp (5M), Cp(CO)₂(SiH₂)W-C≡C-W(SiH₂)(CO)₂Cp (10), (MeO)₃W≡C-C≡W(OMe)₃ (11), Cp(CO)₂W≡CH (12), and Cp(CO)₂W(CCH)(SiH₂) (3M) and Experimental Parameters of Cp*(CO)₂W(SiPh₂) (μ -CC)(SiPh₂)W(CO)₂Cp* (5)

	5M	5	10	11	12	$3M^b$
W1-Si1	2.485	2.4801(14)	2.387			2.616
W2-Si2	2.492	2.4773(13)	2.387			
W1-C1	2.043	2.089(5)	2.104	1.781	1.804	2.014
W2-C2	2.034	2.068(4)	2.105	1.781		
Si1-C1	1.881	1.876(5)				1.968
Si2-C2	1.890	1.898(5)				
Si1-C2	2.908					1.957
Si2-C1	2.827					
C1-C2	1.337	1.343(6)	1.242	1.378		1.299
W1-Si1-C1	54.0	55.23(15)				49.7
W2-Si2-C2	53.0	54.49(13)				
W1-C1-C2	152.0	151.1(3)	179.0	180.0		152.1
W2-C2-C1	159.0	165.1(4)	179.2	179.8		
^a The DFT (B3PW91)/BS-I method was employed. Bond lengths are						
given in angstroms and bond angles in degrees. ^b Reference 18a.						

The W–C distance in **5M** is moderately shorter than in **10** and somewhat longer than in **3M**. However, it is considerably longer than the W–C double-bond distance (about 1.9 Å)⁵⁴ and much longer than the W–C triple-bond distances of **11** and **12**. Also, the W–C bond index is somewhat larger in **5M** than in **10**, is similar to that of **3M**, and is much smaller than in **11** and **12**. All these results rule out the possibility that **5M** involves a W–C Scheme 5





Figure 8. Geometries of $H_2SiCCSiH_2$ (13) and $[H_2SiCCSiH_2]^{2-}$ (13-an). Bond lengths are given in angstroms and bond angles in degrees. Wiberg bond indexes (from DFT(B3PW91)/BS-II NBO calculations) are given in parentheses. For 13d and 13d-an, the geometry was optimized except for the SiCC angle and SiCCSi dihedral angle, which were taken to be the same as those of 5M. The geometries of 13 and 13-an were optimized by the DFT(B3PW91)/BS-I method at triplet and singlet states, respectively.

multiple bond. The WCC angle is 156° in **5M**, while it is about 180° in **10**, including a typical W–ethynediyl bond. Also, the WCCW dihedral angle is 89° in **5M**, while it is 24° in **10**. These results suggest that the W–C bond of **5M** is much different from that of a pure ethynediyl complex.

The C1-C2 distance of **5M** is considerably longer than that of **10**, somewhat longer than that of **3M**, and somewhat shorter than that of **11**. Consistent with the bond distance, the C1-C2 bond index is considerably smaller in **5M** than in **3M** and much smaller than in **10**, but moderately larger than in **11**. This C1-C2 distance of **5M** is similar to that of a C-C double bond and considerably longer than that of the 1,4-disilabutatriene H₂Si=C=C=SiH₂ (**13**), which is a silicon analogue of the butatriene H₂C=C=C=CH₂ (Figure 8).⁵⁵ The CC bond index of **5M** is between those of C-C single and C=C double bonds and is much smaller than that of **13** (Figure 8).⁵⁵ From all these results, it is concluded that the C1-C2 bond of **5M** is much

weaker than those of the pure ethynediyl complex 10 and 1,4disilabutatriene 13.

The Si1-C1 and Si2-C2 distances of **5M** are considerably shorter than the Si-C1 distance of **3M**, but the Si1-C2 and Si2-C1 distances of **5M** are much longer than the Si-C2 distance of **3M** (Figure 7 and Table 1). The Si1-C1 and Si2-C2 bond indices of **5M** are somewhat larger than the Si-C1 and Si-C2 bond indices of **3M**. On the other hand, the Si1-C2 and Si2-C1 bond indices (0.065 and 0.075, respectively) are very small in **5M**, as expected from the geometry of **5M**. These Si1-C1 and Si2-C2 distances of **5M** are similar to a Si-C single bond, and their bond indices are somewhat smaller than that of the Si-C single bond.⁵⁶

It is worth comparing the bond distances and bond indices among the H₂SiCCSiH₂ moieties of 5M, 1,4-disilabutatriene $H_2Si=C=C=SiH_2$ (13), and its dianion $[H_2SiCCSiH_2]^{2-}$ (13an) (Figure 8), where the geometries of 13 and 13-an were optimized at the triplet and singlet states, respectively.⁵⁷ The Si-C1 and Si-C2 distances of 13 and 13-an are moderately shorter than the Si1-C1 and Si2-C2 distances of 5M, while the C1–C2 distances of 13 and 13-an are considerably shorter than that of 5M. Consistently, the Si-C1 and Si-C2 bond indices of 13 and 13-an are somewhat larger and the C1–C2 bond index is considerably larger than those of 5M. Hence, the Si1-C1 and Si2-C2 bonds of 5M are somewhat weaker and the C1-C2 bond of 5M is considerably weaker than those of 13 and 13-an. All these results indicate that the Si1-C1 and Si2-C2 bonding interactions of 5M can be understood to be a Si-C single bond. It is noted that the SiCCSi dihedral angle is 89° in 5M but 180° in 13 and 13-an, indicating that the SiCCSi moiety of 5M is considered not to be a disilabutatriene. For a clearer understanding, we calculated $H_2SiCCSiH_2$ (13d) and $[H_2SiCCSiH_2]^{2-1}$ (13d-an), whose SiCC angle and SiCCSi dihedral angle were taken to be the same as those of 5M, but the other moieties were optimized at the triplet and singlet states, respectively (see Figure 8). Apparently, the Si-C bond indices are somewhat larger and the C1–C2 bond index is considerably larger in both 13d and 13dan than in 5M, as shown in Figure 8. These results indicate that the $H_2Si-C-C-SiH_2$ moiety of **5M** is much different from that of 13d and 13d-an, suggesting that various CT interactions are formed between the SiH₂, CC, and W moieties in 5M to significantly change the electronic structure of the H₂SiCCSiH₂ moiety in 5M, as will be discussed below in detail. We also calculated the 1,4-disila-1,3-butadiene H₂Si=CH-CH=SiH₂ (14), which is a silicon analogue of 1,3-butadiene, $H_2C=CH-$ CH=CH₂, and the deprotonated 1,4-disilabutadiene [H₂SiC- $CSiH_2$ ²⁻ (14-an) (see the Supporting Information, Figure S9). The Si-C and C-C bond indices of 14 and 14-an are much different from those of 5M, suggesting that the H₂Si- $C-C-SiH_2$ moiety of **5M** is different from that of the deprotonated disilabutadiene (see the Supporting Information for the details).

The W atomic and its d orbital populations of **5M** are similar to those of **3M** but somewhat smaller than those of **10** (Table 2). The electron population of the SiH₂ moiety is moderately smaller in **5M** than in **3M** but much smaller than in **10**, indicating that the SiH₂ moiety of **5M** is much different from that of the pure silylene complex **10**. The electron population of the CC moiety is considerably larger in **5M** than in **10**, **3M**, and acetylene (HC=CH).⁵⁸ These results indicate that the CC moiety of **5M** is different from those of the pure ethynediyl complex **10** and the acetylide—silylene complex **3M**. It is also noted that the

Table 2. NBO^{*a*} Populations of Several Important Atoms and Groups in $Cp(CO)_2W(SiH_2)(\mu$ -CC)(SiH₂)W(CO)₂Cp (5M), $Cp(CO)_2(SiH_2)W-C\equiv C-W(SiH_2)(CO)_2Cp$ (10), and $Cp(CO)_2W(CCH)(SiH_2)$ (3M)

	5M	10	3M	
W	74.214	74.373	74.240	
d	5.879	5.958	5.874	
Si	13.022	13.207	13.070	
SiH ₂	15.322	15.564	15.350	
C1	6.493	6.265	6.186	
C2	6.464	6.296	6.563	
CC	12.957	12.560	12.749	
^a DFT(B3PW91)/BS-II NBO calculations.				

population of the CC moiety of **5M** is somewhat larger than those of **13** and **13d-an**,⁵⁹ while it is somewhat smaller than in **13d** and **13-an**.⁵⁹ The population of the SiH₂ moiety of **5M** is considerably smaller than those of **13**, **13d**, **13-an**, and **13d-an**.⁵⁹ These populations of the CC and SiH₂ moieties of **5M** are considerably different from those of the deprotonated disilabutadiene $[H_2SiCCSiH_2]^{2-}$ (**14-an**) (see the Supporting Information for details). From these results, it is concluded that the $H_2Si-C-C-SiH_2$ moiety of **5M** is neither a disilabutatriene nor a disilabutadiene dianion and the C-C moiety has a significant population on the π^* orbital.

4.2. MO Analyses and Population in Fragment MOs. To get a clear picture of the bonding interactions, we inspected the MOs of **5M** (Figure 9) and we analyzed the MOs by representing them with a linear combination of the MOs of fragments, using eq 1,^{60,61} where **5M** is considered to consist of five moieties, as shown in Scheme 6.

$$\psi_{i}(ABCDE) = \sum_{j} a_{ij}\varphi_{j}(A) + \sum_{k} b_{ik}\varphi_{k}(B) + \sum_{l} c_{il}\varphi_{l}(C) + \sum_{m} d_{im}\varphi_{m}(D) + \sum_{n} e_{in}\varphi_{n}(E)$$
(1)

 $\psi_i(\text{ABCDE})$ represents the *i*th MO of the total system ABCDE, $\varphi_j(A)$ is the *j*th MO of fragment $[\text{Cp}(\text{CO})_2\text{W}]_A^+$, $\varphi_k(B)$ is the *k*th MO of the fragment $(\text{SiH}_2)_B$, $\varphi_l(C)$ is the *l*th MO of fragment $[\text{CC}]^{2-}_{C}$, $\varphi_m(D)$ is the *m*th MO of the fragment $(\text{SiH}_2)_D$, and $\varphi_n(E)$ is the *n*th MO of the fragment $[\text{Cp}(\text{CO})_2\text{W}]_E^+$, where the suffixes A–E correspond to the moieties A–E shown in Scheme 6. a_{ij} , b_{ik} , c_{ib} , d_{im} , and e_{in} are expansion coefficients of $\varphi_j(A)$, $\varphi_k(B)$, $\varphi_l(C)$, $\varphi_m(D)$, and $\varphi_n(E)$, respectively. We evaluated the electron population of the fragment MO by eq 2

$$\rho_j(\mathbf{A}) = \sum_{i}^{occ} [a_{ij}^2 + \sum_{k} a_{ij} b_{ik} S_{jk} + \sum_{l} a_{ij} c_{il} S_{jl} + \sum_{m} a_{ij} d_{im} S_{jm} + \sum_{n} a_{ij} e_{in} S_{jn}]$$
(2)

where $\rho_j(A)$ represents how much electron population $\varphi_j(A)$ possesses in the total system ABCDE and S_{jk} is the overlap integral between $\varphi_j(A)$ and $\varphi_k(B)$. The sum of the populations of all MOs of the fragment A is the same as the sum of the Mulliken atomic populations in the fragment A.

Important MOs of $[Cp(CO)_2W]^+$ are LUMO+2, LUMO+1, LUMO, HOMO, and HOMO-1, which mainly consist of the

d orbitals of the W center. They are named $\varphi_{LUMO+2}(W)$ etc. hereafter; see Figure 10A for these MOs. In SiH₂, the HOMO and LUMO play important roles to form CT interactions in **5M**. The LUMO mainly consists of an empty p orbital, and the HOMO is a lone pair orbital (Figure 10B). The LUMO and HOMO are named φ_{p}^{Si} and φ_{lp}^{Si} respectively. In $[CC]^{2-}, \pi^*, \pi,$ and lone pair orbitals play important roles in forming CT interactions. The degenerate LUMOs are two π^* orbitals, which are perpendicular to each other. They are named $\varphi_{\pi1^*}^{CC}$ and $\varphi_{\pi2^*}^{CC}$, respectively (Figure 10C). HOMO and HOMO-2 are two lone pair orbitals, which are named φ_{lp1}^{CC} and φ_{lp2}^{CC} , respectively. The degenerate HOMO-1's are two π orbitals, which are named $\varphi_{\pi1}^{CC}$ and φ_{p}^{CC} .

HOMO, HOMO-1, HOMO-2, and HOMO-3 of 5M are doubly degenerate; see Figure 9 and Figure S11 in the Supporting Information for these MOs. As shown by the weights of fragment MOs of Scheme 7A, the HOMO of 5M mainly consists of the occupied d orbital of W2 (d_{occ}^W) which overlaps with $\varphi^{CC}_{\pi^*}$ in a bonding way. This corresponds to π -back-donation from W2 (d^{W}_{occ}) to the CC moiety ($\phi^{CC}_{\pi^*}$); see CT($d^{W}_{occ} \rightarrow \phi^{CC}_{\pi^*}$) in Scheme 8. Another back-donation from W1 d^{W}_{occ} to ϕ^{Si1}_{μ} of SiH₂ is involved in this HOMO; see CT($d^{W}_{occ} \rightarrow \phi^{Si}_{\mu}$). HOMO-1 mainly consists of d^{W}_{occ} . As shown in Scheme 7B, HOMO-2 involves several kinds of CT interactions which are formed between the W, CC, and SiH₂, as follows: d^W_{occ} of W1 largely participates in HOMO-2, into which the unoccupiof W1 largely participates in HOMO-2, into which the unoccupi-ed $\varphi_{\pi^*}^{CC}$ and φ_{p}^{Si1} mix in a bonding way. These interactions correspond to $CT(d_{occ}^{W} \rightarrow \varphi_{\pi^*}^{CC})$ and $CT(d_{occ}^{W} \rightarrow \varphi_{p}^{Si})$ (see Scheme 8). Also, d_{unoc}^{W} of W2 largely participates in this HOMO-2 into which the occupied $\varphi_{p}^{Si2} \rightarrow \varphi_{p}^{CC}$ and $\varphi_{\pi^*}^{CC}$ moderately mix in a bonding way with the d_{unoc}^{W} orbital. These correspond to $CT(\varphi_{p}^{Si} \rightarrow d_{unoc}^{W})$, $CT(\varphi_{p}^{CC} \rightarrow d_{unoc}^{W})$, and $CT(\varphi_{\pi^*}^{CC} \rightarrow d_{unoc}^{W})$ (see Scheme 8). However, the presence of $\varphi_{\pi^*}^{CC}$ and $\varphi_{\pi^*}^{CC}$ is not clearly observed in this HOMO-2 (Figure 9). This is interpreted in terms of the π orbital polariza-(Figure 9). This is interpreted in terms of the π orbital polarization of the CC moiety, as follows: as shown in Scheme 9A, the mixing of $\varphi_{\pi^*}^{CC}$ into $\varphi_{\pi^*}^{CC}$ considerably increases the contribution of the C1 p orbital but considerably decreases that of the C2 p orbital. This polarized π_1 bonding orbital is observed in HOMO-2. In the π_2 space perpendicular to the π_1 , the reverse polarization occurs to increase the p orbital of C2 and decrease the p orbital of C1. These polarizations lead to nearly equivalent atomic populations of the C1 and C2 atoms (Table 2) and simultaneously lead to the weakening of the π bonding nature in **5M**. Also, the φ_{p}^{si} and φ_{p}^{si} orbitals are not clearly observed in HOMO-2, though their weights are somewhat large, as shown in Scheme 7B. This is because the bonding mixing of φ_{p}^{Si} and the antibonding mixing of $\varphi^{\rm Si}_{\ \rm lp}$ with $d^{\rm W}_{\ \rm occ}$ of the W lead to a distorted bonding orbital, as shown in Scheme 9B. As shown in Scheme 7C, HOMO-3 mainly consists of $\varphi^{CC}_{\tau\tau}$ which overlaps with φ_{p}^{Si} and d_{unoc}^{W} in a bonding way. These correspond to $CT(\varphi_{\pi}^{CC} \rightarrow \varphi_{p}^{Si})$ and $CT(\varphi_{\pi}^{CC} \rightarrow d_{unoc}^{W})$ (see Scheme 8). HOMO-4 and HOMO-6 involve the bonding interaction between φ^{CC}_{lp} and d^{W}_{unoc} as shown in Figure 9, which corresponds to $CT(\varphi^{CC}_{lp} \rightarrow d^{W}_{unoc})$. Though $CT(\varphi^{CC}_{\pi} \rightarrow \varphi^{Si}_{p})$ is found in HOMO-3, $CT(\varphi^{Si}_{lp} \rightarrow \varphi^{CC}_{\pi^*})$ is not clearly observed in the MOs of **5M**, unlike the case for **3M**. This is because $\varphi_{\rm lp}^{\rm Si}$ expands toward the W center in 5M but toward the CC moiety in 3M.

As shown in Table 3, the population of $\varphi_{HOMO-1}(W)$ is close to 2.0e in **5M** and the population of the $\varphi_{HOMO}(W)$ is similar to that of $Cp(CO)_2(SiH_2)W-C \equiv C-W(SiH_2)(CO)_2Cp$ (10) but



Figure 9. Several important Kohn–Sham MOs in $Cp(CO)_2W(SiH_2)(\mu$ -CC)(SiH_2)W(CO)_2Cp (5M). Orbital energies (in eV) are given in parentheses. HOMO, HOMO-1, HOMO-2, and HOMO-3 are doubly degenerate; see Figure S11 in the Supporting Information for the other set.

is considerably smaller than that of $Cp(CO)_2W(CCH)(SiH_2)$ (3M). Because 10 has an acetylenic structure (W-C=C-W), it is a d⁴ complex (+II oxidation state of W). Thus, the similar population of $\varphi_{HOMO}(W)$ indicates that 5M is understood to be a d⁴ complex as well. It is likely that the considerably smaller population of $\varphi_{HOMO}(W)$ in 10 than in 3M arises from the larger $CT(\varphi_{HOMO}(W) \rightarrow \varphi_p^{Si})$,⁶² which will be discussed below in more detail. The population of φ_p^{Si} is moderately larger in 5M than in 10 but somewhat smaller than in 3M. The population of $\varphi_{\pi}^{CC}{}_{\pi}$ in 5M is similar to that of 3M but considerably smaller than that of 10. These results indicate that $CT(\varphi_{\pi}^{CC} \rightarrow \varphi_p^{Si})$ occurs to an extent similar to that in 3M. This conclusion is supported by the geometry of 5M and the feature of HOMO-3; the geometry suggests the presence of Si-C bonding interactions, and HOMO-3 displays the presence of a bonding overlap between $\varphi_{\text{si}p}^{\text{Si}}$ and $\varphi_{\text{cc}\pi}^{\text{CC}}$ (see HOMO-3 of Figure 9). The population of $\varphi_{\text{lp}}^{\text{Si}p}$ is considerably larger in **5M** than in **3M** but considerably smaller than in **10** (Table 3). The population of $\varphi_{\pi^*}^{\text{CC}}$ is somewhat larger in **5M** than in **3M** but considerably larger than in **10**. Though the poor overlap between $\varphi_{\text{lp}}^{\text{Si}}$ and $\varphi_{\pi^*}^{\text{CC}}$ in **5M** suggests that $\text{CT}(\varphi_{\text{lp}}^{\text{Si}} \rightarrow \varphi_{\pi^*}^{\text{CC}})$ is considerably weaker in **5M** than in **3M**, the population of $\varphi_{\pi^*}^{\text{CC}}$ is large in **5M**. These results indicate that $\text{CT}(d_{\sigma \text{cc}}^{\text{CC}} \rightarrow \varphi_{\pi^*}^{\text{CC}})$ is stronger in **5M** than in **3M**. The considerably smaller population in $\varphi_{\text{HOMO}}(\text{W})$ of **5M** also support this conclusion. The population of $\varphi_{\text{lp1}}^{\text{CC}}$ in **5M** is similar to that of **10** but moderately larger than that of **3M**. The population of $\varphi_{\text{lp2}}^{\text{CC}}$ is somewhat smaller in **5M** than in **10**. These results indicate that $\text{CT}(\varphi_{\text{lp2}}^{\text{CC}} \rightarrow \varphi_{\pi^*}^{\text{CC}})$ is moderately larger than that of **5M** than in **5**







Figure 10. Several important Kohn–Sham MOs in $[Cp(CO)_2W]^+$, SiH₂, and $[CC]^{2-}$. In part C, the LUMO and HOMO-1 are doubly degenerate. The other orbital perpendicular to this picture exists beside this orbital.

4.4. Summary of the Bonding Nature of **5M**. The CT interactions discussed above are shown in Scheme 8. As discussed above, the C–C bond in **5M** is weaker than a typical C–C triple bond but is comparable to a C–C double bond. This result is interpreted as follows: $CT(d_{occ}^{W} \rightarrow \varphi_{\pi}^{CC})$ and $CT(\varphi_{\pi}^{CC} \rightarrow \varphi_{\pi}^{Si})$ considerably weaken the C–C bond of **5M**. The mixing of φ_{π}^{CC} into φ_{π}^{CC} into φ_{π}^{CC} orbital polarization of the CC moiety in one plane and reverse π orbital polarization in the perpendicular plane. These polarizations are also responsible for considerable weakening of the CC bond. Because $CT(\varphi_{\mu}^{Si} \rightarrow \varphi_{\pi^*}^{CC})$ is considerably weak in **5M** due to a poor overlap between them, only $CT(\varphi_{\pi}^{CC} \rightarrow \varphi_{p}^{Si})$ contributes to the Si–C bonding interaction in **5M**. The Si1–C1 bond index of **5M** is somewhat larger than the Si–C1 bond index of **3M**, but the Si1–C2 bond index of **5M** is much smaller than the Si–C2 bond index of **3M**. This is because the C1 p_{π} orbital overlaps with φ_{p}^{Si} in **5M** but the C2 p_{π} orbital cannot overlap with φ_{p}^{Si} in **5M**

(see Figure 7 for the orientation of SiH₂). Also, $CT(\varphi_{lp}^{Si} \rightarrow d^{W}_{unoc})$ and $CT(d^{W}_{occ} \rightarrow \varphi_{p}^{Si})$ are formed in **5M**. Because the lone pair of SiH₂ expands toward the W, the above CTs are stronger in **5M** than in **3M** and, hence, the W–Si bond of **5M** is somewhat stronger than that of **3M**.

The above results lead to the following conclusions. (1) The $H_2SiCCSiH_2$ moiety is not understood to be a disilabutatriene or a metal-substituted disilabutadiene. (2) The CC moiety can be understood as an ethynediyl dianion and the SiH₂ moiety as a silylene. (3) The bonding nature should be understood in terms of various CT interactions between the W, SiH₂, and CC moieties (see Scheme 8). Though it is difficult to understand the $H_2SiCCSiH_2$ moiety as disilabutatriene or metal-substituted disilabutatiene, the conclusions (2) and (3) are not inconsistent with the experimental and computational results.

CONCLUDING REMARKS

The ethynediyl-bridged bis(silylene) dinuclear complexes $Cp^*(CO)_2M(SiPh_2)(\mu$ -CC)(SiPh_2)M(CO)_2Cp* (5, M = W; 6, M = Mo) were synthesized by the reaction of Ph_2HSiC=C-SiHPh_2 with 2 equiv of acetonitrile complexes 1a and 2, respectively, via activation of two Si-H bonds of the bis(silyl)-acetylene. X-ray crystal analysis of 5 and 6 revealed a novel linkage between the ethynediyl bridge and two $Cp^*(CO)_2M$ -(SiPh_2) moieties. Two M-Si-C three-membered-ring skeletons are linked nearly perpendicularly to each other. The W-Si bond distance of 5 is considerably shorter than that of the mononuclear acetylide-silylene complex 3b, and the ethynediyl bond distance is significantly elongated from the triple-bond distance. These structural features are rationalized by the theoretical calculations described below.

Reaction of the tungsten acetonitrile complex 1a with 1 equiv of $Ph_2HSiC \equiv CSiHPh_2$ afforded a mixture of mononuclear acetylide—silylene complex 7 and dinuclear complex 5. Addition of 1a to the mixture led to the conversion of 7 to 5, indicating the intermediacy of 7 in the production of 5 in the 1:2 reaction of the bis(silyl)acetylene with 1a. A similar 1:1 reaction using the molybdenum acetonitrile complex 2 also afforded a mixture of mononuclear and dinuclear complexes. In contrast to the tungsten system, however, the equilibrium of two mononuclear complexes, acetylide—silylene complex 8 and silapropargyl/alkynylsilyl complex 9, was strongly suggested by variable-temperature NMR studies of the mixture. Treatment of the equilibrium mixture with 2 resulted in their clean conversion to dinuclear complex 6.

The bonding nature and electronic structure of **5** were disclosed by a DFT study of the model complex $Cp(CO)_2W(SiH_2)(\mu$ -CC)(SiH_2)W(CO)₂Cp (**5M**, Cp = η^5 -C₅H₅). The computational results demonstrate that **5M** is neither a 1,4-disilabutatriene-bridged dinuclear tungsten complex nor a cumulenic (W=C=C=W) complex but an ethynediyl-bridged bis(silylene) dinuclear tungsten complex which contains various charge transfer (CT) interactions (see Scheme 8) between the tungsten (W), silylene (SiH₂), and ethynediyl (CC), as follows. (1) CTs occur from the lone pairs (φ^{CC}_{lp}) and π orbital ($\varphi^{CC}_{\pi^*}$) of the ethynediyl to the unoccupied d orbital (d^W_{unoc}) of the W and from the occupied d orbital (d^W_{occ}) of the W to the π^* orbital ($\varphi^{CC}_{\pi^*}$) of the ethynediyl. (2) CTs occur from the lone pair orbital (φ^{Si}_{lp}) of the silylene to d^W_{unoc} and from d^W_{occ} to the empty p orbital (φ^{Si}_{p}) of the silylene. (3) CT occurs from φ^{CC}_{π} to φ^{Si}_{p} , which leads to considerably strong Si–C bonding interactions and considerably large elongation of the C–C

Scheme 7. Weights (in Percent) of Fragment MOs



Scheme 8. Bonding Nature of 5M



distance. (4) The mixing of φ^{CC}_{π} into $\varphi^{CC}_{\pi^*}$ induces π orbital polarization of the CC moiety in one plane and a reverse π orbital polarization in the perpendicular plane. These polarizations in addition to the CT($d^{W}_{occ} \rightarrow \varphi^{CC}_{\pi^*}$) also participate in the C–C

Scheme 9



bond weakening of the ethynediyl. Thus, **5M** is understood to be a new category of an ethynediyl-bridged bis(silylene) dinuclear transition-metal complex including interesting CT interactions and polarizations. Table 3. Populations^{*a*} of Fragment MOs in Cp(CO)₂W(SiH₂)-(μ -CC)(SiH₂)W(CO)₂Cp (5M), Cp(CO)₂(SiH₂)W-C=C-W(SiH₂)(CO)₂Cp (10), and Cp(CO)₂W(CCH)(SiH₂) (3M)

	5M	10	3M	
$[Cp(CO)_2W]^+$				
$\varphi_{\text{LUMO+2}}(W)$	0.013	0.015	0.011	
$\varphi_{\text{LUMO+1}}(W)$	0.376	0.638	0.411	
$\varphi_{\text{LUMO}}(W)$	1.157	0.794	0.835	
$\varphi_{\rm HOMO}(W)$	1.489	1.454	1.778	
$\varphi_{\text{HOMO-1}}(W)$	1.863	1.910	1.844	
SiH ₂				
φ^{Si}_{P}	0.575	0.540	0.665	
$\varphi^{\rm Si}_{\ \ lp}$	0.941	1.256	0.793	
	$[C_2]^{2-}$ or $[C_2]^{2-}$	CCH] ⁻		
$\varphi^{CC}_{\pi^*}$	0.453 ^b	0.097 ^b	0.397	
$\varphi^{\rm CC}_{lp1}$	1.277	1.276	1.264	
φ^{CC}_{π}	1.492 ^c	1.812 ^c	1.469	
φ^{CC}_{lp2}	1.472	1.635		

^{*a*} DFT(B3PW91)/BS-II calculations. See Table S1 in the Supporting Information for BS-III calculations. ^{*b*} Average of the populations in $\varphi^{\rm CC}_{\pi^{+}1}$ and $\varphi^{\rm CC}_{\pi^{-}2}$. ^{*c*} Average of the populations in $\varphi^{\rm CC}_{\pi^{-}1}$ and $\varphi^{\rm CC}_{\pi^{-}2}$.

EXPERIMENTAL SECTION

General Procedures. All materials were manipulated under an atmosphere of nitrogen in a glovebox or by standard vacuum and Schlenk techniques. NMR spectra were recorded on a JEOL JNM-GSX400 or a Bruker AV-600 spectrometer, and IR spectra were obtained on a Shimadzu FTIR-8100 M spectrometer. Benzene, hexane, pentane, toluene, toluene- d_8 , and THF- d_8 were distilled from sodium benzophenone ketyl, and dichloromethane- d_2 was distilled from calcium hydride. Ph₂HSiC \equiv CSiHPh₂,⁶³ Cp*(CO)₂W(NCMe)Me (1a),^{19a} and Cp*-(CO)₂Mo(NCMe)Me (2)^{19c} were synthesized according to the literature methods. ¹³C-enriched CO (99.3%) was purchased from Isotec and used without further purification.

Synthesis of Cp*(CO)₂W(SiPh₂)(*u*-CC)(SiPh₂)W(CO)₂Cp* (5). On a vacuum line, toluene (6 mL) was vacuum-transferred into a reaction flask containing 1a (100 mg, 0.23 mmol) and Ph₂HSiC=C-SiHPh₂ (43 mg, 0.11 mmol) at -196 °C. The mixture was thawed at -70 °C and warmed to room temperature with stirring. After 90 min at room temperature, the volatiles were removed in vacuo. The residual solid was washed with hexane (1 mL) and then with hexane/toluene (1.1/0.9 mL) to give 5 as an air-sensitive orange solid (69 mg, 55%). Data for 5 are as follows. ¹H NMR (400 MHz, CD_2Cl_2 , 27 °C): δ 1.91 (s, 30H, Cp*), 7.0-7.1 (br m, 4H, Ph), 7.1-7.2 (br m, 6H, Ph), 7.45-7.55 (br s, 6H, Ph), 7.7–7.8 (br s, 4H, Ph). ¹H NMR (600 MHz, CD₂Cl₂, -90 °C): δ 1.75 (br s, 30H, Cp*), 6.7-7.0 (br s, 4H, Ph), 7.0-7.35 (br m, 6H, Ph), 7.35–7.7 (br s, 6H, Ph), 7.7–8.0 (br s, 4H, Ph). ${}^{13}C{}^{1}H{}$ NMR (100 MHz, CD₂Cl₂, 27 °C): δ 11.0 (C₅Me₅), 104.4 (C₅Me₅), 127.4 (Ph), 128.2 (Ph), 129.8 (Ph), 130.7 (Ph), 134.3 (Ph), 136.3 (Ph), 137.2 (Ph), 137.9 (Ph), 222.0 (CO), 223.5 (CO), 235.8 (µ-CC). ¹³C{¹H} NMR (150 MHz, CD₂Cl₂, -90 °C): δ 10.0 (br, C₅Me₅), 10.2 (br, C₅Me₅), 103.2 (br, C₅Me₅), 126.0 (br, Ph), 127.4 (Ph), 130.2 (br, Ph), 131.2 (br, Ph), 133.4 (br, Ph), 134.4 (br, Ph), 136.4 (br, Ph), 137.5 (br, Ph), 220.7 (br, CO), 221.5 (br, CO), 223.6 (br, CO), 231.6 (br, μ-CC), 235.2 (br, μ-CC). ²⁹Si{¹H} NMR (119 MHz, C₇D₈, 27 °C): δ -21.2 (br). ²⁹Si{¹H} NMR (119 MHz, CD₂Cl₂, -90 °C): δ -17.2, -29.8. Anal. Calcd for $C_{50}H_{50}O_4Si_2W_2 \cdot C_7H_8$: C, 55.62; H, 4.75. Found: C, 55.48; H, 4.85.

Synthesis of Cp*(CO)₂Mo(SiPh₂)(µ-CC)(SiPh₂)Mo(CO)₂Cp* (6). On a vacuum line, toluene (2.5 mL) was vacuum-transferred into a reaction flask containing 2 (60 mg, 0.17 mmol) and Ph₂HSiC=C-SiHPh₂ (32 mg, 0.082 mmol) at -196 °C. The mixture was thawed at -70 °C and warmed to room temperature with stirring. After 30 min at room temperature, the volatiles were removed in vacuo. The residual solid was washed with hexane $(2 \times 2 \text{ mL})$ to give 6 as an air-sensitive orange solid (41 mg, 51%). Data for 6 are as follows. ¹H NMR (400 MHz, CD₂Cl₂, 27 °C): δ 1.81 (s, 30H, Cp*), 6.6–7.8 (vbr m, 20H, Ph). ¹H NMR (400 MHz, CD₂Cl₂, -90 °C): δ 1.58 (s, 15H, Cp*), 1.69 (s, 15H, Cp*), 6.85 (br s, 4H, Ph), 7.05-7.25 (br m, 6H, Ph), 7.35-7.6 (br m, 6H, Ph), 7.84 (br m, 4H, Ph). ¹³C{¹H} NMR (150 MHz, CD₂Cl₂, 27 °C): δ 11.1 (C₅Me₅), 105.5 (C₅Me₅), 127.8 (br, Ph), 130.4 (br, Ph), 135.4 (vbr, Ph), 136.7 (br, Ph), 230.2 (br, CO), 240.1 (br, μ-CC). ¹³C{¹H} NMR (150 MHz, CD₂Cl₂, -90 °C): δ 9.9 (C₅Me₅), 10.3 (C₅Me₅), 104.3 (C₅Me₅), 104.5 (C₅Me₅), 126.2 (Ph), 127.4 (Ph), 128.4 (Ph), 130.1 (Ph), 130.5 (Ph), 130.9 (Ph), 133.6 (Ph), 133.9 (Ph), 134.3 (Ph), 135.1 (Ph), 135.7 (Ph), 136.9 (Ph), 137.0 (Ph), 226.6 (CO), 228.8 (CO), 230.6 (CO), 231.5 (CO), 239.8 (µ-CC), 241.2 (µ-CC). ²⁹Si{¹H} NMR (119 MHz, CD₂Cl₂, -90 °C): δ –5.0, 5.3. Anal. Calcd for $C_{50}H_{50}O_4Si_2Mo_2 \cdot C_7H_8$: C, 64.89; H, 5.54. Found: C, 64.87; H, 5.79. Synthesis of ¹³CO-Enriched Cp*(CO)₂Mo(SiPh₂)(μ -CC)-

Synthesis of ¹³CO-Enriched Cp*(CO)₂Mo(SiPh₂)(μ -CC)-(SiPh₂)Mo(CO)₂Cp* (6*). In a 50 mL Schlenk flask containing Cp*(CO)₃MoMe (279 mg, 0.84 mmol) and benzene (10.5 mL) was introduced ¹³CO (2.0 mmol). The solution was irradiated with a 100 W medium-pressure Hg lamp with vigorous stirring for 15 min at 10 °C. After removal of the volatiles, hexane (9.5 mL) was added, and the solution was filtered to remove an insoluble orange solid. The solvent was removed in vacuo, and the residual solid was sublimed at 70 °C to give ¹³CO-enriched Cp*(CO)₃MoMe (239 mg, 86%), which was converted to ¹³CO-enriched 2* by photolysis in MeCN in 30% yield in a manner similar to the synthesis of 2.^{19c} The reaction of Ph₂HSiC=CSiHPh₂ (33 mg, 0.084 mmol) with 2* (60 mg, 0.17 mmol) gave 6* (14 mg, 17%) after recrystallization from toluene/pentane.

1:1 Reaction of 1a with Ph₂HSiC=CSiHPh₂. On a vacuum line, toluene- d_8 (0.5 mL) was vacuum-transferred into an NMR tube containing 1a (7 mg, 16 μ mol) and Ph₂HSiC=CSiHPh₂ (6 mg, 15 μ mol) at -196 °C, and the tube was flame-sealed. The mixture was thawed at -70 °C and warmed to room temperature. After 5 min at room temperature, the ¹H NMR spectrum showed the formation of 7 and 5 in a ratio of 76 to 24. From a preparative-scale reaction of 1a (100 mg, 0.23 mmol) with Ph₂HSiC=CSiHPh₂ (90 mg, 0.23 mmol) in toluene (5.3 mL), an air-sensitive orange solid (24 mg) was isolated in ca. 95% purity by removing the solvent and washing the residual solid with hexane and pentane. Attempts to purify 7 by recrystallization were unsuccessful, and it was characterized by low-temperature ¹H, ¹³C, and ²⁹Si NMR spectra. Data for 7 are as follows. ¹H NMR (400 MHz, toluene- d_{8} , 27 °C): δ 1.69 (s, 15H, Cp*), 5.41 (s, 1H, SiH), 7.00-7.05 (m, 6H, Ph), 7.05-7.10 (m, 6H, Ph), 7.47-7.60 (m, 4H, Ph), 7.67-7.75 (m, 4H, Ph). ¹H NMR (600 MHz, THF- d_8 , $-70 \,^{\circ}$ C): δ 1.86 (s, 15H, Cp*), 4.97 (s, 1H, SiH), 7.01-7.75 (m, 20H, Ph). ¹³C{¹H} NMR (150 MHz, THFd₈, -70 °C): δ 11.0 (C₅Me₅), 103.6 (C₅Me₅), 128.4 (Ph), 128.5 (Ph), 128.7 (Ph), 128.8 (Ph), 129.1 (Ph), 130.3 (Ph), 130.5 (Ph), 130.7 (Ph), 131.2 (Ph), 132.3 (Ph), 132.6 (Ph), 134.0 (Ph), 135.5 (Ph), 135.9 (Ph), 136.5 (Ph), 137.7 (WCC), 186.5 (WCC), 226.2 (CO), 230.7 (CO). ²⁹Si{¹H} NMR (79 MHz, toluene- d_8 , 27 °C): δ –39.2 (SiHPh₂). The WSiPh₂ signal was not observed. ²⁹Si{¹H} NMR (119 MHz, THF-d₈, -70 °C): $\delta -46.7 (^{1}J_{\text{WSi}} = 41 \text{ Hz}, \text{WSiPh}_{2}), -39.0 (\text{SiHPh}_{2}).$

1:1 Reaction of 2 with Ph₂HSiC=CSiHPh₂. On a vacuum line, toluene- d_8 (0.5 mL) was vacuum-transferred into an NMR tube containing **2** (8 mg, 23 μ mol) and Ph₂HSiC=CSiHPh₂ (9 mg, 23 μ mol) at -196 °C, and the tube was flame-sealed. The mixture was thawed at -70 °C and warmed to room temperature. After 20 min at room temperature, the ¹H NMR spectrum showed the formation of mononuclear

	$5 \cdot C_7 H_8$	6 ⋅ C ₇ H ₈
formula	$C_{50}H_{50}O_4Si_2W_2 \cdot C_7H_8$	$C_{50}H_{50}O_4Si_2Mo_2 \cdot C_7H_8$
fw	1230.95	1055.13
cryst size (mm)	$0.10\times0.10\times0.10$	$0.20\times0.20\times0.10$
cryst syst	monoclinic	monoclinic
space group	$P2_{1}/n$	$P2_1/n$
a (Å)	15.754(4)	15.703(4)
b (Å)	17.657(5)	17.614(4)
c (Å)	18.402(4)	18.481(4)
β (deg)	91.8710(10)	92.0150(10)
$V(Å^3)$	5116(2)	5109(2)
Ζ	4	4
F(000)	2432	2176
μ (Mo K $lpha$) (cm ⁻¹)	4.590	5.817
no. of rflns collected	71 469	79 189
no. of unique reflns	11 510	11 501
$R_{\rm int}$	0.054	0.113
no. of variables	556	556
R1 $(I > 2\sigma(I))$	0.0292	0.0601
wR2 (all data)	0.0672	0.1397
GOF	0.822	0.875

and dinuclear complexes in a composition ratio of 82 to 18. From a preparative-scale reaction of 2 (90 mg, 0.26 mmol) with Ph₂HSiC=C-SiHPh₂ (104 mg, 0.266 mmol) in toluene (5.5 mL), an air-sensitive yellow solid (74 mg, 42%) was isolated. Variable-temperature ¹H NMR analysis of a THF- d_8 solution of the solid revealed an equilibrium mixture of two complexes, which were characterized as 8 and 9 on the basis of low-temperature ¹H, ¹³C, and ²⁹Si NMR spectra. Data for 8 and 9 are as follows. ¹H NMR (400 MHz, toluene- d_8 , 27 °C): δ 1.64 (s, 15H, Cp*), 5.44 (s, 1H, SiH), 7.03-7.09 (m, 12H, Ph), 7.46-7.58 (m, 4H, Ph), 7.59–7.69 (m, 4H, Ph). ¹H NMR (600 MHz, THF-*d*₈, -80 °C): δ 1.62 (s, 15H, Cp*, 9), 1.76 (s, 15H, Cp*, 8), 4.90 (s, 1H, SiH, 8), 5.80 (s, 1H, SiH, 9), 6.80-8.10 (m, 40H, Ph). ¹³C{¹H} NMR (150 MHz, THF-d₈, 27 °C): δ 10.9 (C₅Me₅), 104.8 (C₅Me₅), 128.6 (Ph), 128.8 (Ph), 130.5 (Ph), 130.9 (Ph), 133.0 (Ph), 133.1 (Ph), 135.9 (Ph), 136.4 (Ph), 236.6 (CO). The signals of MoCC were not observed. ${}^{13}C{}^{1}H{}$ NMR (150 MHz, THF-d₈, -90 °C): δ 10.8 (C₅Me₅, 9), 11.1 (C₅Me₅, 8), 90.9 (Ph₂SiCC, 9), 103.0 (Ph₂SiCC, 9), 104.4 (C₅Me₅, 9), 104.7 (C₅Me₅, 8), 128.9 (Ph), 129.3 (Ph), 130.9 (Ph), 131.2 (Ph), 131.3 (Ph), 131.5 (Ph), 131.7 (Ph), 132.0 (Ph), 132.9 (Ph), 134.3 (Ph), 134.5 (Ph), 135.6 (Ph), 135.9 (Ph), 136.0 (Ph), 136.2 (Ph), 136.4 (Ph), 137.0 (Ph), 143.7 (MoCC, 8), 190.5 (MoCC, 8), 233.6 (CO), 236.5 (CO), 237.9 (CO), 238.6 (CO). ²⁹Si{¹H} NMR (79 MHz, THF- d_8 , 27 °C): δ – 38.0 (SiHPh₂). The MoSiPh₂ signal was not observed. ²⁹Si{¹H} NMR $(119 \text{ MHz}, \text{THF-}d_{8i}, -90 \,^{\circ}\text{C}): \delta - 39.0 \,(\text{SiHPh}_{2i}, 8), -24.0 \,(\text{SiHPh}_{2i}, 9),$ -14.4 (MoSiPh₂, 8), 55.2 (MoSiPh₂, 9). Anal. Calcd for C₃₈H₃₆O₂Si₂₋ Mo: C, 67.44; H, 5.36. Found: C, 66.77; H, 5.34.

X-ray Crystal Structure Determinations. Selected crystallographic data for $5 \cdot C_7 H_8$ and $6 \cdot C_7 H_8$ are given in Table 4. Single crystalls of $5 \cdot C_7 H_8$ and $6 \cdot C_7 H_8$ were obtained by recrystallization from toluene/ hexane and toluene/pentane, respectively. The diffraction data were collected on a Rigaku AFC10/Saturn instrument with graphite-monochromated Mo K α radiation at -100 °C. The data were processed using CrystalClear⁶⁴ and corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR97 or SHELXS-97),^{65,66} and expanded using Fourier techniques (DIRDIF99).⁶⁷ All non-hydrogen atoms were refined anisotropically except for disordered toluene, with site occupation factors of 0.65/0.35 for 5 and 0.70/0.30 for 6. Hydrogen atoms for the dinuclear complexes were refined using the riding model. The refinement was carried out using full-matrix least-squares methods on F^2 with SHELXL-97.⁶⁸ All calculations were performed using the CrystalStructure crystallographic software package.⁶⁹

Computational Details. The geometry of $Cp(CO)_2W(SiH_2)(\mu-CC)(SiH_2)W(CO)_2Cp$ (**5M**) was optimized with density functional theory (DFT), where the B3PW91 functional^{70,71} was employed for the exchange-correlation term, because this functional presented better agreement of the optimized geometry of $Cp(CO)_2W(CCH)(SiH_2)$ (**3M**)^{18a} with the experimental geometry of **3b**^{19b} than does the B3LYP functional.^{70,72} We ascertained that none of the equilibrium geometries exhibited any imaginary frequency.

Two kinds of basis set systems, BS-I and BS-II, were mainly used in this work. In BS-I, core electrons of W were replaced with the effective core potentials (ECPs)⁷³ and their valence electrons were represented by the (341/321/21) basis sets.⁷³ The usual cc-pVDZ⁷⁴ basis sets were employed for Si, C, and O, and the usual 6-31G⁷⁵ basis set was used for H. This BS-I system was used for geometry optimization. In BS-II, the core electrons of W were replaced with the Stuttgart-Dresden-Bonn (SDB) ECPs and their valence electrons were represented by the (311111/ 22111/411/11) basis sets.^{76,77} For the other atoms, the cc-pVTZ basis sets⁷⁴ were employed, where the f polarization function was excluded to save computational time. This BS-II system was used to evaluate the Wiberg bond index⁷⁸ and population changes. Another basis set system, BS-III, was employed to check the reliability of the Mulliken population analysis with the BS-II system, because a very diffuse function tends to present an unreasonable Mulliken population in several cases. In BS-III, the valence electrons of W were represented by the (541/541/111/1) basis set,^{72,79,80} where its core electrons were replaced with the same ECPs as those of BS-I. For the other atoms, the same basis sets as those of BS-I were employed. The BS-III-calculated Mulliken populations are similar to the BS-II-calculated values (see Table S1 in the Supporting Information). Hence, we present only the BS-II-calculated populations in the discussion.

The Gaussian 03 program package (revision C.02)⁸¹ was used for all these computations. NBO population analysis was carried out with the method proposed by Weinhold et al.⁸² Molecular orbitals were drawn with the MOLEKEL program package (version 4.3).⁸³

ASSOCIATED CONTENT

Supporting Information. CIF files containing X-ray crystallographic data for complexes **5** and **6**, figures giving the NMR spectra of **5**–**9**, text giving the complete reference of Gaussian 03, a table giving DFT/BS-III-calculated Mulliken populations in fragment MOs of **5M**, text giving a comparison between **5M** and **14**, and tables of Cartesian coordinates and total energies of **5M**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sakaba@m.tohoku.ac.jp (H.S.); sakaki@moleng.kyoto-u. ac.jp (S.S.).

Present Address

[#]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA

ACKNOWLEDGMENT

This work was financially supported by Grants-in-Aid on basic research for Scientific Research (Nos. 1835005 and 22550051), Priority Areas for "Molecular Theory" (No. 461), Specially Promoted Research (No. 22000009), the NAREGI project from the Ministry of Education, Science, Sports, and Culture, and a Research Grant of the Japan Society for the Promotion of Science for Young Scientists. Some of the theoretical calculations were performed with the SGI workstation at the Institute for Molecular Science, Okazaki, Japan.

REFERENCES

(1) (a) Corey, J. Y.; Braddock-Wilking, J. Chem. Rev. **1999**, 99, 175. (b) Kubas, G. J. Metal Dihydrogen and σ -Bond Complexes; Kluwer Academic/Plenum Publishers: New York, 2001; Chapter 11. (c) Lin, Z. Chem. Soc. Rev. **2002**, 31, 239. (d) Sakaki, S. Top. Organomet. Chem. **2005**, 12, 31. (e) Corey, J. Y. Chem. Rev. **2011**, 111, 863.

(2) (a) Ueno, K.; Masuko, A.; Ogino, H. Organometallics 1999, 18, 2694. (b) Minglana, J. J. G.; Okazaki, M.; Tobita, H.; Ogino, H. Chem. Lett. 2002, 31, 406. (c) Okazaki, M.; Suzuki, E.; Miyajima, N.; Tobita, H.; Ogino, H. Organometallics 2003, 22, 4633. (d) Okazaki, M.; Minglana, J. J. G.; Yamahira, N.; Tobita, H.; Ogino, H. Can. J. Chem. 2003, 81, 1350. (e) Sato, T.; Okazaki, M.; Tobita, H. Chem. Lett. 2004, 33, 868. (f) Suzuki, E.; Okazaki, M.; Tobita, H. Chem. Lett. 2005, 34, 1026. (g) Koshikawa, H.; Okazaki, M.; Matsumoto, S.; Ueno, K.; Tobita, H.; Ogino, H. Chem. Lett. 2005, 34, 1412. (h) Suzuki, E.; Komuro, T.; Okazaki, M.; Tobita, H. Organometallics 2010, 29, 5296. (j) Hashimoto, H.; Suzuki, T.; Tobita, H. Dalton Trans 2010, 39, 9386.

(3) (a) Sakaba, H.; Tsukamoto, M.; Hirata, T.; Kabuto, C.; Horino, H. J. Am. Chem. Soc. 2000, 122, 11511. (b) Sakaba, H.; Hirata, T.; Kabuto, C.; Horino, H. Chem. Lett. 2001, 30, 1078.

(4) Choo, T. N.; Kwok, W.-H.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. J. Organomet. Chem. **2002**, 645, 235.

(5) Ingleson, M.; Fan, H.; Pink, M.; Tomaszewski, J.; Caulton, K. G. J. Am. Chem. Soc. 2006, 128, 1804.

(6) Rankin, M. A.; MacLean, D. F.; Schatte, G.; McDonald, R.; Stradiotto, M. J. Am. Chem. Soc. 2007, 129, 15855.

(7) (a) Klei, S. R.; Tilley, T. D.; Bergman, R. G. J. Am. Chem. Soc. 2000, 122, 1816. (b) Mork, B. V.; Tilley, T. D. J. Am. Chem. Soc. 2001, 123, 9702. (c) Klei, S. R.; Tilley, T. D.; Bergman, R. G. Organometallics 2002, 21, 3376. (d) Feldman, J. D.; Peters, J. C.; Tilley, T. D. Organometallics 2002, 21, 4065. (e) Mork, B. V.; Tilley, T. D. Angew. Chem., Int. Ed. 2003, 42, 357. (f) Glaser, P. B.; Wanandi, P. W.; Tilley, T. D. Organometallics 2004, 23, 693. (g) Mork, B. V.; Tilley, T. D. J. Am. Chem. Soc. 2004, 126, 4375. (h) Mork, B. V.; Tilley, T. D. J. Am. Chem. Soc. 2004, 126, 4375. (h) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. J. Am. Chem. Soc. 2004, 126, 10428. (i) Glaser, P. B.; Tilley, T. D. Organometallics 2004, 23, 5799. (j) Hayes, P. G.; Beddie, C.; Hall, M. B.; Waterman, R.; Tilley, T. D. J. Am. Chem. Soc. 2006, 128, 428. (k) Calimano, E.; Tilley, T. D. J. Am. Chem. Soc. 2009, 131, 11161. (l) Shinohara, A.; McBee, J.; Tilley, T. D. Inorg. Chem. 2009, 48, 8081. (m) Hayes, P. G.; Waterman, R.; Glaser, P. B.; Tilley, T. D. Organometallics 2009, 28, 5082.

(8) (a) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. Organometallics
2002, 21, 1326. (b) Watanabe, T.; Hashimoto, H.; Tobita, H. Angew.
Chem., Int. Ed. 2004, 43, 218. (c) Tobita, H.; Matsuda, A.; Hashimoto,
H.; Ueno, K.; Ogino, H. Angew. Chem., Int. Ed. 2004, 43, 221. (d)
Hashimoto, H.; Matsuda, A.; Tobita, H. Chem. Lett. 2005, 34, 1374. (e)
Hirotsu, M.; Nunokawa, T.; Ueno, K. Organometallics 2006, 25, 1554. (f)
Ochiai, M.; Hashimoto, H.; Tobita, H. Angew. Chem., Int. Ed. 2007, 46, 8192.
(g) Hashimoto, H.; Sato, J.; Tobita, H. Organometallics 2009, 28, 3963.

(9) Simons, R. S.; Gallucci, J. C.; Tessier, C. A.; Youngs, W. J. J. Organomet. Chem. 2002, 654, 224.

(10) Gusev, D. G.; Fontaine, F.-G.; Lough, A. J.; Zargarian, D. Angew. Chem., Int. Ed. 2003, 42, 216.

(11) Renkema, K. B.; Werner-Zwanziger, U.; Pagel, M. D.; Caulton, K. G. J. Mol. Catal. A: Chem. 2004, 224, 125.

(12) Yoo, H.; Carroll, P. J.; Berry, D. H. J. Am. Chem. Soc. 2006, 128, 6038.

(13) Takaoka, A.; Mendiratta, A.; Peters, J. C. Organometallics 2009, 28, 3744.

(14) Reviews of silylene complexes: (a) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10. (b) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Chapter 35. (c) Ogino, H. *Chem. Rec.* **2002**, *2*, 291. (d) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493. (e) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712.

(15) Recent studies of base-stabilized silvlene complexes: (a) Ueno, K.; Sakai, M.; Ogino, H. Organometallics 1998, 17, 2138. (b) Tobita, H.; Sato, T.; Okazaki, M.; Ogino, H. J. Organomet. Chem. 2000, 611, 314. (c) Sato, T.; Tobita, H.; Ogino, H. Chem. Lett. 2001, 30, 854. (d) Okada, H.; Okazaki, M.; Tobita, H.; Ogino, H. Chem. Lett. 2003, 32, 876. (e) Begum, R.; Komuro, T.; Tobita, H. Chem. Lett. 2007, 36, 650. (f) Klei, S. R.; Tilley, T. D.; Bergman, R. G. Organometallics 2001, 20, 3220. (g) Sakaba, H.; Hirata, T.; Kabuto, C.; Kabuto, K. Organometallics 2006, 25, 5145. (h) Sakaba, H.; Hirata, T.; Kabuto, C.; Kabuto, K. J. Organomet. Chem. 2007, 692, 402. (i) Sharma, H. K.; Pannell, K. H. Organometallics 2001, 20, 7. (j) Zhang, Y.; Cervantes-Lee, F.; Pannell, K. H. J. Organomet. Chem. 2001, 634, 102. (k) Zhang, Y.; Pannell, K. H. Organometallics 2003, 22, 1766. (1) Simons, R. S.; Galat, K. J.; Bradshaw, J. D.; Youngs, W. J.; Tessier, C. A.; Aullón, G.; Alvarez, S. J. Organomet. Chem. 2001, 628, 241. (m) Meltzer, A.; Präsang, C.; Driess, M. J. Am. Chem. Soc. 2009, 131, 7232. (n) Yang, W.; Fu, H.; Wang, H.; Chen, M.; Ding, Y.; Roesky, H. W.; Jana, A. Inorg. Chem. 2009, 48, 5058. (o) Li, J.; Merkel, S.; Henn, J.; Meindl, K.; Döring, A.; Roesky, H. W.; Ghadwal, R. S.; Stalke, D. Inorg. Chem. 2010, 49, 775. (p) Jungton, A.-K.; Meltzer, A.; Präsang, C.; Braun, T.; Driess, M.; Penner, A. Dalton Trans. 2010, 39, 5436. (g) Muraoka, T.; Shimizu, Y.; Kobayashi, H.; Ueno, K.; Ogino, H. Organometallics 2010, 29, 5423. (r) Wang, W.; Inoue, S.; Yao, S.; Driess, M. J. Am. Chem. Soc. 2010, 132, 15890. (s) Tavcar, G.; Sen, S. S.; Azhakar, R.; Thorn, A.; Roesky, H. W. Inorg. Chem. 2010, 49, 10199. See also refs 2-6.

(16) Recent studies of base-free silylene complexes: (a) Wanandi, P. W.; Glaser, P. B.; Tilley, T. D. J. Am. Chem. Soc. 2000, 122, 972. (b) Dysard, J. M.; Tilley, T. D. Organometallics 2000, 19, 4726. (c) Klei, S. R.; Tilley, T. D.; Bergman, R. G. Organometallics 2002, 21, 4648. (d) Feldman, J. D.; Mitchell, G. P.; Nolte, J.-O.; Tilley, T. D. Can. J. Chem. 2003, 81, 1127. (e) Glaser, P. B.; Tilley, T. D. J. Am. Chem. Soc. 2003, 125, 13640. (f) Calimano, E.; Tilley, T. D. J. Am. Chem. Soc. 2008, 130, 9226. (g) Hashimoto, H.; Matsuda, A.; Tobita, H. Organometallics 2006, 25, 472. (h) Hashimoto, H.; Ochiai, M.; Tobita, H. J. Organomet. Chem. 2007, 692, 36. (i) Watanabe, T.; Hashimoto, H.; Tobita, H. J. Am. Chem. Soc. 2007, 129, 11338. (j) Ochiai, M.; Hashimoto, H.; Tobita, H. Dalton Trans. 2009, 1812. (k) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Powell, D.; West, R. Organometallics 2000, 19, 3263. (1) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Millevolte, A. J.; Powell, D. R.; West, R. J. Organomet. Chem. 2001, 636, 17. (m) Amoroso, D.; Haaf, M.; Yap, G. P. A.; West, R.; Fogg, D. E. Organometallics 2002, 21, 534. (n) Evans, W. J.; Perotti, J. M.; Ziller, J. W.; Moser, D. F.; West, R. Organometallics 2003, 22, 1160. (o) Nakata, N.; Fujita, T.; Sekiguchi, A. J. Am. Chem. Soc. 2006, 128, 16024. (p) Takanashi, K.; Lee, V. Y.; Yokoyama, T.; Sekiguchi, A. J. Am. Chem. Soc. 2009, 131, 916. (q) Avent, A. G.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. J. Organomet. Chem. 2003, 686, 321. (r) Neumann, E.; Pfaltz, A. Organometallics 2005, 24, 2008. (s) Zhang, M.; Liu, X.; Shi, C.; Ren, C.; Ding, Y.; Roesky, H. W. Z. Anorg. Allg. Chem. 2008, 634, 1755. (t) Meltzer, A.; Präsang, C.; Milsmann, C.; Driess, M. Angew. Chem., Int. Ed. 2009, 48, 3170. (u) Kong, L.; Zhang, J.; Song, H.; Cui, C. Dalton Trans. 2009, 5444. (v) Calimano, E.; Tilley, T. D. Organometallics 2010, 29, 1680. (w) Cade, I. A.; Hill, A. F.; Kaempfe, A.; Wagler, J. Organometallics 2010, 29, 4012. (x) Watanabe, C.; Inagawa, Y.; Iwamoto, T.; Kira, M. Dalton Trans. 2010, 39, 9414. See also refs 7-13.

(17) (a) Cundari, T. R.; Gordon, M. S. J. Phys. Chem. 1992, 96, 631.
(b) Marquez, A.; Sanz, J. F. J. Am. Chem. Soc. 1992, 114, 2903. (c) Jacobsen, H.; Ziegler, T. Organomettallics 1995, 14, 224. (d) Boehme, C.; Frenking, G. Organometallics 1998, 17, 5801. (e) Arnold, F. P., Jr. Organometallics 1999, 18, 4800. (f) Besora, M.; Maseras, F.; Lledós, A.; Eisenstein, O. Inorg. Chem. 2002, 41, 7105. (g) Pandey, K. K.; Lein, M.; Frenking, G. Organometallics 2004, 23, 2944. (h) Beddie, C.; Hall, M. B.

J. Am. Chem. Soc. 2004, 126, 13564. (i) Besora, M.; Maseras, F.; Lledós, A.; Eisenstein, O. Organometallics 2006, 25, 4748.

(18) (a) Ray, M.; Nakao, Y.; Sato, H.; Sakaba, H.; Sakaki, S. J. Am.
 Chem. Soc. 2006, 128, 11927. (b) Ray, M.; Nakao, Y.; Sato, H.; Sakaki, S.
 Organometallics 2007, 26, 4413. (c) Ray, M.; Nakao, Y.; Sato, H.; Sakaba,
 H.; Sakaki, S. Organometallics 2009, 28, 65.

(19) (a) Sakaba, H.; Watanabe, S.; Kabuto, C.; Kabuto, K. J. Am. Chem. Soc. 2003, 125, 2842. (b) Sakaba, H.; Yoshida, M.; Kabuto, C.; Kabuto, K. J. Am. Chem. Soc. 2005, 127, 7276. (c) Yabe-Yoshida, M.; Kabuto, C.; Kabuto, K.; Kwon, E.; Sakaba, H. J. Am. Chem. Soc. 2009, 131, 9138. (d) Sakaba, H.; Yabe-Yoshida, M.; Oike, H.; Kabuto, C. Organometallics 2010, 29, 4115.

(20) Recent examples of silacyclopropene formation from a silylene and an alkyne: (a) Gaspar, P. P.; Beatty, A. M.; Chen, T.; Haile, T.; Lei, D.; Winchester, W. R.; Braddock-Wilking, J.; Rath, N. P.; Klooster, W. T.; Koetzle, T. F.; Mason, S. A.; Albinati, A. Organometallics **1999**, *18*, 3921. (b) Ostendorf, D.; Saak, W.; Weidenbruch, M.; Marsmann, H. Organometallics **2002**, *21*, 636. (c) Ohshita, J.; Honda, N.; Nada, K.; Iida, T.; Mihara, T.; Matsuo, Y.; Kunai, A.; Naka, A.; Ishikawa, M. Organometallics **2003**, *22*, 2436. See also: (d) Ishikawa, M.; Kumada, M. Adv. Organomet. Chem. **1981**, *19*, 51.

(21) Reviews: (a) Diederich, F.; Rubin, Y. Angew. Chem., Int. Ed. Engl.
1992, 31, 1101. (b) Beck, W.; Niemer, B.; Wieser, M. Angew. Chem., Int. Ed.
Engl. 1993, 32, 923. (c) Lang, H. Angew. Chem., Int. Ed. Engl. 1994, 33, 547.
(d) Bruce, M. I.; Low, P. L. Adv. Organomet. Chem. 2004, 50, 179.

(22) (a) Appel, M.; Heidrich, J.; Beck, W. Chem. Ber 1987, 120, 1087. (b) Heidrich, J.; Stelman, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C. Organometallics 1990, 9, 1296.

(23) (a) Frank, K. G.; Selegue, J. P. J. Am. Chem. Soc. **1990**, 112, 6414. (b) Koutsantonis, G. A.; Selegue, J. P. J. Am. Chem. Soc. **1991**, 113, 2316.

(24) Davies, J. A.; El-Ghanam, M.; Pinkerton, A. A.; Smith, D. A. J. Organomet. Chem. **1991**, 409, 367.

(25) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. J. Am. Chem. Soc. 1991, 113, 8466.

(26) (a) Chen, M. C.; Tsai, Y. J.; Lin, Y. C.; Tseng, T. W.; Lee, G. H.; Wang, Y. Organometallics **1991**, *10*, 378. (b) Yang, Y. L.; Wang, L. J. J.; Lin, Y. C.; Huang, S. L.; Chen, M. C.; Lee, G. H.; Wang, Y. Organometallics **1997**, *16*, 1573.

(27) Ramsden, J. A.; Weng, W.; Arif, A. M.; Gladysz, J. A. J. Am. Chem. Soc. 1992, 114, 5890.

(28) Sünkel, K.; Birk, U.; Robl, C. Organometallics 1994, 13, 1679.
(29) (a) Akita, M.; Takabuchi, A.; Terada, M.; Ishii, N.; Tanaka, M.; Morooka, Y. Organometallics 1994, 13, 2516. (b) Akita, M.; Moro-oka, Y. Bull. Soc. Jpn. 1995, 68, 420. (c) Akita, M.; Chung, M. C.; Sakurai, A.; Sugimoto, S.; Terada, M.; Tanaka, M.; Morooka, Y. Organometallics 1997, 16, 4882.

(30) Long, N. J.; Williams, C. K. Angew. Chem., Int. Ed. Engl. 2003, 42, 2586 and references therein.

(31) Binger, P.; Müller, P.; Philipps, P.; Gabor, B.; Mynott, R.; Herrmann, A. T.; Langhauser, F.; Krüger, C. *Chem. Ber.* **1992**, *125*, 2209.

(32) Bruce, M. I.; Costuas, K.; Ellis, B. G.; Halet, J. F.; Low, P. J.; Moubaraki, B.; Murray, K. S.; Ouddaï, N.; Perkins, G. J.; Skelton, B. W.; White, A. H. *Organometallics* **2007**, *26*, 3735.

(33) De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Angew. Chem., Int. Ed. Engl. **1995**, 34, 1092.

(34) (a) LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. J. Am. Chem. Soc. **1986**, 108, 6382. (b) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. J. Am. Chem. Soc. **1989**, 111, 9056.

(35) Kheradmandan, S.; Venkatesan, K.; Blacque, O.; Schmalle, H. W.; Berke, H. *Chem. Eur. J.* **2004**, *10*, 4872.

(36) Listemann, M. L.; Schrock, R. R. Organometallics 1985, 4, 74.

(37) (a) Gilbert, T. M.; Rogers, R. D. J. Organomet. Chem. **1991**, 421, C1. (b) Gilbert, T. M.; Rogers, R. D. Acta Crystallogr., Sect. C **1993**, 49, 677.

(38) Caulton, K. G.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B.; Xue, Z. Organometallics **1992**, *11*, 321. (39) Woodworth, B. E.; White, P. S.; Templeton, J. L. J. Am. Chem. Soc. **1998**, 120, 9028.

(40) Colebatch, A. L.; Cordiner, R. L.; Hill, A. F.; Nguyen, K. T. H. D.; Shang, R.; Willis, A. C. *Organometallics* **2009**, *28*, 4394.

(41) (a) Belanzoni, P.; Nazzareno, Re.; Rosi, M.; Sgamellotti, A.; Floriani, C. *Organometallics* **1996**, *15*, 4264. (b) Angelis, F. D.; Nazzareno, Re.; Rosi, M.; Sgamellotti, A.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1997**, 3841. (c) Belanzoni, P.; Nazzareno, Re.; Sgamellotti, A.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1997**, 4773. (d) Belanzoni, P.; Sgamellotti, A.; Nazzareno, Re.; Floriani, C. *Inorg. Chem.* **2000**, *39*, 1147.

(42) Ouddaï, N.; Costuas, K.; Bencharif, M.; Saillard, J.-Y.; Halet, J.-F. C. R. Chim. 2005, 8, 1336.

(43) For Si-H bond activation of R₂HSiC≡CSiHR₂ by transitionmetal complexes, see: (a) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, 63, 107. (b) Corriu, R. J. P.; Moreau, J. J. E.; Praet, H. *Organometallics* **1989**, *8*, 2779. (c) Schneider, D.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 700. (d) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089. (e) Ohff, A.; Kosse, P.; Baumann, W.; Tillack, A.; Kempe, R.; Goerls, H.; Burlakov, V. V.; Rosenthal, U. *J. Am. Chem. Soc.* **1995**, *117*, 10399. (f) Peulecke, N.; Ohff, A.; Kosse, P.; Tillack, A.; Spannenberg, A.; Kempe, R.; Baumann, W.; Burlakov, V. V.; Rosenthal, U. *Chem. Eur. J.* **1998**, *4*, 1852. (g) Lamač, M.; Spannenberg, A.; Baumann, W.; Jiao, H.; Fischer, C.; Hansen, S.; Arndt, P.; Rosenthal, U. *J. Am. Chem. Soc.* **2010**, *132*, 4369.

(44) Pin, C.-W.; Peng, J.-J.; Shiu, C.-W.; Chi, Y.; Peng, S.-M.; Lee, G.-H. Organometallics 1998, 17, 438.

(45) Mathur, P.; Mukhopadhyay, S.; Lahiri, G. K.; Chakraborty, S.; Thone, C. Organometallics **2002**, *21*, 5209.

(46) Wrackmeyer, B.; Milius, W.; Tok, O. L. Chem. Eur. J. 2003, 9, 4732.

(47) This type of coodination of the Si=C moiety has not been reported so far. For related silene complexes $L_n M(\eta^2 - R_2 SiCR_2)$, see: (a) Lewis, C; Wrighton, M. S. J. Am. Chem. Soc. 1983, 105, 7768. (b) Randolph, C. L.; Wrighton, M. S. Organometallics 1987, 6, 365. (c) Campion, B. K.; Heyn, R. H.; Tilley, T. D. J. Am. Chem. Soc. 1988, 110, 7558. (d) Campion, B. K.; Heyn, R. H.; Tilley, T. D. J. Am. Chem. Soc. 1990, 112, 4079. (e) Koloski, T. S.; Carroll, P. J.; Berry, D. H. J. Am. Chem. Soc. 1990, 112, 6405. (f) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. J. Am. Chem. Soc. 1993, 115, 5527. (g) Koloski, T. S.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. Organometallics 1994, 13, 489. (h) Figge, L. K.; Carroll, P. J.; Berry, D. H. Organometallics 1996, 15, 209. (i) Dioumaev, V. K.; Plössl, K.; Carroll, P. J.; Berry, D. H. J. Am. Chem. Soc. 1999, 121, 8391. (j) Dioumaev, V. K.; Plössl, K.; Carroll, P. J.; Berry, D. H. Organometallics 2000, 19, 3374. (k) Klei, S. R.; Tilley, T. D.; Bergman, R. G. Organometallics 2001, 20, 3220. (1) Kuroda, S.; Dekura, F.; Sato, Y.; Mori, M. J. Am. Chem. Soc. 2001, 123, 4139. (m) Dioumaev, V. K.; Carroll, P. J.; Berry, D. H. Angew. Chem., Int. Ed. 2003, 42, 3947. (n) Bravo-Zhivotovskii, D.; Peleg-Vasserman, H.; Kosa, M.; Molev, G.; Botoshanskii, M.; Apeloig, Y. Angew. Chem., Int. Ed. 2004, 43, 745.

(48) The interesting possibility of 1,4-disilabutatriene coordination to a mononuclear metal center has been discussed for 1-zircona-2,5-disilacyclopent-3-yne: Lamač, M.; Spannenberg, A.; Jiao, H.; Hansen, S.; Baumann, W.; Arndt, P.; Rosenthal, U. *Angew. Chem., Int. Ed.* **2010**, *49*, 2937.

(49) In relation to 1,4-disilabutatriene coordination, μ -trans-butatriene coordination has been found in the dinuclear complexes Cp₂M-(H₂CCCCH₂)MCp₂ (M = Ti,⁵⁰ Zr⁵¹), which have almost planar MCCCCM skeletons and have been best described as a 2,5-dimetallabicyclo[2.2.0]hex-1(4)-ene structure.⁵⁰ The contribution of the corresponding 2,5-dimetalla-3,6-disilabicyclo[2.2.0]hex-1(4)-ene type structure to complexes 5 and 6 is, however, ruled out because of the nearly perpendicular geometry of the MSiCCSiM (M = W, Mo) moieties and very small Si1–C2 and Si2–C1 bond indices (0.065 and 0.075, respectively) compared to the Si1–C1 and Si2–C2 bond indices (0.705 and 0.675, respectively) for **5M**, a model complex of **5**. See Figure 7A and the theoretical study in the text.

(50) (a) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Parameswaran, P.; Jemmis, E. D. *Chem. Commun.* 2004, 2074. (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. Organometallics 2005, 24, 456.

(51) (a) Suzuki, N.; Watanabe, T.; Iwasaki, M.; Chihara, T. Organometallics **2005**, 24, 2065. (b) Suzuki, N.; Hashizume, D. Coord. Chem. Rev. **2010**, 254, 1307.

(52) In structurally related four-legged piano-stool complexes, cistrans and cis-cis interconversion by pseudorotation has been reported. For example, see: (a) Faller, J. W.; Anderson, A. S. J. Am. Chem. Soc. **1970**, 92, 5852. (b) Faller, J. W.; Anderson, A. S.; Jakubowski, A. J. Organomet. Chem. **1971**, 27, C47. (c) Scharrer, E.; Chang, S.; Brookhart, M. Organometallics **1995**, 14, 5686 and references therein.

(53) Carter, J. D.; Kingsbury, K. B.; Wilde, A.; Schoch, T. K.; Carolyn, J. L.; Pham, E. K.; McElwee-White, L. J. Am. Chem. Soc. 1991, 113, 2947.

(54) We optimized the typical W-carbene complex $Cp(CO)_2W$ -(CH₂)(CCH) by the DFT(B3PW91)/BS-I method.

(55) The C–C distances are 1.542, 1.334, and 1.210 Å and the C–C bond indices are 1.043, 2.052, and 3.001 in ethane (H_3C-CH_3) , ethylene $(H_2C=CH_2)$, and acetylene (HC=CH), respectively, where the geometries were optimized with the DFT/BS-I method and the bond indices were evaluated with the DFT/BS-II method.

(56) The Si–C distances are 1.895 and 1.717 Å and the Si–C bond indices are 0.884 and 1.818 in H_3 Si–C H_3 and H_2 Si=C H_2 , respectively.

(57) We calculated here a triplet state of disilabutatriene ($H_2Si-CC-SiH_2$) because we found instability in its closed-shell singlet wave function. However, we calculated the closed-shell singlet wave function for disilabutatriene dianion ($[H_2Si-CC-SiH_2]^{2-}$) because the closed-shell singlet wave function has no instability.

(58) The population of the CC moiety of acetylene is 12.467e.

(59) The populations of the CC moiety are 12.933e, 12.859e, 13.083e, and 13.014e for 13, 13d-an, 13d, and 13-an, respectively. The populations of the SiH₂ moiety are 15.533e, 15.468e, 16.493e, and 16.557e for 13, 13d, 13-an, and 13d-an, respectively.

(60) Dapprich, S.; Frenking, G. J. Phys. Chem. 1995, 99, 9352.

(61) Burdett, J. K. Struct. Bonding (Berlin) 1976, 31, 67.

(62) The population of $\varphi_{HOMO}(W)$ was calculated to be 1.787e in the typical ethynediyl-bridged dinuclear tungsten complex $Cp(CO)_3W-C \equiv C-W(CO)_3Cp$. This population is considerably larger than that (1.454e) of $Cp(CO)_2(SiH_2)W-C \equiv C-W(SiH_2)(CO)_2Cp$ (10), indicating that back-donation from W to SiH₂ is considerably larger in 10 than that from W to CO in $Cp(CO)_3W-C \equiv C-W(CO)_3Cp$.

(63) Sekigawa, S.; Shimizu, T.; Ando, W. *Tetrahedron* 1993, 49, 6359.
(64) (a) *CrystalClear* 1.3.6; Rigaku and Rigaku/MSC, The Woodlands,

TX. (b) Pflugrath, J. W. Acta Crystallogr. **1999**, D55, 1718.

(65) SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giovanni, M.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G. J.; Spagna, R. J. Appl. Crystallogr. **1999**, 32, 115.

(66) Sheldrick, G. M. SHELXS-97, Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

(67) DIRDIF99: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 Program System*; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1999.

(68) Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

(69) CrystalStructure 3.8.0: Crystal Structure Analysis Package; Rigaku and Rigaku/MSC, The Woodlands, TX, 2000–2006.

(70) (a) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.

(71) (a) Perdew, J. P. In *Electronic Structure of Solids* '91; Ziesche, P., Eschrig, H., Eds.; Akademic Verlag: Berlin, 1991; p 11. (b) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671. (c) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1993**, *48*, 4978. (d) Perdew, J. P.; Burke, K.; Wang, Y. *Phys Rev. B* **1996**, *54*, 16533.

(72) (a) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Chem. Phys. Lett. 1989, 157, 200. (73) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.

(74) (a) Dunning, T. H., Jr J. Chem. Phys. 1989, 90, 1007. (b) Woon,
 D. E.; Dunning, T. H., Jr. J. Chem. Phys. 1993, 98, 1358.

(75) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. J. Chem. Phys. 1971, 54, 724. (b) Hehre, W.; Ditchfield, R.; Pople, J. A. J. Chem. Phys. 1972, 56, 2257.

(76) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Theor. Chim. Acta 1990, 77, 123.

(77) Martin, J. M. L.; Sundermann, A. J. Chem. Phys. 2001, 114, 3408.

(78) Wiberg, K. B. Tetrahedron 1968, 24, 1083.

(79) Couty, M.; Hall, M. B. J. Comput. Chem. 1996, 17, 1359.

(80) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, 208, 111.

(81) Pople, J. A.; et al. *Gaussian 03, Revision C.02,* Gaussian Inc., Wallingford, CT, 2004. See ref S1 in the Supporting Information for the complete reference of Gaussian 03.

(82) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

(83) (a) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLE-KEL* 4.3; Swiss Center for Scientific Computing, Manno, Switzerland, 2000–2002. (b) Portmann, S.; Lüthi, H. P. *MOLEKEL*, An Interactive Molecular Graphics Tool. *Chimia* 2000, *54*, 766.