Supporting information

Synthesis, Structure, and Reactivity of a Pyridine-Stabilized Silanonetungsten Complex

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1.1 General Procedure of X-ray crystal structure determination. The X-ray intensity data were collected on a RIGAKU XtaLAB P200 Imaging Plate diffractmeter with graphite monochromated Mo Kα radiation at 120 K. Empirical absorption corrections were applied. The structure was solved by direct and Fourier transform methods using the SHELX-97 systems.[1] All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on *F2* with all reflections. All hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters.

1.2 X-ray crystal structure determination of $Cp^*(OC)_2W\{O=SiMes_2(py)\}(SiMe_3)\cdot CH_2Cl_2$ ($\mathbf{1b\cdot CH_2Cl_2}$). A single crystal of **1b**・CH_2Cl_2 suitable for X-ray crystal structure determination was obtained by recrystallization from CH_2Cl_2:hexane:pyridine (4:3:1). The final residue R1 and the weighted wR2 were 0.0401 and 0.0925, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters are listed in Tables S1, S2, S3, and S4, respectively. ORTEP drawing of **1b** with atomic numbering schemes is shown in Figure S1.

Table S1. Crystal data and structure refinement for complex **1b · CH_2Cl_2**.

Complex	$Cp^*(OC)_2W\{O=SiMes_2(py)\}(SiMe_3)\cdot CH_2Cl_2$ (**1b · CH_2Cl_2**)
Empirical formula	$C_{39}H_{53}Cl_2NO_3Si_2W$
Formula weight	894.74
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 14.969(5) Å α = 91.880(5)° b = 16.001(5) Å β = 109.446(6)° c = 19.069(6) Å γ = 110.618(5)°
Volume (Å^3)	3972(2)
Z	4
D_{calc} (Mg / m^3)	1.496
Absorption coefficient (mm^{-1})	3.139
F(000)	1816
Crystal Size (mm^3)	0.18 × 0.11 × 0.06
Theta Range for data collection (°)	2.752 – 27.531
Index ranges	$-19 \le h \le 19$, $-20 \le k \le 20$, $-24 \le l \le 23$
Reflections collected	66119
Independent reflections [R(int)]	18079 [0.1020]
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	1.000 and 0.833
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18079 / 22 / 921
Goodness-of-fit on F^2	1.010
Final R indices[a] [$I > 2\sigma(I)$]	$R1$ = 0.0336, $wR2$ = 0.0903
R indices[a] (all data)	$R1$ = 0.0401, $wR2$ = 0.0925
Largest difference in peak and hole (eÅ^{-3})	2.580 and -1.272

[a] $R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.
$wR2 = [\Sigma[w\,(Fo^2 - Fc^2)^2] / \Sigma[w\,(Fo^2)^2]]^{0.5}$,
calc $w = 1 / [\sigma^2(Fo^2) + (0.0493P)^2]$ where $P = (Fo^2 + 2Fc^2) / 3$.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1b · CH_2Cl_2**. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	*U*(eq)[a)]
Molecule 1				
W(1)	6922(1)	3052(1)	325(1)	17(1)
Si(1)	4960(1)	2293(1)	114(1)	25(1)
Si(2)	8457(1)	1981(1)	-162(1)	17(1)
O(1)	6470(2)	1428(2)	1195(2)	38(1)
O(2)	5613(2)	2508(2)	-1400(2)	35(1)
O(3)	8057(2)	2658(2)	112(1)	20(1)
N(1)	7295(2)	1170(2)	-997(2)	19(1)
C(1)	6623(3)	2001(2)	830(2)	24(1)
C(2)	6087(3)	2642(2)	-751(2)	23(1)
C(3)	4592(3)	2147(3)	978(2)	37(1)
C(4)	4336(3)	1095(3)	-422(2)	31(1)
C(5)	4098(3)	2861(3)	-458(2)	38(1)
C(6)	8694(3)	1130(2)	466(2)	20(1)
C(7)	8919(3)	1316(2)	1250(2)	22(1)
C(8)	9018(3)	657(3)	1699(2)	30(1)
C(9)	8923(3)	-183(3)	1404(2)	30(1)
C(10)	8762(3)	-342(2)	643(2)	29(1)
C(11)	8666(3)	291(2)	178(2)	24(1)
C(12)	9130(3)	2234(2)	1653(2)	27(1)
C(13)	9021(4)	-895(3)	1885(3)	49(1)
C(14)	8567(3)	45(3)	-631(2)	32(1)
C(15)	9473(2)	2514(2)	-572(2)	17(1)
C(16)	10485(3)	2521(2)	-254(2)	21(1)
C(17)	11157(3)	2832(2)	-632(2)	22(1)
C(18)	10884(3)	3150(2)	-1311(2)	22(1)
C(19)	9931(3)	3203(2)	-1586(2)	22(1)
C(20)	9225(3)	2908(2)	-1225(2)	19(1)
C(21)	10892(3)	2246(3)	500(2)	28(1)
C(22)	11605(3)	3425(2)	-1730(2)	28(1)
C(23)	8234(3)	3055(2)	-1566(2)	23(1)
C(24)	7263(3)	981(2)	-1706(2)	24(1)

C(25)	6377(3)	391(3)	-2273(2)	33(1)
C(26)	5500(3)	-15(3)	-2123(2)	34(1)
C(27)	5537(3)	171(2)	-1393(2)	31(1)
C(28)	6441(3)	761(2)	-848(2)	24(1)
C(29)	6968(3)	4520(2)	321(2)	24(1)
C(30)	6923(3)	4275(2)	1029(2)	24(1)
C(31)	7863(3)	4186(2)	1445(2)	23(1)
C(32)	8477(3)	4363(2)	1000(2)	23(1)
C(33)	7916(3)	4549(2)	294(2)	24(1)
C(34)	6231(3)	4827(3)	-247(2)	36(1)
C(35)	6183(3)	4365(3)	1377(2)	35(1)
C(36)	8170(3)	4009(3)	2249(2)	32(1)
C(37)	9554(3)	4401(2)	1220(2)	31(1)
C(38)	8342(3)	4855(2)	-300(2)	35(1)
Cl(1)	5463(1)	4994(1)	7671(1)	73(1)
Cl(2)	7508(1)	5797(1)	7611(1)	89(1)
C(81)	6540(6)	5965(4)	7981(4)	126(4)
Molecule 2				
W(2)	8068(1)	1827(1)	5112(1)	18(1)
Si(3)	7564(1)	208(1)	5493(1)	32(1)
Si(4)	6777(1)	3390(1)	5012(1)	19(1)
O(4)	8127(2)	1920(2)	6765(2)	46(1)
O(5)	5944(2)	495(2)	3965(2)	35(1)
O(6)	7500(2)	2894(2)	4991(1)	23(1)
N(2)	6318(2)	2970(2)	5803(2)	20(1)
C(39)	8058(3)	1877(2)	6133(2)	27(1)
C(40)	6708(3)	1002(2)	4433(2)	22(1)
C(41)	8531(4)	32(4)	6358(3)	67(2)
C(42)	7225(4)	-816(3)	4774(3)	56(1)
C(43)	6355(3)	-110(3)	5710(2)	31(1)
C(44)	7480(3)	4653(2)	5329(2)	22(1)
C(45)	7239(3)	5281(2)	4870(2)	27(1)
C(46)	7745(3)	6208(2)	5153(2)	28(1)
C(47)	8472(3)	6548(2)	5875(2)	29(1)
C(48)	8753(3)	5940(2)	6308(2)	27(1)
C(49)	8285(3)	5004(2)	6045(2)	24(1)

C(50)	6464(4)	5011(3)	4065(2)	42(1)
C(51)	8969(3)	7552(2)	6174(3)	37(1)
C(52)	8711(3)	4420(3)	6558(2)	30(1)
C(53)	5482(3)	2982(2)	4201(2)	22(1)
C(54)	5340(3)	2539(2)	3494(2)	24(1)
C(55)	4359(3)	2141(2)	2932(2)	26(1)
C(56)	3497(3)	2170(3)	3033(2)	30(1)
C(57)	3648(3)	2666(3)	3707(2)	32(1)
C(58)	4615(3)	3073(3)	4289(2)	25(1)
C(59)	6233(3)	2537(3)	3297(2)	27(1)
C(60)	2444(3)	1721(3)	2417(2)	44(1)
C(61)	4678(3)	3631(3)	4968(2)	36(1)
C(62)	6418(3)	3487(2)	6419(2)	24(1)
C(63)	6098(3)	3122(3)	6974(2)	28(1)
C(64)	5640(3)	2187(3)	6892(2)	31(1)
C(65)	5521(3)	1652(3)	6256(2)	30(1)
C(66)	5871(3)	2061(2)	5723(2)	26(1)
C(67)	9186(3)	2889(2)	4596(2)	28(1)
C(68)	9765(3)	2851(2)	5345(2)	26(1)
C(69)	9745(3)	1955(3)	5368(2)	30(1)
C(70)	9123(3)	1436(2)	4634(2)	30(1)
C(71)	8766(3)	2017(2)	4151(2)	27(1)
C(72)	9081(3)	3732(3)	4321(3)	39(1)
C(73)	10436(3)	3662(3)	5964(3)	45(1)
C(74)	10442(4)	1698(4)	6013(3)	54(1)
C(75)	9070(4)	538(3)	4337(3)	50(1)
C(76)	8160(3)	1733(3)	3315(2)	44(1)
Cl(3A)	6873(6)	-1183(8)	2639(5)	182(5)
Cl(4A)	6577(2)	-2718(3)	3246(3)	107(2)
C(82A)	6639(10)	-2299(9)	2514(7)	94(5)
Cl(3B)	6914(9)	-1142(6)	2638(4)	174(7)
Cl(4B)	6912(3)	-3162(3)	2764(2)	78(2)
C(82B)	6515(15)	-2260(12)	2954(16)	114(8)

Table S3. Bond lengths [Å] and angles [°] for **1b** • CH_2Cl_2.

Molecule 1			
W(1)-C(1)	1.956(4)	C(10)-C(11)	1.382(5)
W(1)-C(2)	1.957(4)	C(11)-C(14)	1.526(5)
W(1)-O(3)	2.154(2)	C(15)-C(20)	1.414(5)
W(1)-C(29)	2.325(3)	C(15)-C(16)	1.427(5)
W(1)-C(30)	2.335(3)	C(16)-C(17)	1.389(4)
W(1)-C(33)	2.347(3)	C(16)-C(21)	1.510(5)
W(1)-C(31)	2.404(3)	C(17)-C(18)	1.393(5)
W(1)-C(32)	2.421(3)	C(18)-C(19)	1.381(5)
W(1)-Si(1)	2.6328(13)	C(18)-C(22)	1.504(4)
Si(1)-C(4)	1.888(4)	C(19)-C(20)	1.403(4)
Si(1)-C(3)	1.901(4)	C(20)-C(23)	1.512(5)
Si(1)-C(5)	1.907(4)	C(24)-C(25)	1.384(5)
Si(2)-O(3)	1.561(2)	C(25)-C(26)	1.375(6)
Si(2)-C(15)	1.890(3)	C(26)-C(27)	1.392(6)
Si(2)-C(6)	1.891(3)	C(27)-C(28)	1.379(5)
Si(2)-N(1)	1.918(3)	C(29)-C(33)	1.422(5)
O(1)-C(1)	1.173(4)	C(29)-C(30)	1.434(5)
O(2)-C(2)	1.170(4)	C(29)-C(34)	1.501(5)
N(1)-C(28)	1.345(4)	C(30)-C(31)	1.427(5)
N(1)-C(24)	1.357(4)	C(30)-C(35)	1.512(4)
C(6)-C(7)	1.414(5)	C(31)-C(32)	1.413(4)
C(6)-C(11)	1.415(4)	C(31)-C(36)	1.515(5)
C(7)-C(8)	1.398(5)	C(32)-C(33)	1.434(5)
C(7)-C(12)	1.511(5)	C(32)-C(37)	1.503(5)
C(8)-C(9)	1.381(5)	C(33)-C(38)	1.493(5)
C(9)-C(10)	1.388(5)	Cl(1)-C(81)	1.705(7)
C(9)-C(13)	1.504(5)	Cl(2)-C(81)	1.900(10)
C(1)-W(1)-C(2)	107.54(14)	C(2)-W(1)-C(29)	94.57(13)
C(1)-W(1)-O(3)	87.18(11)	O(3)-W(1)-C(29)	122.72(11)
C(2)-W(1)-O(3)	87.60(11)	C(1)-W(1)-C(30)	108.82(13)
C(1)-W(1)-C(29)	143.90(13)	C(2)-W(1)-C(30)	122.57(13)

O(3)-W(1)-C(30)	136.51(11)	C(15)-Si(2)-C(6)	115.11(14)
C(29)-W(1)-C(30)	35.86(12)	O(3)-Si(2)-N(1)	104.35(13)
C(1)-W(1)-C(33)	152.13(14)	C(15)-Si(2)-N(1)	104.79(13)
C(2)-W(1)-C(33)	99.59(13)	C(6)-Si(2)-N(1)	99.06(13)
C(30)-W(1)-C(33)	59.10(11)	Si(2)-O(3)-W(1)	154.91(15)
C(1)-W(1)-C(31)	97.01(13)	C(24)-N(1)-Si(2)	126.3(2)
C(2)-W(1)-C(31)	153.02(13)	C(28)-N(1)-Si(2)	115.2(2)
O(3)-W(1)-C(31)	104.98(11)	C(28)-N(1)-C(24)	118.5(3)
C(29)-W(1)-C(31)	58.50(12)	O(1)-C(1)-W(1)	173.6(3)
C(30)-W(1)-C(31)	35.00(12)	O(2)-C(2)-W(1)	171.6(3)
C(33)-W(1)-C(31)	58.11(12)	C(7)-C(6)-C(11)	117.3(3)
C(1)-W(1)-C(32)	117.26(14)	C(7)-C(6)-Si(2)	120.9(2)
C(2)-W(1)-C(32)	132.09(13)	C(11)-C(6)-Si(2)	121.8(2)
O(3)-W(1)-C(32)	78.82(10)	C(8)-C(7)-C(6)	120.4(3)
C(29)-W(1)-C(32)	58.10(12)	C(8)-C(7)-C(12)	116.6(3)
C(30)-W(1)-C(32)	57.79(11)	C(6)-C(7)-C(12)	122.9(3)
O(3)-W(1)-C(33)	87.72(10)	C(9)-C(8)-C(7)	121.8(3)
C(29)-W(1)-C(33)	35.43(12)	C(8)-C(9)-C(10)	117.5(3)
C(1)-W(1)-Si(1)	67.84(10)	C(8)-C(9)-C(13)	121.9(4)
C(2)-W(1)-Si(1)	69.33(10)	C(10)-C(9)-C(13)	120.6(3)
O(3)-W(1)-Si(1)	137.42(7)	C(11)-C(10)-C(9)	122.7(3)
C(29)-W(1)-Si(1)	95.25(9)	C(10)-C(11)-C(6)	120.1(3)
C(30)-W(1)-Si(1)	85.38(9)	C(10)-C(11)-C(14)	116.6(3)
C(33)-W(1)-Si(1)	129.99(9)	C(6)-C(11)-C(14)	123.3(3)
C(31)-W(1)-Si(1)	111.64(8)	C(20)-C(15)-C(16)	118.2(3)
C(32)-W(1)-Si(1)	142.93(8)	C(20)-C(15)-Si(2)	119.2(2)
C(33)-W(1)-C(32)	34.97(12)	C(16)-C(15)-Si(2)	122.5(2)
C(31)-W(1)-C(32)	34.04(11)	C(17)-C(16)-C(15)	119.4(3)
C(4)-Si(1)-C(3)	102.01(18)	C(17)-C(16)-C(21)	117.3(3)
C(4)-Si(1)-C(5)	103.01(19)	C(15)-C(16)-C(21)	123.2(3)
C(3)-Si(1)-C(5)	102.37(19)	C(16)-C(17)-C(18)	122.3(3)
C(4)-Si(1)-W(1)	112.63(12)	C(19)-C(18)-C(17)	117.9(3)
C(3)-Si(1)-W(1)	118.20(14)	C(19)-C(18)-C(22)	121.2(3)
C(5)-Si(1)-W(1)	116.52(14)	C(17)-C(18)-C(22)	120.9(3)
O(3)-Si(2)-C(15)	114.06(13)	C(18)-C(19)-C(20)	122.2(3)
O(3)-Si(2)-C(6)	116.71(14)	C(19)-C(20)-C(15)	119.5(3)

C(19)-C(20)-C(23)	116.4(3)	C(32)-C(31)-C(30)	108.2(3)
C(15)-C(20)-C(23)	124.1(3)	C(32)-C(31)-C(36)	126.6(3)
N(1)-C(24)-C(25)	121.6(3)	C(30)-C(31)-C(36)	125.1(3)
C(26)-C(25)-C(24)	119.8(3)	C(32)-C(31)-W(1)	73.62(19)
C(25)-C(26)-C(27)	118.4(4)	C(30)-C(31)-W(1)	69.84(19)
C(28)-C(27)-C(26)	119.5(4)	C(36)-C(31)-W(1)	126.0(2)
N(1)-C(28)-C(27)	122.1(3)	C(31)-C(32)-C(33)	108.4(3)
C(33)-C(29)-C(30)	107.9(3)	C(31)-C(32)-C(37)	127.4(3)
C(33)-C(29)-C(34)	124.9(3)	C(33)-C(32)-C(37)	124.2(3)
C(30)-C(29)-C(34)	126.7(3)	C(31)-C(32)-W(1)	72.34(19)
C(33)-C(29)-W(1)	73.15(19)	C(33)-C(32)-W(1)	69.71(19)
C(30)-C(29)-W(1)	72.46(19)	C(37)-C(32)-W(1)	125.9(2)
C(34)-C(29)-W(1)	126.9(3)	C(29)-C(33)-C(32)	107.7(3)
C(31)-C(30)-C(29)	107.8(3)	C(29)-C(33)-C(38)	127.1(3)
C(31)-C(30)-C(35)	123.7(3)	C(32)-C(33)-C(38)	124.6(3)
C(29)-C(30)-C(35)	126.2(3)	C(29)-C(33)-W(1)	71.42(19)
C(31)-C(30)-W(1)	75.16(19)	C(32)-C(33)-W(1)	75.32(19)
C(29)-C(30)-W(1)	71.68(18)	C(38)-C(33)-W(1)	125.9(2)
C(35)-C(30)-W(1)	132.4(2)	Cl(1)-C(81)-Cl(2)	107.9(4)

Molecule 2

W(2)-C(39)	1.950(4)	Si(4)-N(2)	1.905(3)
W(2)-C(40)	1.950(4)	O(4)-C(39)	1.173(4)
W(2)-O(6)	2.146(2)	O(5)-C(40)	1.176(4)
W(2)-C(70)	2.310(3)	N(2)-C(66)	1.348(4)
W(2)-C(69)	2.324(4)	N(2)-C(62)	1.349(4)
W(2)-C(68)	2.367(4)	C(44)-C(49)	1.417(5)
W(2)-C(71)	2.374(3)	C(44)-C(45)	1.419(5)
W(2)-C(67)	2.421(3)	C(45)-C(46)	1.395(5)
W(2)-Si(3)	2.6297(13)	C(45)-C(50)	1.518(6)
Si(3)-C(43)	1.891(4)	C(46)-C(47)	1.383(6)
Si(3)-C(41)	1.904(5)	C(47)-C(48)	1.384(5)
Si(3)-C(42)	1.904(5)	C(47)-C(51)	1.509(5)
Si(4)-O(6)	1.560(2)	C(48)-C(49)	1.401(5)
Si(4)-C(44)	1.886(4)	C(49)-C(52)	1.516(5)
Si(4)-C(53)	1.904(4)	C(53)-C(58)	1.417(4)

C(53)-C(54)	1.417(5)	C(67)-C(71)	1.419(5)
C(54)-C(55)	1.400(5)	C(67)-C(72)	1.502(5)
C(54)-C(59)	1.504(5)	C(68)-C(69)	1.426(5)
C(55)-C(56)	1.382(5)	C(68)-C(73)	1.509(6)
C(56)-C(57)	1.395(5)	C(69)-C(70)	1.423(6)
C(56)-C(60)	1.514(6)	C(69)-C(74)	1.500(6)
C(57)-C(58)	1.404(5)	C(70)-C(71)	1.442(5)
C(58)-C(61)	1.505(5)	C(70)-C(75)	1.493(5)
C(62)-C(63)	1.369(5)	C(71)-C(76)	1.506(6)
C(63)-C(64)	1.387(5)	Cl(3A)-C(82A)	1.687(13)
C(64)-C(65)	1.385(5)	Cl(4A)-C(82A)	1.585(13)
C(65)-C(66)	1.376(5)	Cl(3B)-C(82B)	1.865(17)
C(67)-C(68)	1.418(5)	Cl(4B)-C(82B)	1.812(14)

C(39)-W(2)-Si(3)	68.52(11)	C(70)-W(2)-C(68)	58.86(13)
C(40)-W(2)-Si(3)	68.32(10)	C(69)-W(2)-C(68)	35.37(12)
O(6)-W(2)-Si(3)	137.85(7)	C(39)-W(2)-C(71)	157.86(14)
C(70)-W(2)-Si(3)	86.52(9)	C(40)-W(2)-C(71)	93.80(13)
C(69)-W(2)-Si(3)	91.65(10)	O(6)-W(2)-C(71)	99.17(11)
C(68)-W(2)-Si(3)	125.21(9)	C(70)-W(2)-C(71)	35.82(13)
C(71)-W(2)-Si(3)	116.12(9)	C(68)-W(2)-C(71)	58.27(13)
C(67)-W(2)-Si(3)	144.40(8)	C(39)-W(2)-C(67)	130.03(14)
C(39)-W(2)-C(40)	107.54(14)	C(40)-W(2)-C(67)	119.07(14)
C(39)-W(2)-O(6)	87.65(12)	O(6)-W(2)-C(67)	77.43(10)
C(40)-W(2)-O(6)	88.03(12)	C(70)-W(2)-C(67)	58.08(12)
C(39)-W(2)-C(70)	129.77(15)	C(69)-W(2)-C(67)	58.04(13)
C(40)-W(2)-C(70)	101.84(14)	C(68)-W(2)-C(67)	34.43(13)
O(6)-W(2)-C(70)	133.68(11)	C(71)-W(2)-C(67)	34.42(12)
C(39)-W(2)-C(69)	99.94(15)	C(43)-Si(3)-C(41)	104.3(2)
C(40)-W(2)-C(69)	135.91(14)	C(43)-Si(3)-C(42)	101.36(19)
O(6)-W(2)-C(69)	127.52(11)	C(41)-Si(3)-C(42)	101.7(3)
C(70)-W(2)-C(69)	35.77(14)	C(43)-Si(3)-W(2)	111.04(12)
C(39)-W(2)-C(40)	107.54(14)	C(41)-Si(3)-W(2)	117.24(17)
C(39)-W(2)-C(68)	100.69(14)	C(42)-Si(3)-W(2)	119.09(16)
C(40)-W(2)-C(68)	151.75(13)	O(6)-Si(4)-C(44)	113.02(14)
O(6)-W(2)-C(68)	92.15(11)	O(6)-Si(4)-C(53)	116.45(15)

C(44)-Si(4)-C(53)	116.89(15)	C(62)-C(63)-C(64)	118.7(3)
O(6)-Si(4)-N(2)	104.06(13)	C(65)-C(64)-C(63)	119.3(3)
C(44)-Si(4)-N(2)	104.62(14)	C(66)-C(65)-C(64)	119.1(4)
C(53)-Si(4)-N(2)	98.89(14)	C(68)-C(67)-C(71)	108.9(3)
O(4)-C(39)-W(2)	175.1(3)	C(68)-C(67)-C(72)	125.0(4)
O(5)-C(40)-W(2)	172.1(3)	C(71)-C(67)-C(72)	126.1(4)
C(49)-C(44)-Si(4)	120.1(3)	C(68)-C(67)-W(2)	70.71(19)
C(45)-C(44)-Si(4)	122.2(3)	C(71)-C(67)-W(2)	70.99(19)
C(49)-C(44)-C(45)	117.7(3)	C(72)-C(67)-W(2)	126.4(2)
C(46)-C(45)-C(44)	119.5(3)	C(67)-C(68)-C(69)	108.2(3)
C(46)-C(45)-C(50)	116.7(3)	C(67)-C(68)-C(73)	124.9(4)
C(44)-C(45)-C(50)	123.9(3)	C(69)-C(68)-C(73)	126.1(4)
C(47)-C(46)-C(45)	122.7(3)	C(67)-C(68)-W(2)	74.9(2)
C(46)-C(47)-C(48)	117.8(3)	C(69)-C(68)-W(2)	70.7(2)
C(46)-C(47)-C(51)	121.2(3)	C(73)-C(68)-W(2)	128.7(3)
C(48)-C(47)-C(51)	120.9(4)	C(70)-C(69)-C(68)	107.6(3)
C(47)-C(48)-C(49)	121.7(4)	C(70)-C(69)-C(74)	127.4(4)
C(48)-C(49)-C(44)	120.2(3)	C(68)-C(69)-C(74)	123.8(4)
C(48)-C(49)-C(52)	116.1(3)	C(70)-C(69)-W(2)	71.6(2)
C(44)-C(49)-C(52)	123.6(3)	C(68)-C(69)-W(2)	73.98(19)
C(58)-C(53)-C(54)	117.5(3)	C(74)-C(69)-W(2)	129.6(3)
C(58)-C(53)-Si(4)	121.6(3)	C(69)-C(70)-C(71)	108.4(3)
C(54)-C(53)-Si(4)	120.8(2)	C(69)-C(70)-C(75)	126.8(4)
C(55)-C(54)-C(53)	120.4(3)	C(71)-C(70)-C(75)	122.8(4)
C(55)-C(54)-C(59)	117.6(3)	C(69)-C(70)-W(2)	72.63(19)
C(53)-C(54)-C(59)	121.8(3)	C(71)-C(70)-W(2)	74.51(18)
C(56)-C(55)-C(54)	122.4(3)	C(75)-C(70)-W(2)	131.6(3)
C(55)-C(56)-C(57)	117.1(3)	C(67)-C(71)-C(70)	106.9(3)
C(55)-C(56)-C(60)	121.0(4)	C(67)-C(71)-C(76)	128.8(4)
C(57)-C(56)-C(60)	121.8(4)	C(70)-C(71)-C(76)	124.0(3)
C(56)-C(57)-C(58)	122.6(3)	C(67)-C(71)-W(2)	74.59(19)
C(57)-C(58)-C(53)	119.6(3)	C(70)-C(71)-W(2)	69.67(18)
C(57)-C(58)-C(61)	117.0(3)	C(76)-C(71)-W(2)	125.8(2)
C(53)-C(58)-C(61)	123.2(3)	Cl(4A)-C(82A)-Cl(3A)	111.6(8)
N(2)-C(62)-C(63)	122.3(3)	Cl(4B)-C(82B)-Cl(3B)	124.1(10)

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1b • CH_2Cl_2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Molecule 1						
W(1)	17(1)	17(1)	18(1)	3(1)	10(1)	5(1)
Si(1)	20(1)	29(1)	26(1)	2(1)	12(1)	7(1)
Si(2)	19(1)	16(1)	17(1)	1(1)	9(1)	6(1)
O(1)	34(2)	35(2)	43(2)	21(1)	18(1)	7(1)
O(2)	34(2)	51(2)	20(1)	5(1)	10(1)	16(1)
O(3)	21(1)	21(1)	23(1)	3(1)	13(1)	9(1)
N(1)	23(2)	15(1)	20(1)	2(1)	10(1)	6(1)
C(1)	20(2)	25(2)	23(2)	1(1)	9(2)	5(1)
C(2)	24(2)	23(2)	24(2)	3(1)	14(2)	7(1)
C(3)	28(2)	43(2)	38(2)	0(2)	21(2)	4(2)
C(4)	22(2)	31(2)	30(2)	-2(2)	11(2)	0(2)
C(5)	28(2)	49(3)	41(2)	2(2)	12(2)	19(2)
C(6)	22(2)	17(2)	21(2)	1(1)	9(1)	6(1)
C(7)	24(2)	21(2)	22(2)	4(1)	11(1)	8(1)
C(8)	35(2)	29(2)	25(2)	7(2)	12(2)	11(2)
C(9)	36(2)	28(2)	27(2)	9(2)	11(2)	13(2)
C(10)	37(2)	19(2)	31(2)	3(2)	12(2)	11(2)
C(11)	27(2)	22(2)	24(2)	1(1)	10(2)	11(2)
C(12)	39(2)	27(2)	19(2)	3(2)	13(2)	14(2)
C(13)	79(4)	36(2)	35(2)	18(2)	19(2)	27(2)
C(14)	50(3)	27(2)	29(2)	4(2)	18(2)	24(2)
C(15)	21(2)	15(2)	17(2)	-1(1)	9(1)	7(1)
C(16)	22(2)	19(2)	22(2)	-1(1)	9(1)	8(1)
C(17)	19(2)	22(2)	24(2)	0(1)	9(1)	7(1)
C(18)	24(2)	16(2)	26(2)	0(1)	13(2)	4(1)
C(19)	28(2)	22(2)	21(2)	5(1)	12(2)	9(1)
C(20)	19(2)	14(2)	20(2)	-1(1)	8(1)	3(1)
C(21)	20(2)	37(2)	27(2)	6(2)	7(2)	12(2)
C(22)	31(2)	25(2)	35(2)	5(2)	21(2)	9(2)
C(23)	24(2)	21(2)	24(2)	6(1)	10(2)	7(1)
C(24)	29(2)	20(2)	21(2)	3(1)	11(2)	6(2)
C(25)	47(3)	29(2)	17(2)	0(2)	10(2)	11(2)

C(26)	32(2)	23(2)	31(2)	-3(2)	2(2)	2(2)
C(27)	29(2)	21(2)	35(2)	0(2)	12(2)	2(2)
C(28)	26(2)	19(2)	24(2)	2(1)	11(2)	4(1)
C(29)	33(2)	18(2)	24(2)	4(1)	13(2)	10(2)
C(30)	22(2)	23(2)	28(2)	-1(1)	14(2)	6(1)
C(31)	26(2)	16(2)	23(2)	0(1)	11(2)	4(1)
C(32)	21(2)	13(2)	33(2)	-2(1)	14(2)	1(1)
C(33)	32(2)	18(2)	26(2)	3(1)	17(2)	7(2)
C(34)	45(3)	31(2)	38(2)	11(2)	14(2)	23(2)
C(35)	35(2)	34(2)	40(2)	-4(2)	24(2)	9(2)
C(36)	34(2)	27(2)	26(2)	-1(2)	9(2)	4(2)
C(37)	22(2)	21(2)	43(2)	-2(2)	12(2)	1(2)
C(38)	54(3)	21(2)	38(2)	9(2)	33(2)	9(2)
Cl(1)	70(1)	87(1)	61(1)	11(1)	16(1)	36(1)
Cl(2)	80(1)	67(1)	116(1)	-23(1)	58(1)	7(1)
C(81)	164(8)	32(3)	89(5)	23(3)	-10(5)	-14(4)

Molecule 2

W(2)	18(1)	18(1)	20(1)	3(1)	9(1)	6(1)
Si(3)	29(1)	29(1)	43(1)	16(1)	18(1)	13(1)
Si(4)	18(1)	20(1)	19(1)	0(1)	9(1)	6(1)
O(4)	47(2)	56(2)	24(2)	1(1)	15(1)	7(2)
O(5)	30(2)	34(2)	26(2)	3(1)	8(1)	-2(1)
O(6)	23(1)	24(1)	27(1)	4(1)	14(1)	9(1)
N(2)	16(1)	22(1)	21(2)	0(1)	7(1)	4(1)
C(39)	24(2)	24(2)	25(2)	0(2)	9(2)	1(2)
C(40)	23(2)	21(2)	19(2)	3(1)	11(2)	3(1)
C(41)	52(3)	65(3)	86(4)	51(3)	19(3)	25(3)
C(42)	66(3)	29(2)	101(4)	18(2)	64(3)	20(2)
C(43)	34(2)	29(2)	29(2)	7(2)	18(2)	7(2)
C(44)	18(2)	20(2)	27(2)	0(1)	10(1)	6(1)
C(45)	23(2)	26(2)	31(2)	3(2)	11(2)	8(2)
C(46)	27(2)	23(2)	38(2)	9(2)	17(2)	11(2)
C(47)	25(2)	23(2)	46(2)	5(2)	24(2)	7(2)
C(48)	20(2)	26(2)	32(2)	-5(2)	11(2)	2(1)
C(49)	21(2)	25(2)	29(2)	3(2)	13(2)	8(1)

C(50)	49(3)	31(2)	34(2)	11(2)	3(2)	12(2)
C(51)	30(2)	23(2)	57(3)	1(2)	21(2)	5(2)
C(52)	21(2)	27(2)	34(2)	-1(2)	4(2)	8(2)
C(53)	20(2)	23(2)	21(2)	2(1)	9(1)	6(1)
C(54)	30(2)	21(2)	23(2)	5(1)	14(2)	9(2)
C(55)	31(2)	25(2)	17(2)	3(1)	7(2)	7(2)
C(56)	27(2)	31(2)	22(2)	5(2)	5(2)	4(2)
C(57)	21(2)	47(2)	27(2)	2(2)	8(2)	12(2)
C(58)	21(2)	34(2)	20(2)	1(2)	8(2)	10(2)
C(59)	32(2)	34(2)	19(2)	3(2)	12(2)	14(2)
C(60)	32(2)	54(3)	26(2)	0(2)	2(2)	3(2)
C(61)	28(2)	54(3)	28(2)	-7(2)	7(2)	23(2)
C(62)	24(2)	26(2)	22(2)	-2(1)	8(2)	10(2)
C(63)	24(2)	37(2)	21(2)	-2(2)	9(2)	10(2)
C(64)	27(2)	40(2)	28(2)	9(2)	15(2)	11(2)
C(65)	25(2)	30(2)	31(2)	3(2)	12(2)	4(2)
C(66)	22(2)	27(2)	27(2)	-3(2)	13(2)	3(2)
C(67)	26(2)	24(2)	45(2)	12(2)	26(2)	12(2)
C(68)	17(2)	24(2)	36(2)	-3(2)	12(2)	3(1)
C(69)	21(2)	33(2)	40(2)	8(2)	15(2)	12(2)
C(70)	30(2)	22(2)	49(2)	6(2)	28(2)	10(2)
C(71)	25(2)	33(2)	27(2)	5(2)	19(2)	8(2)
C(72)	39(2)	35(2)	60(3)	21(2)	35(2)	17(2)
C(73)	28(2)	39(2)	51(3)	-12(2)	15(2)	-4(2)
C(74)	33(3)	62(3)	71(4)	27(3)	16(2)	27(2)
C(75)	56(3)	28(2)	86(4)	8(2)	53(3)	16(2)
C(76)	39(2)	67(3)	30(2)	4(2)	22(2)	17(2)
Cl(3A)	93(5)	272(12)	101(6)	22(6)	39(4)	-23(5)
Cl(4A)	60(2)	101(3)	164(4)	38(2)	45(2)	32(2)
C(82A)	51(7)	117(11)	81(9)	-40(9)	-9(6)	29(7)
Cl(3B)	185(10)	117(6)	31(3)	31(4)	-31(4)	-94(6)
Cl(4B)	72(3)	105(3)	76(3)	18(2)	36(2)	47(2)
C(82B)	93(11)	122(14)	230(20)	137(15)	127(14)	87(11)

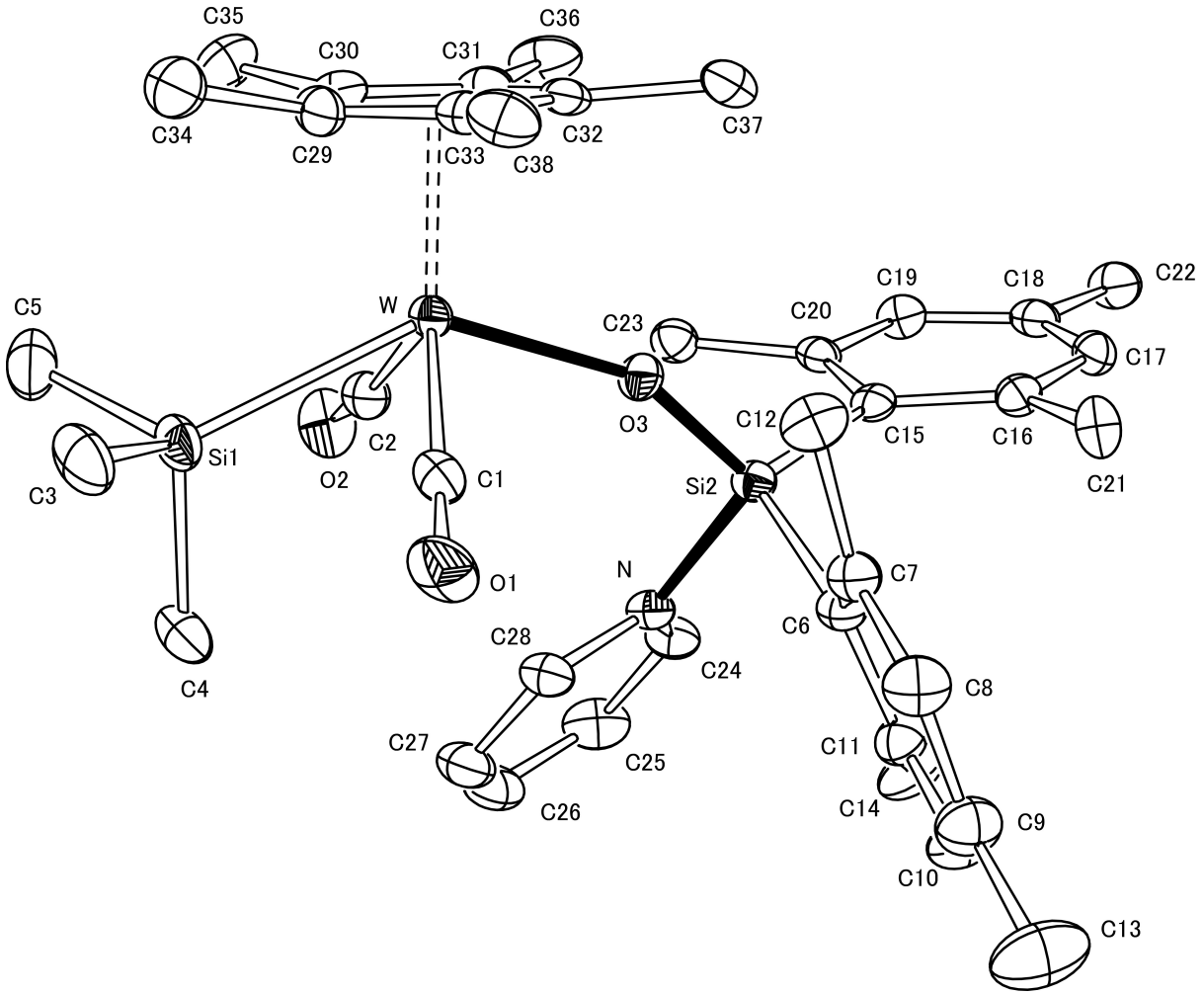

Figure S1. ORTEP drawing of **1b**. (thermal ellipsoids at the 50% probability level).

1.3 X-ray crystal structure determination of Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (5). A single crystal of **5** suitable for X-ray crystal structure determination was obtained by recrystallization from toluene:hexane (1:4). The final residue *R*1 and the weighted *wR*2 were 0.0360 and 0.0654, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters are listed in Tables S5, S6, S7, and S8, respectively. ORTEP drawing of **5** with atomic numbering schemes is shown in Figure S2.

Table S5. Crystal data and structure refinement for complex **5**.

Complex	Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (**5**)
Empirical formula	$C_{36}H_{55}O_3PSi_2W$
Formula weight	806.80
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	*P*-42$_1$*c*
Unit cell dimensions	*a* = 28.087(2) Å
	b = 28.087(2) Å
	c = 9.4238(7) Å
Volume (Å^3)	7434.2(12)
Z	8
D_{calc} (Mg / m^3)	1.442
Absorption coefficient (mm^{-1})	3.247
F(000)	3296
Crystal Size (mm^3)	0.10 × 0.03 × 0.03
Theta Range for data collection (°)	2.603 – 27.514
Index ranges	$-36 \le h \le 36$, $-36 \le k \le 27$, $-12 \le l \le 12$
Reflections collected	62159
Independent reflections [*R*(int)]	8541 [0.0984]
Absorption correction	Multi-scan
Maximum and minimum transmission	1.000 and 0.827
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8541 / 0 / 405
Goodness-of-fit on F^2	0.982
Final *R* indices[a] [$I > 2\sigma(I)$]	$R1 = 0.0289$, $wR2 = 0.0636$
R indices[a] (all data)	$R1 = 0.0360$, $wR2 = 0.0654$
Largest difference in peak and hole (eÅ^{-3})	1.758 and -0.766

[a] $R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.
$wR2 = [\Sigma[w\,(Fo^2 - Fc^2)^2] / \Sigma[w\,(Fo^2)^2]]^{0.5}$,
calc $w = 1 / [\sigma^2(Fo^2) + (0.0217P)^2]$ where $P = (Fo^2 + 2Fc^2) / 3$.

Table S6. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **5**. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	*U*(eq)[a)]
W	7183(1)	9803(1)	8542(1)	17(1)
P	7631(1)	9183(1)	9840(2)	20(1)
Si(1)	7848(1)	10592(1)	9930(2)	18(1)
Si(2)	6491(1)	10196(1)	11540(2)	24(1)
O(1)	6319(2)	9183(2)	9523(5)	35(1)
O(2)	7851(1)	10144(1)	8876(4)	20(1)
O(3)	7365(1)	10503(1)	10916(4)	21(1)
C(1)	6632(2)	9422(2)	9186(7)	26(1)
C(2)	7018(2)	10193(2)	10284(6)	19(1)
C(3)	7867(2)	9387(2)	11534(8)	26(1)
C(4)	7310(2)	8649(2)	10363(8)	37(2)
C(5)	8149(2)	8920(3)	9004(8)	35(2)
C(6)	7811(2)	11178(2)	8906(6)	22(1)
C(7)	8193(2)	11288(2)	7988(7)	22(1)
C(8)	8175(3)	11684(2)	7114(7)	32(2)
C(9)	7784(3)	11999(2)	7114(7)	33(2)
C(10)	7420(2)	11895(2)	8017(8)	33(2)
C(11)	7416(2)	11495(2)	8913(6)	25(1)
C(12)	8637(2)	10979(2)	7900(7)	28(1)
C(13)	7780(3)	12437(3)	6178(9)	53(2)
C(14)	6981(2)	11424(2)	9808(8)	32(2)
C(15)	8366(2)	10623(2)	11242(6)	20(1)
C(16)	8325(2)	10934(2)	12418(7)	24(1)
C(17)	8689(2)	10969(2)	13404(7)	28(1)
C(18)	9107(2)	10705(2)	13281(7)	28(2)
C(19)	9143(2)	10403(2)	12161(8)	33(2)
C(20)	8786(2)	10354(2)	11134(6)	24(1)
C(21)	7898(2)	11251(2)	12642(7)	28(1)

C(22)	9505(3)	10762(3)	14328(9)	47(2)
C(23)	8891(2)	10011(2)	9931(8)	31(2)
C(24)	6514(3)	10724(3)	12747(8)	38(2)
C(25)	5905(2)	10217(3)	10576(8)	39(2)
C(26)	6518(3)	9661(3)	12728(7)	34(2)
C(27)	7393(2)	9565(2)	6170(6)	26(1)
C(28)	7386(3)	10069(2)	6143(6)	33(2)
C(29)	6928(3)	10230(2)	6520(8)	36(2)
C(30)	6630(2)	9813(3)	6721(7)	32(2)
C(31)	6934(2)	9405(2)	6493(8)	23(1)
C(32)	7806(3)	9267(3)	5666(9)	48(2)
C(33)	7796(3)	10370(3)	5716(8)	64(3)
C(34)	6760(4)	10740(3)	6559(10)	69(3)
C(35)	6099(3)	9821(4)	6769(8)	61(3)
C(36)	6767(3)	8896(2)	6367(9)	41(2)

Table S7. Bond lengths [Å] and angles [°] for **5**.

W-C(1)	1.975(7)	C(7)-C(12)	1.521(9)
W-C(2)	2.027(6)	C(8)-C(9)	1.410(10)
W-O(2)	2.131(4)	C(9)-C(10)	1.361(10)
W-C(30)	2.315(6)	C(9)-C(13)	1.514(9)
W-C(31)	2.339(7)	C(10)-C(11)	1.405(9)
W-C(29)	2.363(7)	C(11)-C(14)	1.499(9)
W-C(27)	2.407(6)	C(15)-C(20)	1.407(8)
W-C(28)	2.450(6)	C(15)-C(16)	1.416(9)
W-P	2.4717(15)	C(16)-C(17)	1.384(9)
P-C(5)	1.812(7)	C(16)-C(21)	1.509(9)
P-C(4)	1.816(7)	C(17)-C(18)	1.394(9)
P-C(3)	1.822(7)	C(18)-C(19)	1.359(10)
Si(1)-O(2)	1.602(4)	C(18)-C(22)	1.498(9)
Si(1)-O(3)	1.664(4)	C(19)-C(20)	1.401(9)
Si(1)-C(15)	1.910(6)	C(20)-C(23)	1.515(9)
Si(1)-C(6)	1.912(6)	C(27)-C(31)	1.399(9)
Si(2)-C(24)	1.871(7)	C(27)-C(28)	1.418(9)
Si(2)-C(26)	1.877(7)	C(27)-C(32)	1.508(10)
Si(2)-C(25)	1.880(7)	C(28)-C(29)	1.410(11)
Si(2)-C(2)	1.896(6)	C(28)-C(33)	1.483(10)
O(1)-C(1)	1.152(8)	C(29)-C(30)	1.452(10)
O(3)-C(2)	1.437(7)	C(29)-C(34)	1.508(10)
C(6)-C(7)	1.413(9)	C(30)-C(31)	1.447(8)
C(6)-C(11)	1.422(8)	C(30)-C(35)	1.491(10)
C(7)-C(8)	1.385(9)		

C(1)-W-C(2)	82.2(3)	C(2)-W-C(30)	116.1(2)
C(1)-W-O(2)	152.6(2)	O(2)-W-C(30)	134.0(2)
C(2)-W-O(2)	80.71(19)	C(1)-W-C(31)	76.1(2)
C(1)-W-C(30)	73.1(3)	C(2)-W-C(31)	149.2(2)

O(2)-W-C(31)	126.93(18)	C(4)-P-C(3)	101.7(3)
C(30)-W-C(31)	36.2(2)	C(5)-P-W	118.7(2)
C(1)-W-C(29)	106.6(3)	C(4)-P-W	117.6(2)
C(2)-W-C(29)	108.0(2)	C(3)-P-W	113.4(2)
O(2)-W-C(29)	99.0(2)	O(2)-Si(1)-O(3)	103.5(2)
C(30)-W-C(29)	36.2(2)	O(2)-Si(1)-C(15)	115.8(2)
C(31)-W-C(29)	59.1(2)	O(3)-Si(1)-C(15)	105.4(2)
C(1)-W-C(27)	109.1(2)	O(2)-Si(1)-C(6)	111.3(2)
C(2)-W-C(27)	163.4(2)	O(3)-Si(1)-C(6)	111.5(2)
O(2)-W-C(27)	92.66(18)	C(15)-Si(1)-C(6)	109.2(3)
C(30)-W-C(27)	58.6(2)	C(24)-Si(2)-C(26)	105.7(3)
C(31)-W-C(27)	34.3(2)	C(24)-Si(2)-C(25)	107.5(4)
C(29)-W-C(27)	57.7(2)	C(26)-Si(2)-C(25)	110.5(4)
C(1)-W-C(28)	129.2(3)	C(24)-Si(2)-C(2)	110.8(3)
C(2)-W-C(28)	129.5(2)	C(26)-Si(2)-C(2)	109.7(3)
O(2)-W-C(28)	78.1(2)	C(25)-Si(2)-C(2)	112.5(3)
C(30)-W-C(28)	57.9(2)	Si(1)-O(2)-W	116.2(2)
C(31)-W-C(28)	56.9(2)	C(2)-O(3)-Si(1)	114.4(3)
C(29)-W-C(28)	34.0(3)	O(1)-C(1)-W	176.8(6)
C(27)-W-C(28)	33.9(2)	O(3)-C(2)-Si(2)	105.6(3)
C(1)-W-P	82.25(19)	O(3)-C(2)-W	120.6(4)
C(2)-W-P	95.53(17)	Si(2)-C(2)-W	133.4(3)
O(2)-W-P	78.23(11)	C(7)-C(6)-C(11)	117.3(5)
C(30)-W-P	135.82(18)	C(7)-C(6)-Si(1)	117.1(4)
C(31)-W-P	102.92(15)	C(11)-C(6)-Si(1)	125.4(5)
C(29)-W-P	155.63(19)	C(8)-C(7)-C(6)	120.8(6)
C(27)-W-P	98.00(16)	C(8)-C(7)-C(12)	117.2(6)
C(28)-W-P	123.59(19)	C(6)-C(7)-C(12)	122.1(5)
C(5)-P-C(4)	100.4(3)	C(7)-C(8)-C(9)	122.2(6)
C(5)-P-C(3)	102.4(3)	C(10)-C(9)-C(8)	116.7(6)
O(2)-W-P	78.23(11)	C(10)-C(9)-C(13)	122.3(7)
C(8)-C(9)-C(13)	121.0(7)	C(18)-C(19)-C(20)	123.0(6)

C(9)-C(10)-C(11)	123.6(6)	C(19)-C(20)-C(15)	119.9(6)
C(10)-C(11)-C(6)	119.4(6)	C(19)-C(20)-C(23)	116.0(6)
C(10)-C(11)-C(14)	116.9(6)	C(15)-C(20)-C(23)	124.1(5)
C(6)-C(11)-C(14)	123.7(5)	C(28)-C(27)-C(32)	123.9(7)
C(20)-C(15)-C(16)	117.1(5)	C(31)-C(27)-W	70.2(4)
C(20)-C(15)-Si(1)	124.5(4)	C(28)-C(27)-W	74.7(4)
C(16)-C(15)-Si(1)	118.3(4)	C(32)-C(27)-W	129.4(5)
C(17)-C(16)-C(15)	120.6(6)	C(29)-C(28)-C(27)	109.1(6)
C(17)-C(16)-C(21)	116.9(6)	C(29)-C(28)-C(33)	126.5(7)
C(15)-C(16)-C(21)	122.4(5)	C(27)-C(28)-C(33)	124.3(8)
C(16)-C(17)-C(18)	122.0(6)	C(29)-C(28)-W	69.6(4)
C(19)-C(18)-C(17)	117.3(6)	C(27)-C(28)-W	71.4(4)
C(19)-C(18)-C(22)	121.5(6)	C(33)-C(28)-W	127.3(5)
C(17)-C(18)-C(22)	121.1(6)		

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W	18(1)	16(1)	16(1)	0(1)	-1(1)	1(1)
P	23(1)	16(1)	23(1)	1(1)	-2(1)	2(1)
Si(1)	19(1)	16(1)	19(1)	0(1)	0(1)	0(1)
Si(2)	22(1)	29(1)	23(1)	0(1)	5(1)	0(1)
O(1)	27(2)	38(3)	39(3)	3(2)	3(2)	-10(2)
O(2)	17(2)	22(2)	21(2)	-3(2)	5(2)	-2(2)
O(3)	21(2)	21(2)	22(2)	-4(2)	2(2)	-2(2)
C(1)	26(3)	27(3)	25(3)	-2(3)	-1(3)	1(3)
C(2)	22(3)	21(3)	14(3)	-4(3)	-4(2)	3(2)
C(3)	32(3)	24(3)	23(3)	1(3)	-4(3)	4(3)
C(4)	38(4)	17(3)	55(5)	7(3)	-3(3)	-2(3)
C(5)	29(4)	39(4)	38(4)	-4(3)	0(3)	16(3)
C(6)	27(3)	16(3)	21(3)	-4(2)	-8(3)	-3(2)
C(7)	27(3)	19(3)	21(3)	-4(2)	-7(3)	-4(3)
C(8)	37(4)	34(4)	25(3)	5(3)	-9(3)	-16(3)
C(9)	44(4)	24(3)	31(3)	7(3)	-13(3)	-9(3)
C(10)	32(4)	22(3)	44(4)	0(3)	-12(3)	3(3)
C(11)	31(3)	21(3)	23(3)	-3(2)	-10(3)	-1(3)
C(12)	26(3)	30(4)	27(3)	0(3)	1(3)	-4(3)
C(13)	58(5)	38(4)	64(6)	26(4)	-17(5)	-11(4)
C(14)	32(4)	25(3)	40(4)	-3(3)	-6(3)	9(3)
C(15)	19(3)	18(3)	22(3)	2(2)	5(2)	-4(2)
C(16)	26(3)	22(3)	23(3)	7(3)	-1(3)	-8(2)
C(17)	37(3)	27(3)	20(3)	4(3)	-7(3)	-13(3)
C(18)	27(3)	29(3)	27(4)	9(3)	-6(3)	-6(3)
C(19)	25(3)	26(3)	49(4)	15(3)	-5(3)	-1(3)
C(20)	24(3)	19(3)	29(4)	3(2)	-2(3)	-5(2)
C(21)	30(4)	28(3)	27(3)	-8(3)	-3(3)	-3(3)

C(22)	49(5)	47(5)	46(5)	9(4)	-22(4)	-4(4)
C(23)	25(3)	29(3)	41(4)	0(3)	0(3)	4(3)
C(24)	35(4)	47(5)	33(4)	-12(3)	16(3)	2(3)
C(25)	25(3)	53(5)	39(4)	-3(4)	6(3)	11(3)
C(26)	37(4)	40(4)	25(4)	4(3)	6(3)	2(3)
C(27)	27(3)	35(4)	17(3)	-1(3)	-5(3)	1(3)
C(28)	56(5)	31(4)	12(3)	1(3)	-4(3)	-14(3)
C(29)	65(5)	25(3)	17(3)	-1(4)	-7(4)	8(3)
C(30)	26(3)	42(4)	29(4)	-3(3)	-10(3)	12(3)
C(31)	23(3)	25(3)	22(3)	-5(3)	-6(3)	-2(2)
C(32)	43(4)	70(6)	31(4)	-5(4)	-2(4)	18(4)
C(33)	83(6)	86(7)	22(4)	-1(4)	2(4)	-52(6)
C(34)	142(9)	38(4)	26(4)	3(4)	-23(6)	37(5)
C(35)	33(4)	117(8)	33(5)	-1(5)	-9(3)	27(5)
C(36)	56(4)	34(4)	33(4)	-6(4)	-2(4)	-16(3)

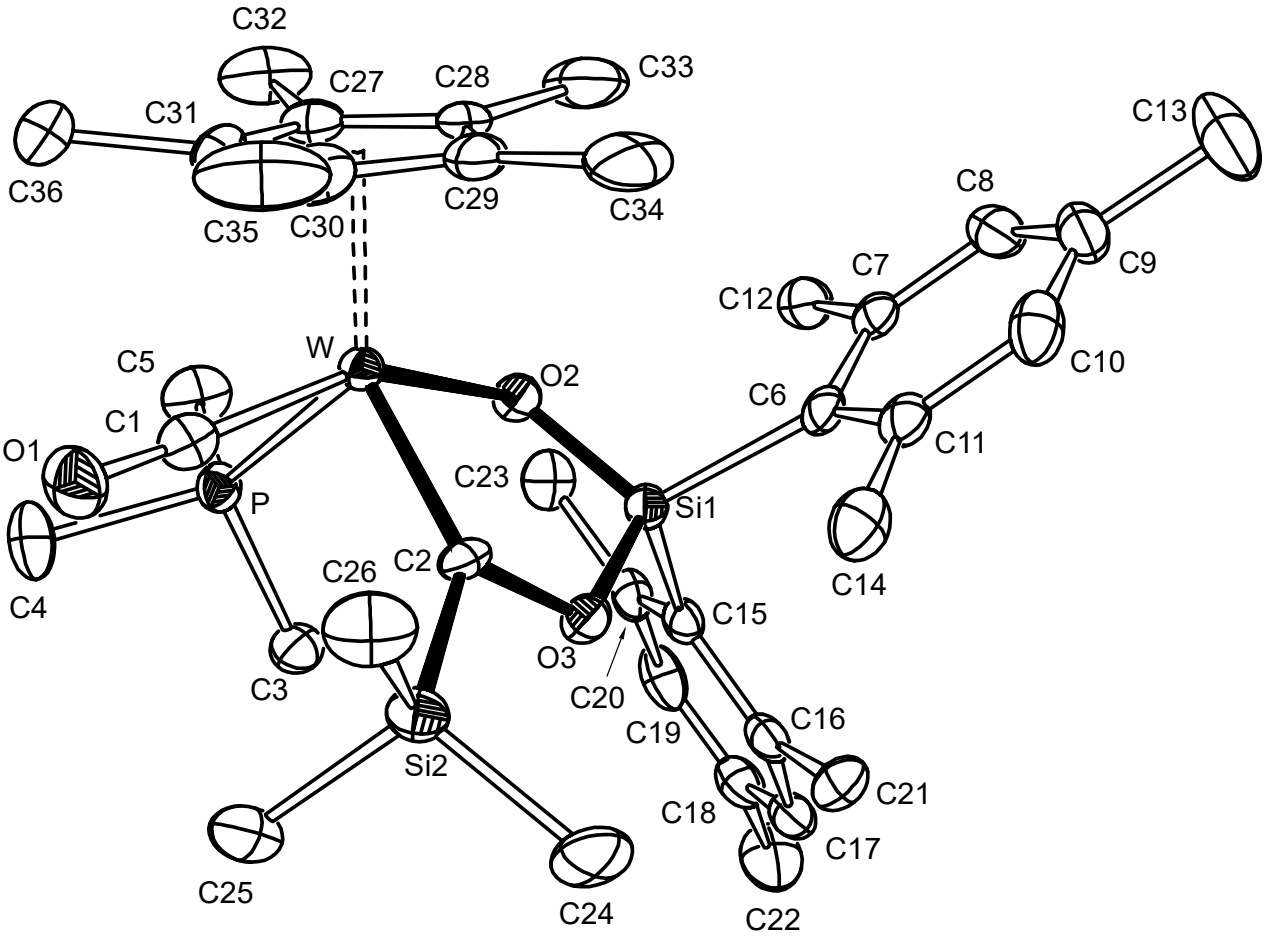

Figure S2. ORTEP drawing of **5**. (thermal ellipsoids at the 50% probability level).

1.4 X-ray crystal structure determination of Cp*W(OSiMes$_2$O){≡C(SiMe$_3$)}(PMe$_3$) (7). A single crystal of **7** suitable for X-ray crystal structure determination was obtained by recrystallization from toluene:hexane (1:5). The final residue *R*1 and the weighted *wR*2 were 0.0273 and 0.0696, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters are listed in Tables S9, S10, S11, and S12, respectively. ORTEP drawing of **7** with atomic numbering schemes is shown in Figure S3.

Table S9. Crystal data and structure refinement for complex **7**.

Complex	Cp*W(OSiMes$_2$O){≡C(SiMe$_3$)}(PMe$_3$) (**7**)
Empirical formula	$C_{35}H_{55}O_2PSi_2W$
Formula weight	778.79
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	*a* = 41.020(5) Å
	b = 10.8934(11) Å β = 107.113(2)°
	c = 16.9740(19) Å
Volume (Å^3)	7249.0(14)
Z	8
D_{calc} (Mg / m^3)	1.427
Absorption coefficient (mm^{-1})	3.325
F(000)	3184
Crystal Size (mm^3)	0.17 × 0.12 × 0.11
Theta Range for data collection (°)	2.942 – 27.548
Index ranges	$-52 \le h \le 53$, $-14 \le k \le 14$, $-22 \le l \le 22$
Reflections collected	57813
Independent reflections [*R*(int)]	8310 [0.0691]
Absorption correction	Multi-scan
Maximum and minimum transmission	1.000 and 0.827
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8310 / 0 / 387
Goodness-of-fit on F^2	1.159
Final *R* indices[a] [$I > 2\sigma(I)$]	*R*1 = 0.0256, *wR*2 = 0.0692
R indices[a] (all data)	*R*1 = 0.0273, *wR*2 = 0.0696
Largest difference in peak and hole (eÅ^{-3})	2.454 and -1.113

[a]$R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.
$wR2 = [\Sigma[w\,(Fo^2 - Fc^2)^2] / \Sigma[w\,(Fo^2)^2]]^{0.5}$,
calc $w = 1 / [\sigma^2(Fo^2) + (0.0660P)^2 + 327.4912P]$ where $P = (Fo^2 + 2Fc^2) / 3$.

Table S10. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **7**. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	*U*(eq)[a)]
W	8651(1)	3435(1)	5157(1)	14(1)
P	8929(1)	2464(1)	4192(1)	22(1)
Si(1)	9491(1)	4835(1)	6017(1)	21(1)
Si(2)	8603(1)	1501(1)	6169(1)	16(1)
O(1)	8644(1)	1515(2)	5242(1)	18(1)
O(2)	8544(1)	2980(2)	6230(1)	17(1)
C(1)	9071(1)	4085(3)	5570(2)	18(1)
C(2)	9616(1)	5932(5)	5299(3)	42(1)
C(3)	9834(1)	3648(4)	6334(3)	40(1)
C(4)	9478(1)	5749(3)	6941(2)	27(1)
C(5)	9007(1)	963(3)	6965(2)	19(1)
C(6)	9201(1)	1696(3)	7627(2)	21(1)
C(7)	9497(1)	1225(4)	8188(2)	25(1)
C(8)	9617(1)	50(4)	8113(2)	26(1)
C(9)	9431(1)	-661(3)	7457(2)	26(1)
C(10)	9131(1)	-233(3)	6888(2)	20(1)
C(11)	9108(1)	3011(3)	7748(2)	26(1)
C(12)	9946(1)	-416(5)	8712(3)	39(1)
C(13)	8946(1)	-1079(3)	6196(2)	31(1)
C(14)	8228(1)	528(3)	6246(2)	18(1)
C(15)	8047(1)	-312(3)	5638(2)	23(1)
C(16)	7781(1)	-1008(3)	5769(2)	24(1)
C(17)	7681(1)	-916(3)	6475(2)	24(1)
C(18)	7854(1)	-71(3)	7066(2)	22(1)
C(19)	8122(1)	642(3)	6962(2)	19(1)
C(20)	8120(1)	-516(4)	4818(2)	31(1)
C(21)	7393(1)	-1688(4)	6586(3)	34(1)
C(22)	8291(1)	1544(3)	7639(2)	24(1)
C(23)	9280(1)	1498(4)	4775(3)	31(1)
C(24)	9139(1)	3403(4)	3599(3)	39(1)
C(25)	8676(1)	1386(4)	3430(3)	33(1)
C(26)	8052(1)	3773(3)	4191(2)	24(1)

C(27)	8056(1)	4201(3)	4967(2)	22(1)
C(28)	8312(1)	5155(3)	5207(2)	18(1)
C(29)	8449(1)	5351(3)	4545(2)	20(1)
C(30)	8300(1)	4463(3)	3927(2)	24(1)
C(31)	7829(1)	2770(4)	3710(3)	37(1)
C(32)	7837(1)	3766(4)	5471(3)	30(1)
C(33)	8385(1)	5884(3)	5989(2)	26(1)
C(34)	8681(1)	6390(3)	4465(2)	24(1)
C(35)	8313(1)	4516(4)	3053(2)	34(1)

Table S11. Bond lengths [Å] and angles [°] for **7**.

W-C(1)	1.802(3)	C(7)-C(8)	1.391(5)
W-O(2)	2.056(2)	C(8)-C(9)	1.387(5)
W-O(1)	2.097(2)	C(8)-C(12)	1.519(5)
W-C(28)	2.350(3)	C(9)-C(10)	1.400(5)
W-C(29)	2.369(3)	C(10)-C(13)	1.510(5)
W-C(30)	2.432(3)	C(14)-C(19)	1.410(5)
W-P	2.4898(9)	C(14)-C(15)	1.415(5)
W-C(27)	2.508(3)	C(15)-C(16)	1.399(5)
W-C(26)	2.547(4)	C(15)-C(20)	1.523(5)
P-C(24)	1.819(4)	C(16)-C(17)	1.379(5)
P-C(23)	1.822(4)	C(17)-C(18)	1.392(5)
P-C(25)	1.827(4)	C(17)-C(21)	1.509(5)
Si(1)-C(1)	1.855(4)	C(18)-C(19)	1.398(5)
Si(1)-C(3)	1.870(4)	C(19)-C(22)	1.517(5)
Si(1)-C(4)	1.870(4)	C(26)-C(27)	1.393(5)
Si(1)-C(2)	1.881(4)	C(26)-C(30)	1.438(5)
Si(2)-O(1)	1.630(2)	C(26)-C(31)	1.504(5)
Si(2)-O(2)	1.637(2)	C(27)-C(28)	1.447(5)
Si(2)-C(5)	1.897(4)	C(27)-C(32)	1.491(5)
Si(2)-C(14)	1.906(3)	C(28)-C(29)	1.414(4)
C(5)-C(6)	1.417(5)	C(28)-C(33)	1.499(5)
C(5)-C(10)	1.418(5)	C(29)-C(30)	1.426(5)
C(6)-C(7)	1.401(5)	C(29)-C(34)	1.510(5)
C(6)-C(11)	1.512(5)		
C(1)-W-O(2)	100.27(12)	O(1)-W-C(28)	140.57(10)
C(1)-W-O(1)	113.30(12)	C(1)-W-C(29)	89.72(13)
O(2)-W-O(1)	71.80(9)	O(2)-W-C(29)	117.53(10)
C(1)-W-C(28)	100.39(13)	O(1)-W-C(29)	154.00(11)
O(2)-W-C(28)	82.92(10)	C(28)-W-C(29)	34.85(11)

C(1)-W-C(30)	114.17(14)	C(25)-P-W	117.64(14)
O(2)-W-C(30)	130.15(11)	C(1)-Si(1)-C(3)	110.05(18)
O(1)-W-C(30)	120.14(11)	C(1)-Si(1)-C(4)	109.03(16)
C(28)-W-C(30)	57.12(11)	C(3)-Si(1)-C(4)	109.32(19)
C(29)-W-C(30)	34.51(12)	C(1)-Si(1)-C(2)	114.33(18)
C(1)-W-P	81.57(10)	C(3)-Si(1)-C(2)	107.5(2)
O(2)-W-P	137.64(7)	C(4)-Si(1)-C(2)	106.5(2)
O(1)-W-P	68.90(6)	O(1)-Si(2)-O(2)	96.40(12)
C(28)-W-P	138.86(8)	O(1)-Si(2)-C(5)	111.91(14)
C(29)-W-P	104.75(8)	O(2)-Si(2)-C(5)	111.99(14)
C(30)-W-P	84.30(9)	O(1)-Si(2)-C(14)	112.71(14)
C(1)-W-C(27)	134.50(13)	O(2)-Si(2)-C(14)	113.89(14)
O(2)-W-C(27)	74.98(10)	C(5)-Si(2)-C(14)	109.48(14)
O(1)-W-C(27)	107.98(11)	Si(2)-O(1)-W	94.76(10)
C(28)-W-C(27)	34.46(11)	Si(2)-O(2)-W	96.14(11)
C(29)-W-C(27)	56.57(11)	W-C(1)-Si(1)	176.5(2)
C(30)-W-C(27)	55.18(11)	C(6)-C(5)-C(10)	117.3(3)
P-W-C(27)	132.31(8)	C(6)-C(5)-Si(2)	124.0(3)
C(1)-W-C(26)	145.46(13)	C(10)-C(5)-Si(2)	118.7(3)
O(2)-W-C(26)	100.85(11)	C(7)-C(6)-C(5)	120.3(3)
O(1)-W-C(26)	99.15(11)	C(7)-C(6)-C(11)	117.3(3)
C(28)-W-C(26)	55.88(12)	C(5)-C(6)-C(11)	122.4(3)
C(29)-W-C(26)	56.21(12)	C(8)-C(7)-C(6)	122.3(3)
C(30)-W-C(26)	33.48(12)	C(9)-C(8)-C(7)	117.4(3)
P-W-C(26)	100.34(9)	C(9)-C(8)-C(12)	121.5(4)
C(27)-W-C(26)	31.97(11)	C(7)-C(8)-C(12)	121.0(4)
C(24)-P-C(23)	101.4(2)	C(8)-C(9)-C(10)	122.2(3)
C(24)-P-C(25)	103.4(2)	C(9)-C(10)-C(5)	120.5(3)
C(23)-P-C(25)	101.9(2)	C(9)-C(10)-C(13)	118.1(3)
C(24)-P-W	120.53(14)	C(5)-C(10)-C(13)	121.4(3)
C(23)-P-W	109.27(13)	C(19)-C(14)-C(15)	117.2(3)
C(19)-C(14)-Si(2)	118.0(2)	C(26)-C(27)-W	75.5(2)

C(15)-C(14)-Si(2)	124.8(3)	C(28)-C(27)-W	66.79(18)
C(16)-C(15)-C(14)	120.0(3)	C(32)-C(27)-W	123.3(2)
C(16)-C(15)-C(20)	116.0(3)	C(29)-C(28)-C(27)	108.0(3)
C(14)-C(15)-C(20)	124.0(3)	C(29)-C(28)-C(33)	127.0(3)
C(17)-C(16)-C(15)	122.9(3)	C(27)-C(28)-C(33)	124.7(3)
C(16)-C(17)-C(18)	117.1(3)	C(29)-C(28)-W	73.32(19)
C(16)-C(17)-C(21)	120.9(4)	C(27)-C(28)-W	78.76(19)
C(18)-C(17)-C(21)	122.1(4)	C(33)-C(28)-W	119.3(2)
C(17)-C(18)-C(19)	121.9(3)	C(28)-C(29)-C(30)	107.4(3)
C(18)-C(19)-C(14)	120.8(3)	C(28)-C(29)-C(34)	126.4(3)
C(18)-C(19)-C(22)	117.7(3)	C(30)-C(29)-C(34)	125.9(3)
C(14)-C(19)-C(22)	121.5(3)	C(28)-C(29)-W	71.83(18)
C(27)-C(26)-C(30)	107.9(3)	C(30)-C(29)-W	75.2(2)
C(27)-C(26)-C(31)	126.3(4)	C(34)-C(29)-W	123.4(2)
C(30)-C(26)-C(31)	125.8(3)	C(29)-C(30)-C(26)	108.3(3)
C(27)-C(26)-W	72.5(2)	C(29)-C(30)-C(35)	124.7(3)
C(30)-C(26)-W	68.89(19)	C(26)-C(30)-C(35)	124.2(3)
C(31)-C(26)-W	124.3(3)	C(29)-C(30)-W	70.32(19)
C(26)-C(27)-C(28)	108.2(3)	C(26)-C(30)-W	77.6(2)
C(26)-C(27)-C(32)	126.6(3)	C(35)-C(30)-W	133.0(3)
C(28)-C(27)-C(32)	125.2(3)		

Symmetry transformations used to generate equivalent atoms:

Table S12. Anisotropic displacement parameters (Å^2 × 10^3) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W	16(1)	13(1)	13(1)	-1(1)	6(1)	-1(1)
P	28(1)	20(1)	24(1)	-5(1)	16(1)	-3(1)
Si(1)	16(1)	23(1)	24(1)	-3(1)	7(1)	-2(1)
Si(2)	21(1)	14(1)	15(1)	-1(1)	7(1)	-2(1)
O(1)	26(1)	15(1)	17(1)	-2(1)	10(1)	-2(1)
O(2)	23(1)	16(1)	16(1)	2(1)	11(1)	1(1)
C(1)	19(2)	17(2)	20(2)	2(1)	7(1)	2(1)
C(2)	35(2)	54(3)	41(2)	2(2)	15(2)	-19(2)
C(3)	25(2)	42(2)	49(3)	-16(2)	4(2)	8(2)
C(4)	26(2)	23(2)	31(2)	-5(2)	6(2)	0(2)
C(5)	20(2)	17(2)	21(2)	2(1)	10(1)	-1(1)
C(6)	25(2)	22(2)	18(2)	-1(1)	10(1)	-5(1)
C(7)	22(2)	29(2)	24(2)	-1(1)	7(1)	-5(2)
C(8)	22(2)	32(2)	27(2)	6(2)	12(2)	1(2)
C(9)	24(2)	22(2)	34(2)	5(2)	14(2)	5(1)
C(10)	23(2)	17(2)	23(2)	1(1)	10(1)	-3(1)
C(11)	30(2)	22(2)	24(2)	-7(1)	7(2)	-7(2)
C(12)	25(2)	53(3)	37(2)	8(2)	8(2)	6(2)
C(13)	36(2)	17(2)	36(2)	-4(2)	7(2)	1(2)
C(14)	18(2)	15(2)	21(2)	1(1)	5(1)	0(1)
C(15)	23(2)	19(2)	26(2)	-1(1)	5(1)	-2(1)
C(16)	24(2)	18(2)	28(2)	-1(1)	2(2)	-7(1)
C(17)	18(2)	22(2)	31(2)	8(1)	4(1)	-2(1)
C(18)	21(2)	24(2)	24(2)	5(1)	10(1)	-1(1)
C(19)	18(2)	17(2)	22(2)	3(1)	5(1)	1(1)
C(20)	34(2)	32(2)	28(2)	-11(2)	9(2)	-13(2)
C(21)	25(2)	33(2)	43(2)	8(2)	6(2)	-8(2)
C(22)	25(2)	24(2)	26(2)	0(1)	10(2)	-4(1)

C(23)	32(2)	30(2)	38(2)	-5(2)	19(2)	6(2)
C(24)	53(3)	32(2)	46(3)	-3(2)	35(2)	-5(2)
C(25)	43(2)	31(2)	29(2)	-13(2)	16(2)	-6(2)
C(26)	18(2)	26(2)	24(2)	-1(1)	0(1)	2(1)
C(27)	20(2)	22(2)	23(2)	4(1)	7(1)	3(1)
C(28)	19(2)	18(2)	16(1)	2(1)	6(1)	3(1)
C(29)	24(2)	21(2)	18(2)	7(1)	8(1)	7(1)
C(30)	26(2)	30(2)	16(2)	2(1)	5(1)	6(2)
C(31)	28(2)	39(2)	38(2)	-10(2)	0(2)	-5(2)
C(32)	21(2)	32(2)	40(2)	4(2)	14(2)	-1(2)
C(33)	35(2)	21(2)	22(2)	-1(1)	11(2)	4(2)
C(34)	31(2)	21(2)	24(2)	5(1)	14(2)	1(1)
C(35)	44(2)	42(2)	16(2)	2(2)	9(2)	8(2)

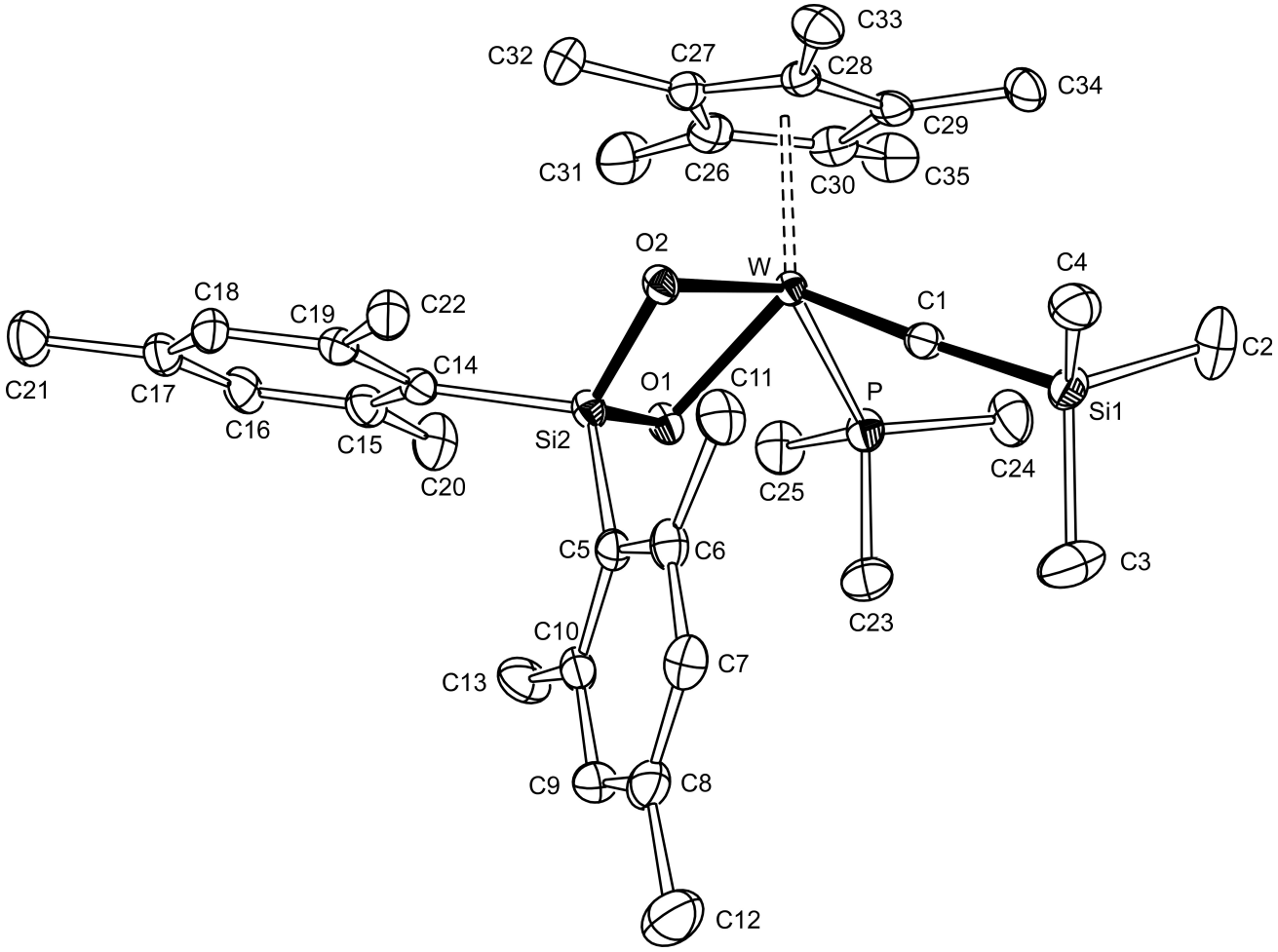

Figure S3. ORTEP drawing of **7**. (thermal ellipsoids at the 50% probability level).

2.1 NMR and IR spectra of 1b, 5, and 7. ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectra of **1b** (Figures S4, S5, S6, and S7), ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR and IR spectra of **5** (Figures S8, S9, S10, S11, and S12) and **7** (Figures S13, S14, S15, S16 and S17) are shown below.

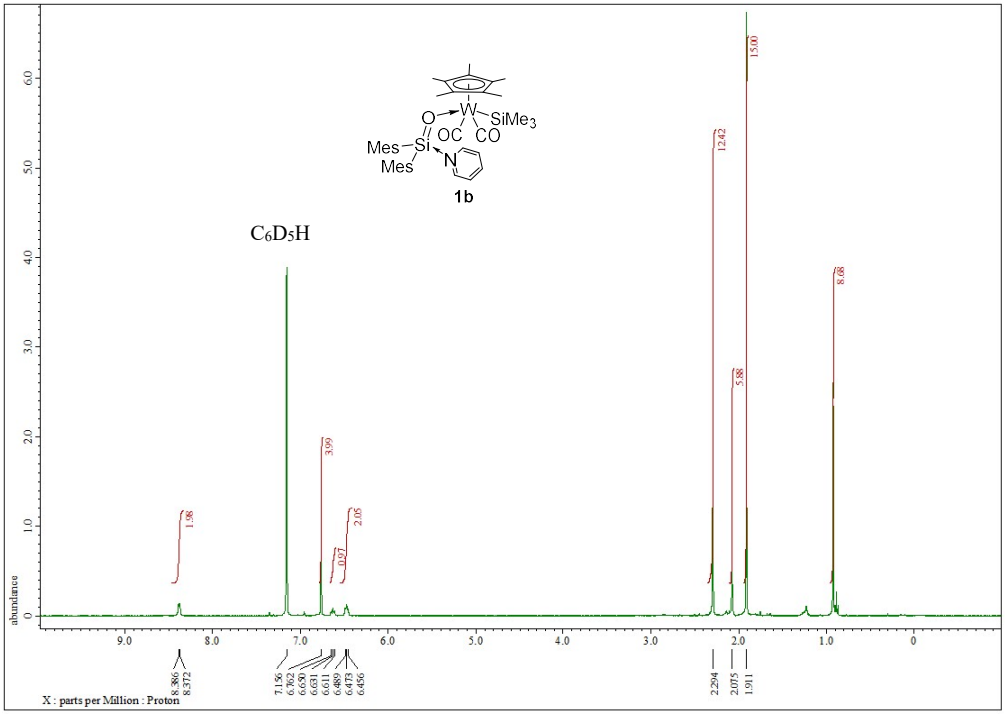

Figure S4. ^{1}H NMR spectrum of Cp*(OC)$_2$W{O=SiMes$_2$(py)}(SiMe$_3$) (**1b**) (300 MHz, C_6D_6).

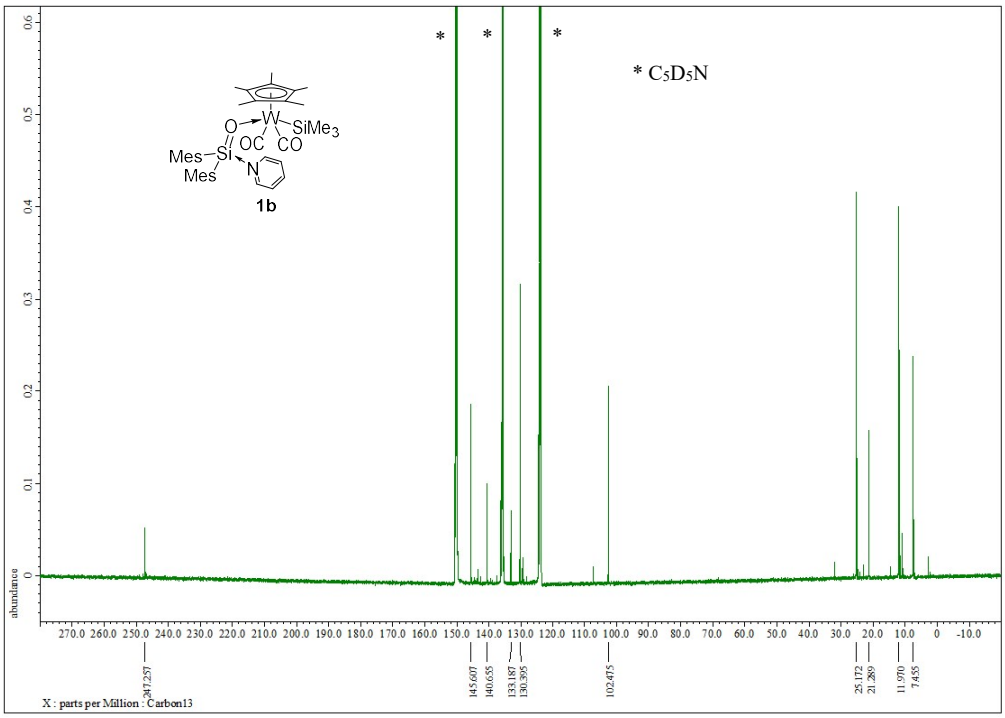

Figure S5. ^{13}C NMR spectrum of Cp*(OC)$_2$W{O=SiMes$_2$(py)}(SiMe$_3$) (**1b**) (150.6 MHz, C_5D_5N).

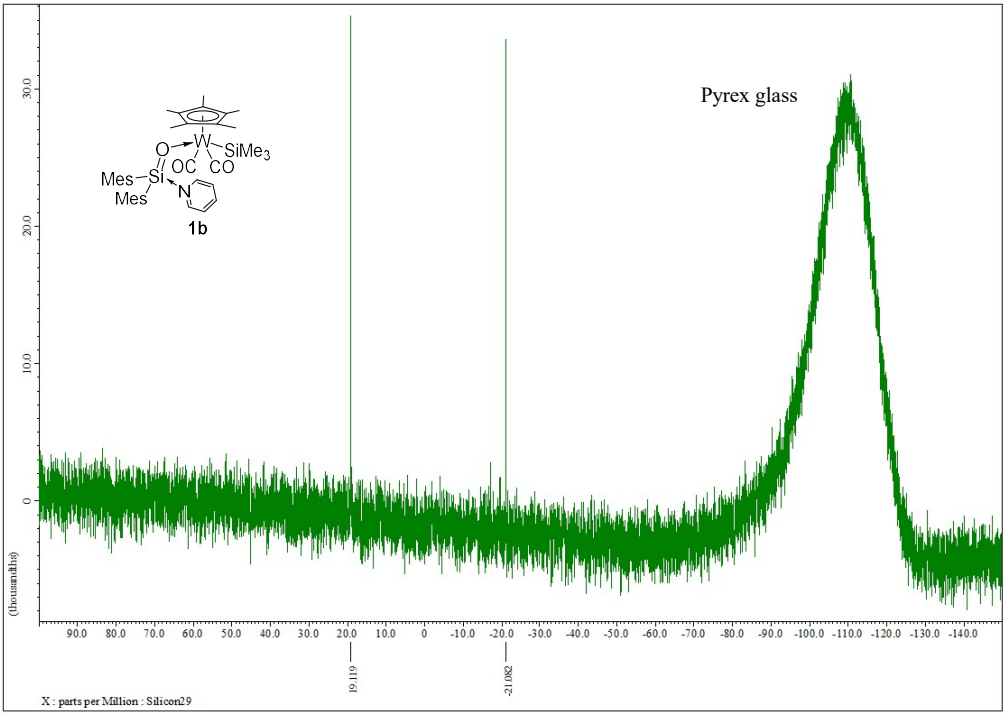

Figure S6. ^{29}Si NMR spectrum of Cp*(OC)$_2$W{O=SiMes$_2$(py)}(SiMe$_3$) (**1b**) (119.4 MHz, C_5D_5N).

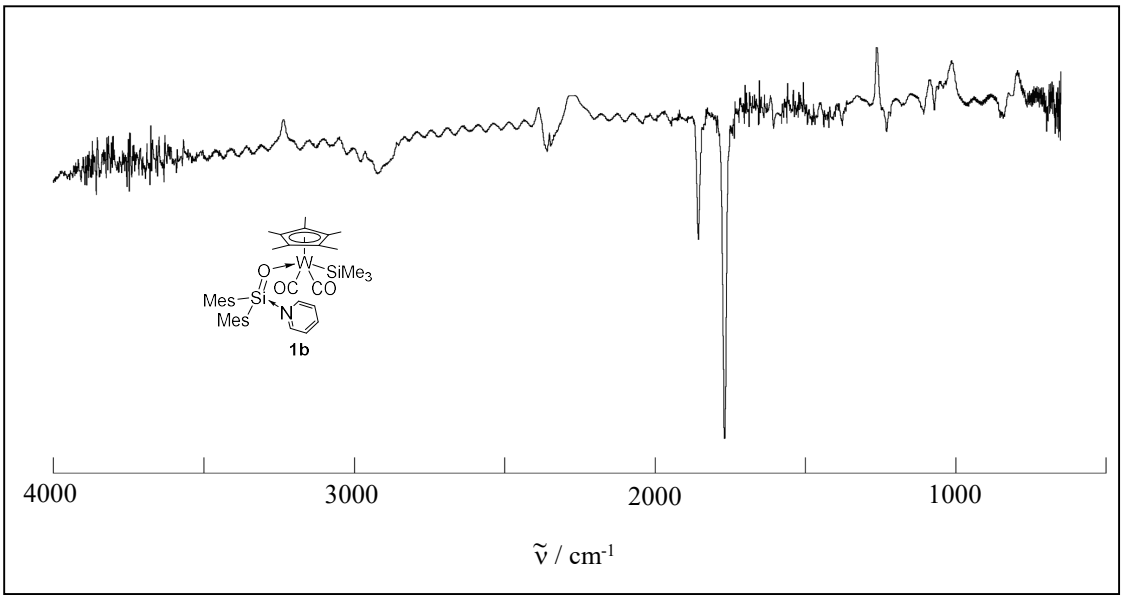

Figure S7. IR spectrum of Cp*(OC)$_2$W{O=SiMes$_2$(py)}(SiMe$_3$) (**1b**) (C_6D_6).

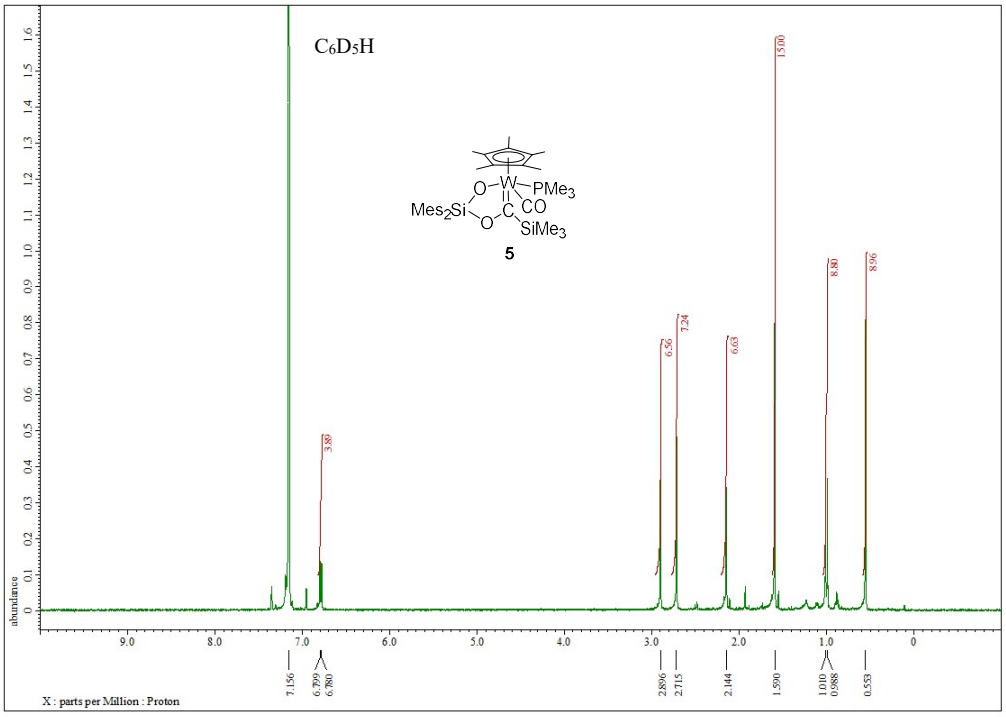

Figure S8. ^{1}H NMR spectrum of Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (**5**) (300 MHz, C_6D_6).

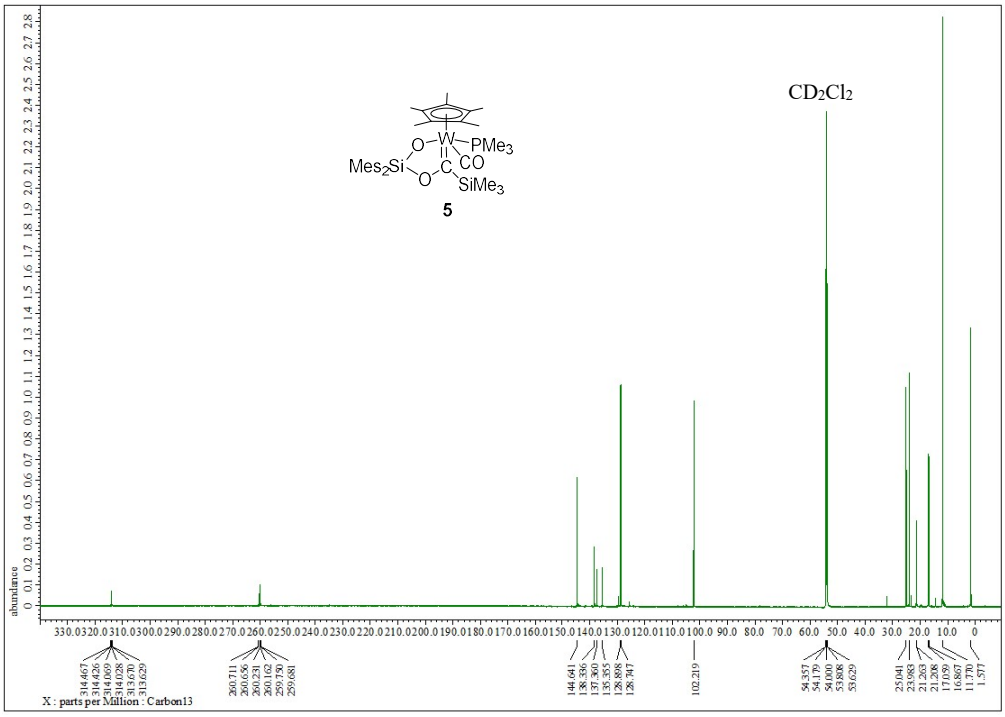

Figure S9. ^{13}C NMR spectrum of Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (**5**) (150.6 MHz, CD_2Cl_2).

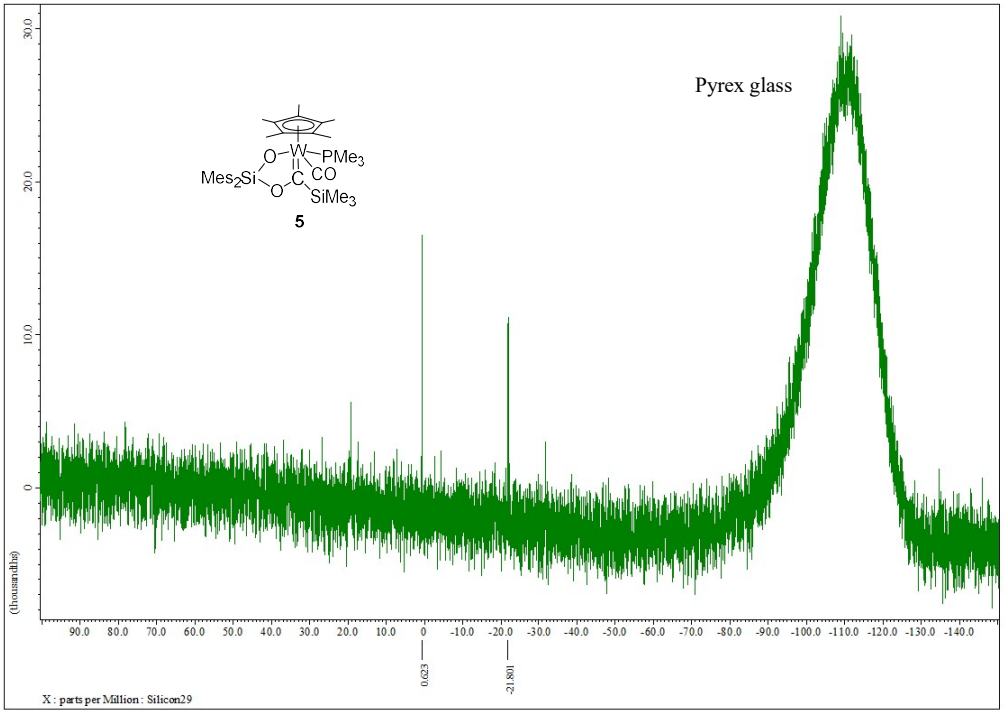

Figure S10. ^{29}Si NMR spectrum of Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (**5**) (119.4 MHz, C_6D_6).

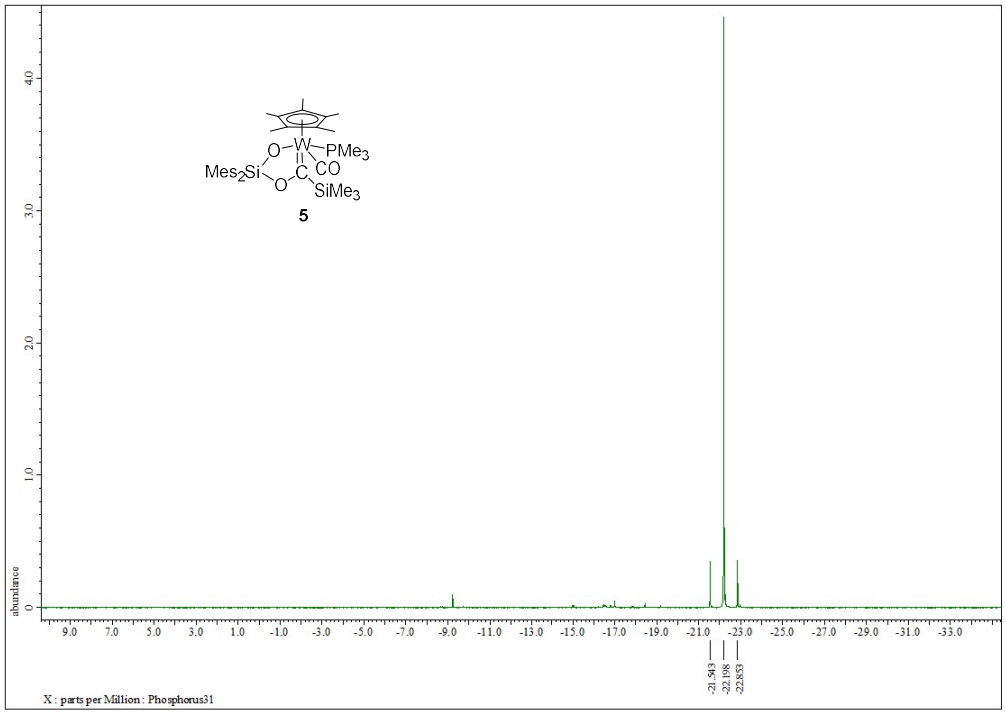

Figure S11. ^{31}P NMR spectrum of Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (**5**) (242.9 MHz, C_6D_6).

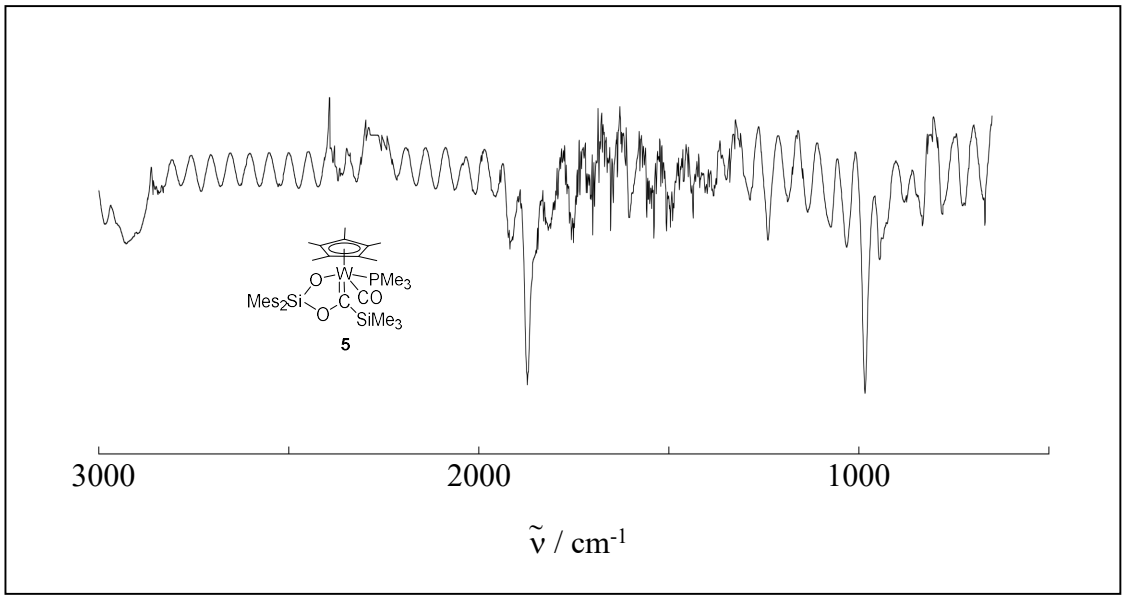

Figure S12. IR spectrum of Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (**5**) (C$_6$D$_6$).

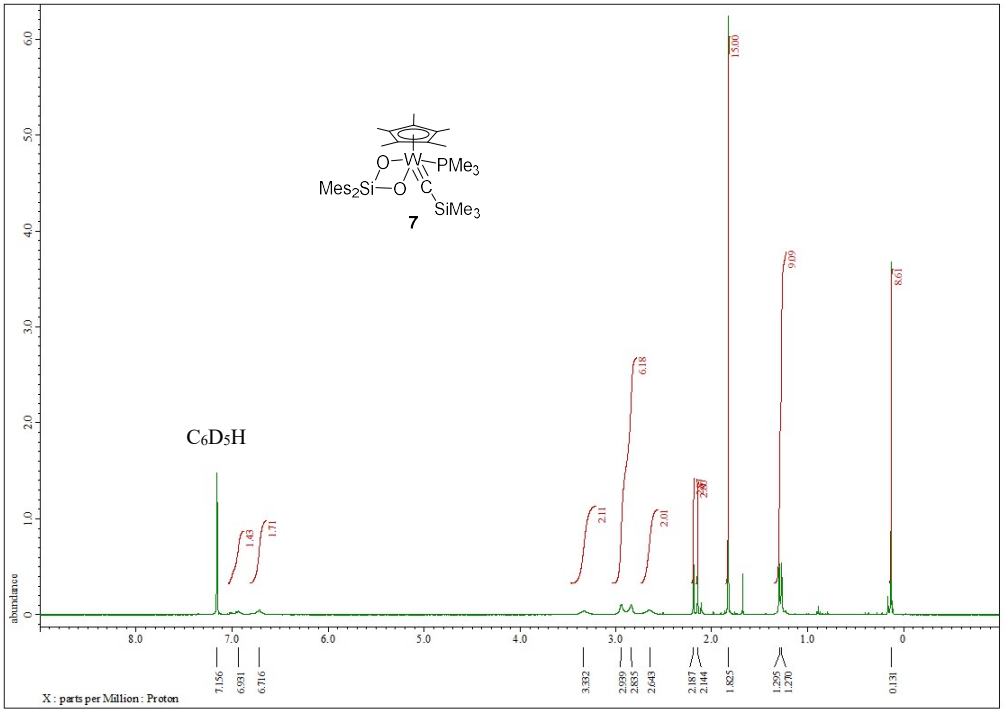

Figure S13. ^{1}H NMR spectrum of Cp*(OC)W(OSiMes$_2$O){≡C(SiMe$_3$)}(PMe$_3$) (**7**) (400 MHz, C$_6$D$_6$).

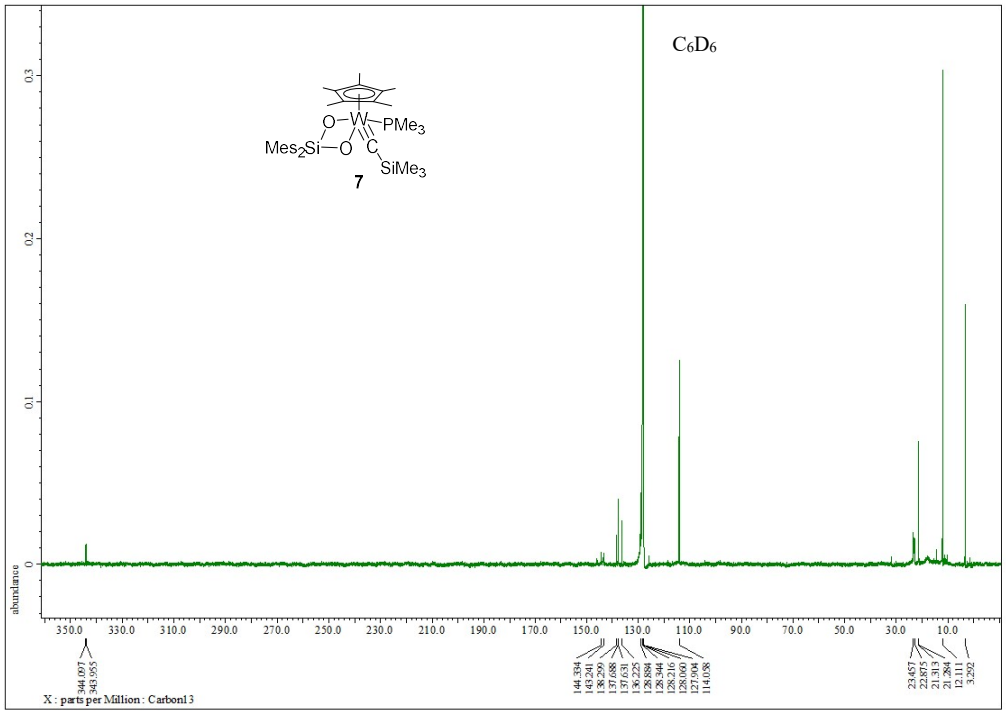

Figure S14. ^{13}C NMR spectrum of Cp*(OC)W(OSiMes$_2$O){≡C(SiMe$_3$)}(PMe$_3$) (**7**) (150.9 MHz, C_6D_6).

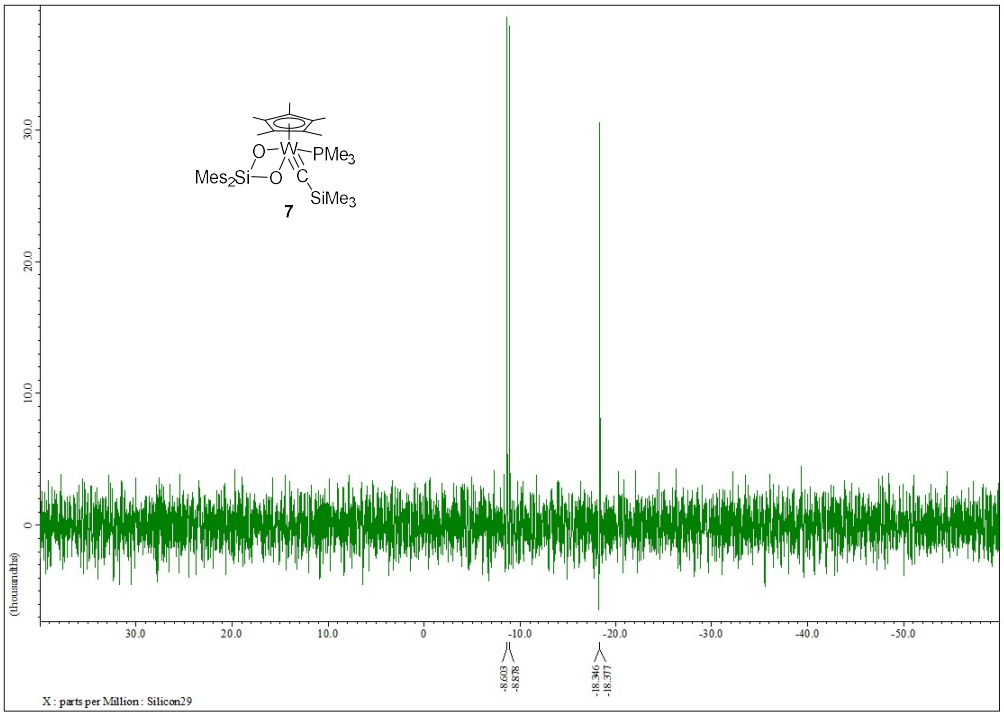

Figure S15. ^{29}Si NMR spectrum of Cp*(OC)W(OSiMes$_2$O){≡C(SiMe$_3$)}(PMe$_3$) (**7**) (119.2 MHz, C_7D_8).

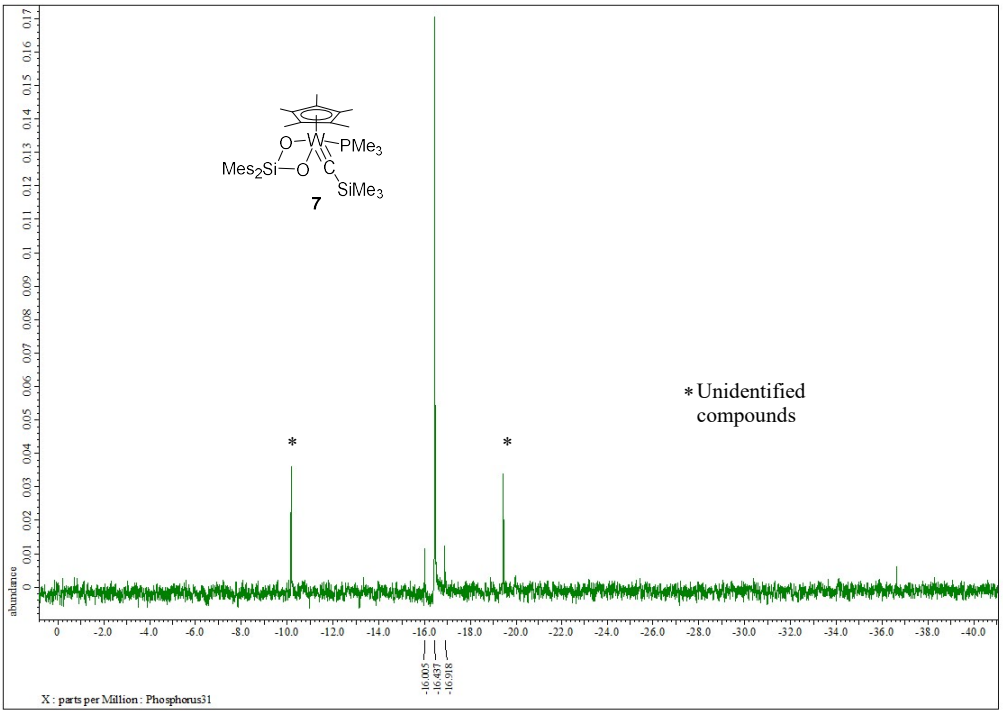

Figure S16. ^{31}P NMR spectrum of Cp*(OC)W{≡C(SiMe$_3$)}(OSiMes$_2$O)(PMe$_3$) (**7**) (242.9 MHz, C_6D_6).

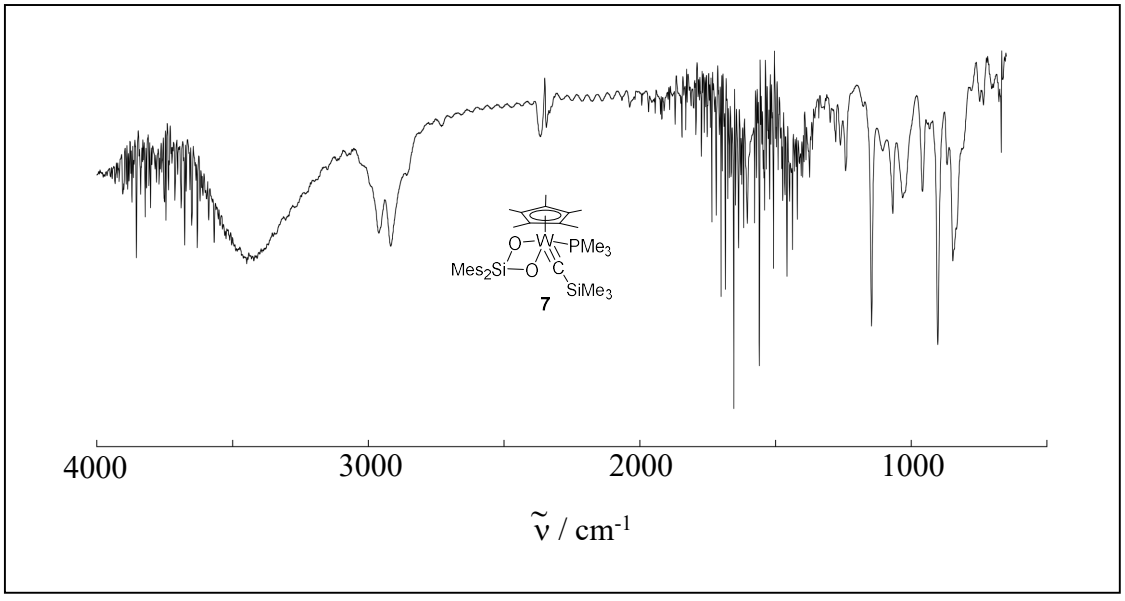

Figure S17. IR spectrum of Cp*(OC)W(OSiMes$_2$O){≡C(SiMe$_3$)}(PMe$_3$) (**7**) (KBr).

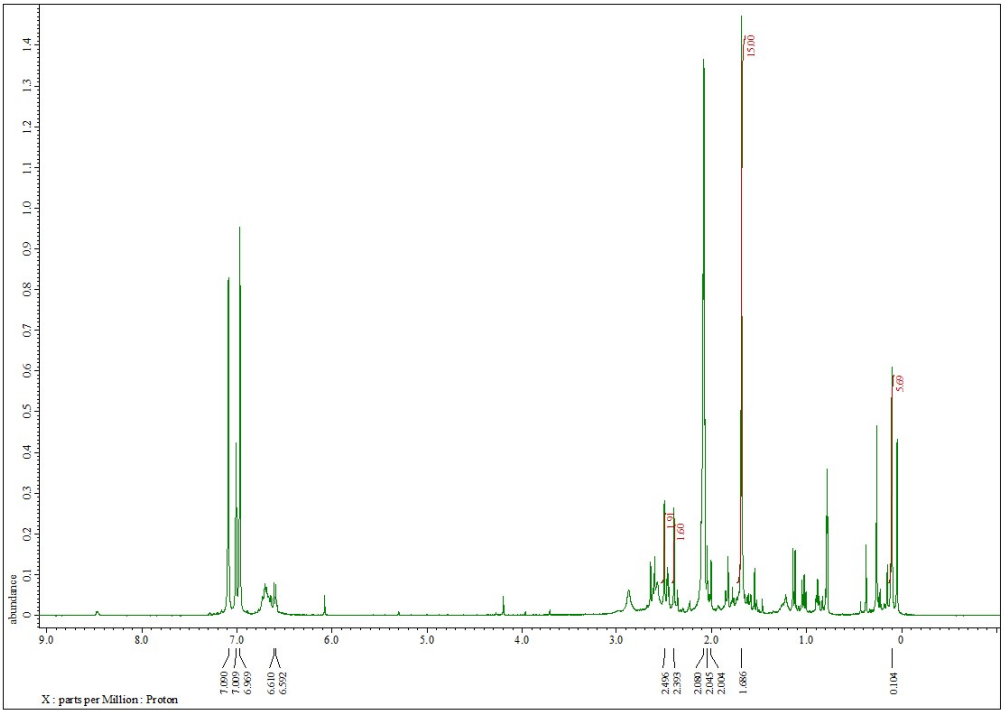

Figure S18. ^{1}H NMR spectrum of a resultant mixture in the reaction of Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (**5**) with 1 atm CO in C_7D_8 at 60 °C for 2 h (300 MHz, C_7D_8).

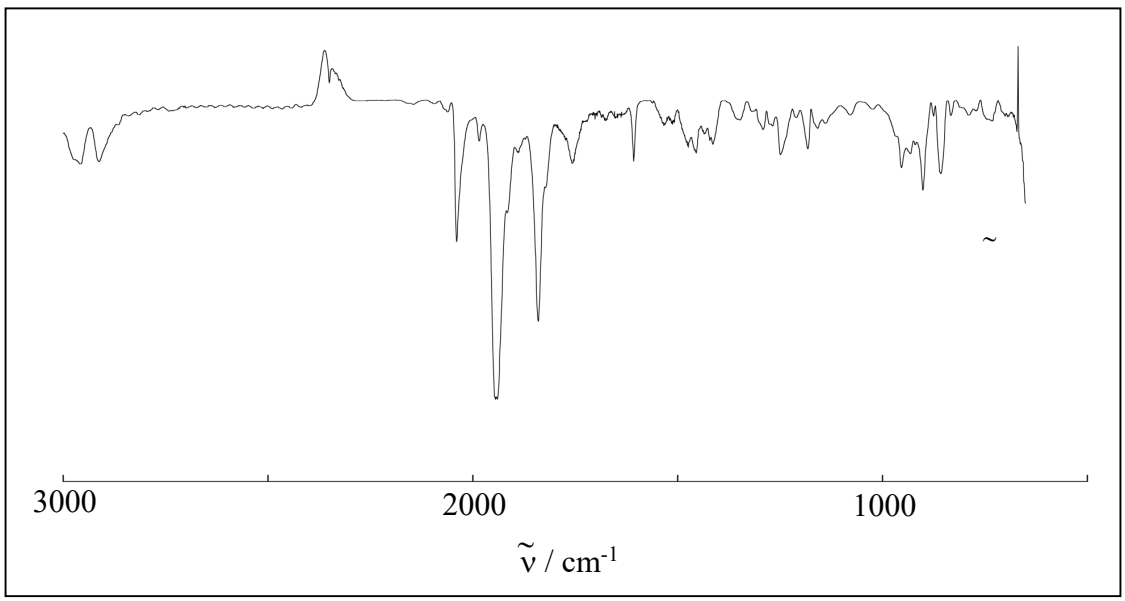

Figure S19. IR spectrum of a resultant mixture in the reaction of Cp*(OC)W{=C(SiMe$_3$)OSiMes$_2$O}(PMe$_3$) (**5**) with 1 atm CO in C_7D_8 at 60 °C for 2 h (C_7D_8).

References

1. Sheldrick, G. M., SHELX-97, Program for Crystal Structure Determination, University of Göttingen, Göttingen, Germany, 1997.