



Direct Conversion of a Si–C(aryl) Bond to Si–Heteroatom Bonds in the Reactions of η^3 - α -Silabenzyl Molybdenum and Tungsten Complexes with 2-Substituted Pyridines

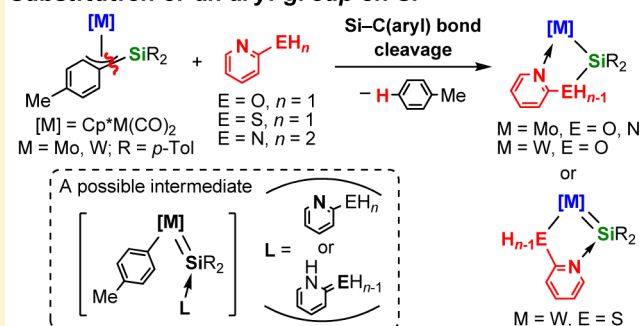
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S Supporting Information

ABSTRACT: η^3 - α -Silabenzyl complexes $\text{Cp}^*\text{M}(\text{CO})_2\{\eta^3(\text{Si}_i\text{C}_i\text{C})\text{-Si}(p\text{-Tol})_3\}$ ($\text{M} = \text{Mo}$ (**1-Mo**), W (**1-W**)) reacted with 2-substituted pyridines $\text{NC}_5\text{H}_4(2\text{-EH}_n)$ ($\text{E} = \text{O}, \text{S}$ ($n = 1$); N ($n = 2$)) under mild conditions to give M-Si-E-C-N ($\text{E} = \text{O}, \text{N}$), W-Si-N-C-S , and M-E-C-N ($\text{E} = \text{S}, \text{N}$) metallacycles depending on the metal M or heteroatom E . These three kinds of metallacycles were characterized by spectroscopy, elemental analysis, and X-ray crystallography. The first two silametallacycles take on some silylene complex character and are considered to form via (aryl)silylene complex intermediates generated by cleavage of the Si–C(aryl) bond in the η^3 - α -silabenzyl ligand of **1-Mo** and **1-W**.

Substitution of an aryl group on Si

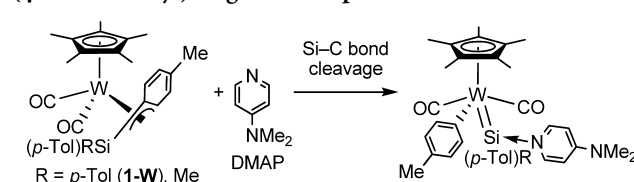


INTRODUCTION

Activation of robust Si–C(aryl) bonds induced by transition-metal complexes is of considerable interest because this can be applied to the direct functionalization of arylsilanes.¹ Many catalytic and stoichiometric reactions via Si–C(aryl) bond activation have been developed using late-transition-metal complexes.^{1,2} In these reactions, oxidative addition of Si–C(aryl) bonds to low-valent metal centers plays a crucial role.² In contrast, the counterparts using early-transition-metal complexes have received less attention.

In addition to the oxidative addition, 1,2-migration of aryl substituents on silicon to metal in coordinatively unsaturated arylsilyl complexes producing (aryl)silylene complexes has been proposed as a crucial process for a few Si–C(aryl) bond activation reactions.^{2b,3} We have recently found a reversible 1,2-aryl migration in tungsten–silicon complexes⁴ and finally succeeded in isolation of key intermediates of this migration reaction, i.e. η^3 - α -silabenzyl complexes $\text{Cp}^*\text{W}(\text{CO})_2\{\eta^3(\text{Si}_i\text{C}_i\text{C})\text{-Si}(p\text{-Tol})_2\text{R}\}$ ($\text{R} = p\text{-Tol}$ (**1-W**), Me), the first silicon analogues of η^3 -benzyl complexes.^{5a} We also found that the reaction of these complexes with 4-(dimethylamino)pyridine (DMAP) gave DMAP-stabilized (aryl)silylene complexes $\text{Cp}^*\text{W}(\text{CO})_2(p\text{-Tol})\{\text{Si}(p\text{-Tol})\text{R-DMAP}\}$ via Si–C(aryl) bond cleavage (1,2-aryl migration) (Scheme 1). This result prompted us to examine the reactions of the η^3 - α -silabenzyl tungsten complex **1-W** and its molybdenum analogue **1-Mo**^{5b} with 2-substituted pyridines $\text{NC}_5\text{H}_4(2\text{-EH}_n)$ ($\text{E} = \text{O}, \text{S}$ ($n = 1$); $\text{E} = \text{N}$ ($n = 2$)). These substrates bear multiple nucleophilic heteroatoms (N and E) that can attack the electrophilic silicon atom as well as protic hydrogen(s) on E that can protonate the metal center. As a result, we developed unique conversion reactions via Si–C(aryl)

Scheme 1. 1,2-Aryl Migration in the Reaction of (η^3 - α -Silabenzyl)tungsten Complexes with DMAP



bond cleavage and arene elimination to give silametallacycles. We report here the direct conversion of a Si–C(aryl) bond to Si–heteroatom bonds starting from **1-W** and **1-Mo**.

RESULTS AND DISCUSSION

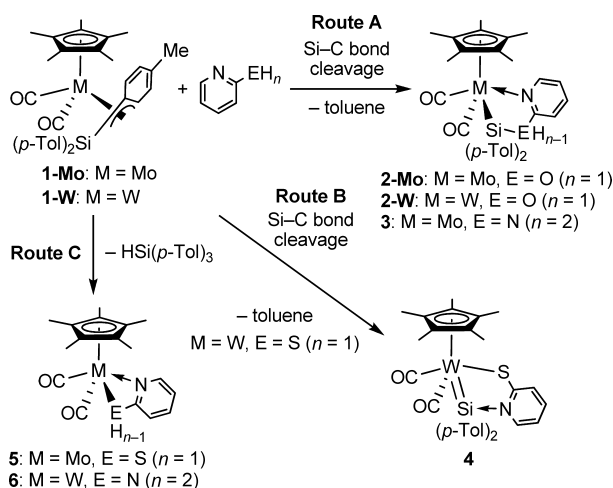
Reactions of η^3 - α -Silabenzyl Complexes **1-Mo and **1-W** with 2-Substituted Pyridines.** **1-Mo** and **1-W** reacted with 2-substituted pyridines (2-hydroxypyridine, 2-mercaptopyridine, and 2-aminopyridine) to give three kinds of metallacycles **2–6** depending on the metal and the 2- EH_n substituent (routes A–C in Scheme 2). Complexes **1-Mo** and **1-W** reacted with 2-hydroxypyridine at room temperature in C_6D_6 to give the M-Si-O-C-N five-membered-ring complexes $\text{Cp}^*\text{M}(\text{CO})_2\{\kappa^2(\text{Si}_i\text{N})\text{-Si}(p\text{-Tol})_2(\text{OC}_5\text{H}_4\text{N})\}$ (**2-Mo**, $\text{M} = \text{Mo}$; **2-W**, $\text{M} = \text{W}$) in 76% and 57% NMR yields, respectively (route A in Scheme 2). **2-Mo** and **2-W** were isolated in 58% and 24% yields, respectively, by the same reactions conducted in toluene. Reaction of molybdenum complex **1-Mo** with 2-aminopyridine in toluene at 40 °C also gave the similar Mo-Si-N-C-N

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Scheme 2. Reactions of η^3 - α -Silabenzyl Complexes **1-Mo** and **1-W** with 2-Substituted Pyridines



five-membered-ring complex $\text{Cp}^*\text{Mo}(\text{CO})_2[\kappa^2(\text{Si}_i\text{N})\text{-Si}(\text{p-Tol})_2\{\text{N}(\text{H})\text{C}_5\text{H}_4\text{N}\}]$ (**3**) in 50% isolated yield (route A in Scheme 2).

Monitoring of these reactions by ^1H NMR spectroscopy showed the formation of toluene together with **2** or **3** (see the Experimental Section). This indicates that the η^2 -coordinated *p*-tolyl moiety in the η^3 - α -silabenzyl ligand of **1** is eliminated as a toluene molecule via Si-C(*p*-Tol) bond cleavage followed by C-H reductive elimination from the metal center. Interestingly, in contrast to these reactions resulting in the formation of molybdenum complexes **2-Mo** and **3** via Si-C(aryl) bond cleavage, we have recently reported that the reaction of **1-Mo** with DMAP afforded the DMAP-coordinated silylmolybdenum complex $\text{Cp}^*\text{Mo}(\text{CO})_2(\text{DMAP})\{\text{Si}(\text{p-Tol})_3\}$ exclusively via dissociation of the coordinated aromatic carbons in **1-Mo**.^{5b}

Reaction of tungsten complex **1-W** with 2-mercaptopyridine at room temperature in toluene afforded a different type of silametallacycle, i.e. the W-Si-N-C-S five-membered-ring complex $\text{Cp}^*\text{W}(\text{CO})_2[\kappa^2(\text{S}_i\text{N})\text{-(SC}_5\text{H}_4\text{N})\text{Si}(\text{p-Tol})_2]$ (**4**), in 38% isolated yield via Si-C(*p*-Tol) bond cleavage (route B in Scheme 2). NMR monitoring of the same reaction in C_6D_6 showed that **4** and toluene were formed as the main products in 54% and 63% NMR yields, respectively.⁶

On the other hand, reaction of molybdenum complex **1-Mo** with 2-mercaptopyridine at room temperature in toluene gave the Mo-S-C-N four-membered-ring complex $\text{Cp}^*\text{Mo}(\text{CO})_2[\kappa^2(\text{S}_i\text{N})\text{-(SC}_5\text{H}_4\text{N})]$ (**5**) in 76% isolated yield (route C in Scheme 2). NMR monitoring of the same reaction in C_6D_6 revealed that hydrosilane $\text{HSi}(\text{p-Tol})_3$ was formed quantitatively together with **5** (91% NMR yield). This clearly shows that the η^3 - α -silabenzyl ligand of **1-Mo** and the SH hydrogen of the 2-mercaptopyridine were eliminated as $\text{HSi}(\text{p-Tol})_3$ via Mo-Si bond cleavage. A similar four-membered-ring complex was obtained by the reaction of tungsten complex **1-W** with 2-aminopyridine at room temperature in C_6D_6 : the W-N-C-N four-membered-ring complex $\text{Cp}^*\text{W}(\text{CO})_2[\kappa^2(\text{N}_i\text{N})\text{-(NC}_5\text{H}_4\text{N}(\text{H}))]$ (**6**) and $\text{HSi}(\text{p-Tol})_3$ were formed in 63% and 62% NMR yields, respectively, via W-Si bond cleavage (route C in Scheme 2). Complex **6** was isolated in ca. 31% yield as a crude product from a mixture of the same reaction in toluene.

Characterization of Metallacycles 2–6. The molecular structures of **2-Mo**, **2-W**, and **3** were determined by X-ray crystallography (Figure S1 (Supporting Information), Figure 1,

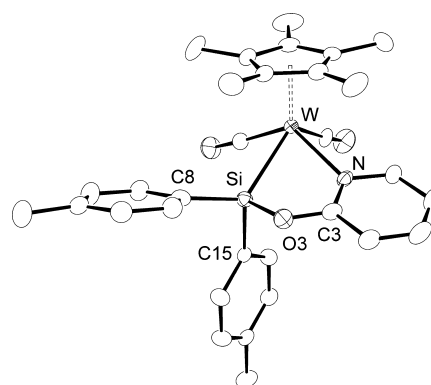
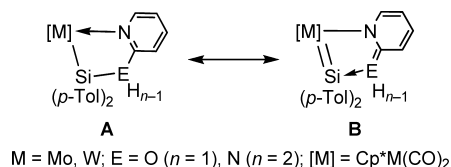


Figure 1. Crystal structure of **2-W**. Selected bond distances (Å) and angles (deg): W-Si 2.5072(10), W-N 2.241(4), Si-O3 1.742(3), O3-C3 1.321(6), N-C3 1.363(6); Si-W-N 71.32(9), W-Si-O3 99.32(10), W-Si-C8 125.06(14), W-Si-C15 119.45(13), C8-Si-C15 105.21(18), W-N-C3 121.3(3), O3-C3-N 118.8(4).

and Figure S2 (Supporting Information), respectively), revealing that these complexes have a five-membered chelate ring formed by $\kappa^2(\text{Si}_i\text{N})$ coordination of a 2-pyridyloxysilyl or 2-pyridylaminosilyl ligand. The Mo-Si bond distances of **2-Mo** (2.5038(10) Å) and **3** (2.5243(15) Å)⁷ and the W-Si bond distance of **2-W** (2.5072(10) Å) are much shorter than the corresponding M-Si bond distances of silyl complexes $\text{Cp}^*\text{M}(\text{CO})_2(\text{DMAP})\{\text{Si}(\text{p-Tol})_3\}$ (2.6218(10) Å ($\text{M} = \text{Mo}$)^{5b} and 2.6110(13) Å ($\text{M} = \text{W}$)^{4c}). On the other hand, the M-Si distances of **2** and **3** are slightly longer than or are in the range of those of usual base-stabilized silylene complexes (Mo-Si , 2.4439(14)–2.5008(9) Å; W-Si , 2.445(2)–2.573(4) Å).⁸ The sums of the bond angles among the three bonds except for the Si-O or Si-N bond around the silicon atoms of **2-Mo**, **2-W**, and **3** (350.0(4), 349.7(4), and 344.9(5)°, respectively) are nearly intermediate between the tetrahedral (329°) and trigonal (360°) angles. These features of bond distances and angles indicate that the silicon moieties in **2** and **3** take on some silylene ligand character.

The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of molybdenum complexes **2-Mo** and **3** and tungsten complex **2-W** show signals at 95.5, 65.4, and 92.3 ppm, respectively. These signals are shifted substantially downfield in comparison with the corresponding signals of silyl complexes $\text{Cp}^*\text{M}(\text{CO})_2(\text{DMAP})\{\text{Si}(\text{p-Tol})_3\}$ (34.7 ppm ($\text{M} = \text{Mo}$)^{5b} and 24.3 ppm ($\text{M} = \text{W}$)^{4c}) and are shifted slightly upfield in comparison with those of donor-stabilized bis(silylene) molybdenum and tungsten complexes $\text{Cp}^*\text{M}(\text{CO})_2\{\text{Si}(\text{Me})_2\}\cdots\text{Do}\cdots\{\text{Si}(\text{Me})_2\}$ ($\text{M} = \text{Mo}$, 117.6 (Do = OMe) and 80.5 (Do = NEt_2) ppm; $\text{M} = \text{W}$, 99.3 (Do = OMe) ppm).⁹ These observations also support the silylene complex character of complexes **2** and **3**. Thus, each of the structures of complexes **2** and **3** can be drawn as a resonance of two canonical forms: (pyridine)silyl complex form A and base-stabilized (amido)silylene complex form B (Scheme 3). Similar resonance forms

Scheme 3. Two Possible Canonical Forms for Five-Membered-Ring Complexes **2** and **3**



have been proposed for several previously reported M–Si–O–C–N and M–Si–N–C–N five-membered-ring complexes.¹⁰

On the other hand, X-ray crystal structure analysis revealed that complex **4** has an unprecedented W–Si–N–C–S five-membered chelate ring where the nitrogen of the 2-pyridinethiolato moiety is bound to the silicon atom (Figure 2).

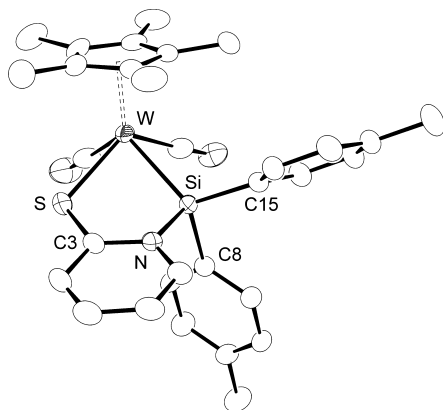


Figure 2. Crystal structure of **4**. Selected bond distances (Å) and angles (deg): W–S 2.4807(13), W–Si 2.4928(12), S–C3 1.728(5), Si–N 1.886(4), N–C3 1.363(6); S–W–Si 75.07(4), W–S–C3 112.02(16), W–Si–C8 121.19(14), W–Si–C15 119.02(15), C8–Si–C15 103.98(19), W–Si–N 107.37(12), S–C3–N 119.8(4).

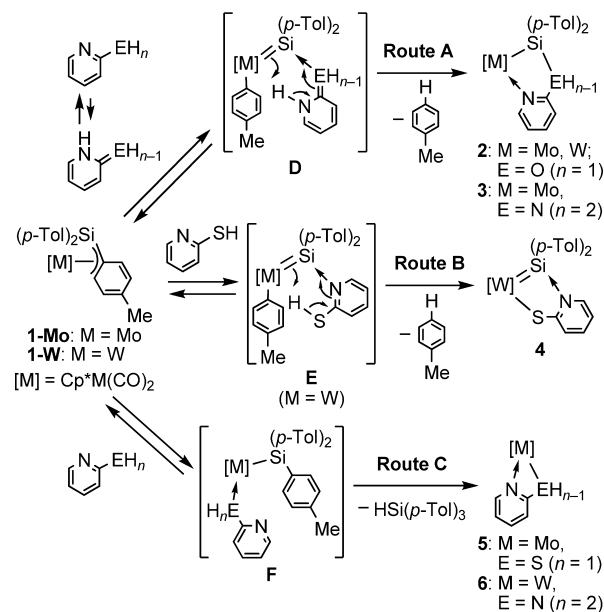
The W–Si bond distance (2.4928(12) Å), which is slightly shorter than that of **2-W** (2.5072(10) Å), is comparable with that of the related base-stabilized silylene complex $\text{Cp}^*\text{W}(\text{CO})_2\{\kappa^2(\text{Si},\text{C})\text{-SiMe}_2(\text{NMe}_2\text{C}_6\text{H}_4)\}$ (**C**) bearing a W–Si–N–C–C five-membered ring (2.487(3) Å).^{4a} The sum of the bond angles among the three bonds except for the Si–N bond around the silicon atom of **4** (344.2(4)°) is nearly at the middle of the tetrahedral (329°) and trigonal (360°) angles. The Si–N(py) bond distance of **4** (1.886(4) Å) is longer than normal Si–N single-bond distances (1.71–1.75 Å)⁸ and is close to the Si–N dative bond distance for the DMAP-stabilized silylene tungsten complex $\text{Cp}^*\text{W}(\text{CO})_2(p\text{-Tol})\{\text{=Si}(p\text{-Tol})\text{-Me-DMAP}\}$ (1.898(11) Å).^{4c} The S–C3 bond distance of **4** (1.728(5) Å) is located at the longer end of the range of normal S=C double-bond distances (1.60–1.72 Å)⁸ while being nearly at the shorter end of the range of normal S–C(sp²) single-bond distances (1.71–1.76 Å).⁸ The W–S bond distance of **4** (2.4807(13) Å) is slightly shorter than that of the thiolato tungsten complex $\text{CpW}(\text{CO})_3\{\text{S}(\text{benzothiazolyl})\}$ (2.500(3) Å).¹¹ The ²⁹Si{¹H} NMR spectrum of **4** in C₆D₆ appears as a singlet at 103.0 ppm with ¹⁸³W satellites (*J*_{WSi} = 101 Hz), which is shifted downfield in comparison with that of **2-W** (92.3 ppm). The δ_{Si} and *J*_{WSi} values are close to those of base-stabilized silylene tungsten complex **C** (115.0 ppm and *J*_{WSi} = 103 Hz).^{4a} According to the aforementioned discussion on the crystal structure and the ²⁹Si NMR data, **4** can be best described as a base-stabilized silylene(thiolato) complex.

X-ray crystal structure analysis revealed that complex **5** adopts a four-legged piano-stool geometry bearing a Mo–S–C–N four-membered ring (Figure S3 in the Supporting Information). The Mo–S (2.514(2) Å) and Mo–N (2.182(7) Å) bond distances of **5** are similar to the corresponding bond distances of the known Mo–S–C–N four-membered-ring complex $\text{CpMo}(\text{CO})_2\{\kappa^2(\text{S},\text{N})\text{-SC}_5\text{H}_4\text{N}\}$ (2.5227(9) and 2.183(2) Å, respectively).¹² Complex **6** was identified by comparing the

¹H NMR and IR spectroscopic data with those of the sample synthesized by an alternative method: i.e., the reaction of methyl(pyridine) tungsten complex $\text{Cp}^*\text{W}(\text{CO})_2(\text{py})\text{Me}^{13}$ with 2-aminopyridine. Complex **6** prepared by the latter reaction was characterized by ¹H and ¹³C NMR, IR, and mass spectroscopy and elemental analysis (see the Experimental Section).

Possible Reaction Pathways for the Formation of Metallacycles 2–6. Possible formation mechanisms of **2–6** by the reactions of $\eta^3\text{-}\alpha$ -silybenzyl complexes **1-Mo** and **1-W** with 2-substituted pyridines are illustrated in Scheme 4.

Scheme 4. Possible Formation Mechanisms of Complexes **2–6**



In the reactions of **1-Mo** and **1-W** with 2-hydroxypyridine and of **1-Mo** with 2-aminopyridine (route A in Scheme 2), the oxygen atom of the pyridone tautomer of 2-hydroxypyridine or the nitrogen atom of the pyridonimine tautomer of 2-aminopyridine attacks the sterically encumbered silicon atom of **1** to give base-stabilized silylene complex intermediates **D**.¹⁴ A possible driving force of this nucleophilic attack is the high affinity of electronegative oxygen and nitrogen for silicon. Proton transfer from nitrogen to metal in **D** and C–H reductive elimination of toluene then takes place to produce M–Si–E–C–N five-membered-ring complexes **2** and **3** (route A in Scheme 4).

In the reaction of tungsten complex **1-W** with 2-mercaptopyridine (route B in Scheme 2), the nitrogen of 2-mercaptopyridine attacks the silicon atom of **1-W** to give silylene complex intermediate **E**. Alternative nucleophilic attack of the sulfur atom of the thiopyridone tautomer^{14b} of 2-mercaptopyridine instead of the pyridine nitrogen is unlikely because of the much lower affinity of sulfur to silicon in comparison with that of nitrogen.¹⁵ Intermediate **E** is subsequently converted into the W–Si–N–C–S five-membered-ring complex **4** via proton transfer from sulfur to tungsten in **E** followed by toluene elimination (route B in Scheme 4).

On the other hand, in the reaction of molybdenum complex **1-Mo** with 2-mercaptopyridine, the corresponding silylene complex intermediate **E** (M = Mo) is thought to be less stable than silyl complex intermediate **F** (M = Mo, E = S). This low

stability of **E** ($M = Mo$) is probably caused by less effective π -type overlap of the vacant 3p orbital of silicon with a 4d orbital of molybdenum in comparison with that with a larger 5d orbital of tungsten in **E** ($M = W$).^{5b} Thus, intermediate **F** ($M = Mo$, $E = S$) is formed by coordination of the sulfur atom on the metal center.¹⁶ Protonation of the metal center by a coordinated SH hydrogen followed by reductive elimination of hydrosilane then occurs to give the Mo–S–C–N four-membered-ring complex **5** (route C in Scheme 4).

In the reactions of **1** with 2-aminopyridine, it is possible that both silylene complex **D** ($E = N$) and silyl complex **F** ($E = N$) are generated. In the reaction of molybdenum complex **1-Mo**, protonation of the metal center by coordinated 2-aminopyridine in **F** ($M = Mo$, $E = N$) is unlikely to occur, due to the weak acidity of the NH_2 group of 2-aminopyridine.¹⁷ Instead, protonation of the metal center by the silicon-bound imino tautomer in intermediate **D** ($M = Mo$, $E = N$) occurs predominantly because the NH hydrogen of the pyridonimine tautomer coordinated to the electropositive silylene silicon is considered to be sufficiently acidic for this protonation. As a result, five-membered-ring complex **3** is formed similarly to the reaction of **1** with 2-hydroxypyridine (route A in Scheme 4). The much slower rate of this reaction (reaction conditions: 40 °C, 72 h) in comparison with those of other reactions of **1** with 2-substituted pyridines (reaction conditions: room temperature, 10 min to 1.5 h) is possibly caused by the lower stability of the silylene complex intermediate **D** ($M = Mo$, $E = N$) in comparison with the silyl complex intermediate **F** ($M = Mo$, $E = N$), leading to an equilibrium shift from **D** to **F** in the reaction system. In the case of tungsten complex **1-W**, protonation of the tungsten center of **F** ($M = W$, $E = N$) is likely to occur possibly because of the higher basicity of tungsten in comparison with that of molybdenum, which leads to the formation of four-membered-ring complex **6** via reductive elimination of hydrosilane (route C in Scheme 4). By comparison, generation of silylene complex intermediate **D** ($M = W$, $E = N$) is considered to be unfavorable because the proportion of the imine tautomer of 2-aminopyridine is very low in the tautomeric equilibrium.^{14a}

CONCLUSION

We developed a method for direct conversion of a Si–C(aryl) bond to Si–E bonds ($E = O, N$) by stoichiometric reactions of η^3 - α -sila-benzyl complexes **1-Mo** and **1-W** with 2-substituted pyridines under mild conditions. In these reactions, Si–C(aryl) bond cleavage and toluene elimination occur to give silametallacycles **2–4** via generation of silylene complex intermediates. Further study aiming at application of these reactions to the catalytic functionalization of arylsilanes is currently under way.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under dry argon or nitrogen in a glovebox.

Materials. Hexane was dried using a Glass Contour alumina column (Nikko Hansen & Co., Ltd.). Toluene was dried using an MBRAUN Solvent Purification System, further dried over CaH_2 , and vacuum-transferred. Benzene- d_6 was dried over CaH_2 and vacuum-transferred. 2-Hydroxypyridine and 2-aminopyridine were recrystallized from a toluene solution. 2-Mercaptopyridine was purchased from Sigma-Aldrich and used as received. All solvents were stored under argon over 4 Å molecular sieves in a glovebox. $Cp^*Mo(CO)_2\{\eta^3(Si(C,C)-Si(p-Tol)_3\}$ (**1-Mo**)^{5b} and $Cp^*W(CO)_2(py)Me$ ¹³ were prepared according to the literature methods. $Cp^*W(CO)_2\{\eta^3(Si(C,C)-Si(p-Tol)_3\}$ (**1-W**)^{5a} was synthesized by a new method starting from $Cp^*W(CO)_2(py)Me$ as described below.

Spectroscopic Measurements. 1H , $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE 300 or Bruker AVANCE III 400 Fourier transform spectrometer. Chemical shifts are reported in parts per million. Coupling constants (J) and line widths at half-height ($\Delta\nu_{1/2}$) are given in Hz. $^{29}Si\{^1H\}$ NMR measurements were performed using the DEPT pulse sequence. The residual proton (7.15 ppm) and the carbon resonances (128.0 ppm) of benzene- d_6 were used as internal references for 1H and ^{13}C NMR chemical shifts, respectively. Aromatic proton and carbon are abbreviated as ArH and ArC, respectively. Pyridyl proton and carbon are abbreviated as pyH and pyC, respectively. $^{29}Si\{^1H\}$ NMR chemical shifts were referenced to $SiMe_4$ (0 ppm) as an external standard. All NMR data were collected at room temperature unless otherwise indicated. Infrared spectra were measured for samples included in KBr pellets using a Horiba FT-730 or FT-720 spectrometer. High-resolution mass spectra (HRMS) and mass spectra were recorded on a Bruker Daltonics solarix 9.4T spectrometer operating in the electrospray ionization (ESI) mode or atmospheric pressure chemical ionization (APCI) mode or on a Shimadzu GC-MS QP-2010 SE spectrometer operating in the electron impact (EI) mode. Elemental analyses were carried out using a J-Science Lab JM11 microanalyzer. Measurements of some mass spectra and elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

Synthesis of $Cp^*Mo(CO)_2\{\kappa^2(Si,Mo-Si(p-Tol)_2(OC_5H_4N)\}$ (**2-Mo**).

In a Schlenk tube, **1-Mo** (31 mg, 0.053 mmol) and 2-hydroxypyridine (7 mg, 0.07 mmol) were dissolved in toluene (3 mL). The mixture was stirred at room temperature for 10 min. The resulting orange reaction mixture was concentrated, and then hexane (2 mL) was slowly layered on it. After crystals were precipitated, the mother liquor was removed by a syringe. The crystals were washed with hexane (0.2 mL \times 2) and then dried under vacuum to give **2-Mo** (18 mg, 0.030 mmol) in 58% yield as orange crystals. 1H NMR (300 MHz, C_6D_6): δ 1.48 (s, 15H, Cp^*), 1.94 (s, 3H, C_6H_4Me), 2.21 (s, 3H, C_6H_4Me), 5.89 (ddd, $^3J_{HH} = 7.0$, 6.0 Hz, $^4J_{HH} = 1.4$ Hz, 1H, pyH), 6.39 (br d, $^3J_{HH} = 8.1$ Hz, 1H, pyH), 6.57 (ddd, $^3J_{HH} = 8.1$, 7.0 Hz, $^4J_{HH} = 1.8$ Hz, 1H, pyH), 6.96 (d, $^3J_{HH} = 7.6$ Hz, 2H, ArH), 7.25 (d, $^3J_{HH} = 7.6$ Hz, 2H, ArH), 7.83 (d, $^3J_{HH} = 7.9$ Hz, 2H, ArH), 8.15 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 1.8$ Hz, 1H, pyH), 8.20 (d, $^3J_{HH} = 7.9$ Hz, 2H, ArH). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 10.5 (C_5Me_5), 21.2, 21.6 (C_6H_4Me), 103.4 (C_5Me_5), 112.6, 116.0, 128.79, 128.82, 134.4, 135.7, 137.2, 138.7, 138.8, 139.7, 140.1, 155.4, 168.1 (ArC), 244.8, 248.5 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6): δ 95.5. IR (KBr pellet, cm^{-1}) 1898 (s, ν_{COsym}), 1820 (s, ν_{COasym}). HRMS (ESI positive, additive: NaI): m/z calcd for $[C_{31}H_{33}NO_3SiMo + Na]^+$ 616.1181, found 616.1179. Anal. Calcd for $C_{31}H_{33}NO_3SiMo$: C, 62.93; H, 5.62; N, 2.37. Found: C, 63.15; H, 5.68; N, 2.50.

Synthesis of $Cp^*W(CO)_2\{\kappa^2(Si,Mo-Si(p-Tol)_2(OC_5H_4N)\}$ (**2-W**).

1-W (50 mg, 0.074 mmol) and 2-hydroxypyridine (8 mg, 0.08 mmol) were dissolved in toluene (5 mL) in a Schlenk tube. After the mixture was stirred at room temperature for 10 min, the resulting orange solution was evaporated under vacuum. The residual dark orange oil was purified by silica gel column chromatography using silica gel 60N (spherical, neutral, 100–210 μm , Kanto Chemical Co., Inc.) and toluene as an eluent. An orange fraction was collected, and the solvent was evaporated under vacuum. The residue was recrystallized from toluene/hexane at room temperature. **2-W** (12 mg, 0.018 mmol) was obtained as orange crystals in 24% yield. 1H NMR (400 MHz, C_6D_6): δ 1.55 (s, 15H, Cp^*), 1.95 (s, 3H, C_6H_4Me), 2.22 (s, 3H, C_6H_4Me), 5.78 (ddd, $^3J_{HH} = 6.8$, 6.0 Hz, $^4J_{HH} = 1.4$ Hz, 1H, pyH), 6.40 (ddd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.4$ Hz, $^5J_{HH} = 0.6$ Hz, 1H, pyH), 6.50–6.58 (m, 1H, pyH), 6.97 (d, $^3J_{HH} = 7.5$ Hz, 2H, ArH), 7.25 (d, $^3J_{HH} = 7.4$ Hz, 2H, ArH), 7.84 (d, $^3J_{HH} = 7.9$ Hz, 2H, ArH), 8.14 (d, $^3J_{HH} = 7.9$ Hz, 2H, ArH), 8.21 (ddd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 1.9$ Hz, $^5J_{HH} = 0.6$ Hz, 1H, pyH). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 10.5 (C_5Me_5), 21.2, 21.6 (C_6H_4Me), 102.0 (C_5Me_5), 112.1, 116.3 (pyC), 128.8, 128.9, 134.3, 136.2, 138.2, 138.5, 138.8 (ArC), 140.2 (pyC), 140.7 (ArC), 157.1, 169.7 (pyC), 239.8, 242.1 (CO). $^{29}Si\{^1H\}$ NMR (79.5 MHz, C_6D_6): δ 92.3 (s with satellites, $J_{WSi} = 81$ Hz). IR (KBr pellet, cm^{-1}): 1901 (s, ν_{COsym}), 1809 (s, ν_{COasym}). EI-MS (70 eV): m/z 679 (M^+ , 54),

623 ($M^+ - 2 \text{ CO}$, 100). Anal. Calcd for $\text{C}_{31}\text{H}_{33}\text{NO}_3\text{SiW}$: C, 54.79; H, 4.89; N, 2.06. Found: C, 54.86; H, 4.85; N, 2.24.

Synthesis of $\text{Cp}^*\text{Mo}(\text{CO})_2[\kappa^2(\text{Si},\text{N})\text{-Si}(\text{p-Tol})_2\{\text{N}(\text{H})\text{C}_5\text{H}_4\text{N}\}]$ (3). 1-Mo (26 mg, 0.044 mmol) and 2-aminopyridine (5 mg, 0.05 mmol) were dissolved in toluene (3 mL) in a Schlenk tube. After the solution was stirred at 40 °C for 48 h, the resulting orange reaction mixture was evaporated under vacuum. The residue was dissolved in a minimum amount of toluene, and hexane was then slowly layered on the toluene solution. After crystals were precipitated, the mother liquor was removed using a Pasteur pipet, and the crystals were dried under vacuum. Complex 3 (13 mg, 0.022 mmol) was obtained in 50% yield as orange crystals. ^1H NMR (400 MHz, C_6D_6): δ 1.50 (s, 15H, Cp*), 2.03 (s, 3H, $\text{C}_6\text{H}_4\text{Me}$), 2.27 (s, 3H, $\text{C}_6\text{H}_4\text{Me}$), 4.62 (br s, $\Delta\nu_{1/2} = 3 \text{ Hz}$, 1H, NH), 5.63 (br d, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 1H, pyH), 5.80 (ddd, $^3J_{\text{HH}} = 6.8$, 6.2 Hz, $^4J_{\text{HH}} = 1.2 \text{ Hz}$, 1H, pyH), 6.55 (ddd, $^3J_{\text{HH}} = 8.4$, 6.8 Hz, $^4J_{\text{HH}} = 2.0 \text{ Hz}$, 1H, pyH), 7.02 (d, $^3J_{\text{HH}} = 7.2 \text{ Hz}$, 2H, ArH), 7.26 (d, $^3J_{\text{HH}} = 7.2 \text{ Hz}$, 2H, ArH), 7.75 (d, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, 2H, ArH), 7.89 (d, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, 2H, ArH), 8.10 (dd, $^3J_{\text{HH}} = 6.2 \text{ Hz}$, $^4J_{\text{HH}} = 2.0 \text{ Hz}$, 1H, pyH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ 10.5 (C_5Me_5), 21.3, 21.6 ($\text{C}_6\text{H}_4\text{Me}$), 103.1 (C_5Me_5), 110.4, 112.2 (pyC), 128.6, 128.8, 134.8, 135.4 (ArC), 137.5 (pyC), 137.6, 138.0, 138.3, 142.1 (ArC), 155.8, 166.4 (pyC), 246.1, 249.1 (CO). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.5 MHz, C_6D_6): δ 65.4. IR (KBr pellet, cm^{-1}): 3379 (w, ν_{NH}), 1890 (s, ν_{COsym}), 1805 (s, ν_{COasym}). EI-MS (70 eV): m/z 592 (M^+ , 13), 564 ($M^+ - \text{CO}$, 26), 536 ($M^+ - 2 \text{ CO}$, 100). Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{N}_2\text{O}_2\text{SiMo}$: C, 63.04; H, 5.80; N, 4.74. Found: C, 63.03; H, 5.72; N, 4.71.

Synthesis of $\text{Cp}^*\text{W}(\text{CO})_2[\kappa^2(\text{S},\text{Si})\text{-}(\text{SC}_5\text{H}_4\text{N})\text{Si}(\text{p-Tol})_2]$ (4). 1-W (25 mg, 0.037 mmol) and 2-mercaptopyridine (4 mg, 0.04 mmol) were dissolved in toluene (3 mL). After the mixture was stirred at room temperature for 1.5 h, the solution became red. The solution was concentrated, and then hexane (2 mL) was slowly layered on it. After crystals were precipitated, the mother liquor was removed using a Pasteur pipet, and the crystals were washed with hexane (0.2 mL \times 2). Complex 4 (10 mg, 0.014 mmol) was obtained as dark red crystals in 38% yield. ^1H NMR (400 MHz, C_6D_6): δ 1.69 (s, 15H, Cp*), 1.98 (s, 3H, $\text{C}_6\text{H}_4\text{Me}$), 2.22 (s, 3H, $\text{C}_6\text{H}_4\text{Me}$), 5.71 (ddd, $^3J_{\text{HH}} = 6.8$, 6.2 Hz, $^4J_{\text{HH}} = 1.2 \text{ Hz}$, 1H, pyH), 6.06 (ddd, $^3J_{\text{HH}} = 8.4$, 6.8 Hz, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, 1H, pyH), 7.01 (d, $^3J_{\text{HH}} = 8.0 \text{ Hz}$, 2H, ArH), 7.13–7.18 (m, 2H, ArH), 7.19 (ddd, $^3J_{\text{HH}} = 8.4 \text{ Hz}$, $^4J_{\text{HH}} = 1.2 \text{ Hz}$, $^5J_{\text{HH}} = 0.8 \text{ Hz}$, 1H, pyH), 7.73 (d, $^3J_{\text{HH}} = 8.0 \text{ Hz}$, 2H, ArH), 7.82 (d, $^3J_{\text{HH}} = 8.0 \text{ Hz}$, 2H, ArH), 7.95 (ddd, $^3J_{\text{HH}} = 6.2 \text{ Hz}$, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, $^5J_{\text{HH}} = 0.8 \text{ Hz}$, 1H, pyH). The multiplet ArH signal at 7.13–7.18 ppm was overlapped with the signal of $\text{C}_6\text{D}_5\text{H}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ 10.7 (C_5Me_5), 21.2, 21.4 ($\text{C}_6\text{H}_4\text{Me}$), 102.3 (C_5Me_5), 116.0, 128.6 (pyC), 128.9, 129.0, 135.3 (ArC), 135.4 (pyC), 136.5, 138.3, 138.5, 138.8, 140.1 (ArC), 142.9, 178.6 (pyC), 234.7, 238.1 (CO). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.5 MHz, C_6D_6): δ 103.0 (s with satellites, $J_{\text{WSi}} = 101 \text{ Hz}$). IR (KBr pellet, cm^{-1}): 1900 (s, ν_{COsym}), 1817 (s, ν_{COasym}). EI-MS (70 eV): m/z 695 (M^+ , 50), 667 ($M^+ - \text{CO}$, 8), 639 ($M^+ - 2 \text{ CO}$, 98), 560 (100). Anal. Calcd for $\text{C}_{31}\text{H}_{33}\text{NO}_2\text{SiW}$: C, 53.53; H, 4.78; N, 2.01. Found: C, 53.36; H, 4.69; N, 2.21.

Synthesis of $\text{Cp}^*\text{Mo}(\text{CO})_2[\kappa^2(\text{S},\text{M})\text{-SC}_5\text{H}_4\text{N}]$ (5). 1-Mo (50 mg, 0.085 mmol) and 2-mercaptopyridine (11 mg, 0.099 mmol) were

dissolved in toluene (5 mL). The mixture was stirred at room temperature for 10 min. After evaporation of volatiles under vacuum from the resulting red solution, the residue was recrystallized from toluene/hexane (a 1/2 mixture) at -35°C to give complex 5 (26 mg, 0.065 mmol) in 76% yield as red crystals. ^1H NMR (400 MHz, C_6D_6): δ 1.52 (s, 15H, Cp*), 5.99 (ddd, $^3J_{\text{HH}} = 7.2$, 5.6 Hz, $^4J_{\text{HH}} = 1.2 \text{ Hz}$, 1H, pyH), 6.33 (ddd, $^3J_{\text{HH}} = 8.4 \text{ Hz}$, $^4J_{\text{HH}} = 1.2 \text{ Hz}$, $^5J_{\text{HH}} = 1.0 \text{ Hz}$, 1H, pyH), 6.49 (ddd, $^3J_{\text{HH}} = 8.4$, 7.2 Hz, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, 1H, pyH), 7.40 (ddd, $^3J_{\text{HH}} = 5.6 \text{ Hz}$, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, $^5J_{\text{HH}} = 1.0 \text{ Hz}$, 1H, pyH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ 10.4 (C_5Me_5), 106.6 (C_5Me_5), 115.7, 127.2, 140.2, 151.2, 179.4 (pyC), 257.5, 263.7 (CO). IR (KBr pellet, cm^{-1}): 1928 (s, ν_{COsym}), 1832 (s, ν_{COasym}). EI-MS (70 eV): m/z 399 (M^+ , 15), 371 ($M^+ - \text{CO}$, 4), 343 ($M^+ - 2 \text{ CO}$, 100). HRMS (APCI): m/z calcd for $[\text{C}_{17}\text{H}_{16}\text{NO}_2\text{SMo} + \text{H}]^+$ 400.0263, found 400.0263. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{SMo}$: C, 51.39; H, 4.82; N, 3.53. Found: C, 51.39; H, 4.82; N, 3.52.

Synthesis of $\text{Cp}^*\text{W}(\text{CO})_2[\kappa^2(\text{N},\text{M})\text{-NC}_5\text{H}_4\text{NH}]$ (6). 1-W (50 mg, 0.074 mmol) and 2-aminopyridine (8 mg, 0.08 mmol) were dissolved in toluene (5 mL) in a Schlenk tube. After the mixture was stirred at room temperature for 10 min, the resulting orange solution was evaporated under vacuum. The residual dark orange oil was washed with hexane and then dried under vacuum to give complex 6 as a crude product, which contained an unidentified impurity bearing a Cp* ligand,¹⁹ in ca. 31% yield (11 mg, 0.023 mmol). Complex 6 in the crude product was identified by comparing the IR and ^1H NMR spectra with those of the authentic sample synthesized by the method described below.

Alternative Synthesis of Complex 6 by a Reaction of $\text{Cp}^*\text{W}(\text{CO})_2(\text{py})\text{Me}^{13}$ with 2-Aminopyridine. $\text{Cp}^*\text{W}(\text{CO})_2(\text{py})\text{-Me}$ (50 mg, 0.11 mmol) and 2-aminopyridine (10 mg, 0.11 mmol) were dissolved in toluene (3 mL) in a Schlenk tube. After the mixture was stirred at room temperature for 1 h, the resulting reddish orange solution was evaporated under vacuum. The residue was washed with hexane and dried under vacuum to give complex 6 in 83% yield (43 mg, 0.092 mmol) as an orange-red powder. ^1H NMR (400 MHz, C_6D_6): δ 1.65 (s, 15H, Cp*), 3.50 (br s, $\Delta\nu_{1/2} = 18 \text{ Hz}$, 1H, NH), 5.19 (ddd, $^3J_{\text{HH}} = 8.8 \text{ Hz}$, $^4J_{\text{HH}} = 1.2 \text{ Hz}$, $^5J_{\text{HH}} = 1.0 \text{ Hz}$, 1H, pyH), 5.79 (ddd, $^3J_{\text{HH}} = 6.8$, 5.6 Hz, $^4J_{\text{HH}} = 1.0 \text{ Hz}$, 1H, pyH), 6.67 (ddd, $^3J_{\text{HH}} = 8.2$, 6.8 Hz, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, 1H, pyH), 7.31 (ddd, $^3J_{\text{HH}} = 5.6 \text{ Hz}$, $^4J_{\text{HH}} = 1.6 \text{ Hz}$, $^5J_{\text{HH}} = 1.2 \text{ Hz}$, 1H, pyH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ 10.7 (C_5Me_5), 105.5 (C_5Me_5), 107.3, 110.0, 134.3, 147.7, 169.5 (pyC), 256.7, 261.9 (CO). IR (KBr pellet, cm^{-1}): 3435 (w, ν_{NH}), 1909 (s, ν_{COsym}), 1801 (s, ν_{COasym}). EI-MS (70 eV): m/z 468 (M^+ , 13), 440 ($M^+ - \text{CO}$, 4), 410 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{W}$: C, 43.61; H, 4.31; N, 5.98. Found: C, 43.60; H, 4.33; N, 6.00.

General Procedure for NMR Monitoring of the Reactions of $\eta^3\text{-}\alpha\text{-Silabenzyl}$ Complexes 1 with 2-Substituted Pyridines. These reactions were all carried out by the same procedures, and a general procedure for them is as follows. The $\eta^3\text{-}\alpha\text{-silabenzyl}$ complex 1-Mo or 1-W and Cp_2Fe (internal standard, less than 1 mg) were dissolved in benzene- d_6 (ca. 0.5 mL). The solution was transferred to an NMR tube with a J. Young Teflon valve (5 mm o.d.). A ^1H NMR spectrum of the mixture was measured to determine the ratio of the intensities of the signals of 1-Mo or 1-W and Cp_2Fe . 2-Substituted pyridine was then added to the solution. The reaction was monitored

Table 1. Reaction Conditions and Yields of Products for the NMR Monitoring of the Reactions of 1 with 2-Substituted Pyridines

entry	complex (amount)	substrate (amount)	temp, time ^a	product(s) (NMR yield(s), %)	
1	1-Mo (5 mg, 8 μmol)	2-hydroxypyridine (1 mg, 0.01 mmol)	room temp, 10 min	2-Mo (76)	toluene (quant)
2	1-W (5 mg, 8 μmol)	2-hydroxypyridine (1 mg, 0.01 mmol)	room temp, 10 min	2-W (57)	toluene (quant)
3	1-Mo (6 mg, 0.01 mmol)	2-mercaptopyridine (2 mg, 0.02 mmol)	room temp, 15 min	5 (91)	HSi(p-Tol) ₃ (quant)
4	1-W (5 mg, 8 μmol)	2-mercaptopyridine (1 mg, 9 μmol)	room temp, 1.5 h	4 (54) 7 (16)	toluene (63) HSi(p-Tol) ₃ (14)
5	1-Mo (5 mg, 8 μmol)	2-aminopyridine (1 mg, 0.01 mmol)	40 °C, 72 h	3 (77)	toluene (85)
6	1-W (6 mg, 9 μmol)	2-aminopyridine (1 mg, 0.01 mmol)	room temp, 15 min	6 (63)	HSi(p-Tol) ₃ (62)

^aA period until the signals of 1-Mo or 1-W in a reaction mixture completely disappeared.

by ^1H NMR spectroscopy. The signals of a five- or four-membered-ring complex (2–6) and toluene or $\text{HSi}(p\text{-Tol})_3$ appeared during the reaction. NMR yields of metallacycles 2–6 were determined by comparison of intensities of the Cp^* signals of these complexes with that of the signal of Cp_2Fe . NMR yields of toluene and $\text{HSi}(p\text{-Tol})_3$ were determined by comparison of intensities of the Me signals of toluene and $\text{HSi}(p\text{-Tol})_3$ with that of the signal of Cp_2Fe . Complexes 2–6 were identified by comparing the ^1H NMR spectra with those of the corresponding authentic samples synthesized by the above-mentioned procedures. The amounts of reactants and the NMR yields of products are given in Table 1.

In the reaction of 1-W with 2-mercaptopyridine (entry 4, Table 1), the ^1H NMR spectrum of the reaction mixture showed not only the signals of 4 and toluene but also some other signals of minor products. Two of them were $\text{Cp}^*\text{W}(\text{CO})_2\{\kappa^2(\text{S},\text{N})\text{-SC}_5\text{H}_4\text{N}\}$ (7, a putative structure) and $\text{HSi}(p\text{-Tol})_3$. The structure of 7 was tentatively deduced by ^1H NMR spectroscopy: The chemical shifts of the ^1H NMR signals of 7 are close to the corresponding chemical shifts of the molybdenum analogue 5. ^1H NMR (400 MHz, C_6D_6) data for 7: δ 1.61 (s, 15H, Cp^*), 5.98 (ddd, $^3J_{\text{HH}} = 7.2$, 6.0 Hz, $^4J_{\text{HH}} = 1.4$ Hz, 1H, pyH), 6.14 (ddd, $^3J_{\text{HH}} = 8.6$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, $^5J_{\text{HH}} = 1.0$ Hz, 1H, pyH), 6.41 (ddd, $^3J_{\text{HH}} = 8.6$, 7.2 Hz, $^4J_{\text{HH}} = 1.4$ Hz, 1H, pyH), 7.45 (ddd, $^3J_{\text{HH}} = 6.0$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, $^5J_{\text{HH}} = 1.0$ Hz, 1H, pyH).

Synthesis of $\text{Cp}^*\text{W}(\text{CO})_2\{\eta^3(\text{Si},\text{C},\text{C})\text{-Si}(p\text{-Tol})_3\}$ (1-W). 1-W was synthesized according to the following newly developed method.²⁰ $\text{Cp}^*\text{W}(\text{CO})_2(\text{py})\text{Me}^{13}$ (200 mg, 0.426 mmol), $\text{HSi}(p\text{-Tol})_3$ (130 mg, 0.430 mmol), and BPh_3 (104 mg, 0.430 mmol) were dissolved in toluene (5 mL). The solution was stirred at room temperature for 1 h. After the volatiles were evaporated under vacuum, hexane (20 mL) was added to the residue, and the mixture was stirred at room temperature for 1.5 h. During the stirring, py-BPh₃ was precipitated as a colorless solid. The mixture was filtered to remove py-BPh₃, and the filtrate was concentrated under vacuum. When the concentrated solution was cooled at -35°C , a brown solid was precipitated. After removal of the mother liquor, the residual solid was washed with hexane, and drying the solid under vacuum gave 1-W as a brown powder in 52% yield (150 mg, 0.222 mmol). Complex 1-W was identified by comparing the ^1H NMR and IR spectra with those of the authentic sample.^{5a}

X-ray Crystal Structure Determination. X-ray-quality single crystals of 2-Mo (an orange block), 2-W (an orange-yellow block), 3 (a yellow block), 4 (a dark red block), and 5 (a red block) were obtained from a toluene/hexane (a 1/2 mixture) solution at -35°C for 2-Mo or from a toluene/hexane solution at room temperature for 2-W and 3–5. Intensity data for the analysis were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069\text{ \AA}$) under a cold nitrogen stream ($T = 150\text{ K}$). Numerical absorption corrections were applied to the data. The structures of 2–5 were solved by direct methods using the SHELXS-97²¹ program and refined by full-matrix least-squares techniques on all F^2 data with SHELXL-97.²¹ The asymmetric unit of the single crystal of 3 contains two crystallographically independent molecules, namely, 3-A and 3-B. Anisotropic refinement was applied to all non-hydrogen atoms. All calculations were carried out using Yadokari-XG 2009.²² CCDC reference numbers: 1404813 (2-Mo), 1404814 (2-W), 1404815 (3), 1404816 (4), and 1404817 (5). Crystallographic data are available in the Supporting Information as a CIF file, and selected crystallographic data are also given in Tables S1 (for 2-Mo and 2-W), S2 (for 3 and 4), and S3 (for 5) in the Supporting Information. Crystal structures of 2-Mo, 3, and 5 are depicted in Figures S1–S3, respectively (see the Supporting Information).

■ ASSOCIATED CONTENT

■ Supporting Information

Crystal structures of complexes 2-Mo, 3, and 5 (Figures S1–S3, respectively), NMR spectra of complexes 2–6 (Figures S4–S19), and tables (Tables S1–S3) and a CIF file giving X-ray crystallographic data for 2–5. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00335.

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Notes

The authors declare no competing financial interest.

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(19) The ^1H NMR spectrum of the crude product in C_6D_6 shows a Cp^* signal of the impurity at 1.55 ppm together with the signals of **6** (intensity ratio of the Cp^* signals of **6** and the impurity 1:0.17).

(20) In our previous study, **1-W** had been synthesized by the following two-step method starting from a (DMAP)(methyl)tungsten complex $\text{Cp}^*\text{W}(\text{CO})_2(\text{DMP})\text{Me}$: (1) the reaction of the methyl complex with $\text{HSi}(p\text{-Tol})_3$ to give the DMAP-stabilized aryl(silylene) complex $\text{Cp}^*\text{W}(\text{CO})_2(p\text{-Tol})\{\text{=Si}(p\text{-Tol})_2\cdot\text{DMP}\}$ and (2) the reaction of the resulting silylene complex with BPh_3 .^{4c,5a}

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