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Reactions of Tungsten Acetylide–Silylene Complexes with Pyridines: Direct Observation of Silylene/Silyl Migration in Tungsten Acetylide and Carbyne/Vinylidene Frameworks

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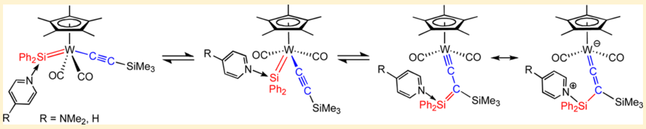
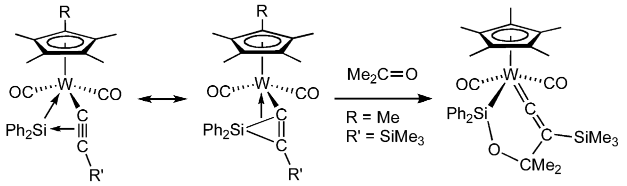
Supporting Information

ABSTRACT: Reaction of acetylide–silylene complex Cp*(CO)$_2$W(SiPh$_2$)(CC^{t}Bu) (**1a**) with 4-(dimethylamino)pyridine (DMAP) gave an equilibrium mixture of DMAP-stabilized silylene acetylide complexes *trans*- and *cis*-Cp*(CO)$_2$W(SiPh$_2$·DMAP)(CC^{t}Bu) (***trans*-4** and ***cis*-4**). The corresponding reaction using Cp*(CO)$_2$W(SiPh$_2$)(CCSiMe$_3$) (**2**) produced the novel DMAP-coordinated silenylcarbyne/silylvinylidene complex Cp*(CO)$_2$W[CC(SiPh$_2$·DMAP)(SiMe$_3$)] (**6a**) as a major product, which was equilibrated with *trans*- and *cis*-Cp*(CO)$_2$W(SiPh$_2$·DMAP)(CCSiMe$_3$) (***trans*-5a** and ***cis*-5a**) via silylene/silyl migration. The novel structures of ***cis*-4** and **6a** were revealed by X-ray crystallography. A mixture of **2** and pyridine exhibited interesting temperature-dependent NMR spectral changes, indicating the formation of *trans*- and *cis*-Cp*(CO)$_2$W(SiPh$_2$·py)(CCSiMe$_3$) (***trans*-5b** and ***cis*-5b**) and Cp*(CO)$_2$W[CC(SiPh$_2$·py)(SiMe$_3$)] (**6b**) at low temperature, while a mixture of **1a** and pyridine showed no such spectral changes.



Recent extensive studies on transition-metal silylene complexes have demonstrated their novel reactivity and important roles in metal-mediated reactions of organosilicon compounds.[1] The silylene center is highly electrophilic and often forms a donor-stabilized silylene complex, typically with a lone-pair donor. We previously reported the synthesis of acetylide–silylene complexes (η^5-C$_5$Me$_4$R)(CO)$_2$W(SiPh$_2$)(CCR′) (**1a**: R = Me, R′ = ^{t}Bu; **1b**: R = Et, R′ = ^{t}Bu; **2**: R = Me, R′ = SiMe$_3$) (Scheme 1),[2] whose unique charge transfer (CT) interactions between the acetylide and silylene ligands have been disclosed by a theoretical study.[3] Considering the CT from the acetylide to the silylene, they can be viewed as an intramolecularly π-bond-donor-stabilized silylene complex, and the electrophilic nature of the silylene ligand has been recently shown by the reaction of **2** with acetone to give the insertion product $\mathrm{Cp^*(CO)_2\overline{W{=}C{=}C(SiMe_3)CMe_2OSi}Ph_2}$ (**3**).[2b] We describe here the reactivity of **1a** and **2** toward typical lone-pair donors, pyridine and 4-(dimethylamino)pyridine (DMAP), demonstrating the formation of novel donor-stabilized silylene acetylide and silenylcarbyne/silylvinylidene complexes.

Scheme 1. Reaction of Acetylide–Silylene Complex 2 with Acetone



1a: R = Me, R′ = ^{t}Bu; **1b**: R = Et, R′ = ^{t}Bu
2: R = Me, R′ = SiMe$_3$

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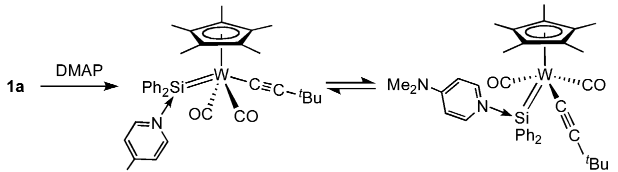
The reaction of **1a** with DMAP in toluene at room temperature resulted in the isolation of a yellow solid in 42% yield (Scheme 2). X-ray analysis of crystals obtained by recrystallization from toluene/hexane showed the interesting structure of DMAP-stabilized silylene acetylide complex ***cis*-4**, which adopts a four-legged piano stool geometry with two *cis*-arranged CO ligands (Figure 1). The W–Si bond distance (2.5125(7) Å) is much shorter than that (2.567(2) Å) of acetylide–silylene complex **1b**[2a] and is in the range (2.45–2.51 Å) for the W–Si bonds of donor-stabilized silylene tungsten complexes.[4] The Si–C1 and Si–C2 interatomic distances (2.436(3) and 3.141(3) Å, respectively) are significantly longer than those (1.937(7) and 2.009(7) Å) of **1b**.[2a] The W–C1–C2 angle (178.6(3)°) is linear, in contrast to the bent geometry

Scheme 2. Reaction of Acetylide–Silylene Complex 1a with DMAP



***trans*-4** ***cis*-4**

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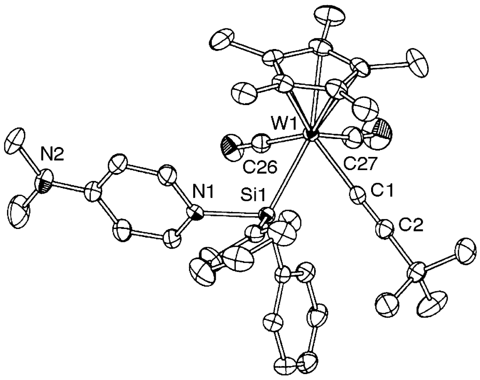


Figure 1. Molecular structures of ***cis*-4** showing thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W1−Si1, 2.5125(7); W1−C1, 2.137(3); Si1−N1, 1.941(3); C1−C2, 1.213(4); Si1−W1−C1, 62.59(7); Si1−W1−C26, 74.40(7); C26−W1−C27, 76.51(12); C1−W1−C27, 83.50(11); W1−C1−C2, 178.6(3).

(153.8(5)°) of the corresponding moiety in **1b**. The C1−C2 bond distance (1.213(4) Å) is shorter than that (1.270(9) Å) of **1b** and comparable to a typical C−C triple bond distance. These observations indicate considerably increased metal−silylene and decreased acetylide−silylene interactions in ***cis*-4** than in **1b**. However, the following feature suggests that a weak acetylide−silylene interaction may still exist in ***cis*-4**; the Si−W−C1 angle (62.59(7)°) between two bulky DMAP-coordinated silylene and *tert*-butylethynyl ligands is the smallest among four basal interligand angles: Si−W−C26 = 74.40(7)°, C1−W−C27 = 83.50(11)°, and C26−W−C27 = 76.51(12)° for the other three angles. Also in comparison with the P−W−C$_\alpha$ angle (75.1(2)°) and W−P distance (2.491(2) Å) of *cis*-Cp(CO)$_2$W(PPh$_3$)(C$_\alpha$≡CPh),[5] whose PPh$_3$ ligand has a bulkiness similar to the SiPh$_2$·DMAP in ***cis*-4**, the Si−W−C1 angle is found to be fairly small.

The ^{1}H NMR spectrum of the isolated solid in toluene-d_8 showed a single ^{t}Bu signal at 20 °C (Figure 2A). When the temperature was lowered, the signal broadened and then decoalesced into two signals in 27:73 ratio at −50 °C. In the ^{29}Si NMR spectrum at −50 °C, minor and major signals were observed at 69.4 ($J_{\rm WSi}$ = 111 Hz) and 41.4 ppm ($J_{\rm WSi}$ = 93 Hz), respectively. The minor component was characterized as *trans*-DMAP-stabilized silylene complex ***trans*-4** on the basis of the ^{29}Si chemical shift and ^{183}W satellites, which are in the ranges (62−145 ppm and 70−132 Hz, respectively) for those of donor-stabilized silylene tungsten complexes.[4] The major component was assigned to ***cis*-4**, and its ^{29}Si resonance is upfield-shifted by 28 ppm compared to that of ***trans*-4**. This upfield shift may result from the weak acetylide−silylene interaction suggested by the X-ray structure, considering the characteristic upfield ^{29}Si resonance (−48.1 ppm) of acetylide−silylene complex **1a**[2a] and the minor contribution of the acetylide−silylene interaction in ***cis*-4**. These VT-NMR experiments demonstrated an equilibrium between *trans* and *cis* isomers of the DMAP-stabilized silylene complex in solution.

Treatment of **2** with DMAP gave a yellow solid in 48% yield, and recrystallization from *p*-xylene/pentane gave single crystals, the X-ray analysis of which revealed the three-legged piano-stool structure **6a** with a unique W−C1−C2−Si1 backbone (Figure 3 and Scheme 3). A characteristic difference was found for the two Si−C bonds. The Si1−C2 bond (1.813(2) Å) is shorter by 2.5% than the Si2−C2 bond (1.859(2) Å). This bond shortening suggests a weak multiple-bond character for the Si1−C2 bond, although the Si1−C2 bond distance is considerably longer than Si═C bond distances (1.74−1.76 Å) of nitrogen donor-stabilized silenes Do·R$_2$Si═CR$_2$,[6,7] and the bond shortening is smaller than that (3.3%) in a typical example, Me$_2$EtN·Me$_2$Si═C(SiMe$_2$Ph)$_2$ (Si═C = 1.761(4) Å and Si−C = 1.822(4) Å for the average of two PhMe$_2$Si−C bonds).[6b] The Si1−N1 bond distance (1.850(2) Å) is intermediate between the Si−N bond distance (1.988(4) Å) of the Me$_2$EtN-stabilized silene and a typical Si−N covalent

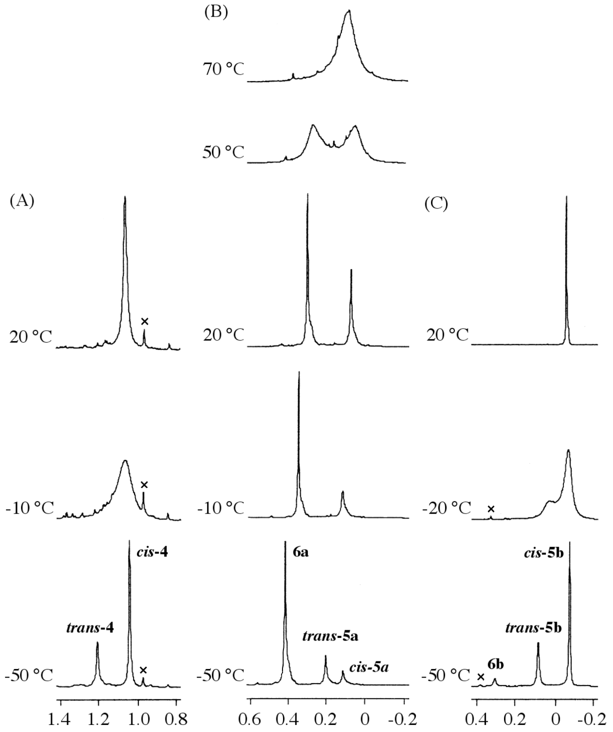


Figure 2. Variable-temperature ^{1}H NMR spectra in toluene-d_8. (A) ^{t}Bu signals of ***trans*-4** and ***cis*-4**. (B) SiMe$_3$ signals of ***trans*-5a**, ***cis*-5a**, and **6a**. (C) SiMe$_3$ signals of ***trans*-5b**, ***cis*-5b**, and **6b**. $^{\rm X}$Impurities.

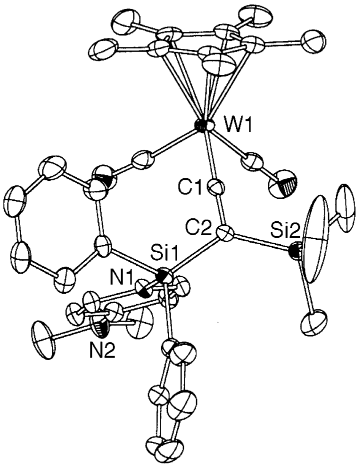
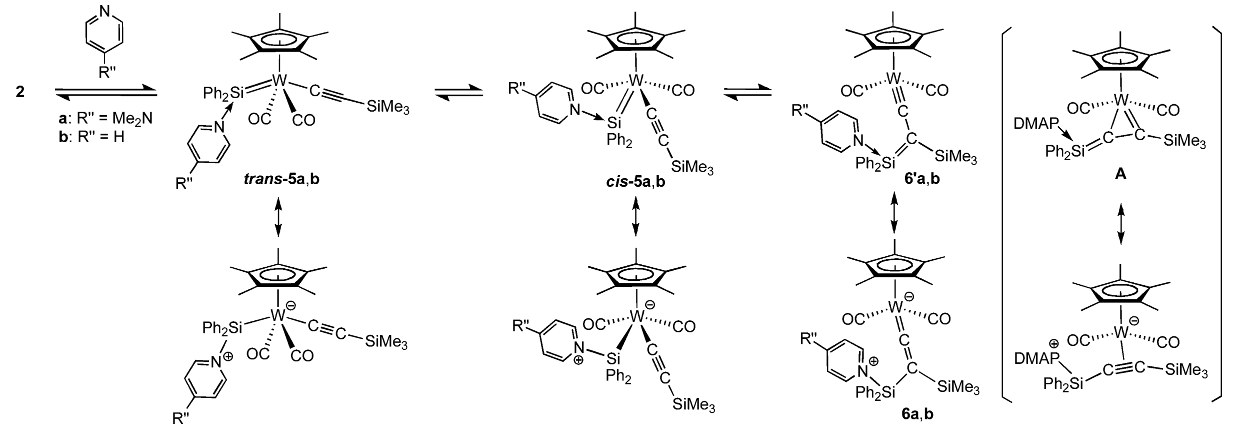


Figure 3. Molecular structure of **6a** showing thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W1−C1, 1.918(2); C1−C2, 1.359(3); Si1−C2, 1.813(2); Si2−C2, 1.859(2); Si1−N1, 1.850(2); W1−C1−C2, 176.55(19); Si1−C2−Si2, 129.29(12); Si1−C2−C1, 111.20(17); Si2−C2−C1, 117.65(17).

Scheme 3. Reactions of Acetylide−Silylene Complex 2 with DMAP and Pyridine



bond distance (1.70−1.76 Å).[8] The W−C1 bond distance (1.918(2) Å) is longer than W≡C bond distances (1.81−1.82 Å) in tungsten carbyne complexes $Cp(CO)_2W{\equiv}CR$ (R = *p*-Tol, $SiPh_3$)[9] and in the range (1.88−1.98 Å) of W═C bond distances in tungsten vinylidene complexes.[10] However, interesting differences were found in comparison of the W−C1−C2 moiety of **6a** with the W═C═C framework of structurally closely related vinylidene complex **3**. The W−C1 bond is 0.04 Å shorter than the *W*═*C*═C bond (1.957(3) Å) of **3**,[2b] whereas the C1−C2 bond (1.359(3) Å) is 0.05 Å longer than the W═*C*═*C* bond (1.309(4) Å). These structural features are attributable to a major contribution of vinylidene form **6a** accompanied by a minor contribution of DMAP-stabilized silenylcarbyne form **6′a**.

In the ^{1}H NMR spectrum of the isolated solid in toluene-d_8 at 20 °C, two $SiMe_3$ signals were observed at 0.31 (major) and 0.08 ppm (minor) (Figure 2B).[11] Although the shape of the major signal did not change in low-temperature measurements, the minor signal became broad at −10 °C and separated into two signals at 0.20 and 0.11 ppm at −50 °C. At this temperature, three components were observed in 70:18:12 ratio, based on the relative intensities of the $SiMe_3$ signals at 0.41, 0.20, and 0.11 ppm, which were characterized as **6a**, ***trans*-5a**, and ***cis*-5a**, respectively. The ^{29}Si NMR spectrum at −60 °C showed three pairs of signals, which were assigned to ***trans*-5a** (68.2 ($SiPh_2$·DMAP) and −29.4 ($SiMe_3$) ppm), ***cis*-5a** (50.5 ($SiPh_2$·DMAP) and −27.9 ($SiMe_3$) ppm), and **6a** (−10.8 ($SiPh_2$·DMAP) and −10.6 ($SiMe_3$) ppm), judging from their relative intensities and ^{1}H−^{29}Si HMBC correlations between the $SiMe_3$ and $SiMe_3$ signals. The chemical shift of the $SiPh_2$·DMAP signal of ***trans*-5a** (68.2 ppm) is very close to that of ***trans*-4** (69.4 ppm), while the $SiPh_2$·DMAP signal of ***cis*-5a** (50.5 ppm) is 9 ppm downfield-shifted from that of ***cis*-4** (41.4 ppm). This difference would be derived from stronger metal−silylene and weaker acetylide−silylene interactions in **2** than in **1b** observed in their molecular structures: W−Si = 2.5474(16) Å and Si−C_β(acetylide) = 2.059(6) Å for **2** and W−Si = 2.567(2) Å and Si−C_β(acetylide) = 2.009(7) Å for **1b**.[2] Compared to these ^{29}Si signals, the $SiPh_2$·DMAP signal of **6a** is considerably upfield-shifted, and the vinylidene-type structure is supported by ^{13}C signals at 320.9 (C_α) and 87.4 (C_β) ppm at −70 °C. The low-temperature NMR measurements indicated fast interconversion between ***trans*-5a** and ***cis*-5a**, similar to the case for ***trans*-4** and ***cis*-4**, and high-temperature measurements demonstrated their slow interconversion with **6a**, as evidenced by coalescence of the $SiMe_3$ signals to give a broad signal at 0.10 ppm at 70 °C (Figure 2B). The latter behavior strongly suggests the first direct observation of interconversion between a metal acetylide and a metal carbyne/vinylidene by silylene/silyl migration; the $SiPh_2$·DMAP moiety in ***trans*-5a**, ***cis*-5a**, and **6a** can be viewed as a resonance hybrid of DMAP-stabilized silylene and 4-(dimethylamino)pyridiniumsilyl groups (Scheme 3). For the isomerization mechanism, the formation of **6a** via metallacyclopropene(η^2-vinyl)/alkyne complex **A**, which is derivable from ***cis*-5a**, might be also conceivable. However, coordination of the η^2-vinyl/alkyne-type ligand having two bulky silyl substituents would cause steric repulsion toward the metal fragment to favor the formation of **6a** rather than that of **A** from ***cis*-5a**. As a supportive example, it has been reported that $(\eta^6\text{-}C_6Me_6)(CO)_2Cr{=}C{=}C(SiMe_3)_2$ is thermodynamically more stable than $(\eta^6\text{-}C_6Me_6)(CO)_2Cr(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$.[12] Considering also a recent theoretical study by Koga et al. that the activation energy for 1,3-silyl migration is considerably lower than those for 1,3-hydrogen and methyl migrations in the conversion of the acetylide complex $(H_3P)_2ClRhR(C{\equiv}CH)$ to the vinylidene complex $(H_3P)_2ClRh{=}C{=}CHR$ (R = SiH_3, 12.84; H, 18.71; CH_3, 25.38 kcal mol^{-1}),[13] 1,3-silylene/silyl migration seems to be favored in the interconversion between ***cis*-5** and **6a**.

Reactivity of **1a** and **2** toward pyridine was also investigated. The room-temperature ^{1}H NMR spectrum of a toluene-d_8 solution of **1a** and pyridine (3 equiv) showed their sharp signals with no observable products, in contrast to the reaction with DMAP, and slight signal broadening was observed only upon cooling to −60 °C. Very interestingly, by contrast, the treatment of **2** with pyridine (3.3 equiv) led to clear temperature-dependent spectral changes. The ^{1}H NMR spectrum at 20 °C showed sharp signals of the starting materials, involving one $SiMe_3$ signal at −0.05 ppm (Figure 2C and see also Supporting Information, Figure S5), whereas three $SiMe_3$ signals assigned to pyridine adducts **6b**, ***trans*-5b**, and ***cis*-5b** were observed at 0.32, 0.09, and −0.07 ppm in a 6:31:63 ratio at −50 °C (Figure 2C). This spectral change indicates that the starting materials are equilibrated with the adducts and that the equilibrium shifts toward the adducts at low temperature. At −60 °C, three sets of ^{29}Si signals were detected: 79.3 (J_{WSi} = 115 Hz, $SiPh_2$·py) and −29.2 ($SiMe_3$) ppm for ***trans*-5b**, 37.8 (vbr, $SiPh_2$·py) and −25.5 (br, $SiMe_3$) ppm for ***cis*-5b**, and −3.6 ($SiPh_2$·py) and −10.3 ($SiMe_3$) ppm for **6b** (Figure 4A). Signal assignments were performed on the basis of the ^{1}H−^{29}Si HMBC spectrum and the similarity of their ^{29}Si chemical shifts to those of ***trans*-4,5a**, ***cis*-4,5a**, and **6a**. The chemical shift and

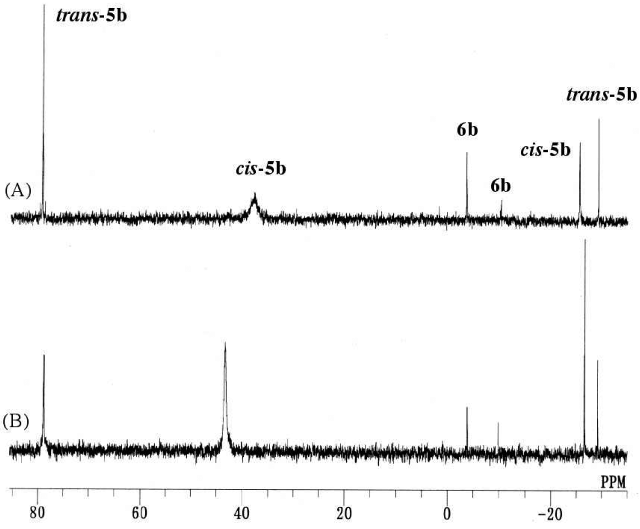


Figure 4. ^{29}Si{^{1}H} NMR spectra of ***trans*-5b**, ***cis*-5b**, and **6b** in toluene-d_8 at −60 °C (A) and at −90 °C (B).

^{183}W satellites for the *Si*Ph_2·py signal of ***trans*-5b** are reasonable for the typical donor-stabilized silylene complex,[4] and the *Si*Ph_2·py signal of ***cis*-5b** is upfield-shifted relative to it, similar to the case for ***cis*-4** and ***cis*-5a**, supporting its *cis*-donor-stabilized silylene structure. Notably, only the signals of ***cis*-5b** were broad at −60 °C and sharpened at −90 °C (Figure 4). In the ^{1}H NMR spectrum at −60 °C, the coordinated pyridine signals of ***trans*-5b** were clearly detected at 8.67, 6.48, and 6.08 ppm (see Supporting Information, Figure S6). On the other hand, the corresponding signals of ***cis*-5b** were observed as coalescent signals with free pyridine at 8.46, 6.89, and 6.55 ppm at −60 °C, and they considerably broadened at −80 °C (see Supporting Information, Figures S6 and S7). These observations imply that the dissociation equilibrium of pyridine is much more facilitated in ***cis*-5b** than in ***trans*-5b**, most likely due to the weak acetylide−silylene interaction remaining in the *cis* isomer. Dissociation of the coordinated donor in the DMAP system is also demonstrated by the reaction of a mixture of ***trans*-5a**, ***cis*-5a**, and **6a** with BPh_3 (1 equiv) in benzene-d_6, leading to the rapid and clean formation of **2** and DMAP·BPh_3.

From the above results, important substituent effects of $SiMe_3$ vs CMe_3 group on the reactivity of acetylide−silylene complexes are derived as follows. The $SiMe_3$ substituent increases the reactivity of an acetylide−silylene complex toward a nitrogen base, as shown by the reactivity of **1a** and **2** toward pyridine. This is ascribed to the stronger metal−silylene and weaker acetylide−silylene interactions in **2** than in **1a**, as evidenced by X-ray structural comparison of **2** and **1b**. The reactions of **1a** and **2** with DMAP demonstrate that the $SiMe_3$ group favors the formation of silylvinylidene/silenylcarbyne complex **6a**, and a similar stabilization effect for a vinylidene-type structure has been observed in their reactions with acetone.[2b] The strength of bases also affects the product distribution. In the reactions of **2**, the weaker base pyridine favors the formation of *cis*-donor-stabilized silylene acetylide complex ***cis*-5b** over *trans* isomer ***trans*-5b**, while the stronger base DMAP overcomes the acetylide−silylene interaction to favor *trans* isomer ***trans*-5a** over *cis* isomer ***cis*-5a**, although the most favorable product is silylvinylidene/silenylcarbyne complex **6a**. Further studies of the acetylide−silylene complexes are in progress to uncover their novel property and reactivity.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Hexane, pentane, toluene, benzene-d_6, and toluene-d_8 were distilled from sodium benzophenone ketyl. 4-(Dimethylamino)pyridine and triphenylborane were purchased from Sigma-Aldrich. $Cp^*(CO)_2W(SiPh_2)(CC^tBu)$ (**1a**),[2a] $Cp^*(CO)_2W(SiPh_2)(CCSiMe_3)$ (**2**),[2b] $Cp^*(CO)_2W(NCMe)Me$,[14] $Ph_2HSiC{\equiv}C^tBu$,[2a] and $Ph_2HSiC{\equiv}CSiMe_3$[2b] were prepared according to the literature methods. NMR spectra were recorded on a Bruker AV-400 or AV-600 spectrometer, and IR spectra were obtained on a Shimadzu FTIR-8100 M spectrometer. High-resolution mass spectra were recorded on a Bruker Daltonics solariX 9.4T FT-ICR mass spectrometer. Mass spectrometric analysis, elemental analysis, and X-ray crystal analysis were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

Reaction of 1a with DMAP. An NMR tube was charged with **1a** (7.0 mg, 11 μmol), DMAP (1.3 mg, 11 μmol), and benzene-d_6 (0.5 mL), and the tube was flame-sealed under vacuum. The ^{1}H NMR spectrum of the solution showed coalescent signals of ***trans*-4** and ***cis*-4** in 87% yield. ^{1}H NMR (400 MHz, benzene-d_6, rt): δ 1.11 (s, 9H, ^{t}Bu), 2.03 (br, 6H, NMe_2), 2.07 (s, 15H, Cp*), 5.82 (s, 2H, DMAP), 7.19−7.27 (m, 2H, Ph), 7.27−7.37 (m, 4H, Ph), 8.00 (br, 2H, DMAP), 8.30 (br, 4H, Ph).

In a preparative reaction, toluene (3 mL) was vacuum transferred to a mixture of $Cp^*(CO)_2W(NCMe)Me$ (100 mg, 0.23 mmol) and $Ph_2HSiC{\equiv}C^tBu$ (64 mg, 0.24 mmol) with cooling in a liquid nitrogen bath. The mixture was thawed at −70 °C and warmed to room temperature with stirring. After 30 min at room temperature, the solvent was removed under vacuum to leave crude **1a**, to which DMAP (30 mg, 0.25 mmol) and toluene (2.5 mL) were added. The mixture was stirred at room temperature for 50 min. After removal of the volatiles, the residual solid was washed with hexane (4 × 2 mL) to give an air-sensitive yellow solid (74 mg, 42% yield based on $Cp^*(CO)_2W(NCMe)Me$). The room-temperature spectrum of the solid was the same as that of the NMR tube reaction, and variable-temperature NMR measurements were performed using toluene-d_8 as a solvent. ^{1}H NMR (600 MHz, toluene-d_8, −60 °C): δ 1.06 (s, ^{t}Bu, ***cis*-4**), 1.23 (s, ^{t}Bu, ***trans*-4**), 1.62 (s, NMe_2, ***trans*-4**), 1.71 (s, NMe_2, ***cis*-4**), 2.08 (s, Cp*, overlapped with a $C_6D_5CD_2H$ signal), 2.15 (s, Cp*, ***cis*-4**), 5.12 (m, DMAP, ***cis*-4**), 5.18 (m, DMAP, ***trans*-4**), 7.22−7.26 (m, Ph), 7.32−7.38 (m, Ph), 7.54 (m, Ph), 7.63 (m, DMAP, ***cis*-4**), 8.14−8.19 (m, Ph), 8.27 (m, DMAP, ***trans*-4**), 8.35 (m, Ph). ^{13}C{^{1}H} NMR (150 MHz, toluene-d_8, −70 °C): δ 11.5 (C_5*Me*$_5$, ***trans*-4**), 11.7 (C_5*Me*$_5$, ***cis*-4**), 30.2 (C*Me*$_3$, ***trans*-4**), 30.6 (C*Me*$_3$, ***cis*-4**), 31.5 (*C*Me_3, ***cis*-4**), 32.7 (*C*Me_3, ***trans*-4**), 38.2 (NMe_2, ***trans*-** and ***cis*-4**), 86.5 (WCC, ***cis*-4**), 89.3 (WCC, ***trans*-4**), 100.0 (C_5Me_5, ***cis*-4**), 100.1 (C_5Me_5, ***trans*-4**), 104.8 (DMAP, ***cis*-4**), 105.1 (DMAP, ***trans*-4**), 127.3, 130.2, 132.5, 135.0, 135.5 (Ph), 136.5 (WCC, ***trans*-4**), 142.9 (Ph), 145.7 (DMAP, ***cis*-4**), 146.2 (WCC, ***cis*-4**), 147.4 (DMAP, ***trans*-4**), 153.9 (DMAP, ***cis*-4**), 154.7 (DMAP, ***trans*-4**), 221.1 (CO, ***trans*-4**), 238.2 (CO, ***cis*-4**), 249.0 (CO, ***cis*-4**). Several acetylide and aromatic carbon signals were not assigned due to their poor intensities or overlap with solvent signals. ^{29}Si{^{1}H} NMR (118 MHz, toluene-d_8, −70 °C): δ 69.4 ($^{1}J_{WSi}$ = 111 Hz, ***trans*-4**), 41.4 ($^{1}J_{WSi}$ = 93 Hz, ***cis*-4**). IR (KBr): ν_{CO} 1892, 1806 cm^{-1}. Anal. Calcd for $C_{37}H_{44}N_2O_2SiW$: C, 58.42; H, 5.83; N, 3.68. Found: C, 58.15; H, 6.03; N, 3.42.

Reaction of 2 with DMAP. An NMR tube was charged with **2** (9.5 mg, 16 μmol), DMAP (2.0 mg, 16 μmol), and benzene-d_6 (0.5 mL), and the tube was flame-sealed under vacuum. The ^{1}H NMR spectrum of the solution showed the coalescent signals of ***trans*-5a** and ***cis*-5a** and the signals of **6a** in 37% (***trans*-5a** + ***cis*-5a**) and 63% (**6a**) yields, respectively. ^{1}H NMR (400 MHz, benzene-d_6, rt): δ 0.13 (s, $SiMe_3$, ***trans*-** and ***cis*-5a**), 0.39 (s, $SiMe_3$, **6a**), 1.84 (s, NMe_2, **6a**), 1.90 (br, NMe_2, ***trans*-** and ***cis*-5a**), 2.03 (s, Cp*, ***trans*-** and ***cis*-5a**), 2.24 (s, Cp*, **6a**), 5.36−5.66 (br, DMAP, ***trans*-** and ***cis*-5a**), 5.66−5.90 (br, DMAP, **6a**), 7.18−7.28 (m, Ph, ***trans*-** and ***cis*-5a** + **6a**), 7.28−7.39 (m, Ph, ***trans*-** and ***cis*-5a** + **6a**), 7.75−8.13 (br, Ph, ***trans*-** and ***cis*-5a** + **6a**), 8.14−8.33 (m, DMAP, ***trans*-** and ***cis*-5a** + **6a**).

In a preparative reaction, toluene (2.5 mL) was vacuum transferred to a mixture of Cp*(CO)$_2$W(NCMe)Me (100 mg, 0.23 mmol) and Ph$_2$HSiC≡CSiMe$_3$ (69 mg, 0.24 mmol) with cooling in a liquid nitrogen bath. The mixture was thawed at −70 °C and warmed to room temperature with stirring. After 30 min at room temperature, the volatiles were removed under vacuum to leave crude **2**, to which DMAP (29 mg, 0.24 mmol) and toluene (2.2 mL) were added. The mixture was stirred at room temperature for 2 h. After removal of the volatiles, the residual solid was washed with hexane (4 mL) and then with hexane/toluene (5 × 3.7 mL/0.3 mL) to give an air-sensitive yellow solid (86 mg, 48% yield based on Cp*(CO)$_2$W(NCMe)Me). The room-temperature spectrum of the powder was the same as that of the NMR tube reaction, and variable-temperature NMR measurements were performed using toluene-d_8 as a solvent. ^{1}H NMR (600 MHz, toluene-d_8, −60 °C): δ 0.12 (s, SiMe$_3$, ***cis*-5a**), 0.21 (s, SiMe$_3$, ***trans*-5a**), 0.42 (s, SiMe$_3$, **6a**), 1.733 (s, NMe$_2$, **6a**), 1.735 (s, NMe$_2$, ***trans*-5a**), 1.78 (s, NMe$_2$, ***cis*-5a**), 2.03 (s, Cp*, ***trans*-5a**), 2.09 (s, Cp*, ***cis*-5a**, overlapped with a C$_6$D$_5$CD$_2$H signal), 2.30 (s, Cp*, **6a**), 5.20 (br m, DMAP, ***trans*-5a**), 5.23 (br m, DMAP, ***cis*-5a**), 5.61 (m, DMAP, **6a**), 7.0−7.6 (br m, Ph), 7.53 (m, DMAP, ***trans*-5a**), 8.15 (m, DMAP, **6a**), 8.2−8.5 (br, Ph). ^{13}C NMR (100 MHz, toluene-d_8, −70 °C): δ 1.1 (SiMe$_3$, ***cis*-5a**), 1.8 (SiMe$_3$, ***trans*-5a**), 2.7 (SiMe$_3$, **6a**), 11.3 (C$_5$*Me*$_5$, ***trans*-5a**), 11.5 (C$_5$*Me*$_5$, ***cis*-5a**), 12.0 (C$_5$*Me*$_5$, **6a**), 38.1 (NMe$_2$, ***trans*-5a**), 38.3 (NMe$_2$, ***cis*-5a**), 38.5 (NMe$_2$, **6a**), 87.4 (WCC, **6a**), 100.4 (*C*$_5$Me$_5$, ***trans*-5a** and ***cis*-5a**), 101.7 (*C*$_5$Me$_5$, **6a**), 105.2 (DMAP, ***cis*-5a**), 106.3 (DMAP, ***trans*-5a**), 106.4 (DMAP, **6a**), 133.9, 134.6, 135.3, 136.7, 145.4, 145.9, 146.9, 154.7, 155.4 (Ph), 234.4 (CO), 237.2 (CO), 237.5 (CO), 247.6 (CO), 320.9 (WCC, **6a**). Several acetylide and aromatic carbon signals were not assigned due to overlap with solvent signals. ^{29}Si NMR (79 MHz, toluene-d_8, −60 °C): δ −29.4 (SiMe$_3$, ↔ δ_H 0.21, ***trans*-5a**), −27.9 (SiMe$_3$, ↔ δ_H 0.12, ***cis*-5a**), −10.8 (SiPh$_2$·DMAP, **6a**), −10.6 (SiMe$_3$, ↔ δ_H 0.42, **6a**), 50.5 (SiPh$_2$·DMAP, ***cis*-5a**), 68.2 (SiPh$_2$·DMAP, ***trans*-5a**); ^{29}Si−^{1}H HMBC correlations are indicated by ↔. IR (KBr): ν_CO 1869, 1767 cm^{-1}. HRMS: calcd for C$_{36}$H$_{44}$N$_2$O$_2$Si$_2$W 776.24503, found 776.25060.

Reaction of 2 with Pyridine. An NMR tube was charged with **2** (40 mg, 0.061 mmol), pyridine (0.20 mmol, 3.3 equiv), and toluene-d_8 (0.6 mL). The tube was flame-sealed under vacuum, and variable-temperature NMR measurements were carried out. ^{1}H NMR (600 MHz, toluene-d_8, −60 °C): δ −0.07 (s, SiMe$_3$, ***cis*-5b**), 0.10 (s, SiMe$_3$, ***trans*-5b**), 0.33 (s, SiMe$_3$, **6b**), 1.95 (s, Cp*, ***trans*-5b**), 1.98 (s, Cp*, ***cis*-5b**), 2.26 (s, Cp*, **6b**), 6.08 (m, py, ***trans*-5b**), 6.48 (m, py, ***trans*-5b**), 6.55 (m, py, free + ***cis*-5b**), 6.89 (m, py, free + ***cis*-5b**), 7.20 (m, Ph), 7.29 (m, Ph), 7.33 (m, Ph), 8.03 (m, Ph), 8.28 (m, Ph), 8.46 (m, py, free + ***cis*-5b**), 8.67 (m, py, ***trans*-5b**). ^{13}C NMR (150 MHz, toluene-d_8, −60 °C): δ 0.5 (SiMe$_3$, ***cis*-5b**), 1.6 (SiMe$_3$, ***trans*-5b**), 2.5 (SiMe$_3$, **6b**), 11.2 (C$_5$*Me*$_5$, ***trans*-5b**), 11.4 (C$_5$*Me*$_5$, ***cis*-5b**), 11.9 (C$_5$*Me*$_5$, **6b**), 100.5 (*C*$_5$Me$_5$, ***trans*-5b**), 100.7 (*C*$_5$Me$_5$, ***cis*-5b**), 102.0 (*C*$_5$Me$_5$, **6b**), 123.6 (py, free + ***cis*-5b**), 124.4 (py, ***trans*-5b**), 129.6, 134.7 (Ph), 134.9 (WCC, ***trans*-5b**), 136.0 (py, free + ***cis*-5b**), 137.1, 138.4, 140.1, 141.1, 141.5, 144.1 (Ph), 148.2 (py, ***trans*-5b**), 149.6 (py, free + ***cis*-5b**), 149.9 (WCC, ***cis*-5b**), 235.6 (CO, ***cis*-5b**), 246.9 (CO, ***cis*-5b**). Several acetylide, vinylidene, carbonyl, and aromatic carbon signals were not assigned due to their poor intensities or overlap with solvent signals. ^{29}Si{^{1}H} NMR (119 MHz, toluene-d_8, −60 °C): δ −29.2 (SiMe$_3$, ↔ δ_H 0.10, ***trans*-5b**), −25.5 (br, SiMe$_3$, ↔ δ_H −0.07, ***cis*-5b**), −10.3 (SiMe$_3$, ↔ δ_H 0.33, **6b**), −3.6 (SiPh$_2$·py, **6b**), 37.8 (vbr, SiPh$_2$·py, ***cis*-5b**), 79.3 (J_WSi = 115 Hz, SiPh$_2$·py, ***trans*-5b**). ^{29}Si−^{1}H HMBC correlations are indicated by ↔.

Reaction of a Mixture of *cis*-5a, *trans*-5a, and 6a with BPh$_3$. BPh$_3$ (3.3 mg, 13 μmol) was added into an NMR tube containing a mixture of ***cis*-5a**, ***trans*-5a**, and **6a** (10 mg, 13 μmol) in benzene-d_6 (0.5 mL), and the tube was flame-sealed under vacuum. The ^{1}H NMR spectrum showed their quantitative conversion into **2** and DMAP·BPh$_3$.

X-ray Crystal Structure Determination. Single crystals of ***cis*-4**·0.5hexane and **6a** were obtained by recrystallization from toluene/hexane and *p*-xylene/pentane, respectively. The diffraction data were collected on a Rigaku Saturn70 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at −100 °C. The structures were solved by direct methods using SHELXS97[15] for ***cis*-4**·0.5hexane and SIR2004[16] for **6a**, and structural refinements were performed by full-matrix least-squares using SCHLXL97 for ***cis*-4**·0.5hexane and CRYSTALS[17] for **6a**. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined using the riding model. Selected crystallographic data are summarized in Table S1 in the Supporting Information.

ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C{^{1}H} NMR spectra and selected crystallographic data (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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