Supporting Information

Hydrogen-bridged bis(silylene) complex as platform for small molecule activation via adjacent metal–ligand cooperation

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Contents

1. Experimental procedures and characterisation data

1.1 General procedures

All manipulations were performed using either standard Schlenk techniques, vacuum line techniques, or in a drybox under an argon atmosphere. Pentane, hexane and toluene were dried over sodium benzophenone ketyl and distilled under nitrogen atmosphere. Benzene-d_6 (C_6D_6) was dried over calcium hydride and then with molecular sieves. $Cp^*W(CO)_2\{Me_2Si\cdots H\cdots Si(^tBu)Me\}$ (**1**)[S1] and $Cp^*W(CO)_2\{Me_2Si\cdots OMe\cdots Si(^tBu)Me\}$ (**A**) [S1] were prepared by the literature procedure. Phenol, *p*-cresol, 2-Adamantanone, and dimethyl aminopyridine (DMAP) were directly used without purification after being purchased. Isopropyl alcohol was dried over calcium hydride and then distilled. 4-Methylbenezenethiol was distilled under nitrogen atmosphere prior to use. Acetone was dried with molecular sieves 3A. Acetophenone, methyl vinyl ketone, methyl vinyl ketone and 3-butyn-2-one were dried with molecular sieves 4A. Diethyl amine was dried over potassium hydroxide and distilled. The ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, ^1H–^1H COSY, and ^1H–$^{29}Si\{^1H\}$ COSY NMR spectra were measured on a Bruker AVANCE-300 or JNM-ECA-600 spectrometers. The ^1H or ^{13}C NMR chemical shifts were referenced to the residual proton (C_6D_5H in C_6D_6: $\delta = 7.15$, $C_6D_5CD_2H$ in $C_6D_5CD_3$: $\delta = 2.09$) and the carbon (C_6D_6: $\delta = 128.0$, $C_6D_5CD_3$: $\delta = 20.4$) of deuterated solvents. The $^{29}Si\{^1H\}$ NMR spectra were referenced to an external standard of tetramethylsilane ($\delta = 0.0$). IR spectra were recorded on a HORIBA FT-730 spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer. High resolution mass spectroscopy and elemental analysis were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

1.2 Reaction of $Cp^*W(CO)_2\{Me_2Si\cdots H\cdots Si(^tBu)Me\}$ (1) with phenol: Formation of $Cp^*W(CO)_2\{Me_2Si\cdots O(Ph)\cdots Si(^tBu)Me\}$ (2)

(a) NMR experiment

An NMR tube equipped with a Teflon valve was charged with **1** (5 mg, 0.009 mmol), C_6Me_6 (< 1 mg, internal standard) and C_6D_6 (0.6 mL). The solution was checked by ^1H NMR and then phenol (1 mg, 0.01 mmol) was added to it. The resulting solution was moved into another NMR tube with a glass joint, which was connected to a vacuum-line system and flame-sealed. Then the ^1H NMR spectrum was measured at room temperature, which showed the formation of $Cp^*W(CO)_2\{Me_2Si\cdots O(Ph)\cdots Si(^tBu)Me\}$ (**2**) in 91% NMR yield.

(b) Preparative experiment

A solution of **1** (45 mg, 84 μmol) and phenol (12 mg, 0.13 mmol) in C_6D_6 (ca. 0.8 mL) was prepared in an NMR tube with a Teflon valve. The sample solution was checked by ^1H NMR, which indicated complete consumption of **1**. All volatiles were removed in vacuo and hexane was added to the residue. The hexane extraction solution was concentrated and kept at –30 °C to afford a white crystalline solid of **2** in 68% yield (36 mg, 0.057 mmol).

2: ^1H NMR (300 MHz, C_6D_6, r.t., δ) 0.37 (s, 3H, SiMe), 0.72 (s, 3H, SiMe), 0.97 (s, 3H, SiMe), 1.12 (s, 9H, ^{t}Bu), 1.96 (s, 15H, Cp^*), 6.77 ~ 6.94 (m, 5H, ArH). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K, δ) 5.8 (SiMe), 8.7 (SiMe), 10.9 (SiMe), 12.5 ($C_5\underline{Me}_5$), 27.9, ($C\underline{Me}_3$), 28.1 ($\underline{C}Me_3$),101.1 ($\underline{C_5}Me_5$), 124.0 (*o*-C), 126.6 (*p*-C), 130.2 (*m*-C), 152.1 (*i*-C), 233.2 (CO), 234.4 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6, DEPT, 298 K, δ) 108.0 (Me_2Si), 121.8 (^{t}BuMeSi).

IR (hexane, cm^{-1}): 1915 ($\nu_{\rm CO}$), 1851 ($\nu_{\rm CO}$). HRMS (ESI positive,, +NaI, *m/z*): Calcd. For [$C_{25}H_{38}O_3Si_2W$]$^+$: [M+Na]$^+$ 649.1766; Found: [M+Na]$^+$ 649.1763. Anal. Calcd. for $C_{25}H_{38}O_3Si_2W$: C, 47.92; H, 6.11. Found: C, 48.05; H, 6.02.

1.3 Reaction of 1 with *p*-cresol: Formation of $Cp^*W(CO)_2\{Me_2Si\cdots O(C_6H_4\text{-}4\text{-}Me)\cdots Si(^tBu)Me\}$ (3)

(a) NMR experiment

In a procedure similar to that of **1.2 (a)**, a solution of **1** (7 mg, 0.01 mmol) and *p*-cresol (2 mg, 0.02 mmol) containing C_6Me_6 (< 1 mg) in C_6D_6 (0.6 mL) was prepared and checked by ^{1}H NMR, which indicated the formation of $Cp^*W(CO)_2\{Me_2Si\cdots O(C_6H_4\text{-}4\text{-}Me)\cdots Si(^tBu)Me\}$ (**3**) in 85% NMR yield.

(b) Preparative experiment

In a 15 mL Schenk flask, to a solution of **1** (53 mg, 0.099 mmol) in toluene (1.5 mL) was added *p*-cresol (19 mg, 0.18 mmol). Soon after that, all volatiles were removed from the solution and the residue was extracted with hexane. The hexane solution was concentrated and layered with hexamethyldisiloxane, and then kept at –30 °C to afford a light-brown solid of **3** in 65% (41 mg, 0.069 mmol).

3: ^{1}H NMR (300 MHz, C_6D_6, r.t., δ) 0.42 (s, 3H, SiMe), 0.75 (s, 3H, SiMe), 0.99 (s, 3H, SiMe),1.15 (s, 9H, ^{t}Bu), 1.94 (s, 3H, *p*-Me), 1.97 (s, 15H, Cp*),6.72 (d, $J_{\rm HH}$ = 8.4 Hz, 2H, Ph), 6.77 (d, $J_{\rm HH}$ = 9.0 Hz, 2H, Ph). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K,δ) 5.8 (SiMe), 8.7 (SiMe), 10.8 (SiMe), 12.5 ($C_5\underline{Me_5}$), 21.2 (*p*-Me), 27.9 ($C\underline{Me_3}$), 28.1 ($\underline{C}Me_3$), 101.1 ($\underline{C}_5Me_5$), 123.7 (*o*-C), 130.8 (*p*-C), 136.3 (*m*-C), 150.0 (*ipso*-C), 233.3 (CO), 234.4 (CO). ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6, DEPT, r.t. K, δ) 106.9 ($J_{\rm Wsi}$ = 93 Hz), 126.4 ($J_{\rm Wsi}$ = 116 Hz). IR (C_6D_6, cm^{-1}) 1905 ($\nu_{\rm CO}$), 1832 ($\nu_{\rm CO}$). HRMS (ESI positive, +NaI, *m/z*) Calcd. For [$C_{26}H_{40}O_3Si_2W$]$^+$: 663.1918 [M+Na]$^+$, Found : 663.1919 [M+Na]$^+$. Anal. Calcd. For $C_{26}H_{40}O_3Si_2W$: C, 48.75; H, 6.29. Found: C, 48.97; H, 6.27.

1.4 Reaction of 1 with isopropyl alcohol: Formation of $Cp^*W(CO)_2\{Me_2Si\cdots O(CHMe_2)\cdot\cdot Si(^tBu)Me\}$ (4)

(a) NMR experiment

In a procedure similar to that of **1.2 (a)**, a solution of **1** (7 mg, 0.01 mmol), isopropyl alcohol (2 mg, 0.03 mmol) and C_6Me_6 (< 1 mg) in C_6D_6 (0.6 mL) was prepared ^{1}H NMR. After 20 min, $Cp^*W(CO)_2\{Me_2Si\cdots O(CHMe_2)\cdot\cdot Si(^tBu)Me\}$ (**4**) was formed in 73% NMR yield. When the sample was prepared using an NMR sample under atmospheric conditions (without using a vacuum line system), a signal of H_2 was observed at 4.46 ppm in the ^{1}H NMR spectrum.

Complex **4** was exactly the same to that obtained by the reaction of **1** with acetone described in the experiment **1.5**, based on the ^{1}H NMR and IR data. For isolation and characterisation of **4**, see below.

1.5 Reaction of 1 with acetone: Formation of 4

(a) NMR experiment

In a procedure similar to that of **1.2 (a)**, to a solution of **1** (7 mg, 0.01 mmol) containing C_6Me_6 (< 1 mg) in C_6D_6 (0.5 mL) was added acetone (3 mg, 0.05 mmol). The solution was soon monitored by ^{1}H NMR, which showed the formation of $Cp^*W(CO)_2\{Me_2Si\cdots O(CHMe_2)\cdots Si(^tBu)Me\}$ (**4**) in 94% NMR yield.

(b) Preparative experiment

In a procedure similar to that of **1.3 (b)**, to a solution of **1** (47 mg, 0.088 mmol) in toluene (1.5 mL) was added acetone (4.1 mL, 0.19 mmol). Removal of volatiles and subsequent crystallisation from hexane gave **4** in 75% (39 mg, 0.066 mmol) as colorless crystals.

4: ^{1}H NMR (300 MHz, C_6D_6, r.t., δ) 0.54 (br, 3H, $SiMe_2$), 0.60 (br, 3H, $SiMe_2$), 0.87 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $OCH\underline{Me}_2$), 0.91 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $OCH\underline{Me}_2$), 1.00 (br, 3H, SiMe), 1.21 (br, 9H, ^{t}Bu), 1.93 (s, 15H, Cp*), 4.2 (sep, $^3J_{HH}$ = 6.6 Hz, 1H, OCH). ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6, DEPT, r.t., δ) 99.3 (Me_2Si), 110.2 (^{t}BuMeSi). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, r.t.,δ) 3.7 (SiMe), 12.4 ($C_5\underline{Me}_5$), 12.6 (SiMe), 13.1 (SiMe), 24.0 ($CH\underline{Me}$), 24.8 ($\underline{C}Me_3$), 28.2 ($CH\underline{Me}$), 28.8 ($C\underline{Me}_3$), 78.5 (OCH), 100.7 ($\underline{C}_5Me_5$), 233.7 (CO), 234.7 (CO). IR (C_6D_6, cm^{-1}) 1898 (ν_{CO}), 1826 (ν_{CO}). HRMS (ESI positive, +NaI, *m/z*) Calcd. For $[C_{22}H_{40}O_3Si_2W+Na]^+$: 615.1918 Found: 615.1915. Anal. Calcd. For $C_{22}H_{40}O_3Si_2W$: C, 44.59; H, 6.80, Found: C, 44.89; H, 6.83.

1.6 Reaction of 1 with 2-adamantanone: Formation of Cp*W(CO)$_2${Me$_2$Si···O(CHC$_9$H$_{14}$)···Si(^{t}Bu)Me} (5)

(a) NMR experiment

In a procedure similar to that of **1.3 (a)**, to a solution of **1** (10 mg, 0.019 mmol) containing C_6Me_6 (< 1 mg) in C_6D_6 (0.5 mL) was added 2-adamantanone (4 mg, 0.03 mmol). The solution was soon monitored by ^{1}H NMR, which showed the formation of Cp*W(CO)$_2${Me$_2$Si···O(CHC$_9$H$_{14}$)···Si(^{t}Bu)Me} (**5**) in 99% NMR yield.

(b) Preparative experiment

In a procedure similar to that of **1.3 (b)**, **1** (42 mg, 0.078 mmol) and 2-adamantanone (18 mg, 0.12 mmol) were dissolved in toluene (1.5 mL). Removal of volatiles and subsequent crystallisation from hexane gave **5** in 58% (22 mg, 0.032 mmol) as light-yellow crystals.

5: ^{1}H NMR (300 MHz, C_6D_6, r.t., δ) 0.72 (s, 3H, $SiMe_2$), 0.78 (s, 3H, $SiMe_2$), 1.05 (s, 3H, SiMe),1.29 (s, 9H, ^{t}Bu), 1.96 (s, 15H, Cp*), 4.32 (br, 1H, OCH). ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6, DEPT, r.t., δ) 99.1 ($^1J_{WSi}$ = 82.9 Hz, Me_2Si), 120.8 ($^1J_{WSi}$ = 116.9 Hz, ^{t}BuMeSi). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, r.t.,δ) 7.4 (SiMe), 9.8 (SiMe), 12.6 ($C_5\underline{Me}_5$), 15.1 (SiMe), 27.4, 27.6, 28.3, 30.1 ($C\underline{Me}_3$), 32.4, 32.6, 33.1,33.3, 37.2, 37.4, 37.5, 39.6, 47.7, 90.0 (OCH), 101.2 ($\underline{C}_5Me_5$), 233.4 (CO), 233.9 (CO). IR (C_6D_6, cm^{-1}) 1894 (ν_{CO}), 1822 (ν_{CO}). HRMS (EI, *m/z*) Calcd. For $[C_{29}H_{48}O_3Si_2W]^+$: 684.2651 Found: 684.2654. Calcd. For $C_{29}H_{48}O_3Si_2W$: C, 50.87; H, 7.07 Found: C, 51.09; H, 7.30.

1.7 Reaction of 1 with ethyl vinyl ketone: Formation of Cp*W(CO)$_2${Me$_2$Si···O[CHEt(C=CH)]···Si(^{t}Bu)Me} (6)

(a) NMR experiment

In a procedure similar to that of **1.3 (a)**, to a solution of **1** (12 mg, 0.022 mmol) containing C_6Me_6 (< 1 mg) in C_6D_6 (0.5 mL) was added ethyl vinyl ketone (3.1 μL, 0.042 mmol). The solution was soon monitored by ^{1}H NMR, which showed the formation of Cp*W(CO)$_2${Me$_2$Si···O[CHEt(C=CH)]···Si(^{t}Bu)Me} (**6**) as a mixture of two diastereomers (dr = 5:3) almost quantitatively.

(b) Preparative experiment

In a procedure similar to that of **1.3 (b)**, **1** (25 mg, 0.046 mmol) and ethyl vinyl ketone (4.8 μL, 0.048 mmol) were dissolved in toluene (1.5 mL). Removal of volatiles and washing with cold hexane of the residue gave a brownish solid of **7** in 60% yield (17 mg, 0.027 mmol) as a mixture of two diastereomers. Complex **7** was thermally unstable and gradually decomposed in solution ($\tau_{1/2}$ ~ 3.5 h).

6: ^{1}H NMR (594 MHz, C_6D_6, r.t., δ) **major**: 0.49 (t, $^3J_{HH}$ = 7.47 Hz, $CH_2\underline{CH_3}$), 0.59 (br, SiMe), 0.61 (br, SiMe), 1.02 (br, SiMe), 1.24 (br, ^{t}Bu), 1.38~1.47 (m, CH_2), 1.65~1.74 (m, CH_2), 1.93 (s, Cp*), 4.32 (br, OCH), 4.82 (d, $^3J_{HH}$ = 17.3 Hz, =CH_2), 4.93 (d, $^3J_{HH}$ = 10.1 Hz, =CH_2), 5.58 (ddd, $^3J_{HH}$ = 17.3 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 9.1 Hz, HC=), **minor**: 0.53 (br, $CH_2\underline{CH_3}$), 0.62 (br, SiMe), 1.03 (br, SiMe), 1.25 (br, ^{t}Bu), 1.50~1.63 (m, CH_2), 1.94 (s, Cp*), 4.35 (br, OCH), 4.86 (d, $^3J_{HH}$ = 17.3 Hz, =CH_2), 4.88 (d, $^3J_{HH}$ = 10.5 Hz, =CH_2), 5.66 (ddd, $^3J_{HH}$ = 17.3 Hz, $^3J_{HH}$ = 10.6, $^3J_{HH}$ = 8.4 Hz, HC=). ^{29}Si{^{1}H} NMR (118 MHz, C_6D_6, IG, r.t., δ) 102.6 (Me_2Si), 115.3 (^{t}BuMeSi). ^{13}C{^{1}H} NMR (149 MHz, C_6D_6, r.t.,δ) **major**: 3.8 (Me), 10.3 (SiMe), 10.3 (SiMe), 11.8 ($C_5\underline{Me_5}$), 12.4 (SiMe), 28.1 ($C\underline{Me_3}$), 88.1 (OCH), 100.1 ($\underline{C}_5Me_5$,, 120.6 (=CH_2), 137.2 (HC=), 232.9 (CO), 234.1 (CO). **minor**: 11.8 ($C_5\underline{Me_5}$), 12.6 (Me), 13.0 (SiMe), 28.2 ($C\underline{Me_3}$), 87.2 (OCH), 119.7 (=CH_2), 135.9 (HC=), 232.9 (CO), 234.1 (CO). IR (C_6D_6, cm^{-1}) 1900 (ν_{CO}), 1832 (ν_{CO}), 1828 (ν_{CO}). HRMS (ESI positive, +NaI, *m/z*) Calcd. For $[C_{24}H_{42}O_3Si_2W+Na]^+$: 641.2074· Found: 641.2076. Anal. Calcd. For $C_{24}H_{42}O_3Si_2W$: C, 46.60; H, 6.84, Found: C, 46.93; H, 6.66.

1.8 Reaction of 1 with methyl vinyl ketone: Cp*W(CO)$_2${Me$_2$Si···O(CHMeCH=CH$_2$)···Si(^{t}Bu)Me} (7)

(a) NMR experiment

In a procedure similar to that of **1.3 (a)**, to a solution of **1** (7 mg, 0.01 mmol) containing C_6Me_6 (< 1 mg) in C_6D_6 (0.5 mL) was added methyl vinyl ketone (7 mg, 0.1 mmol). The solution was soon monitored by ^{1}H NMR, which showed the formation of Cp*W(CO)$_2${Me$_2$Si···O(CHMeCH=CH$_2$)···Si(^{t}Bu)Me} (**7**) in 94% NMR yield.

(b) Preparative experiment

In a procedure similar to that of **1.3 (b)**, **1** (43.5 mg, 0.0814 mmol) in toluene (1.5 mL) was added methyl vinyl ketone (8.6 mg, 0.12 mmol). Removal of volatiles and subsequent crystallisation from hexane gave **7** in 45% yield (17 mg, 0.037 mmol) as a brownish solid. Complex **7** was extremely thermally unstable in solution and the measurements of the ^{29}Si and ^{13}C NMR spectra were unsuccessful because of its decomposition. The structure of **7** was supported by HRMS, the^{1}H NMR and IR data of **7**, which resemble those of **6**.

7: ^{1}H NMR (300 MHz, C_6D_6, r.t., δ) 0.57 (br, 3H, SiMe), 0.59 (br, 3H, SiMe), 0.91~1.11 (6H, SiMe, $CH\underline{Me}$), 1.22 (s, 9H, ^{t}Bu), 1.93 (s, 15H, Cp*), 4.62 (m, 1H, OCH), 4.68~4.89 (m, 2H, =CH_2), 5.66~5.93 (m, 1H, CH). IR (C_6D_6, cm^{-1}) 1900 (ν_{CO}), 1828 (ν_{CO}). HRMS (ESI positive, +NaI, *m/z*) Calcd. For $[C_{23}H_{45}NO_2Si_2W+Na]^+$: 630.2396 Found: 630.2392.

1.9 Reaction of 1 with 3-butyn-2-one: Formation of Cp*W(CO)$_2${Me$_2$Si···O[CHMe(C≡CH)]···Si(^{t}Bu)Me} (8)

(a) NMR experiment

In a procedure similar to that of **1.3 (a)**, to a solution of **1** (14 mg, 0.027 mmol) containing C_6Me_6 (< 1 mg) in C_6D_6 (0.5 mL) was added 3-butyn-2-one (1.8 mg, 0.027 mmol). The solution was soon monitored by ^{1}H NMR, which showed the formation of Cp*W(CO)$_2${Me$_2$Si···O[CHMe(C≡CH)]···Si(^{t}Bu)Me} (**8**) a mixture of two diastereomers (dr = 2:1) in 96% NMR yield.

(b) Preparative experiment

In a procedure similar to that of **1.3 (b)**, **1** (49 mg, 0.092 mmol) in toluene (1.5 mL) was added 3-butyn-2-one (7.4 μL, 0.095 mmol) and the solution was stirred for 40 min. Removal of volatiles and washing with cold hexane of the residue gave **8** in74% (41 mg, 0.068 mmol) as a brownish solid.

In the ^{1}H NMR spectrum, all signals except Cp*of the two diastereomers appeared to be almost overlapped.

8: ^{1}H NMR (300 MHz, C_6D_6, r.t., δ) 0.47 (br, 1H, ≡CH), 0.71 (br, 3H, SiMe), 0.83 (br, 3H, SiMe), 1.00 (br, 3H, SiMe),1.10~1.14 (br, 9H, ^{t}Bu), 1.91 (**minor**) (s, 15H, Cp*) and 1.96 (**major**) (s, 15H, Cp*), 4.60~4.75 (br, 1H, OCH). ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6, DEPT, r.t., δ) 108.2 (Me_2Si), 117.7 (^{t}BuMeSi). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, r.t.,δ) 12.4 ($C_5\underline{Me}_5$), 28.4 ($C\underline{Me}_3$), 28.7 ($\underline{C}Me_3$), 100.8 ($\underline{C_5}Me_5$), 233.1 (CO), 234.6 (CO). IR (C_6D_6, cm^{-1}) 1901 (ν_{CO}), 1832 (ν_{CO}), 1828 (ν_{CO}). HRMS (ESI positive, +NaI, *m/z*) Calcd. For $[C_{23}H_{38}O_3Si_2W+Na]^+$: 625.1761, Found: 625.1760. Anal. Calcd. For $C_{23}C_{38}O_3Si_2W$: C, 45.85; H, 6.36, Found: C, 46.07; H, 6.16.

1.10 Reaction of 1 with diethylamine: Formation of Cp*W(CO)$_2$(=SiMe$_2$←NHEt$_2$)SiH(^{t}Bu)Me (9)

(a) NMR experiment

In a procedure similar to that of **1.3 (a)**, to a solution of **1** (6 mg, 0.01 mmol) containing C_6Me_6 (< 1 mg) in C_6D_6 (0.5 mL) was added diethylamine (2 mg, 0.02 mmol). The solution was soon monitored by ^{1}H NMR, which showed the formation of Cp*W(CO)$_2$(=SiMe$_2$←NHEt$_2$)SiH(^{t}Bu)Me (**9**) in 91% NMR yield.

(b) Preparative experiment

In a procedure similar to that of **1.3 (b)**, **1** (49 mg, 0.092 mmol) in toluene (1.5 mL) was added diethylamine (46 mg, 0.71 mmol) and the solution was stirred for 2 h. Removal of volatiles and subsequent crystallisation of the residue from hexane gave **9** in77% yield (42 mg, 0.069 mmol) as yellow crystals.

9: ^{1}H NMR (300 MHz, C_6D_6, r.t., δ) 0.52 (t, $^3J_{HH}$ = 7.5 Hz, 3H,$CH_2\underline{CH_3}$), 0.57 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $CH_2\underline{CH_3}$), 0.61 (s, 3H, SiMe),0.68 (s, 3H, SiMe), 1.01 (d,$^3J_{HH}$ = 3.9 Hz, 3H, SiMe), 1.55 (s, 9H, ^{t}Bu), 1.92 (s, 15H, Cp*), 2.90 (m, 4H, CH_2), 3.57 (br, 1H, NH), 4.73 (q, $^3J_{HH}$ = 3.9 Hz, 1H, SiH). ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6, DEPT, r.t., δ) 22.9 ($^1J_{WSi}$ = 118 Hz, ^{t}BuMeHSi), 101.4 (Me_2Si). HRMS (ESI positive, +NaI, *m/z*) Calcd. For $[C_{23}H_{45}NO_2Si_2W+Na]^+$: 630.2396, Found: 630.2392.

1.11 Reaction of 1 with dimethyl aminopyridine (DMAP): Formation of Cp*W(CO)$_2$(=SiMe$_2$←dmap)SiH(^{t}Bu)Me (10)

(a) NMR experiment

In a procedure similar to that of **1.3 (a)**, to a solution of **1** (12 mg, 0.022 mmol) containing C_6Me_6 (< 1 mg) in C_6D_6 (0.4 mL) was added DMAP (4 mg, 0.03 mmol). The solution was soon monitored by ^{1}H NMR, which showed the formation of Cp*W(CO)$_2$(=SiMe$_2$←dmap)SiH(^{t}Bu)Me (**10**) in 99% NMR yield.

(b) Preparative experiment

In a procedure similar to that of **1.3 (b)**, **1** (41 mg, 0.077 mmol) in toluene (1.5 mL) was added DMAP (7 mg, 0.06 mmol). Removal of volatiles and washing of the residue with pentane afforded **10** in 88% yield (35 mg, 0.053 mmol) as a yellow-brown solid.

10: ^{1}H NMR (300 MHz, C_6D_6, 298 K, δ) 1.05 (s, 6H, W=SiMe$_2$), 1.06 (d, $^3J_{HH}$ = 3.6 Hz, 3H, W−SiMe), 1.41 (s, 9H, ^{t}Bu), 1.92 (s, 6H, NMe$_2$), 2.02 (s, 15H, Cp*), 4.78 (q, $^1J_{SiH}$ = 157.0 Hz, $^3J_{HH}$ = 3.6 Hz, 1H, SiH), 5.62 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-H of DMAP), 8.24 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-H of DMAP). ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6, DEPT, 298 K, δ) 26.9 ($^1J_{WSi}$ = 70.4 Hz, WSiHMe^{t}Bu), 86.7 ($^1J_{WSi}$ = 114.5 Hz, W=SiMe$_2$←DMAP). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, DEPT, 298 K, δ) −0.4 (W−SiMe), 6.8 (W=SiMe), 7.8 (W=SiMe), 11.3 ($C_5\underline{Me}_5$), 23.7 ($\underline{C}Me_3$), 31.5 ($C\underline{Me}_3$), 38.3 (NMe$_2$), 98.8 ($\underline{C}_5Me_5$), 106.1 (*m*-C of DMAP), 145.0 (*o*-C of DMAP), 155.2 (*p*-C of DMAP), 234.5(CO), 237.9 (CO). IR (C_6D_6, cm^{-1}) 2006 (w, νSiH), 1847 (m, νCO), 1770 (s, νCO). HRMS: (ESI positive, +NaI, *m/z*) Calcd. for $[C_{26}H_{44}N_2O_2Si_2W+Na]^+$: 679.2348, Found: 679.2343.

2. NMR Spectra

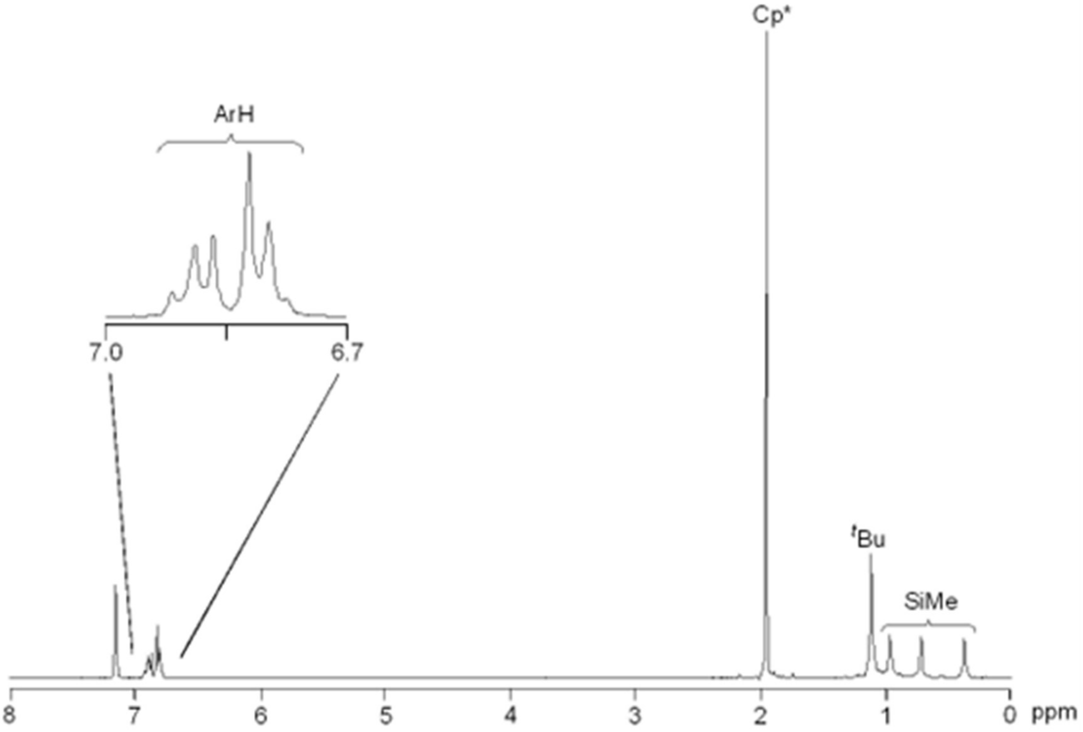


Fig. S1 ^{1}H NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(Ph)···Si(^{t}Bu)Me} (**2**) (300 MHz, C_6D_6).

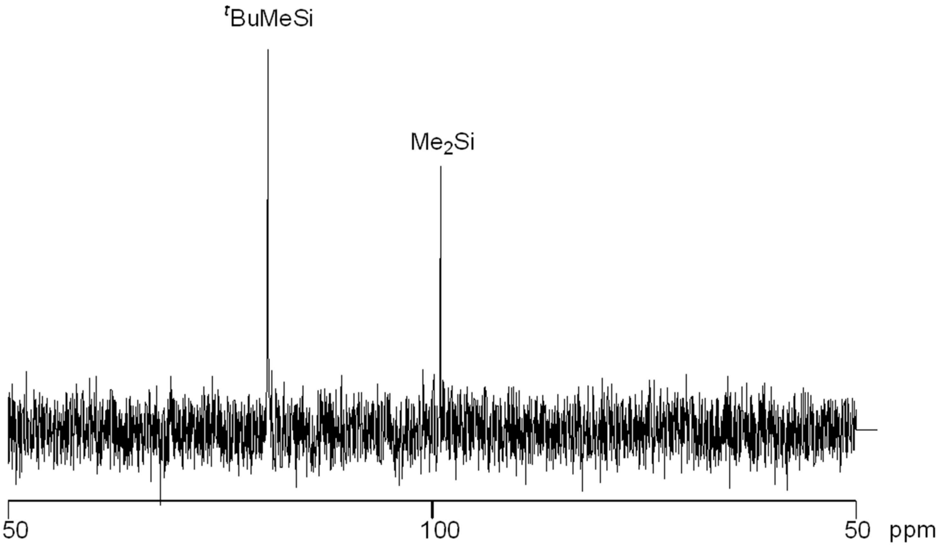


Fig. S2 ^{29}Si{^{1}H} NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(Ph)···Si(^{t}Bu)Me} (**2**) (59.6 MHz, C_6D_6).

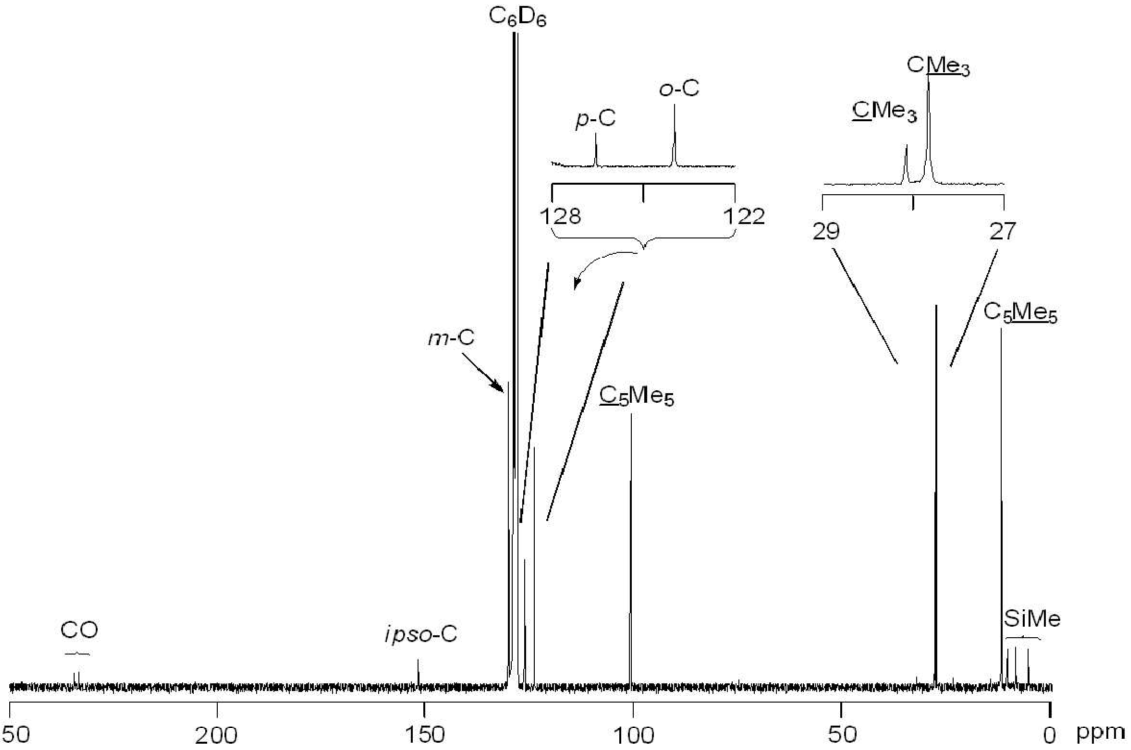


Fig. S3 ^{13}C{^{1}H} NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(Ph)···Si(^{t}Bu)Me} (**2**) (75.5 MHz, C$_6$D$_6$).

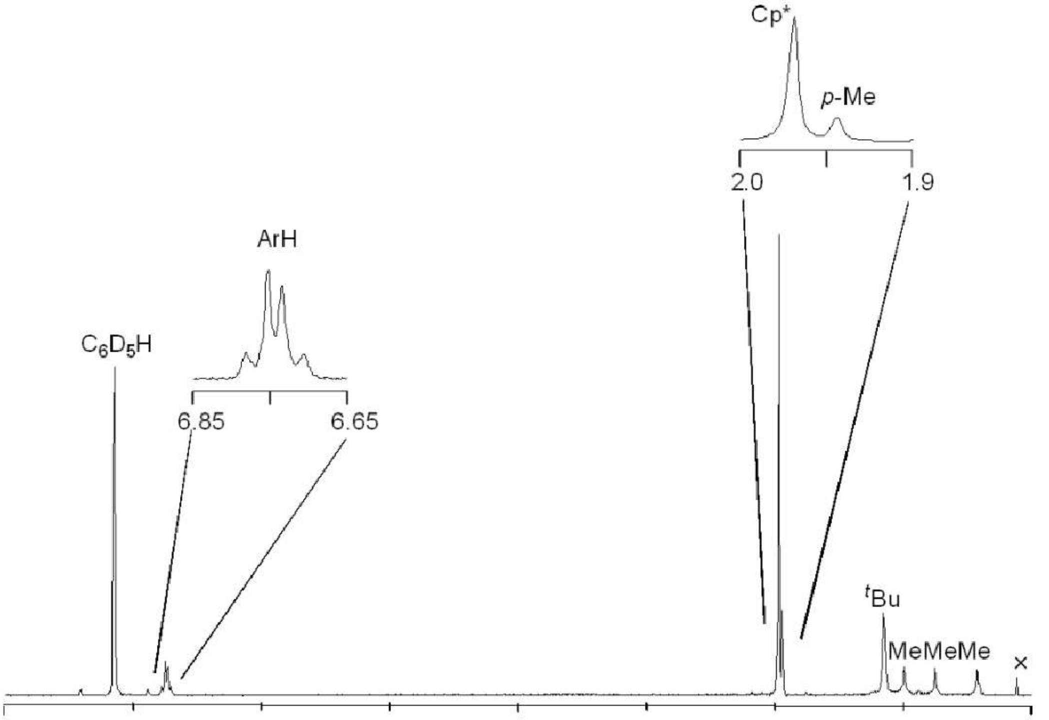


Fig. S4 ^{1}H NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(C$_6$H$_4$-4-Me)···Si(^{t}Bu)Me} (**3**) (300 MHz, C$_6$D$_6$).

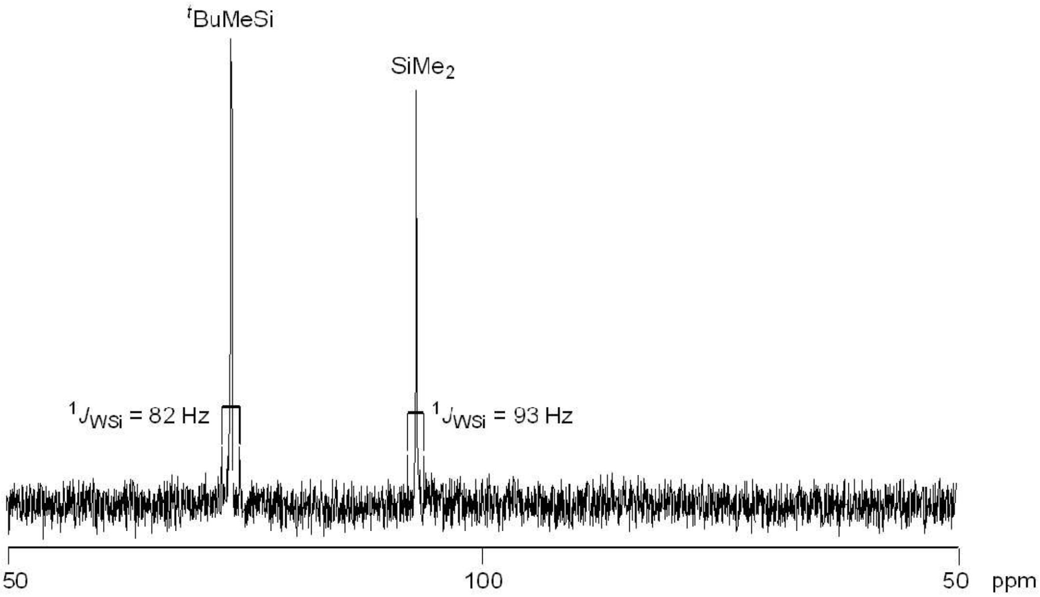


Fig. S5 $^{29}Si\{^1H\}$ NMR spectrum of $Cp^*W(CO)_2\{Me_2Si\cdots O(C_6H_4\text{-}4\text{-}Me)\cdots Si(^tBu)Me\}$ (**3**) (59.6 MHz, C_6D_6).

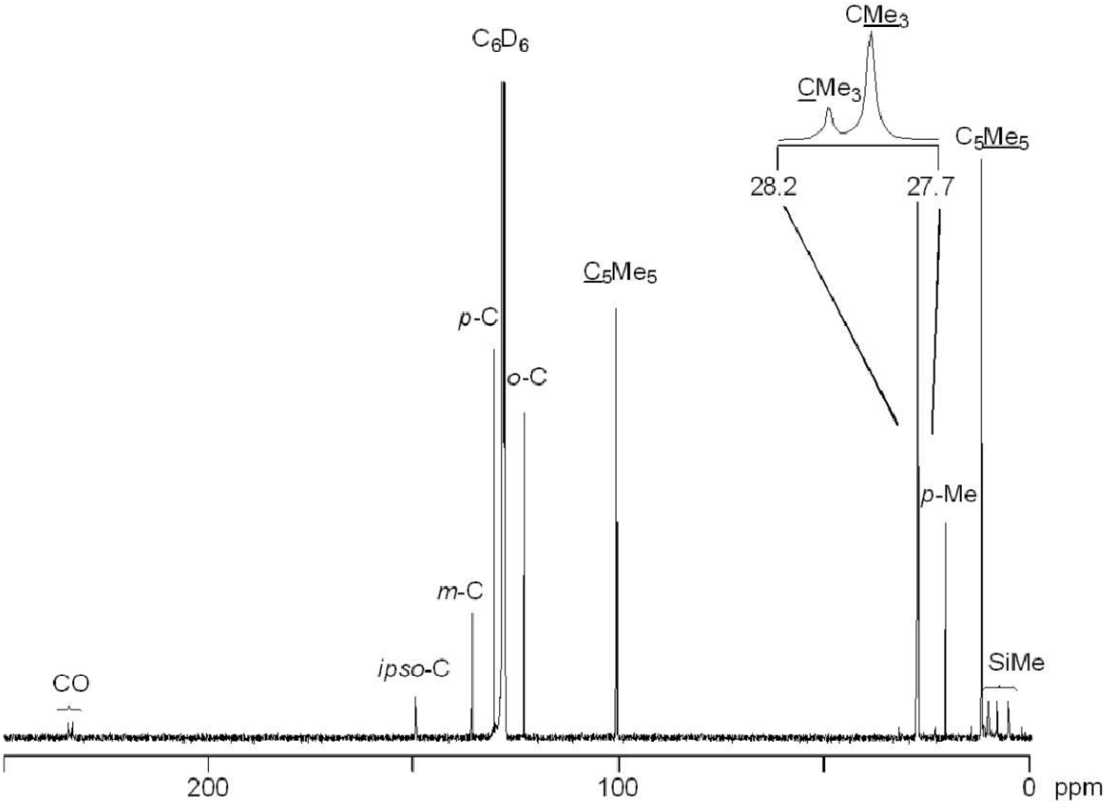


Fig. S6 $^{13}C\{^1H\}$ NMR spectrum of $Cp^*W(CO)_2\{Me_2Si\cdots O(C_6H_4\text{-}4\text{-}Me)\cdots Si(^tBu)Me\}$ (**3**) (75.5 MHz, C_6D_6).

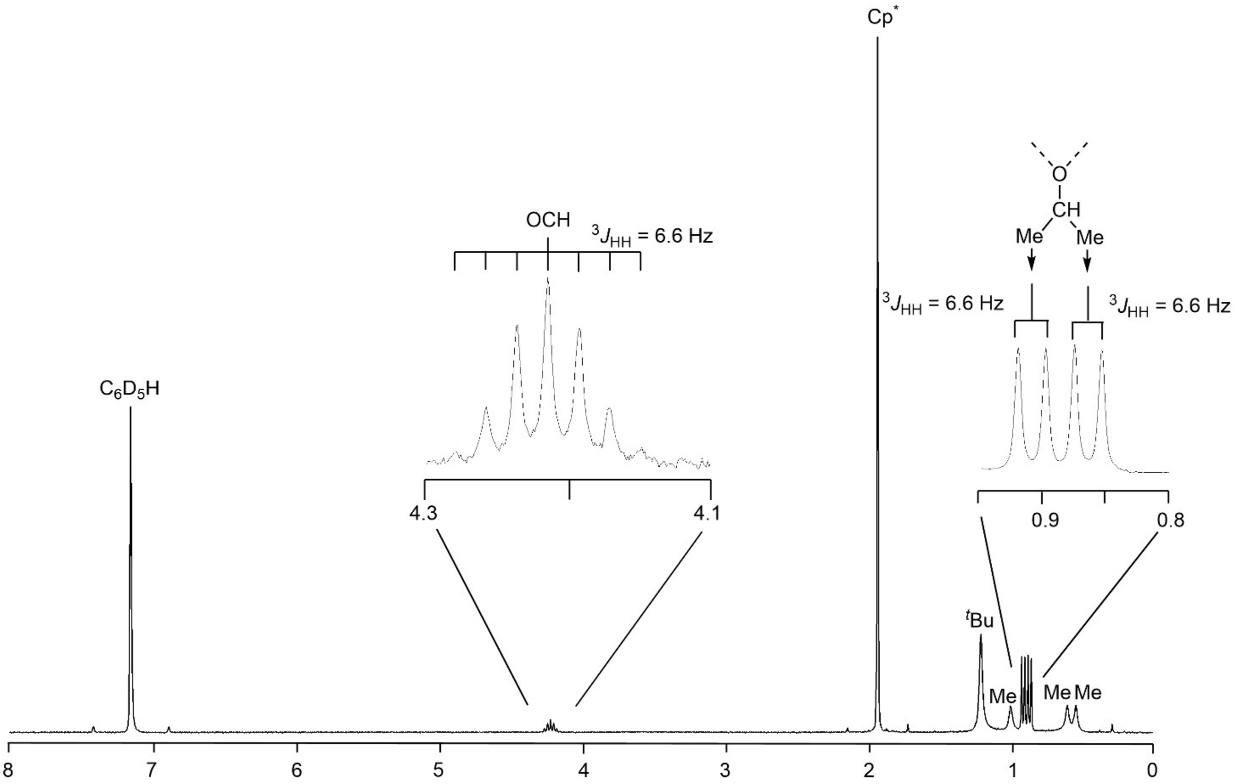


Fig. S7 ^{1}H NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHMe$_2$)···Si(^{t}Bu)Me} (**4**) (300 MHz, C$_6$D$_6$).

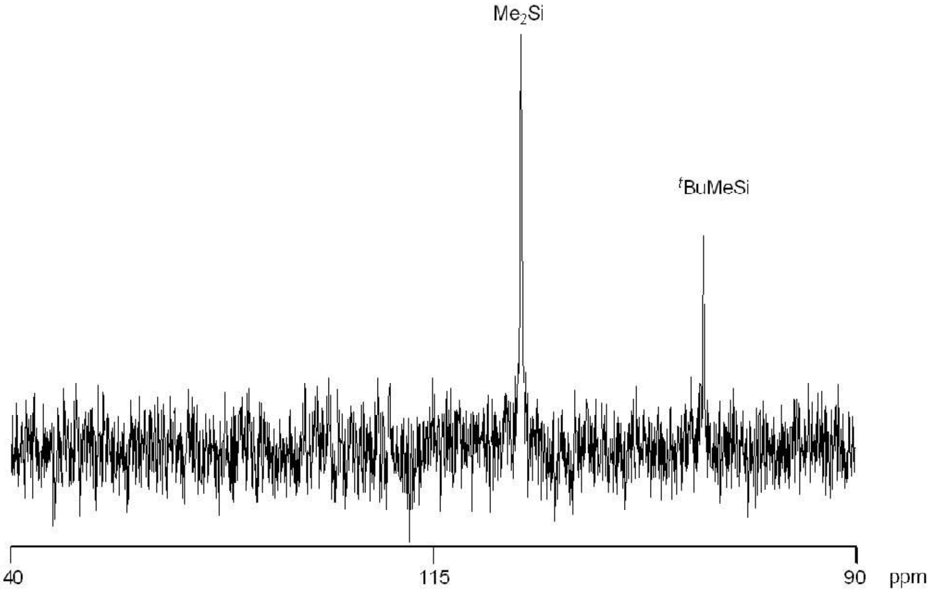


Fig. S8 ^{29}Si{^{1}H} NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHMe$_2$)···Si(^{t}Bu)Me} (**4**) (59.6 MHz, C$_6$D$_6$).

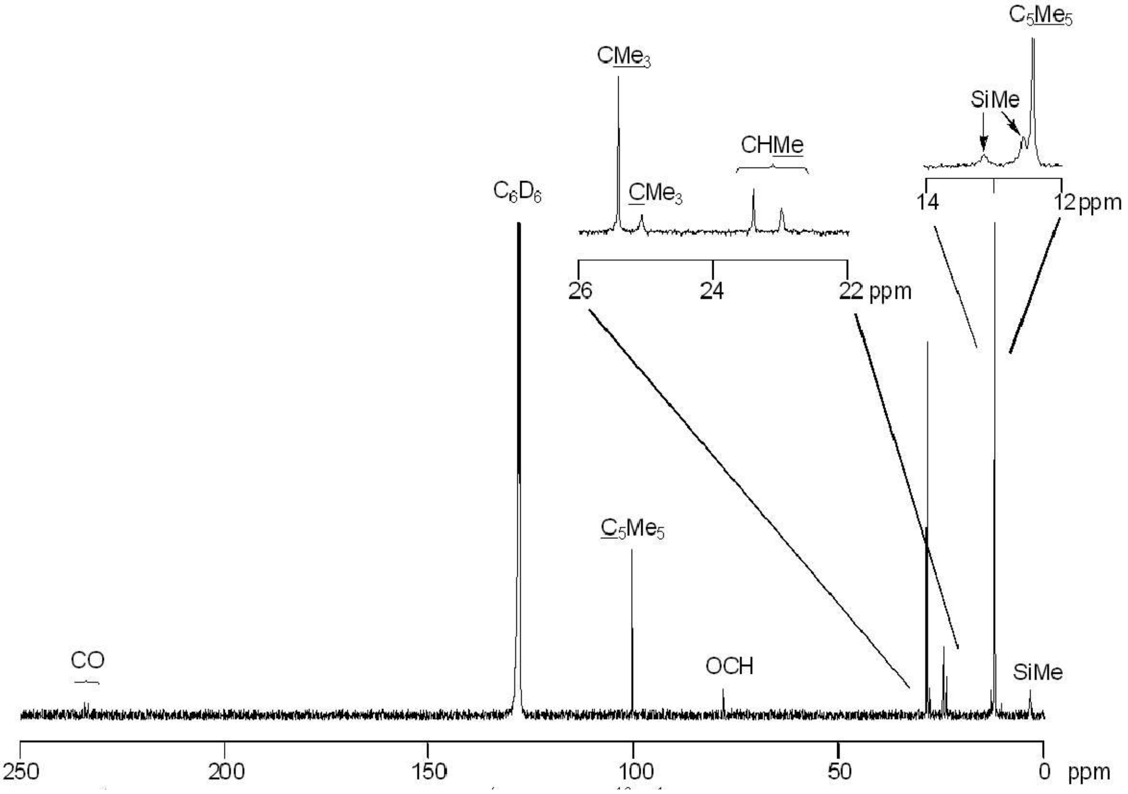


Fig. S9 ^{13}C{^{1}H} NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHMe$_2$)···Si(^{t}Bu)Me} (**4**) (75.5 MHz, C_6D_6).

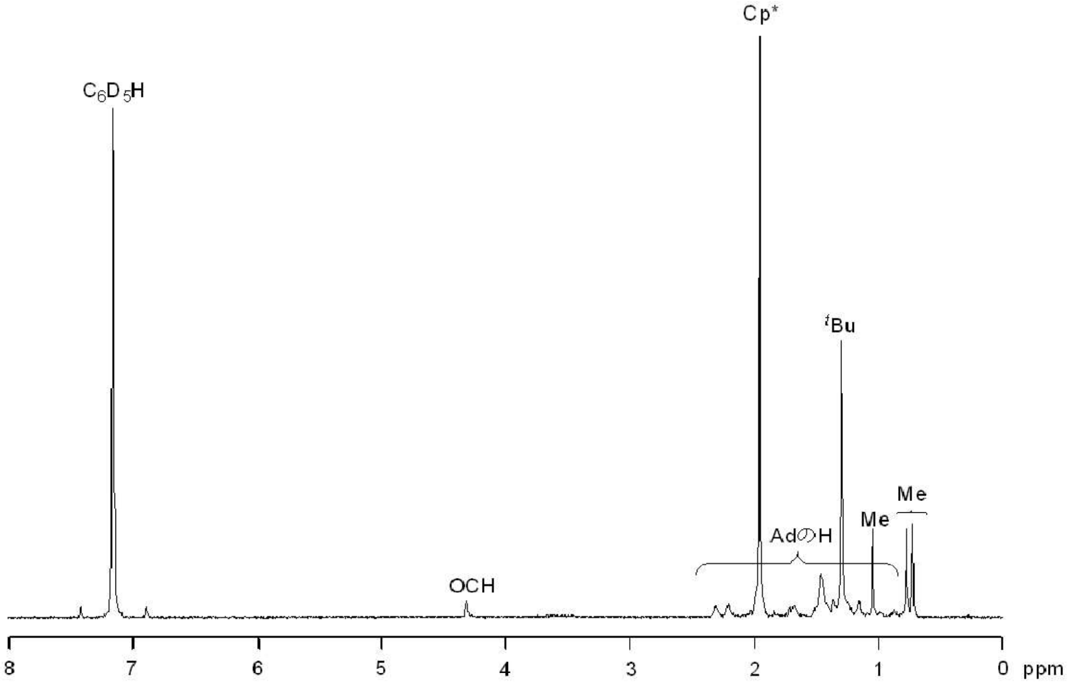


Fig. S10 ^{1}H NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHC$_9$H$_{14}$)···Si(^{t}Bu)Me} (**5**) (300 MHz, C_6D_6).

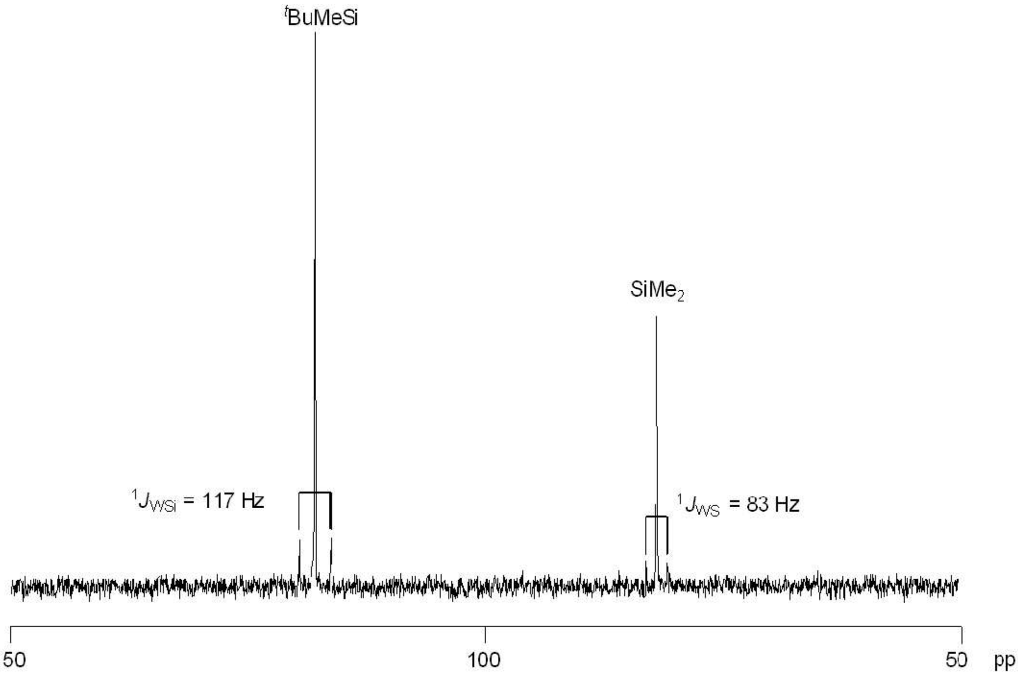


Fig. S11 ^{29}Si{^{1}H} NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHC$_9$H$_{14}$)···Si(^{t}Bu)Me} (**5**) (59.6 MHz, C$_6$D$_6$).

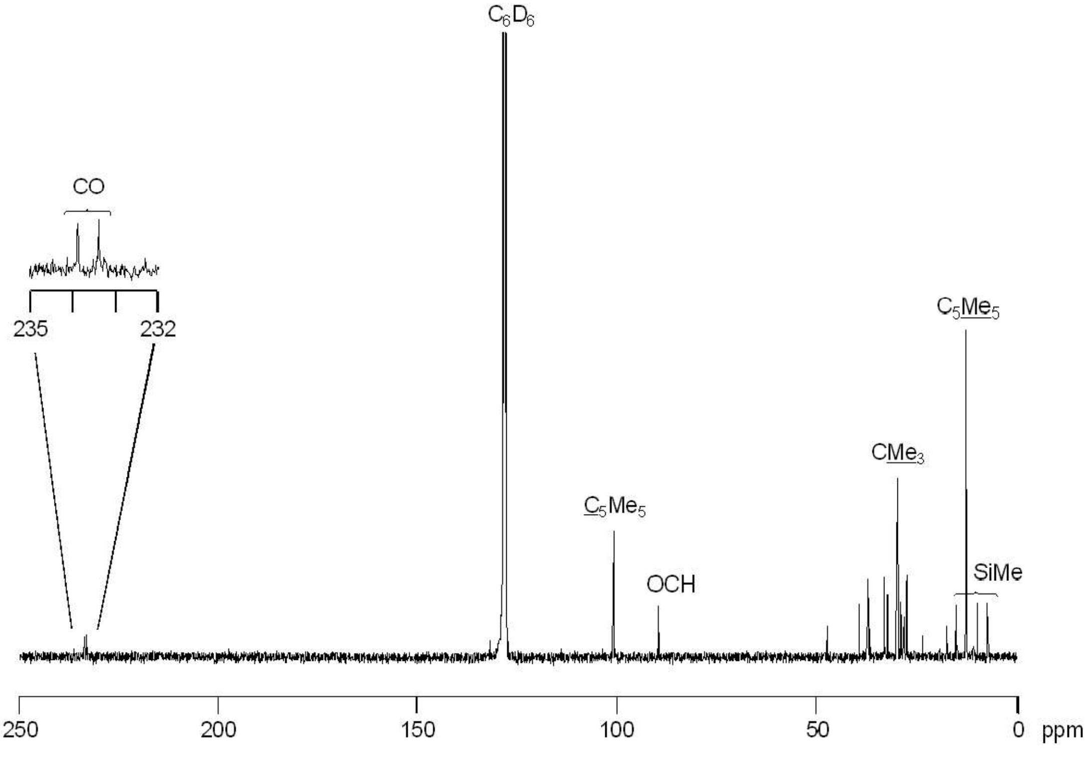


Fig. S12 ^{13}C{^{1}H} NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHC$_9$H$_{14}$)···Si(^{t}Bu)Me} (**5**) (75.5 MHz, C$_6$D$_6$).

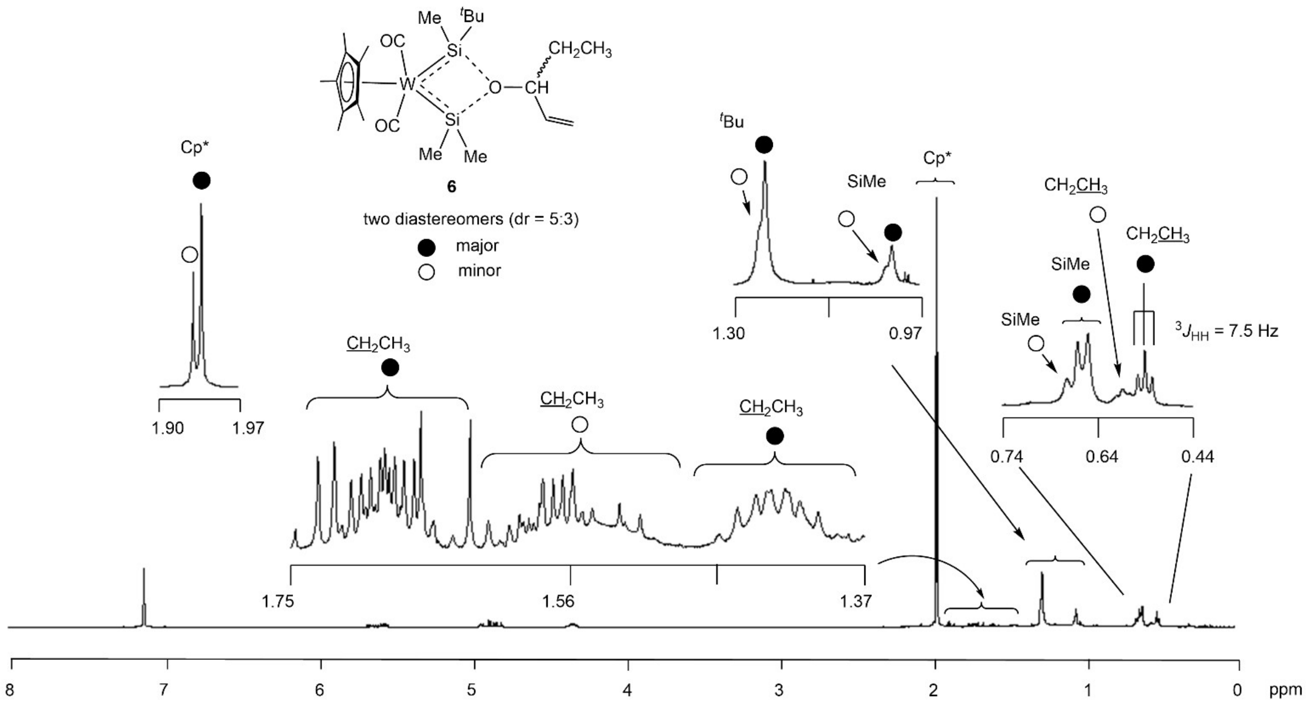


Fig. S13-1 ^{1}H NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHEtCH=CH$_2$)···Si(^{t}Bu)Me} (**6**) with insertion of expanded spectra of the high-field regions (a mixture of two diastereomers, dr = 5:3) (300 MHz, C$_6$D$_6$).

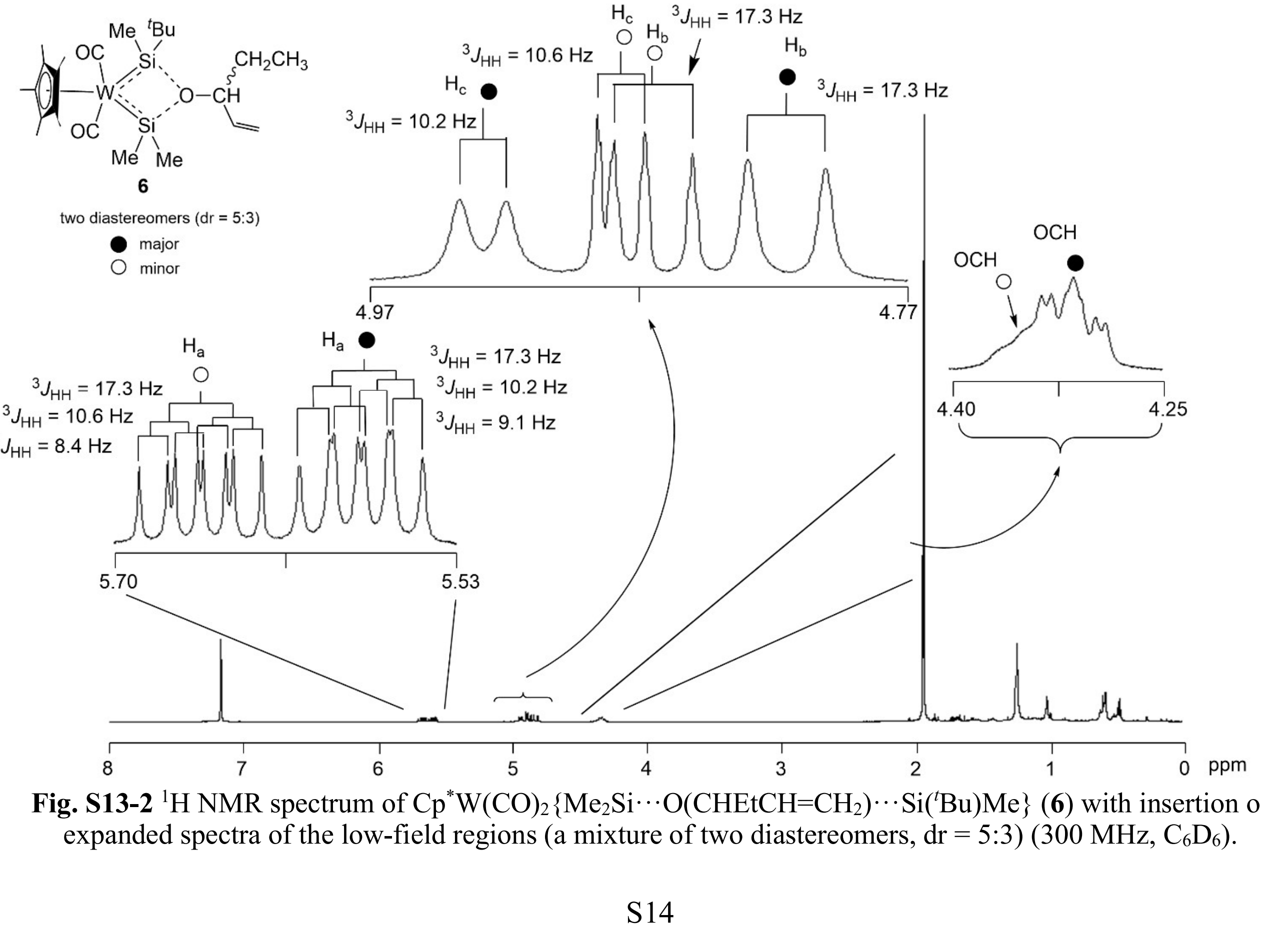
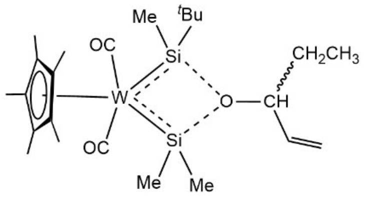


Fig. S13-2 ^{1}H NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHEtCH=CH$_2$)···Si(^{t}Bu)Me} (**6**) with insertion of expanded spectra of the low-field regions (a mixture of two diastereomers, dr = 5:3) (300 MHz, C$_6$D$_6$).



6

two diastereomers (dr = 5:3)

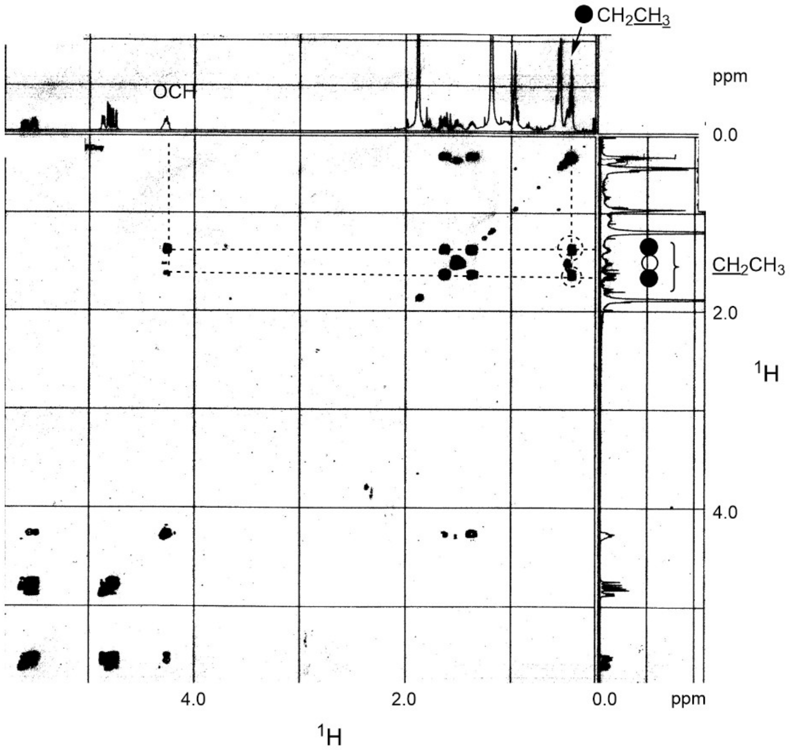


Fig. S14 ^{1}H–^{1}H COSY NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHEtCH=CH$_2$)···Si(^{t}Bu)Me} (**6**) (a mixture of two diastereomers, dr = 5:3) (594.2 MHz, C_6D_6).

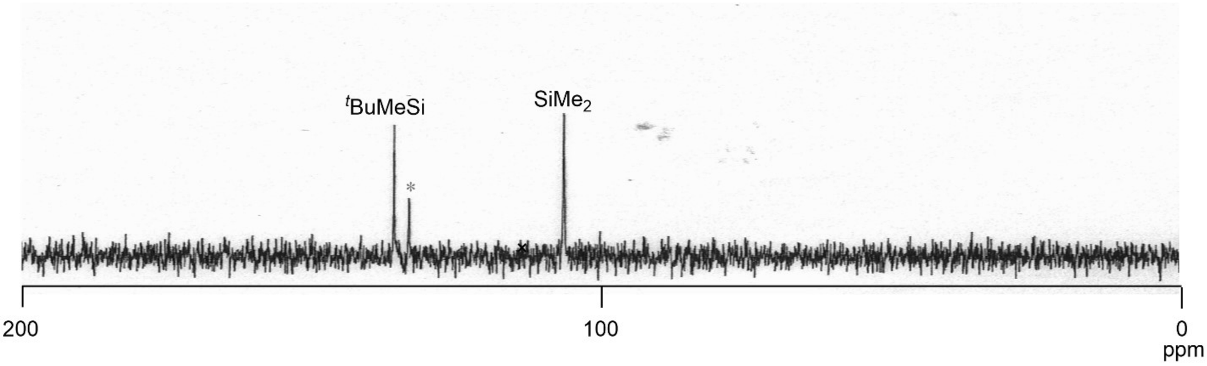
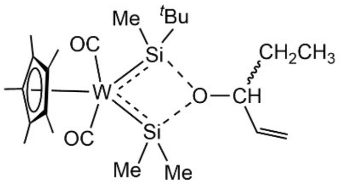


Fig. S15 ^{29}Si{^{1}H} NMR spectrum of Cp*W(CO)$_2${Me$_2$Si···O(CHEtCH=CH$_2$)···Si(^{t}Bu)Me} (**6**) (a mixture of two diastereomers dr = 5:3) (118 MHz, C_6D_6). **6** was thermally unstable in solution and gradually decomposed.
The signal denoted by "*" seems to be decomposed species because there was no correlation between this signal and any other SiMe signals in the ^{1}H–^{29}Si{^{1}H} COSY NMR in **Fig.S16** (below).



6

two diastereomers (dr = 5:3)

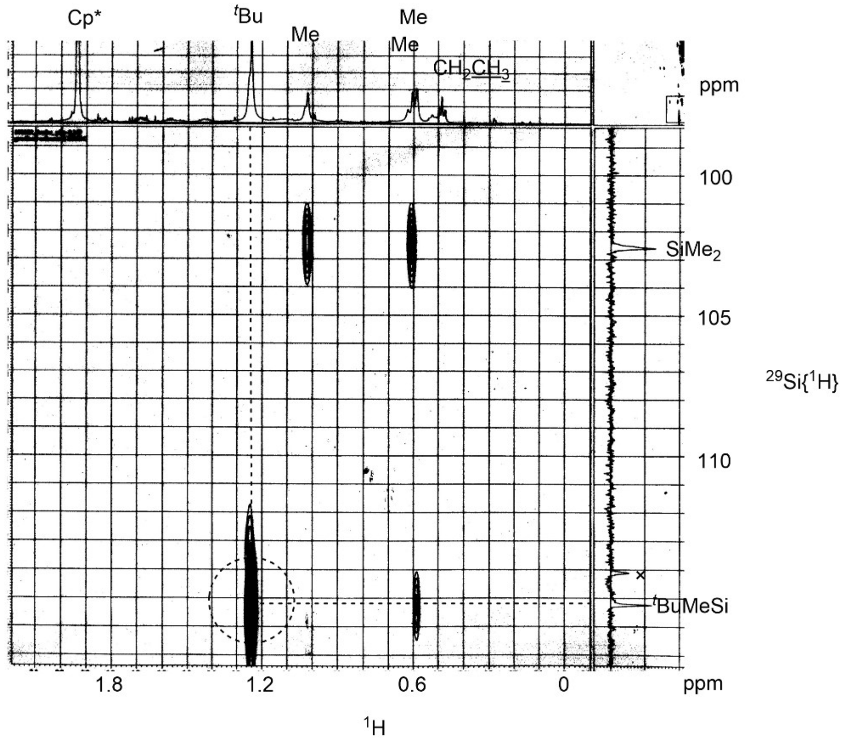


Fig. S16 ^1H–$^{29}Si\{^1H\}$ COSY NMR spectrum of $Cp^*W(CO)_2\{Me_2Si\cdots O(CHEtCH{=}CH_2)\cdots Si(^tBu)Me\}$ (**6**) (a mixture of two diastereomers, dr = 5:3) (594 MHz, C_6D_6).

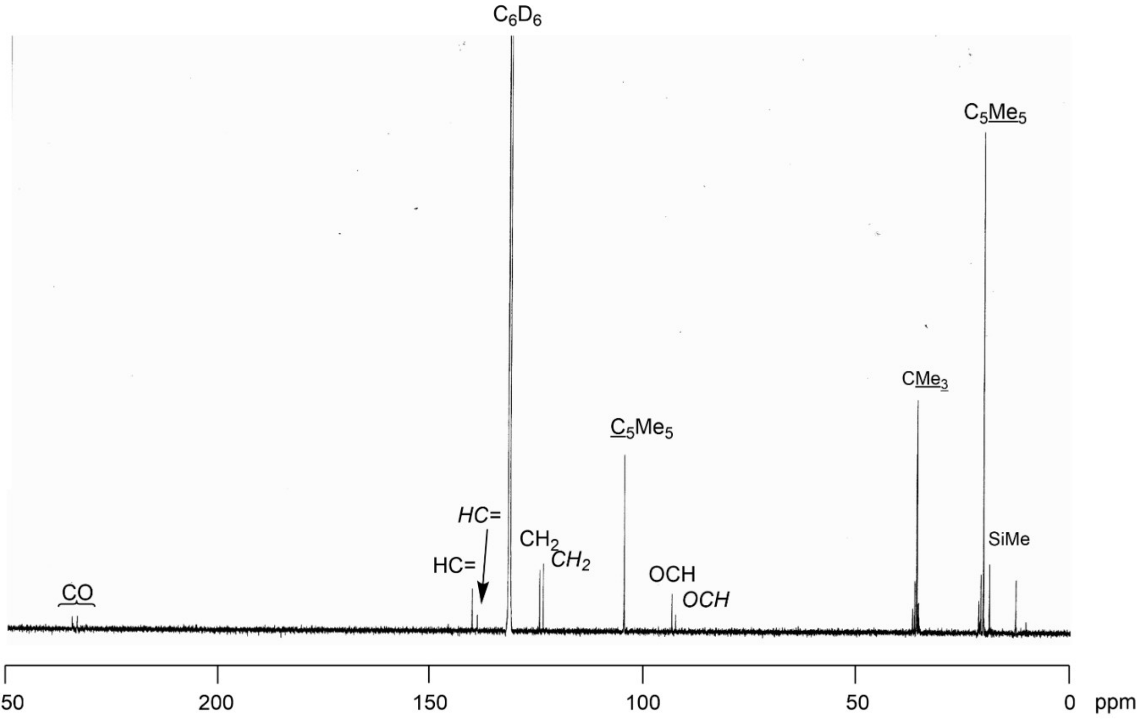


Fig. S17-1 $^{13}C\{^1H\}$ NMR spectrum of $Cp^*W(CO)_2\{Me_2Si\cdots O(CHEtCH{=}CH_2)\cdots Si(^tBu)Me\}$ (**6**) ((a mixture of two diastereomers, dr = 5:3) (149 MHz, C_6D_6).

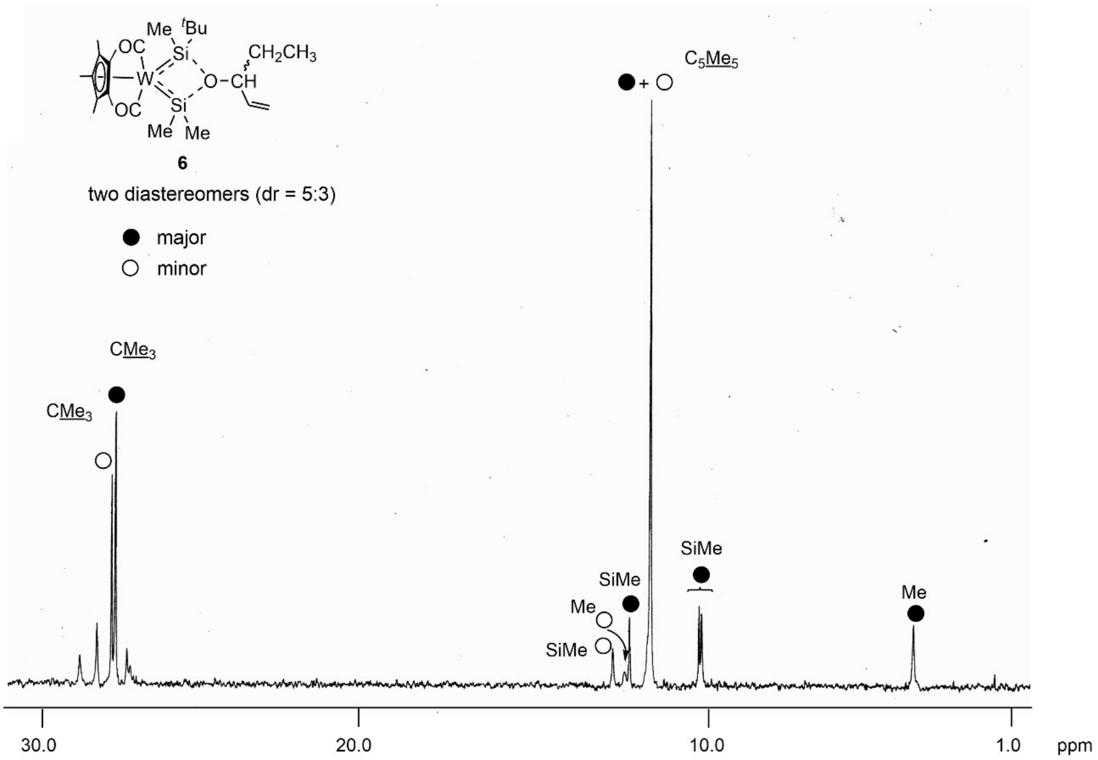


Fig. S17-2 Expanded $^{13}C\{^1H\}$ NMR spectrum of Cp*W(CO)$_2$\{Me$_2$Si···O(CHEtCH=CH$_2$)···Si(^{t}Bu)Me\} (**6**) in a region of 1.0~30 ppm (a mixture of two diastereomers, dr = 5:3). (149 MHz, C$_6$D$_6$).

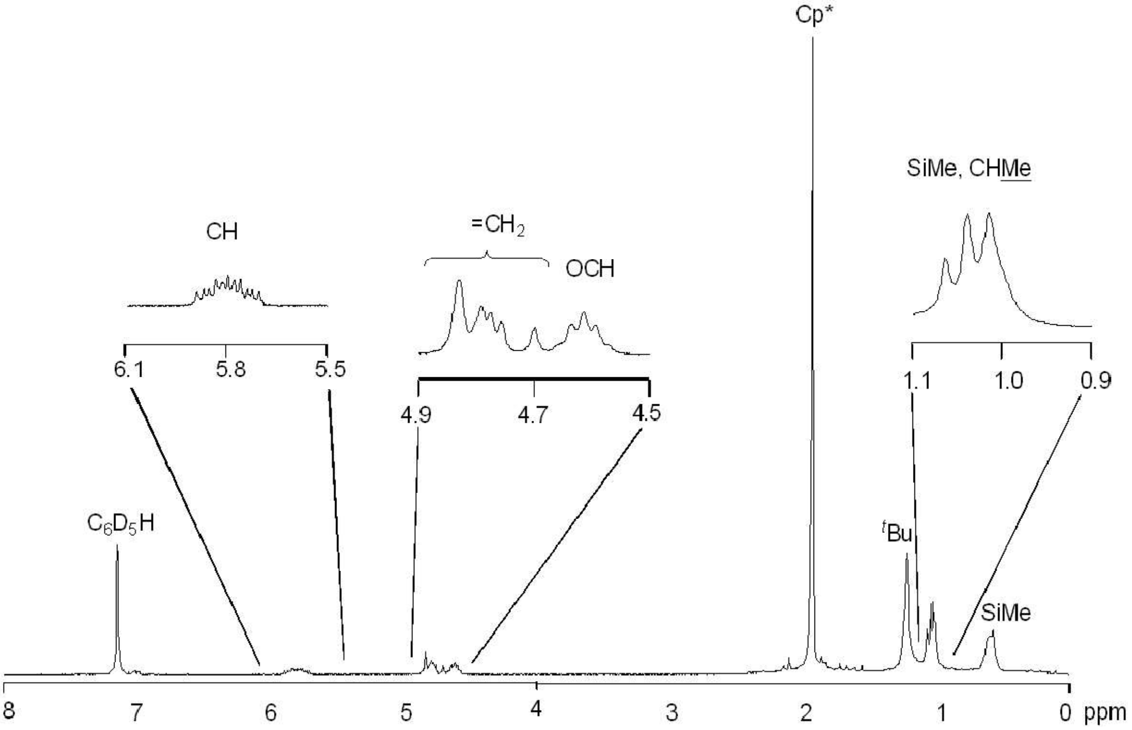


Fig. S18 ^{1}H NMR spectrum of Cp*W(CO)$_2$\{Me$_2$Si···O(CHMeCH=CH$_2$)···Si(^{t}Bu)Me\} (**7**) (300 MHz, C$_6$D$_6$).

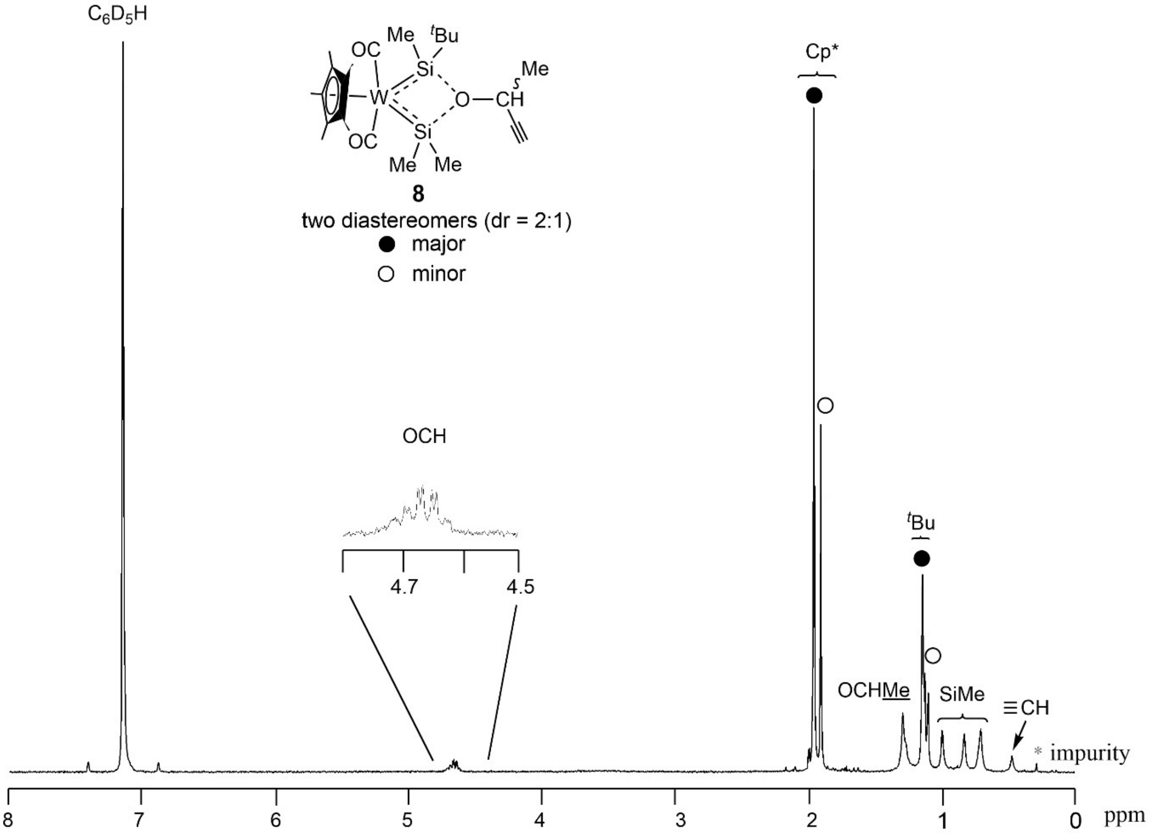


Fig. S19 ^{1}H NMR spectrum of Cp*W(CO)$_2$\{Me$_2$Si···O[CHMe(C≡CH)]···Si(^{t}Bu)Me\} (**8**) (300 MHz, C_6D_6). ((a mixture of two diastereomers, dr = 2:1).

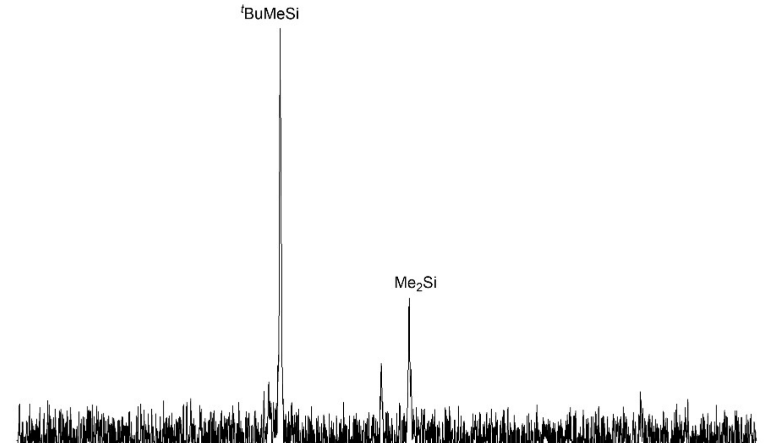


Fig. S20 ^{29}Si\{^{1}H\} NMR spectrum of Cp*W(CO)$_2$\{Me$_2$Si···O[CHMe(C≡CH)]···Si(^{t}Bu)Me\} **(8**) (59.6 MHz, C_6D_6). (a mixture of two diastereomers, dr = 2:1).

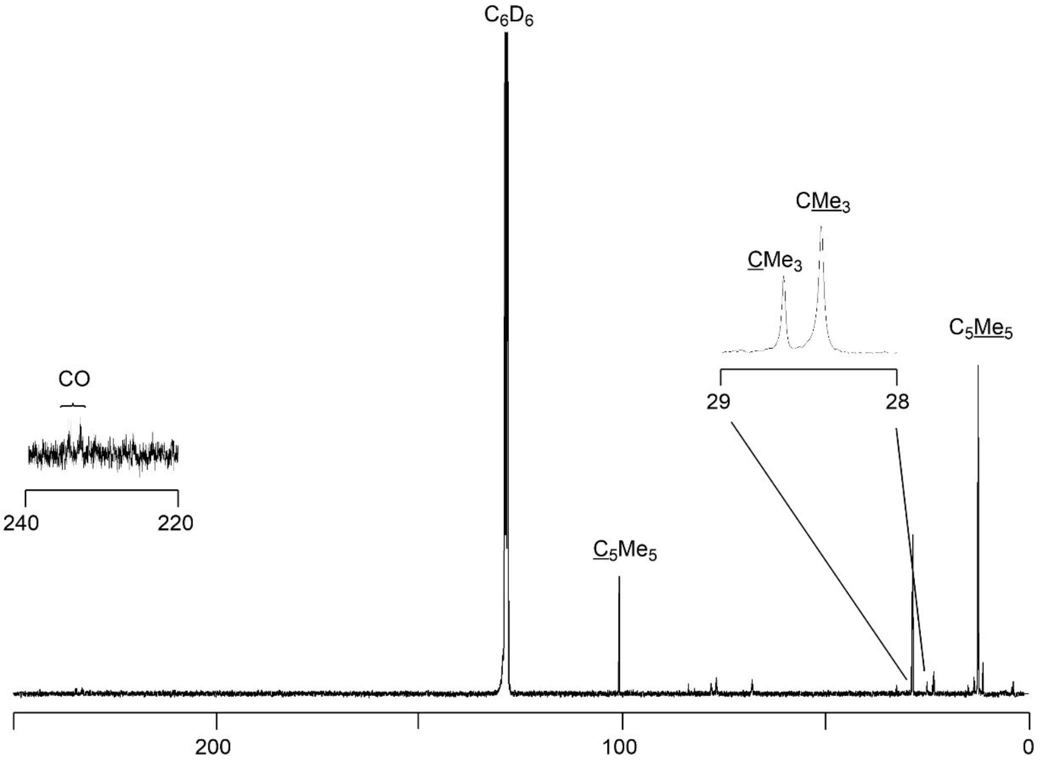


Fig. S21 $^{13}C\{^{1}H\}$ NMR spectrum of $Cp^{*}W(CO)_2\{Me_2Si\cdots O[CHMe(C{\equiv}CH)]\cdots Si(^{t}Bu)Me\}$ (**8**) (75.5 MHz, C_6D_6). (a mixture of two diastereomers, dr = 2:1).

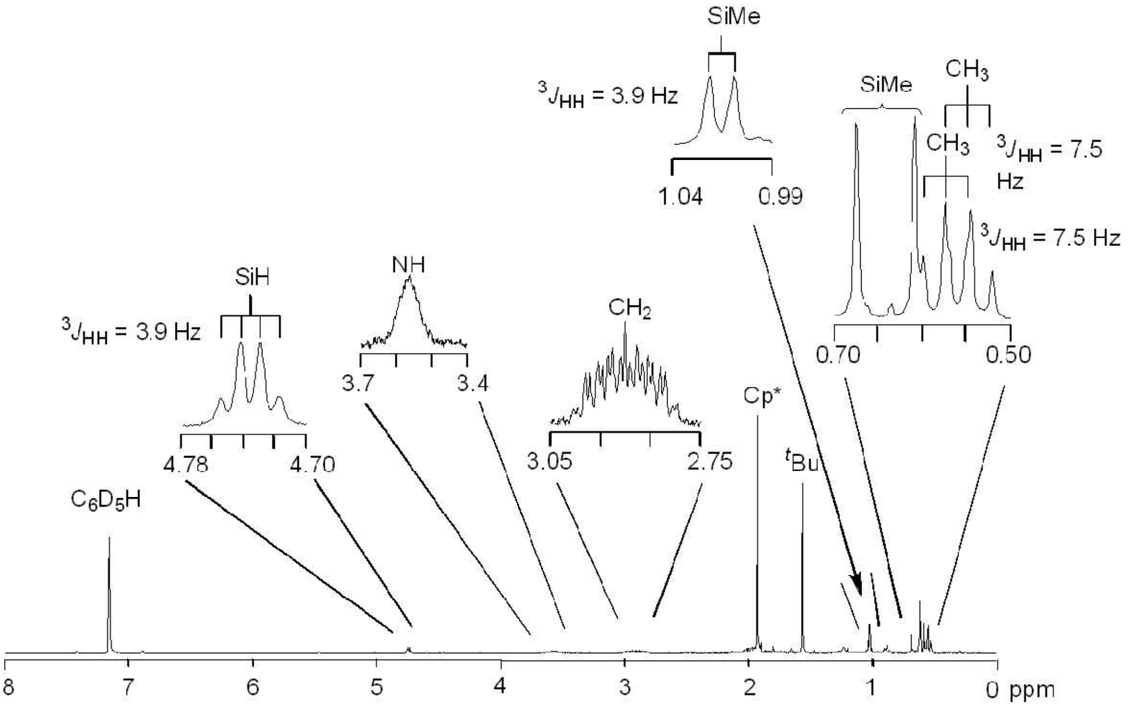


Fig. S22 ^{1}H NMR spectrum of $Cp^{*}W(CO)_2(=SiMe_2{\leftarrow}NHEt_2)SiH(^{t}Bu)Me$ (**9**) (300 MHz, C_6D_6).

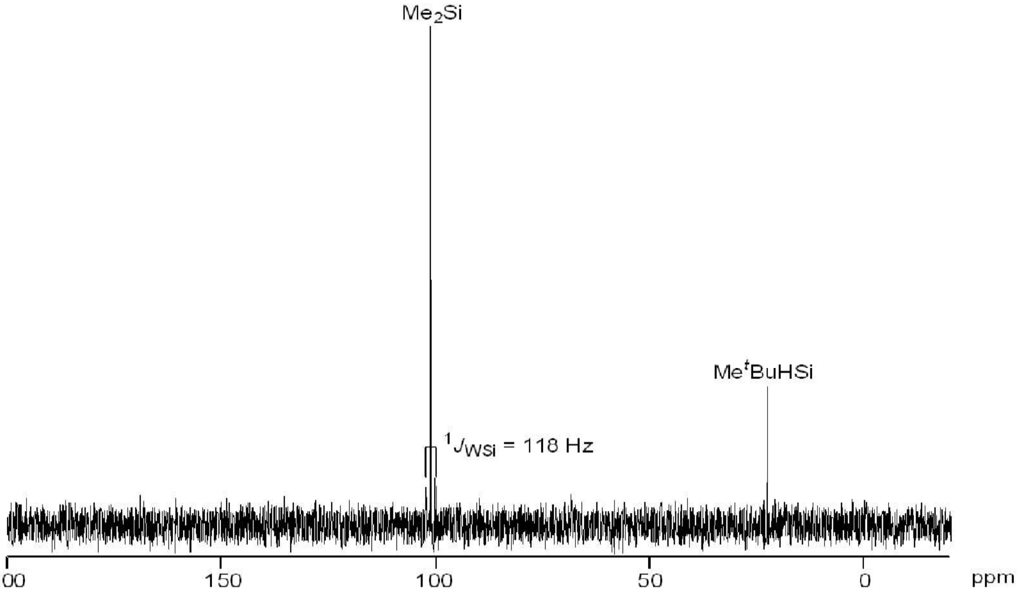


Fig. S23 ^{29}Si{^{1}H} NMR spectrum of Cp*W(CO)$_2$(=SiMe$_2$←NHEt$_2$)SiH(^{t}Bu)Me (**9**) (59.6 MHz, C_6D_6).

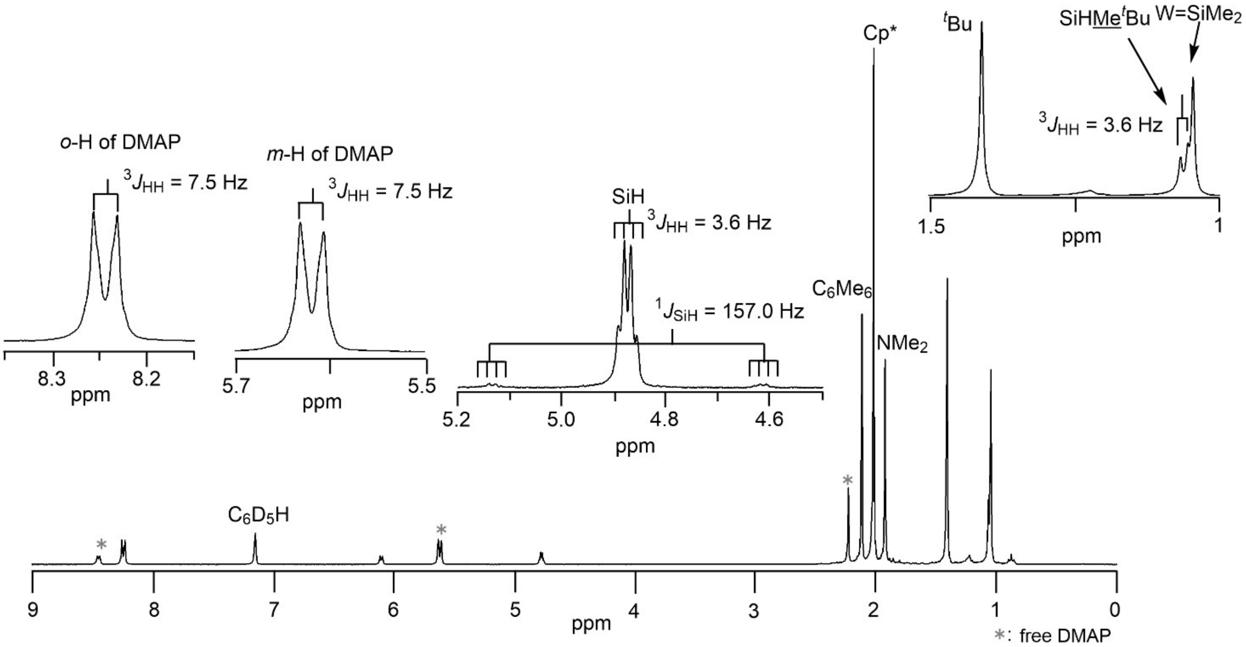


Fig. S24 ^{1}H NMR spectrum of Cp*W(CO)$_2$(=Si Me$_2$←dmap(^{t}Bu)Me (**10**) (300 MHz, C_6D_6).

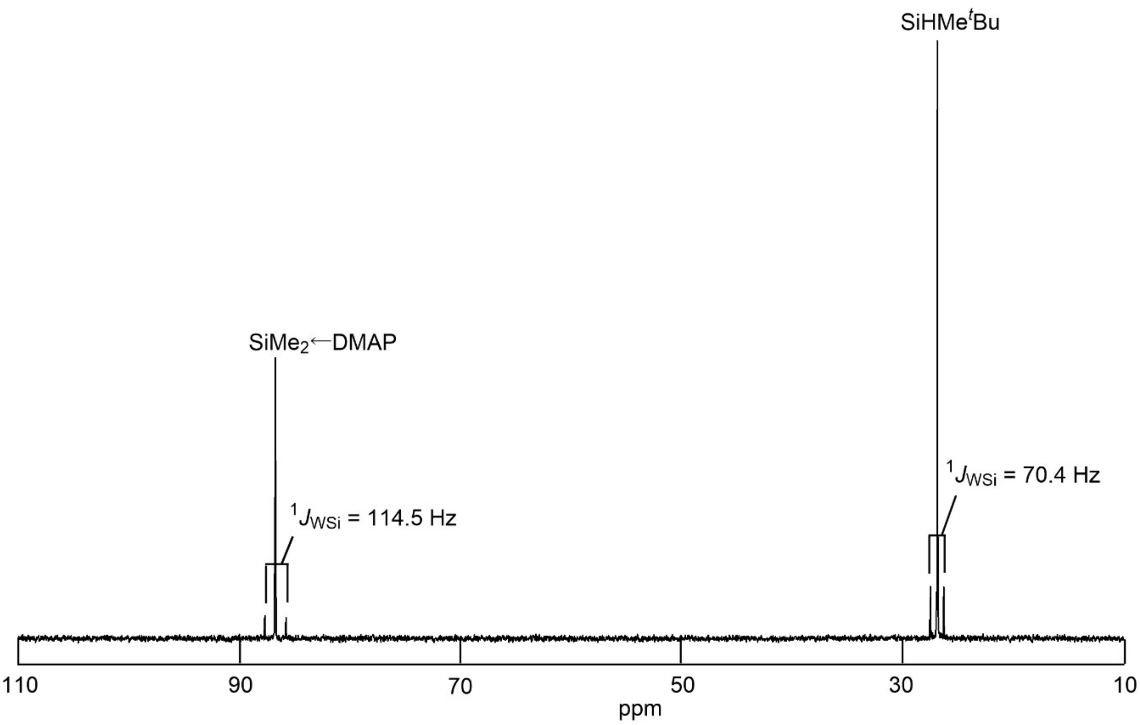


Fig. S25 ^{29}Si{^{1}H} NMR spectrum of Cp*W(CO)$_2$(=SiMe$_2$←dmap)SiH(^{t}Bu)Me (**10**) (59.6 MHz, C_6D_6).

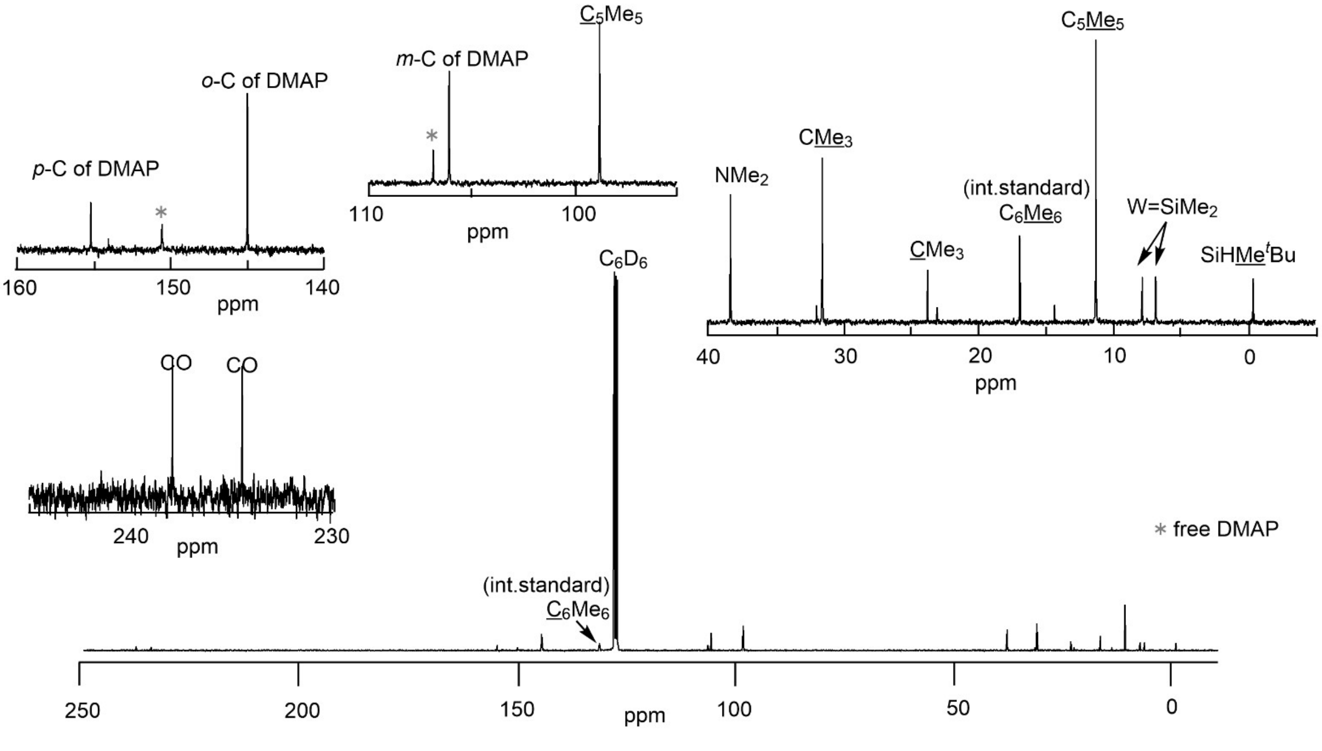


Fig. S26 ^{13}C{^{1}H} NMR spectrum of Cp*W(CO)$_2$(=Si Me$_2$←dmap(^{t}Bu)Me (**10**) (75.5 MHz, C_6D_6).

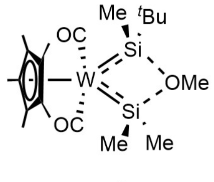
3. X-ray crystal structure analysis

Single crystals suitable for X-ray diffraction measurement of **A**, **5**, **6**, **8** and **10** were coated with a layer of paraffin oil and were mounted on a nylon loop, and held at a position under a cold stream of N_2 on the diffractometer. Diffraction measurements were made on a RIGAKU RAXIS-RAPID Imaging Plate Diffractometer with graphite monochromated Mo-Kα radiation about 150 K. Numerical absorption collection were made using the program NUMBAS.[S2] The structures were solved by Patterson and Fourier transform methods (SHELXS-97)[S3a] and refined by full matrix least-square technique on F^2 with SHELXL-97,[S3b] using Yadokari-XG 2009 software[S4] or Olex2[S5] software as a graphical user interface. All other non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Selected crystallographic data are summarized in Tables S1. Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre: CCDC 2403405 (**A**), CCDC 2403406 (**5**), CCDC 2403407 (**6**), CCDC 2403408 (**8**), CCDC 2403409 (**10**). Crystallographic data are available as a CIF file.

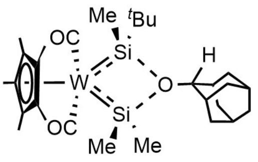
Table S1 Selected Crystallographic Data for Cp*W(CO)$_2${Me$_2$Si···OMe···Si(^{t}Bu)Me} (A), Cp*W(CO)$_2${Me$_2$Si···O(CHC$_9$H$_{14}$)···Si(^{t}Bu)Me} (5), Cp*W(CO)$_2${Me$_2$Si···O[CHEt(C=CH)]···Si(^{t}Bu)Me} (6), Cp*W(CO)$_2${Me$_2$Si···O[CHMe(C≡CH)]···Si(^{t}Bu)Me} (8), Cp*W(CO)$_2$(=SiMe$_2$←dmap)SiH(^{t}Bu)Me (10)

Compound	**A**	**5**	**6**	**8**	**10**
formula	$(C_{20}H_{30}O_3Si_2W)/0.5(C_{12}H_{18})$	$C_{29}H_{48}O_3Si_2W$	$C_{24}H_{41}O_3Si_2W$	$C_{30}H_{46}O_3Si_2W$	$C_{26}H_{44}N_2O_2SiW/C_7H_8$
formula weight	639.60	684.70	617.60	694.70	748.80
crystal system	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
crystal size/mm^3	0.12×0.08 ×0.06	0.20×0.19×0.16	0.44×0.36×0.28	0.23×0.20×0.19	
space group	$P{-}1$	$Pna2_1$	$C2/c$	$P2_1/n$	$Pnma$
a/Å	8.6680(8)	17.1114(6)	26.4496(13)	13.6063(3)	14.2410(2)
b/Å	9.9938(5)	10.5152(5)	15.6024(11)	16.0363(4)	33.3455(6)
c/Å	17.0474(15)	16.3940(5)	15.8880(9)	14.7843(3)	14.4026(4)
α/°	94.187(3)	90	90	90	90
β/°	100.584(4)	90	125.3613(12)	104.0881(6)	90
γ/°	102.745(3)	90	90	90	90
V/Å^3	1405.90(19)	2949.8(2)	5347.0(6)	3128.83(12)	6839.4(2)
Z	2	4	8	4	8
Abs. coeff. /mm^{-1}	4.217	4.025	4.431	3.796	3.478
reflns collected	12194	24271	24861	28824	48122
indep. reflns (R_{int})	6048 (0.0976)	6662 (0.0567)	6123 (0.0598)	6992 (0.0603)	7899 (0.0606)
refin. parameters	304	327	287	308	395
$R1$, $wR2$ (all data)	0.0945, 0.1598	0.0448, 0.0675	0.0304, 0.0855	0.0464,0.1021	0.0736, 0.1634
$R1$, $wR2$ [$I > 2\ \sigma(I)$]	0.0714, 0.1519	0.0370, 0.0658	0.0271, 0.0785	0.0387,0.0990	0.0666, 0.1606
GOF	1.205	1.177	1.229	1.242	1.358

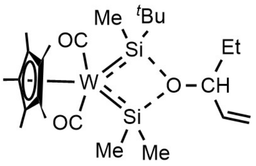
Table S2 Selected Bond Lengths and Angles for A, 5, 6, 8 and 10



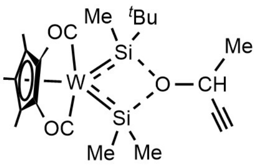
A



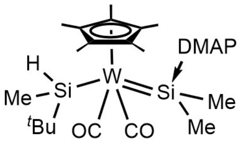
5



6

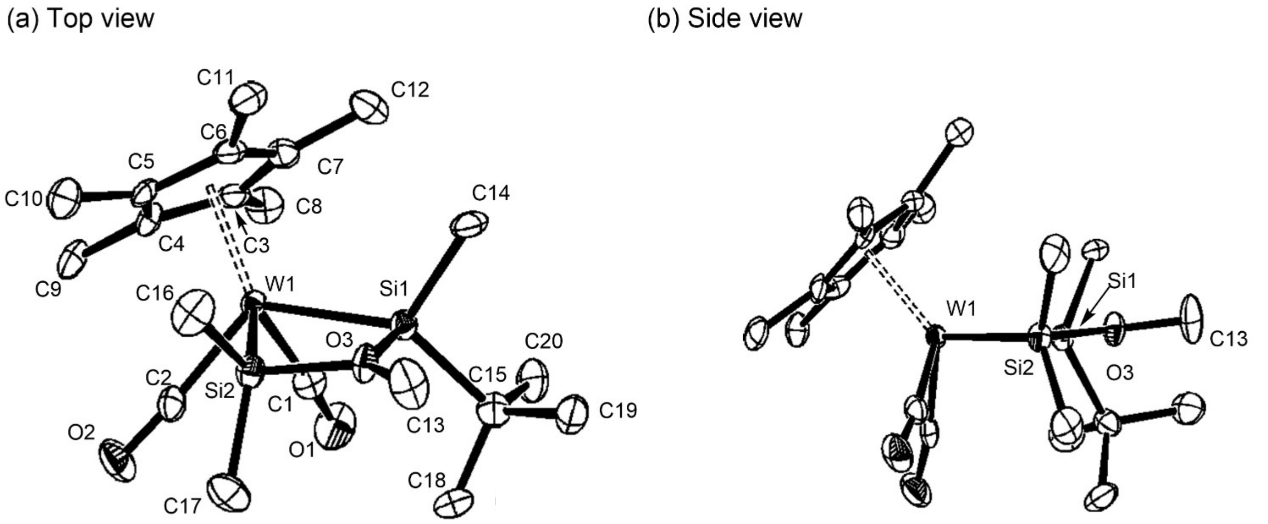


8



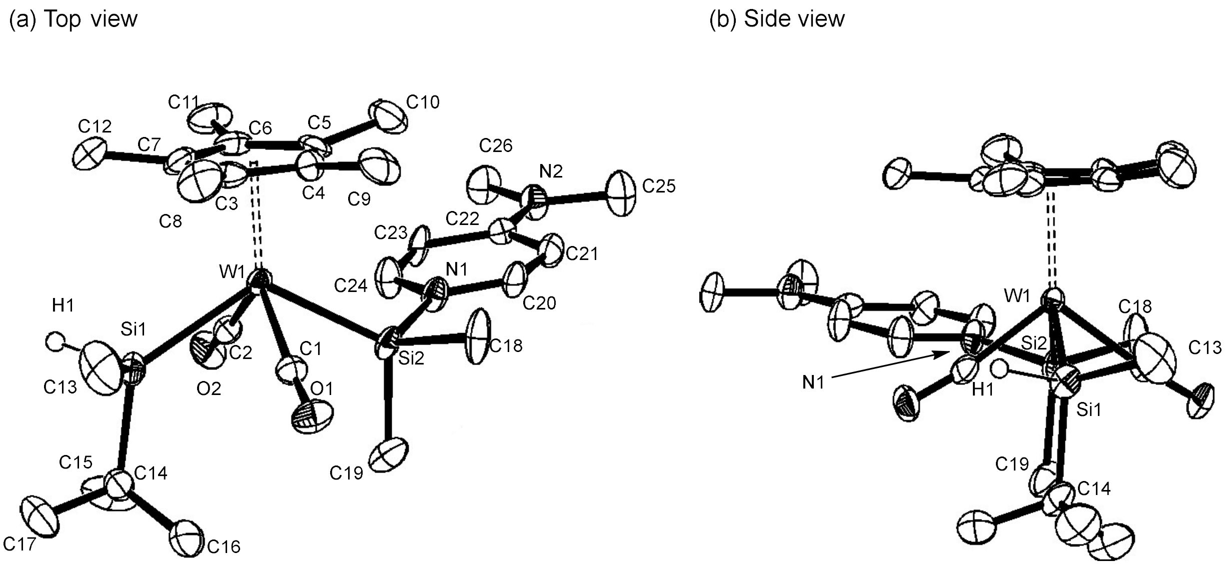
10

Compound	**A**	**5**	**6**	**8**	**10**
Bond length/ Å					
W–Si1(^{t}Bu)	2.537(3)	2.535(3)	2.5188(9)	2.5236(13)	2.586(2)
W–Si2	2.509(3)	2.500(3)	2.5037(9)	2.5049(13)	2.485(2)
Si1–μO	1.795(8)	1.871(8)	1.828(3)	1.829(4)	–
Si2–μO	1.782(7)	1.817(8)	1.813(3)	1.818(4)	–
Si2–N	–	–	–	–	1.908(7)
Bond Angles/°					
W–Si1–μO	98.9(3)	98.8(3)	99.02(9)	99.56(12)	–
W–Si2–μO	100.3(3)	101.6(3)	99.99(9)	100.54(12)	–
Si1–W–Si2	63.82(10)	63.50(5)	64.07(3)	63.90(4)	123.34(8)
Si1–μO–Si2	96.4(4)	92,0(4)	94.02(12)	93.72(16)	–
Dihedral Angle/°					
W–Si1– Si2–μO	172.4(4)	160.26(19)	163.15(13)	165.07(18)	–


(a) Top view

(b) Side view

Fig. S27 X-ray crystal structure of Cp*W(CO)$_2${Me$_2$Si···OMe···Si(^{t}Bu)Me} (**A**).


(a) Top view

(b) Side view

Fig. S28 X-ray crystal structure of Cp*W(CO)$_2$(=SiMe$_2$←dmap)SiH(^{t}Bu)Me (**10**). (a) Top view, (b) Side view.

5. References

S1 H. Hashimoto, Y. Odagiri, Y. Yamada, N. Takagi, S. Sakaki and H. Tobita, *J. Am. Chem. Soc.*2015, **137**, 158.

S2 T. Higashi, *NUMBUS*, Rigaku Corporation, Tokyo, Japan.

S3 (a) G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Determination; University of Göttingen; Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Determination; University of Göttingen; Göttingen, Germany, 1997.

S4 K. Wakita, *Yadokari-XG, Software for Crystal Structure Analyses,* (2001); C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses*, *J. Cryst. Soc. Jpn.,* 2009, **51**, 218.

S5 O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.