

**Reactions of  $d^0$  tungsten alkylidyne complexes with O<sub>2</sub> or H<sub>2</sub>O. Formation of an oxo siloxy complex through unusual silyl migrations**

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**Supplementary Information**

## 1. Experimental section

All manipulations were performed under a dry nitrogen or argon atmosphere with the use of either a glovebox or standard Schlenk techniques. Solvents were purified by distillation from potassium benzophenone ketyl. NMR solvents were dried and stored over 5 Å molecular sieves. NMR spectra were recorded on Bruker AC-250 and AMX-400 Fourier transform spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to solvents (residual protons in the  $^1\text{H}$  spectra).  $^{29}\text{Si}$  chemical shifts were referenced to  $\text{SiMe}_4$ . IR spectra were recorded on a Varian 4100 FT-IR (Excalibur series) spectrometer. Elemental analyses were carried out by E+R Microanalytical Laboratory, Inc., Parsippany, New Jersey.  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**)<sup>S1</sup> was prepared from  $\text{WCl}_3(\text{OMe})_3$  and  $\text{ClMgCH}_2\text{SiMe}_3$  using a procedure similar to that for the preparation of  $(\text{Me}_3\text{CCH}_2)_3\text{W}\equiv\text{CCMe}_3$  (**7**).<sup>S2</sup>  $\text{O}=\text{PMe}_3$  (Organometallics, Inc.) and  $\text{O}_2$  (99.6%, National Welders Supply Co., now Airgas Inc.) were used as received.  $^{13}\text{CO}_2$  (99%  $^{13}\text{C}$ , <1%  $^{18}\text{O}$ ) and  $^{13}\text{CH}_4$  (99%  $^{13}\text{C}$ ) were purchased from Cambridge Isotope Laboratories, Inc. and used as received.

Before each experiment, Schlenk flasks and NMR tubes were dried, under better than 0.01 torr vacuum, by either a Bunsen burner at  $>500\text{ }^\circ\text{C}$  or a HEJET™ Model HJ-500X heat gun (Pamran Co., Inc.) at  $>400\text{ }^\circ\text{C}$ . Earlier studies showed that, under the vacuum, dehydration (the removal of physically adsorbed water) and dehydroxylation (the removal of silanol groups from the silica surface) occurred at  $<100\text{ }^\circ\text{C}$  and  $>200\text{ }^\circ\text{C}$ , respectively.<sup>11</sup>

The reaction of  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  with  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**) was conducted by one of the following three methods:

(a) Both  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ) and  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**) were each dissolved in THF (or  $\text{THF-}d_8$ ). The  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$ ) in THF ( $\text{THF-}d_8$ ) was then added to the solution of **2** in THF ( $\text{THF-}d_8$ ) at a pre-set temperature.

(b) **2** was dissolved in THF (THF-*d*<sub>8</sub>), and added *slowly* pure H<sub>2</sub>O (or D<sub>2</sub>O). This method was usually done with a small amount of water (ca. 5 μL). The added water was less homogeneous than that in (a) above, which may reduce the yields of the products.

(3) H<sub>2</sub>O in THF was added to powders of **2** that were vigorously stirred at -25 °C or 23 °C. In our hands, this method reduced the formation of the trimer **4**, enhancing the yield of **3**.

**Preparation of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>(Me<sub>3</sub>SiC≡)W←O=PMe<sub>3</sub> (**1**).**

Solids of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>W≡CSiMe<sub>3</sub> (**2**, 200 mg, 0.377 mmol) and O=PMe<sub>3</sub> (34.7 mg, 0.377 mmol) were placed in a Schlenk flask, and they were then dissolved in Et<sub>2</sub>O (ca. 15 mL). The mixture was stirred until all O=PMe<sub>3</sub> was dissolved in ca. 10 min. Cooling the solution at -30 °C overnight gave crystals of **1** (136 mg, 0.218 mmol, 57.9% yield). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 400.04 MHz, 23 °C) δ 1.30 (-CH<sub>2</sub>SiMe<sub>3</sub>), 0.842 (d, O=PMe<sub>3</sub>, <sup>2</sup>J<sub>P-H</sub> = 12.7 Hz), 0.533 (≡CSiMe<sub>3</sub>), 0.303 (-CH<sub>2</sub>SiMe<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 100.6 MHz, 23 °C) δ 327.39 (≡CSiMe<sub>3</sub>), 69.56 (CH<sub>2</sub>SiMe<sub>3</sub>), 17.38 (d, O=PMe<sub>3</sub>, <sup>2</sup>J<sub>P-C</sub> = 70.4 Hz), 3.26 (-CH<sub>2</sub>SiMe<sub>3</sub>), 2.19 (≡CSiMe<sub>3</sub>). <sup>31</sup>P NMR (benzene-*d*<sub>6</sub>, H<sub>3</sub>PO<sub>4</sub> internal standard, 161.94 MHz, 23 °C) δ 41.95. Anal. Calcd. C, 36.64, H, 8.25. Found C, 36.45, H, 8.06.

**Preparation of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>(Me<sub>3</sub>SiC≡)W←O=W(OSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> (**12**) from the reaction of **1** with O<sub>2</sub>.**

(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>(Me<sub>3</sub>SiC≡)W←O=PMe<sub>3</sub> (**1**, 86.4 mg, 0.139 mmol) was dissolved in toluene-*d*<sub>8</sub> (ca. 0.5 mL) in a J. Young NMR tube. Three aliquots of 1000 mmHg (0.325 mmol) O<sub>2</sub> were added over a period of 4 days, and product formation was monitored by <sup>1</sup>H NMR spectroscopy. When the reaction was completed, the solution was transferred to a Schlenk flask, and all

volatiles were removed *in vacuo*. The remaining solid was dissolved in pentane and filtered into a solution of  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**) in pentane. Cooling the solution to  $-30\text{ }^\circ\text{C}$  gave crystals of  $(\text{Me}_3\text{SiCH}_2)_3(\text{Me}_3\text{SiC}\equiv)\text{W}\leftarrow\text{O}=\text{W}(\text{OSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3$  (**12**, 25.8 mg, 0.0238 mmol, 17.1%).  $^1\text{H}$  NMR (toluene- $d_8$ , 400.04 MHz,  $23\text{ }^\circ\text{C}$ )  $\delta$  1.640 (6H,  $\text{CH}_2\text{-W=O}$ ;  $^2J_{\text{W-H}} = 10.8$  Hz), 0.697 (6H,  $\text{CH}_2\text{-W}\equiv\text{C}$ ;  $^2J_{\text{W-H}} = 9.8$  Hz), 0.403 (9H,  $\text{Me}_3\text{SiC}\equiv$ ), 0.283 (9H,  $\text{Me}_3\text{Si-O}$ ), 0.241 (27H,  $\text{Me}_3\text{SiCH}_2\text{-W=O}$ ), 0.160 (27H,  $\text{Me}_3\text{SiCH}_2\text{-W}\equiv\text{C}$ ).  $^{13}\text{C}$  NMR (toluene- $d_8$ , 100.6 MHz,  $23\text{ }^\circ\text{C}$ )  $\delta$  343.49 ( $\text{Me}_3\text{SiC}\equiv$ ), 75.77 ( $\text{CH}_2\text{W}\equiv$ ), 62.90 ( $\text{CH}_2\text{W=O}$ ), 2.39 ( $\text{Me}_3\text{SiCH}_2\text{W}\equiv\text{C}$ ), 1.58 ( $\text{Me}_3\text{SiCH}_2\text{W=O}$ ), 2.07 ( $\text{Me}_3\text{SiC}\equiv$ ), 1.99 (O-SiMe<sub>3</sub>).  $^{29}\text{Si}$  NMR (toluene- $d_8$ , 79.49 MHz,  $23\text{ }^\circ\text{C}$ )  $\delta$  10.74 ( $\text{Me}_3\text{Si-O}$ ), -1.50 ( $\text{Me}_3\text{SiCH}_2\text{-W}\equiv\text{C}$ ), -2.97 ( $\text{Me}_3\text{SiCH}_2\text{-W=O}$ ), -19.76 ( $\text{Me}_3\text{SiC}\equiv$ ). Anal. Calcd. for  $\text{C}_{31}\text{H}_{84}\text{O}_2\text{Si}_8\text{W}_2$ : C, 34.43, H, 7.83, Si, 20.78, P, 0.00. Found C, 34.42, H, 7.86, Si, 21.03, P, <0.02. The P analysis was conducted to rule out that the -OSiMe<sub>3</sub> group observed in the X-ray crystal structure of **12** was OPMe<sub>3</sub>.

### ***Quantitative determination of CO<sub>2</sub> yielded from the reaction of***

#### ***(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>(Me<sub>3</sub>SiC≡)W←O=PMe<sub>3</sub> (1) with O<sub>2</sub>.***

In a J. Young NMR tube,  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**, 66 mg, 0.12 mmol),  $\text{O=PMe}_3$  (11.2 mg, 0.12 mmol), and 4,4'-dimethylbiphenyl (5.9 mg, 0.032 mmol, internal standard) were dissolved in ca. 0.5 mL of toluene- $d_8$ .  $^1\text{H}$  NMR spectrum of the solution revealed the nearly quantitative formation of  $(\text{Me}_3\text{SiCH}_2)_3(\text{Me}_3\text{SiC}\equiv)\text{W}\leftarrow\text{O=PMe}_3$  (**1**). The J. Young NMR tube (headspace = 2.8 mL) was then attached to a gas manifold, and the solution was frozen in liquid nitrogen, while most of the J. Young tube was immersed in liquid nitrogen. The  $\text{N}_2$  gas in the J. Young tube was removed *in vacuo*. Approximately 1.3 mmol of  $\text{O}_2$  (0.5 atm) was introduced into a gas manifold (65 mL). The valve on the J. Young NMR tube was opened for approximately 5

s to introduce O<sub>2</sub> gas into the tube. Since the boiling point of O<sub>2</sub> (90.2 K) is high than that (77.4 K) of N<sub>2</sub>, O<sub>2</sub> was condensed into the NMR tube. An HRMS analysis of the production mixture *after* the reaction showed the presence of excess O<sub>2</sub>.

The solution was warmed to room temperature and shaken. <sup>1</sup>H NMR spectrum revealed the formation of O=W(OSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> (**3**, 0.011 mmol, 9.4% yield based on **1**). On a calibrated vacuum line with a volume of 170.7 mL, <sup>13</sup>CO<sub>2</sub> (0.0145 atm, 0.101 mmol) at 23 °C was introduced. The J. Young NMR tube containing the product, attached to the line previously, was opened and allowed to mix with the <sup>13</sup>CO<sub>2</sub> gas in the manifold for approximately 15 min. The NMR tube was frozen by liquid nitrogen to condense the CO<sub>2</sub> gas (<sup>13</sup>CO<sub>2</sub> and <sup>12</sup>CO<sub>2</sub>) and then thawed. The tube was then frozen by liquid nitrogen, and was thawed. This process was repeated for a total of 3 times to allow a good mixing of <sup>13</sup>CO<sub>2</sub> and <sup>12</sup>CO<sub>2</sub>. The tube was frozen again and the valve on the J. Young NMR tube was closed. After the tube was thawed, an HRMS analysis gave <sup>13</sup>CO<sub>2</sub> : <sup>12</sup>CO<sub>2</sub> = 100.00 : 10.14. Thus the yield of CO<sub>2</sub> from the reaction was 0.010 mmol, or ca. 91% of O=W(OSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> (**3**) from the reaction.

***Reaction between powders of 2 and H<sub>2</sub>O at -25 °C to give 3 and then 12.***

Powders of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>W≡CSiMe<sub>3</sub> (**2**, 0.1420 g, 0.2676 mmol) at -25 °C were added a magnetic stir bar. The stir bar in the powders was stirred vigorously, and the powders were slowly added 2 equiv of H<sub>2</sub>O (0.54 mmol, 9.6 μL) in THF (10 mL) *via* syringe. Immediate colour change from yellow to reddish-orange was observed upon addition of the water solution. Stirring continued for 15 h while the solution was gradually warmed to 23 °C. All volatiles were removed *in vacuo* to give **3** as a light brown oil. **3** was found to be unstable. <sup>1</sup>H NMR of **3** (benzene-*d*<sub>6</sub>, 399.79 MHz, 23 °C) δ 1.66 (s, 6H, CH<sub>2</sub>SiMe<sub>3</sub>), 0.27 (s, 9H, OSiMe<sub>3</sub>), 0.24 (s, 27H,

$\text{CH}_2\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (benzene- $d_6$ , 100.54 MHz, 23 °C)  $\delta$  62.88 ( $\text{CH}_2\text{SiMe}_3$ ), 1.99 ( $\text{OSiMe}_3$ ), 1.57 ( $\text{CH}_2\text{SiMe}_3$ ).  $^{29}\text{Si}$  NMR (benzene- $d_6$ , 79.43 MHz, 23 °C)  $\delta$  8.89 ( $\text{OSiMe}_3$ ), -3.41 ( $\text{CH}_2\text{SiMe}_3$ ).

In the preparation of **12** from **3**, **3** prepared above as an oil was added powders of  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**, 0.1420 g, 0.2676 mmol) in THF. THF (5 mL) was added to the mixture and the solution was stirred at 23 °C for 5 h. Volatiles were then removed *in vacuo* to give **12** as a crude product. Recrystallization in  $\text{Et}_2\text{O}$  at -32 °C gave crystals of **12** (88.4 mg, 0.0817 mmol, 30.5% yield).

***Reaction between 2 in THF and H<sub>2</sub>O at -78 °C to give 3 and then 12.***

$(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**, 235 mg, 0.443 mmol) in 5 mL of THF -78 °C was stirred vigorously.  $\text{H}_2\text{O}$  (16  $\mu\text{L}$ ) was added to the solution directly at -78 °C. No reaction was observed at this temperature. The temperature was slowly raised. At -40 °C, the solution became red. The solution was slowly warmed to room temperature over 12 h. The solution was stirred for additional 12 h. Then 1 equiv of **2** (235 mg, 0.443 mmol) was added to the reaction mixture and stirring for 6 h. Removing volatiles *in vacuo*, followed by crystallization with a small amount of  $\text{Et}_2\text{O}$  at -32 °C, yielded crystals of **12** (101.8 mg, 0.0941 mmol, 21.3%).

***Reaction between 2 in THF and H<sub>2</sub>O at 23 °C to give the trimer  $[(\mu\text{-O})\text{W}(\text{CH}_2\text{SiMe}_3)_2(=\text{O})(\text{THF})]_3$  (4).***

$(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**, 508.5 mg, 0.958 mmol) was dissolved in 10 mL of THF at 23 °C with vigorous stirring in a Schlenk flask. When 2 equiv of  $\text{H}_2\text{O}$  (34.5  $\mu\text{L}$ ) was added to the solution, the solution turned to light brown. The mixture was stirred overnight, and volatiles

were then removed *in vacuo*. The solid was then dissolved in 1 mL of hexane. Crystallisation at  $-32\text{ }^{\circ}\text{C}$  yielded white crystals of **4** (113.5 mg, 0.0818 mmol, 25.6% yield) overnight.  $^1\text{H}$  NMR (benzene- $d_6$ , 250.1 MHz)  $\delta$  3.57 (t, 2H, THF), 1.85 (broad, 2H,  $\text{CH}_2\text{SiMe}_3$ ), 1.40 (m, 2H, THF), 0.35 (s, 9H,  $\text{CH}_2\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR (benzene- $d_6$ , 62.9 MHz)  $\delta$  70.0 ( $\text{CH}_2\text{SiMe}_3$ ), 68.0 (THF), 25.8 (THF), 1.73 ( $\text{CH}_2\text{SiMe}_3$ ). **4** was found unstable, decomposing under nitrogen in less than 2 h into a green solid.

***Quantitative determination of  $\text{CH}_4$  yielded from the reaction of  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**) with  $\text{H}_2\text{O}$ .***

A  $\text{H}_2\text{O}$ -THF- $d_8$  solution was made by adding 0.0143 mL of  $\text{H}_2\text{O}$  to 1.000 mL of THF- $d_8$ . In a J. Young NMR tube, powders of  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**, 62.4 mg, 0.118 mmol) and bibenzyl (13.2 mg) as an internal standard were cooled to  $-25\text{ }^{\circ}\text{C}$  and added the  $\text{H}_2\text{O}$ -THF- $d_8$  solution (0.300 mL). The tube was immediately sealed.  $^1\text{H}$  NMR spectrum of the solution revealed the formation of  $\text{O}=\text{W}(\text{OSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3$  (**3**, 0.078 mmol, 66% yield based on **2**). The J. Young NMR tube (headspace = 2.8 mL) was then attached to a gas manifold, and the solution was frozen in liquid nitrogen, while most of the NMR tube was immersed in liquid nitrogen. The  $\text{N}_2$  gas in the NMR tube was removed *in vacuo*. On a calibrated vacuum line with a volume of 129.2 mL,  $^{13}\text{CH}_4$  (0.0153 atm, 0.0814 mmol) at  $23\text{ }^{\circ}\text{C}$  was introduced. The J. Young NMR tube was opened and allowed to mix with the  $^{13}\text{CH}_4$  gas in the manifold for approximately 15 min. The J. Young tube was frozen by liquid nitrogen to condense the  $\text{CH}_4$  gas ( $^{13}\text{CH}_4$  and  $^{12}\text{CH}_4$ ) and then thawed. The tube was then frozen again by liquid nitrogen, and was thawed. This process was repeated for a total of three times to allow a good mixing of  $^{13}\text{CH}_4$  and  $^{12}\text{CH}_4$ . The tube was frozen again and the NMR valve was closed. After the tube was thawed, an HRMS

analysis gave  $^{13}\text{CH}_4 : ^{12}\text{CH}_4 = 100 : 90$ . Thus the yield of  $\text{CH}_4$  from the reaction was 0.073 mmol (0.62% yield based on **2**), and the molar ratio of **3** :  $\text{CH}_4 = 66\% : 62\% \approx 1 : 1$ .

**Reaction of  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**) with  $\text{D}_2\text{O}$ .**

**2** (30 mg, 0.057 mmol) dissolved in THF- $d_8$  (ca. 0.5 mL) at room temperature was transferred to a J. Young NMR tube.  $\text{D}_2\text{O}$  (ca. 5 mg, 0.28 mmol) was added *via* syringe in a glove box, and the NMR tube was sealed immediately. An instant color change from yellow to reddish-orange was observed upon addition of  $\text{D}_2\text{O}$ . Studies with high-resolution mass spectrometry (HRMS) were conducted shortly after  $\text{D}_2\text{O}$  was added.  $^1\text{H}$  NMR spectra of the solution confirmed the formation of  $\text{O}=\text{W}(\text{OSiMe}_3)(\text{CH}_2\text{-}d_n\text{SiMe}_3)_3$  (**3- $d_n$** ) in solution.

In a separate study, **2** (30 mg, 0.057 mmol) dissolved in THF- $d_8$  (ca. 0.5 mL) at room temperature in a J. Young NMR tube was added a  $\text{D}_2\text{O}/\text{THF-}d_8$  solution (126 mg of a  $\text{D}_2\text{O}/\text{THF-}d_8$  mixture, 1.2 mg of  $\text{D}_2\text{O}$ , 0.060 mmol  $\text{D}_2\text{O}$ ) was added *via* syringe in a glove box, and the NMR tube was sealed immediately. Analysis of the gaseous products by HRMS was conducted shortly after  $\text{D}_2\text{O}$  was added, and it gave the following ratios:  $\text{CH}_4 : \text{CH}_3\text{D} : \text{CH}_2\text{D}_2 : \text{CHD}_3 : \text{CD}_4 = 0 : 22 : 100 : 30 : 34(\pm 5)\%$  (Table S2 and Fig. S2). Higher percentages of  $\text{CH}_3\text{D}$  and  $\text{CHD}_3$  were observed. The exchange of HO-Si groups on the NMR tube surface with  $\text{D}_2\text{O}^{11}$  is believed to lead to the formation of HOD and  $\text{CH}_3\text{D}$ .

**$^2\text{D}\{^1\text{H}\}$  NMR study of the reaction between  $(\text{Me}_3\text{SiCH}_2)_3\text{W}\equiv\text{CSiMe}_3$  (**2**) and  $\text{D}_2\text{O}$ .**

**2** (50 mg, 0.094 mmol) dissolved in THF (ca. 0.5 mL) in a J. Young NMR tube at room temperature was added  $\text{D}_2\text{O}$  (ca. 5  $\mu\text{L}$ , 0.28 mmol) *via* syringe in a glove box.  $^2\text{D}\{^1\text{H}\}$  NMR at  $-10^\circ\text{C}$  (Fig. S1) showed a broad peak at 1.55 ppm attributable to the  $\text{CHDSiMe}_3$  and  $\text{CD}_2\text{SiMe}_3$



ligands.

***The analysis of volatile products by mass spectrometry (MS) and high-resolution mass spectrometry (HRMS).***

Electron-ionization mass spectrometry (EI-MS, 70 eV) was conducted on a VG ZAB-EQ double focusing mass spectrometer for the analysis of methane isotopologues. In the HRMS studies, the instrument was tuned to a resolution ( $M/\Delta M \approx 12000$ ) sufficient to discriminate between the various isotopologues of  $\text{CH}_x\text{D}_y$  ( $x + y = 4$ ) and the EI-fragmentation products produced from them (Tables S1-S2). The sample gas was introduced through a needle valve to produce a registered source pressure of ca.  $<10^{-6}$  mBar. Vapour of 90%  $\text{H}_2^{18}\text{O}$ -10%  $\text{H}_2^{16}\text{O}$  in one experiment (Table S1) and  $\text{H}_2^{16}\text{O}$  in another (Table S2) was used as the mass-calibration standard, thus allowing assignment of peaks to the  $\text{CH}_x\text{D}_y$  isotopologues as shown in Tables S1-S2.

***X-ray crystal structure determination for 1, 4 and 12.***

The X-ray crystal structures of **1**, **4** and **12** were determined on a Bruker AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector and a graphite-monochromated Mo source ( $K_\alpha$  radiation, 0.71073 Å) and fitted with an upgraded Nicolet LT-2 low temperature device. Suitable crystals were coated with paratone oil (Exxon) and mounted either on a glass fiber for **1** and **12** under a stream of nitrogen at 173(2) K or on a fiber loop for **4** under a stream of nitrogen at 100(2) K. The structures were solved by direct methods. All non-hydrogen atoms were anisotropically refined. Empirical absorption correction was performed with SADABS.<sup>S3a</sup> Global refinements for the unit cells and data reductions were performed under the Saint

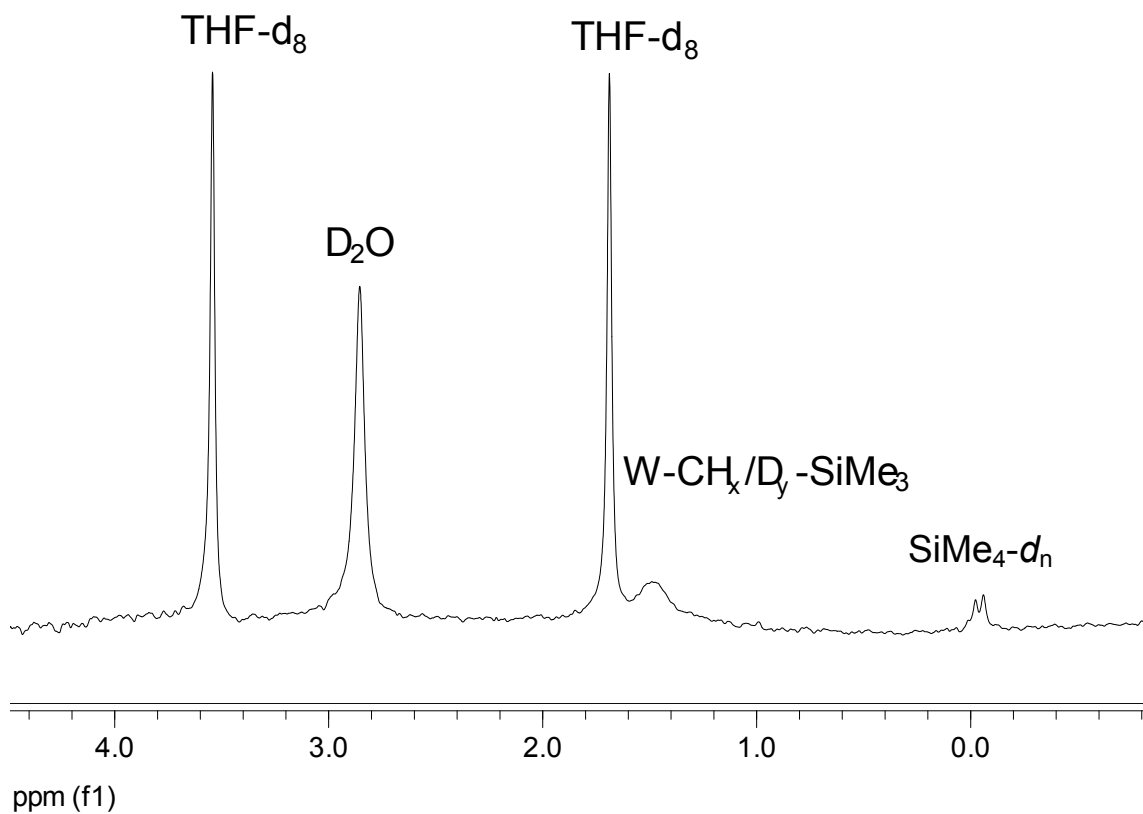
program (Version 6.02). All calculations were performed using SHELXTL (Version 5.1) proprietary software package.<sup>S3b</sup>

## 2. Additional Results and Discussion

<sup>18</sup>O-labeled [<sup>18</sup>O]-**3** was prepared from the reaction of **2** with H<sub>2</sub><sup>18</sup>O. IR spectra of [<sup>16</sup>O] and [<sup>18</sup>O]-**3** reveal that the  $\nu(\text{W}=\text{O})$  fundamental is shifted by 45 cm<sup>-1</sup> from 995 in [<sup>16</sup>O]-**3** to 950 cm<sup>-1</sup> in [<sup>18</sup>O]-**3**. The  $\nu(\text{Si}-\text{O}-\text{W})$  at 901 cm<sup>-1</sup> in [<sup>16</sup>O]-**3** is shifted by 29 cm<sup>-1</sup> to 872 cm<sup>-1</sup> in [<sup>18</sup>O]-**3**. Both isotopic shifts are similar to those in **8**<sup>2f</sup> and silica-supported  $\equiv\text{Si}-\text{O}-\text{V}(=\text{O})\text{Cl}_2$ .<sup>S4</sup>

## References

- S1. R. A. Andersen, M. H. Chisholm, J. F. Gibson, W. W. Reichert, I. P. Rothwell, G. Wilkinson, *Inorg. Chem.*, 1981, **20**, 3934.
- S2. R. R. Schrock, J. Sancho, S. F. Pederson, *Inorg. Synth.* 1989, **26**, 45.
- S3. (a) G. M. Sheldrick, *SADABS, A Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen, Göttingen, Germany, 1996. (b) G. M. Sheldrick, *SHELXL-97, A Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.
- S4. G. L. Rice and S. L. Scott, *J. Mole. Catal. A. Chem.* 1997, **125**, 73.



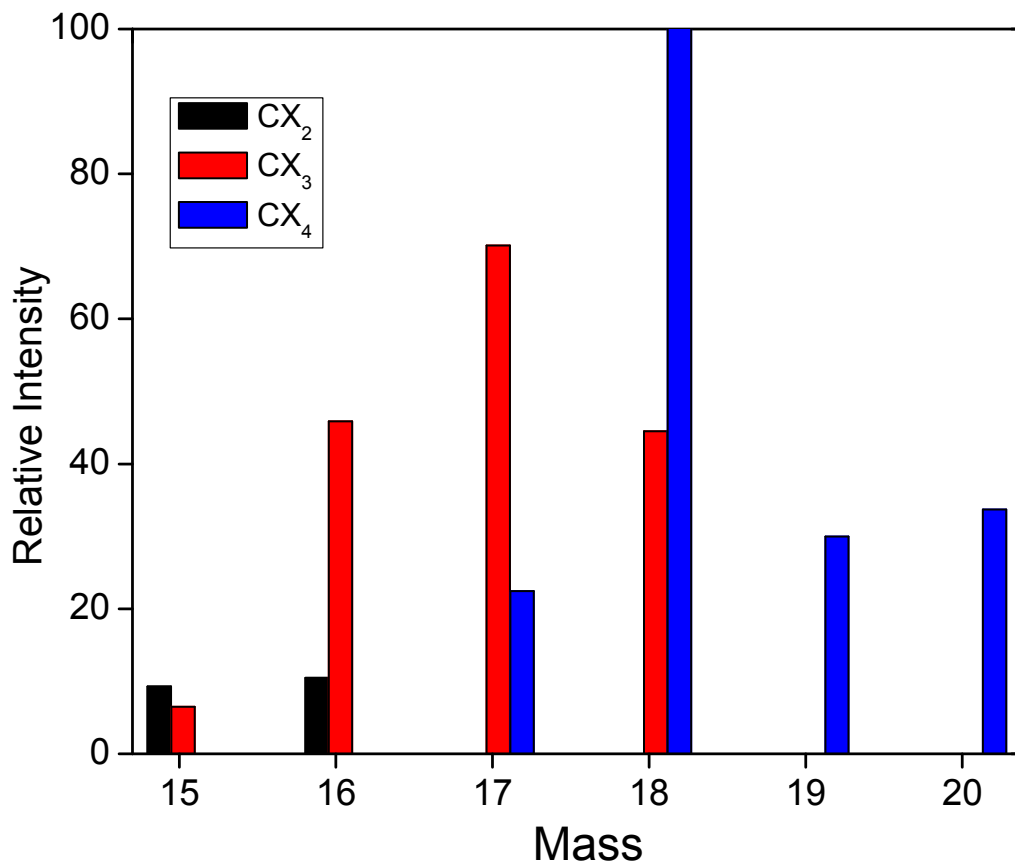
**Fig. S1.**  $^2\text{H}$  NMR spectrum of the  $\alpha\text{-H}$  region in **3** at  $-10\text{ }^\circ\text{C}$ . Non-deuterated THF solvent was used with one drop of  $\text{THF-}d_8$  as reference.  $\text{SiMe}_4\text{-}d_n$  was also observed.

**Table S1.** List of HRMS peaks and their intensities in the 15-20 Dalton region for the reaction of **2** (30 mg) with ca. 5 equiv of D<sub>2</sub>O (5 mg) in a J. Young NMR tube.

Calculated				Observed	
Chemical Species	Mass	#H	#D	Mass	Rel.%
CHD	15.0219	1	1	15.0216	7.8
CH <sub>3</sub>	15.0235	3	0	15.0232	2.1
<sup>16</sup> O	15.9949			15.9949	1.3
CD <sub>2</sub>	16.0282	0	2	16.0282	9.6
CH <sub>2</sub> D	16.0298	2	1	16.0299	31.3
CH <sub>4</sub>	16.0313	4	0		
<sup>16</sup> OH	17.0027			17.0027	2.0
CHD <sub>2</sub>	17.0360	1	2	17.0361	66.2
CH <sub>3</sub> D	17.0376	3	1	17.0378	3.1
<sup>16</sup> OH <sub>2</sub>	18.0106			18.0106	8.9
CD <sub>3</sub>	18.0423	0	3	18.0424	37.3
CH <sub>2</sub> D <sub>2</sub>	18.0439	2	2	18.0440	100.0
<sup>18</sup> OH	19.0070			19.0070	3.5
CHD <sub>3</sub>	19.0501	1	3	19.0501	19.3
<sup>18</sup> OH <sub>2</sub>	20.0148			20.0148	13.2
CD <sub>4</sub>	20.0564	0	4	20.0564	31.5

**Table S2.** List of HRMS peaks and their intensities in the 15-20 Dalton region for the reaction of **2** (30 mg) with ca. 1 equiv of D<sub>2</sub>O (1.2 mg) in a J. Young NMR tube.

Calculated				Observed		
Chemical Species	Mass	#H	#D	Mass (observed)	Mass (calibrated)	Rel. %
CHD	15.0219	1	1	15.0248	15.0202	9.3
CH <sub>3</sub>	15.0235	3	0	15.0265	15.0219	6.5
<sup>16</sup> O	15.9949			15.9988	15.9942	4.5
CD <sub>2</sub>	16.0282	0	2	16.0319	16.0273	10.5
CH <sub>2</sub> D	16.0298	2	1	16.0338	16.0292	45.9
CH <sub>4</sub>	16.0313	4	0			
<sup>16</sup> OH	17.0027			17.0071	17.0025	5.8
CHD <sub>2</sub>	17.0360	1	2	17.0404	17.0358	70.1
CH <sub>3</sub> D	17.0376	3	1	17.0422	17.0376	22.43
<sup>16</sup> OH <sub>2</sub>	18.0106			18.0152	18.0106	23.5
CD <sub>3</sub>	18.0423	0	3	18.0468	18.0422	44.5
CH <sub>2</sub> D <sub>2</sub>	18.0439	2	2	18.0486	18.0440	100.0
CHD <sub>3</sub>	19.0501	1	3	19.0550	19.0504	30.0
CD <sub>4</sub>	20.0564	0	4	20.0616	20.0570	33.7



**Fig. S2.** The HRMS mass spectrum for the methane isotopologues in the 15-20 Dalton region for the reaction of **2** with ca. 1 equiv D<sub>2</sub>O (1.2 mg D<sub>2</sub>O) in a J. Young NMR tube.<sup>11</sup> See Fig. 3 for the reaction of **2** with 5 equiv D<sub>2</sub>O (5 mg D<sub>2</sub>O) in a J. Young NMR tube. Isotopologues of methylene (CX<sub>2</sub>), methyl (CX<sub>3</sub>) and methane (CX<sub>4</sub>) are given in black, red, and blue colours, respectively. <sup>16</sup>OH<sub>2</sub> and its fragments are omitted for clarity.