

Supporting information

Synthesis and Structure of a Pyridine-Stabilized Silanone Molybdenum Complex and its Reactions with PMe₃ and Acetone

Takako Muraoka,^{1*} Yuzuki Suzuki,¹ Masato Tsuchimoto,¹ Gama Trigagema,¹ Keiji Ueno¹ and
Shinji Koyama²

¹ Division of Molecular Science, Graduate School of Science and Technology, Gunma University,
Kiryu 376-8515, Japan

² Division of Mechanical Science and Technology, Graduate School of Science and Technology,
Gunma University, Kiryu 376-8515, Japan

Table of Contents

1. X-ray Crystallographic Determinations of **2b**, **6**, **8** and **9** and Molecular Structures of **2b**, **6**, **8** and **9**

Table S1; Crystal data and structure refinement for complex 2b .	S5
Table S2; Atomic coordinates and equivalent isotropic displacement parameters for 2b .	S6-S7
Table S3; Bond lengths and angles for 2b .	S8-S10
Table S4; Anisotropic displacement parameters for 2b .	S11-S12
Figure S1; ORTEP drawing of 2b .	S13
Table S5; Crystal data and structure refinement for complex 6 .	S14
Table S6; Atomic coordinates and equivalent isotropic displacement for 6 .	S15-S16
Table S7; Bond lengths and angles for 6 .	S17-S19
Table S8; Anisotropic displacement parameters for 6 .	S20-S21
Figure S2; ORTEP drawing of 6 .	S22
Table S9; Crystal data and structure refinement for compound 8 .	S24
Table S10; Atomic coordinates and equivalent isotropic displacement parameters for 8 .	S25-S26
Table S11; Bond lengths and angles for 8 .	S27-S29
Table S12; Anisotropic displacement parameters for 8 .	S30-S31
Figure S3; ORTEP drawing of 8 .	S32
Table S13; Crystal data and structure refinement for compound 9 .	S33
Table S14; Atomic coordinates and equivalent isotropic displacement parameters for 9 .	S34-S35
Table S15; Bond lengths and angles for 9 .	S36-S38
Table S16; Anisotropic displacement parameters for 9 .	S39-S40
Figure S4; ORTEP drawing of 9 .	S41

2. NMR and IR spectra of **2b**, **5b**, **5c**, **6**, **8** and **9** and ^1H NMR spectra of the resultant mixtures in the reaction of **2b** with 1 equivalent of DMAP, in the reaction of **2b** with excess acetone, and in the reaction of **1b** with excess acetone

Figure S5; ^1H NMR spectrum of the reaction of **2b** with 1 equivalent of DMAP. S42

Figure S6; ^1H NMR spectrum of the reaction of **2b** with excess acetone. S42

Figure S7; ^1H NMR spectrum of the reaction of **1b** with excess acetone. S43

Figures S8 – S11; ^1H , ^{13}C and ^{29}Si NMR and IR spectra of complex **2b**. S43-S45

Figures S12 – S15; ^1H , ^{13}C and ^{29}Si NMR and IR spectra of complex **5b**. S45-S47

Figures S16 – S20; ^1H , ^{13}C , ^{29}Si , and ^{31}P NMR and IR spectra of complex **5c**. S47-S49

Figures S21 – S25; ^1H , ^{13}C , ^{29}Si , and ^{31}P NMR and IR spectra of complex **6**. S50-S52

Figures S26 – S29; ^1H , ^{13}C and ^{29}Si NMR and IR spectra of complex **8**. S52-S54

Figures S30 – S33; ^1H , ^{13}C and ^{29}Si NMR and IR spectra of complex **9**. S54-S56

3. References

1.1 General Procedure of X-ray crystal structure determination. The X-ray intensity data was collected on a RIGAKU XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-K α radiation at 150 or 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 F^2 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 Analysis of Cp*(OC)₂Mo{O=SiMe₂(py)}(SiMe₃) (2b) A single crystal suitable for X-ray crystal structure analysis was obtained by recrystallization from toluene/hexane solution of **2b**. The final residue $R1$ and the weighted $wR2$ were 0.0351 and 0.0885, 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 **2b** with atomic numbering schemes is shown in Figure S1.

1.3 X-ray Crystal Structure Analysis of Cp*(OC)Mo(=C(SiMe₃)OSiMe₂O)(PMe₃) (6) A single crystal suitable for X-ray crystal structure analysis was obtained by recrystallization from hexane solution of **6**. The final residue $R1$ and the weighted $wR2$ were 0.0363 and 0.0855, 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 **6** with atomic numbering schemes is shown in Figure S2.

Table S1. Crystal data and structure refinement for complex **2b**.

Complex	Cp*(OC) ₂ Mo(SiMe ₃){O=SiMes ₂ (py)} (2b)
Empirical formula	C ₃₈ H ₅₁ MoNO ₃ Si ₂
Formula weight	721.91
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 32.545(5) \text{ Å}$ $b = 13.0056(18) \text{ Å}$ $\beta = 97.278(3)^\circ$ $c = 17.608(3) \text{ Å}$
Volume (Å ³)	7398(2)
Z	8
D_{calc} (Mg / m ³)	1.297
Absorption coefficient (mm ⁻¹)	3.859
$F(000)$	3040
Crystal Size (mm ³)	0.16 × 0.10 × 0.05
Theta Range for data collection (°)	2.789 – 27.579
Index ranges	$-42 \leq h \leq 42, -16 \leq k \leq 16, -22 \leq l \leq 22$
Reflections collected	64225
Independent reflections [$R(\text{int})$]	8514 [0.1211]
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	1.000 and 0.814
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8514 / 0 / 420
Goodness-of-fit on F^2	0.974
Final R indices ^a [$I > 2\sigma(I)$]	$R1 = 0.0351, wR2 = 0.0885$
R indices ^a (all data)	$R1 = 0.0453, wR2 = 0.0921$
Largest difference in peak and hole (eÅ ⁻³)	0.663 and -0.921

^a $R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.

$wR2 = [\Sigma[w (Fo^2 - Fc^2)^2] / \Sigma[w (Fo^2)^2]]^{0.5}$,

calc $w = 1 / [\sigma^2(Fo^2) + (0.0429P)^2]$ where $P = (Fo^2 + 2Fc^2) / 3$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U(\text{eq})^{\text{a}}$
Mo	1446(1)	140(1)	3607(1)	20(1)
Si(1)	1008(1)	1831(1)	3493(1)	33(1)
Si(2)	1110(1)	−2546(1)	3680(1)	19(1)
O(1)	862(1)	282(1)	2063(1)	39(1)
O(2)	921(1)	410(1)	4954(1)	46(1)
O(3)	1326(1)	−1501(1)	3589(1)	25(1)
N	576(1)	−2167(1)	3941(1)	23(1)
C(1)	1067(1)	224(2)	2652(1)	27(1)
C(2)	1097(1)	284(2)	4420(1)	30(1)
C(3)	1109(1)	2744(2)	4335(2)	48(1)
C(4)	1051(1)	2661(2)	2624(2)	48(1)
C(5)	428(1)	1598(2)	3422(2)	45(1)
C(6)	928(1)	−3284(1)	2772(1)	23(1)
C(7)	675(1)	−4171(2)	2801(1)	27(1)
C(8)	542(1)	−4718(2)	2134(1)	32(1)
C(9)	648(1)	−4425(2)	1428(1)	35(1)
C(10)	890(1)	−3561(2)	1397(1)	34(1)
C(11)	1035(1)	−2990(2)	2048(1)	27(1)
C(12)	538(1)	−4586(2)	3531(1)	32(1)
C(13)	513(1)	−5047(2)	713(2)	52(1)
C(14)	1319(1)	−2105(2)	1921(1)	38(1)
C(15)	1368(1)	−3352(1)	4498(1)	23(1)
C(16)	1369(1)	−3020(2)	5266(1)	28(1)
C(17)	1534(1)	−3653(2)	5868(1)	35(1)
C(18)	1712(1)	−4594(2)	5745(1)	37(1)
C(19)	1745(1)	−4872(2)	5002(2)	35(1)
C(20)	1582(1)	−4275(2)	4374(1)	28(1)
C(21)	1213(1)	−1975(2)	5475(1)	35(1)
C(22)	1872(1)	−5282(2)	6415(2)	55(1)
C(23)	1660(1)	−4637(2)	3589(1)	36(1)
C(24)	391(1)	−1402(2)	3510(1)	28(1)
C(25)	6(1)	−1029(2)	3620(2)	39(1)
C(26)	−194(1)	−1445(2)	4198(2)	44(1)

C(27)	−3(1)	−2225(2)	4640(2)	44(1)
C(28)	380(1)	−2572(2)	4502(1)	33(1)
C(29)	2079(1)	390(2)	3068(1)	33(1)
C(30)	2022(1)	1219(2)	3571(1)	34(1)
C(31)	2040(1)	819(2)	4329(1)	31(1)
C(32)	2096(1)	−255(2)	4291(1)	30(1)
C(33)	2128(1)	−516(2)	3517(1)	32(1)
C(34)	2119(1)	484(3)	2228(2)	52(1)
C(35)	2071(1)	2340(2)	3363(2)	57(1)
C(36)	2054(1)	1432(2)	5060(2)	51(1)
C(37)	2168(1)	−994(2)	4956(2)	47(1)
C(38)	2235(1)	−1572(2)	3258(2)	50(1)

Table S3. Bond lengths [Å] and angles [deg] for **2b**.

Mo-C(1)	1.959(2)	C(9)-C(13)	1.514(3)
Mo-C(2)	1.945(2)	C(10)-C(11)	1.397(3)
Mo-C(29)	2.396(2)	C(11)-C(14)	1.510(3)
Mo-C(30)	2.348(2)	C(15)-C(20)	1.418(3)
Mo-C(31)	2.3469(19)	C(15)-C(16)	1.419(3)
Mo-C(32)	2.353(2)	C(16)-C(17)	1.397(3)
Mo-C(33)	2.400(2)	C(16)-C(21)	1.513(3)
Mo-O(3)	2.1692(14)	C(17)-C(18)	1.381(3)
Mo-Si(1)	2.6156(7)	C(18)-C(19)	1.376(4)
Si(1)-C(3)	1.895(3)	C(18)-C(22)	1.519(3)
Si(1)-C(4)	1.893(3)	C(19)-C(20)	1.399(3)
Si(1)-C(5)	1.900(3)	C(20)-C(23)	1.511(3)
Si(2)-C(6)	1.895(2)	C(24)-C(25)	1.382(3)
Si(2)-C(15)	1.890(2)	C(25)-C(26)	1.386(3)
Si(2)-N	1.9161(16)	C(26)-C(27)	1.380(4)
Si(2)-O(3)	1.5484(14)	C(27)-C(28)	1.376(3)
O(1)-C(1)	1.164(3)	C(29)-C(33)	1.417(3)
O(2)-C(2)	1.173(3)	C(29)-C(30)	1.423(3)
N-C(24)	1.346(3)	C(29)-C(34)	1.505(3)
N-C(28)	1.349(3)	C(30)-C(31)	1.427(3)
C(6)-C(11)	1.417(3)	C(30)-C(35)	1.516(3)
C(6)-C(7)	1.421(3)	C(31)-C(32)	1.412(3)
C(7)-C(8)	1.395(3)	C(31)-C(36)	1.509(3)
C(7)-C(12)	1.512(3)	C(32)-C(33)	1.420(3)
C(8)-C(9)	1.383(3)	C(32)-C(37)	1.510(3)
C(9)-C(10)	1.379(3)	C(33)-C(38)	1.503(3)
C(2)-Mo-C(1)	105.20(9)	C(1)-Mo-C(30)	111.19(8)
C(2)-Mo-O(3)	89.13(7)	O(3)-Mo-C(30)	136.96(7)
C(1)-Mo-O(3)	87.11(7)	C(31)-Mo-C(30)	35.39(7)
C(2)-Mo-C(31)	94.75(8)	C(2)-Mo-C(32)	102.45(9)
C(1)-Mo-C(31)	146.10(8)	C(1)-Mo-C(32)	151.53(8)
O(3)-Mo-C(31)	120.86(7)	O(3)-Mo-C(32)	86.64(6)
C(2)-Mo-C(30)	120.29(9)	C(31)-Mo-C(32)	34.97(8)

C(30)-Mo-C(32)	58.43(7)	C(24)-N-Si(2)	114.10(13)
C(2)-Mo-C(29)	152.81(9)	C(28)-N-Si(2)	127.08(15)
C(1)-Mo-C(29)	97.59(8)	O(1)-C(1)-Mo	175.94(18)
O(3)-Mo-C(29)	106.87(7)	O(2)-C(2)-Mo	173.2(2)
C(31)-Mo-C(29)	58.26(7)	C(11)-C(6)-C(7)	117.49(18)
C(30)-Mo-C(29)	34.88(8)	C(11)-C(6)-Si(2)	122.44(15)
C(32)-Mo-C(29)	58.07(8)	C(7)-C(6)-Si(2)	120.06(15)
C(2)-Mo-C(33)	135.52(8)	C(8)-C(7)-C(6)	120.1(2)
C(1)-Mo-C(33)	116.79(8)	C(8)-C(7)-C(12)	116.17(19)
O(3)-Mo-C(33)	79.40(6)	C(6)-C(7)-C(12)	123.71(18)
C(31)-Mo-C(33)	57.66(8)	C(9)-C(8)-C(7)	122.1(2)
C(30)-Mo-C(33)	57.56(8)	C(10)-C(9)-C(8)	117.99(19)
C(32)-Mo-C(33)	34.74(8)	C(10)-C(9)-C(13)	120.6(2)
C(29)-Mo-C(33)	34.37(8)	C(8)-C(9)-C(13)	121.4(2)
C(2)-Mo-Si(1)	67.15(6)	C(9)-C(10)-C(11)	122.4(2)
C(1)-Mo-Si(1)	66.95(6)	C(10)-C(11)-C(6)	119.9(2)
O(3)-Mo-Si(1)	136.94(4)	C(10)-C(11)-C(14)	115.68(19)
C(31)-Mo-Si(1)	97.39(6)	C(6)-C(11)-C(14)	124.34(18)
C(30)-Mo-Si(1)	85.66(6)	C(20)-C(15)-C(16)	117.61(18)
C(32)-Mo-Si(1)	131.98(6)	C(20)-C(15)-Si(2)	122.13(15)
C(29)-Mo-Si(1)	110.05(6)	C(16)-C(15)-Si(2)	120.20(15)
C(33)-Mo-Si(1)	142.49(6)	C(17)-C(16)-C(15)	119.8(2)
C(4)-Si(1)-C(3)	104.59(12)	C(17)-C(16)-C(21)	117.00(19)
C(4)-Si(1)-C(5)	102.25(13)	C(15)-C(16)-C(21)	123.11(18)
C(3)-Si(1)-C(5)	102.95(12)	C(18)-C(17)-C(16)	122.1(2)
C(4)-Si(1)-Mo	116.49(8)	C(19)-C(18)-C(17)	117.9(2)
C(3)-Si(1)-Mo	115.35(9)	C(19)-C(18)-C(22)	121.5(2)
C(5)-Si(1)-Mo	113.49(8)	C(17)-C(18)-C(22)	120.6(2)
O(3)-Si(2)-C(15)	113.68(8)	C(18)-C(19)-C(20)	122.5(2)
O(3)-Si(2)-C(6)	117.04(8)	C(19)-C(20)-C(15)	119.5(2)
C(15)-Si(2)-C(6)	115.04(9)	C(19)-C(20)-C(23)	117.32(19)
O(3)-Si(2)-N	103.68(7)	C(15)-C(20)-C(23)	123.13(18)
C(15)-Si(2)-N	106.82(8)	N-C(24)-C(25)	121.9(2)
C(6)-Si(2)-N	97.89(8)	C(24)-C(25)-C(26)	119.1(2)
Si(2)-O(3)-Mo	161.02(8)	C(27)-C(26)-C(25)	118.7(2)
C(24)-N-C(28)	118.82(17)	C(28)-C(27)-C(26)	119.7(2)

N-C(28)-C(27)	121.7(2)	C(32)-C(31)-Mo	72.77(11)
C(33)-C(29)-C(30)	107.3(2)	C(30)-C(31)-Mo	72.36(11)
C(33)-C(29)-C(34)	126.7(2)	C(36)-C(31)-Mo	126.47(15)
C(30)-C(29)-C(34)	125.8(2)	C(31)-C(32)-C(33)	107.90(19)
C(33)-C(29)-Mo	72.99(12)	C(31)-C(32)-C(37)	126.9(2)
C(30)-C(29)-Mo	70.74(11)	C(33)-C(32)-C(37)	124.7(2)
C(34)-C(29)-Mo	125.94(15)	C(31)-C(32)-Mo	72.26(11)
C(29)-C(30)-C(31)	108.2(2)	C(33)-C(32)-Mo	74.43(12)
C(29)-C(30)-C(35)	123.6(2)	C(37)-C(32)-Mo	125.23(14)
C(31)-C(30)-C(35)	125.7(2)	C(29)-C(33)-C(32)	108.7(2)
C(29)-C(30)-Mo	74.38(12)	C(29)-C(33)-C(38)	127.2(2)
C(31)-C(30)-Mo	72.25(11)	C(32)-C(33)-C(38)	123.9(2)
C(35)-C(30)-Mo	133.69(17)	C(29)-C(33)-Mo	72.64(12)
C(32)-C(31)-C(30)	107.84(19)	C(32)-C(33)-Mo	70.83(12)
C(32)-C(31)-C(36)	125.0(2)	C(38)-C(33)-Mo	126.63(14)

Symmetry transformations used to generate equivalent atoms:

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

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	22(1)	19(1)	20(1)	-1(1)	3(1)	-3(1)
Si(1)	47(1)	23(1)	28(1)	0(1)	6(1)	6(1)
Si(2)	20(1)	19(1)	19(1)	-1(1)	2(1)	-1(1)
O(1)	41(1)	40(1)	32(1)	-3(1)	-9(1)	2(1)
O(2)	60(1)	44(1)	40(1)	5(1)	27(1)	16(1)
O(3)	26(1)	21(1)	28(1)	-1(1)	7(1)	-1(1)
N	21(1)	25(1)	23(1)	-3(1)	3(1)	-3(1)
C(1)	28(1)	23(1)	30(1)	-1(1)	4(1)	-1(1)
C(2)	31(1)	23(1)	36(1)	2(1)	6(1)	3(1)
C(3)	78(2)	29(1)	38(1)	-6(1)	10(1)	8(1)
C(4)	74(2)	30(1)	41(2)	6(1)	8(1)	10(1)
C(5)	46(1)	45(1)	44(2)	-1(1)	6(1)	20(1)
C(6)	23(1)	24(1)	21(1)	-3(1)	0(1)	5(1)
C(7)	20(1)	28(1)	31(1)	-4(1)	-3(1)	5(1)
C(8)	23(1)	30(1)	42(1)	-11(1)	-6(1)	4(1)
C(9)	24(1)	46(1)	33(1)	-18(1)	-5(1)	13(1)
C(10)	31(1)	45(1)	24(1)	-7(1)	1(1)	13(1)
C(11)	27(1)	31(1)	24(1)	-2(1)	1(1)	11(1)
C(12)	29(1)	28(1)	37(1)	0(1)	-2(1)	-9(1)
C(13)	35(1)	71(2)	47(2)	-35(1)	-8(1)	12(1)
C(14)	54(1)	35(1)	26(1)	-1(1)	15(1)	1(1)
C(15)	21(1)	24(1)	24(1)	2(1)	-1(1)	-5(1)
C(16)	24(1)	34(1)	25(1)	5(1)	0(1)	-8(1)
C(17)	25(1)	53(1)	26(1)	12(1)	-3(1)	-9(1)
C(18)	19(1)	47(1)	43(1)	22(1)	-4(1)	-8(1)
C(19)	20(1)	29(1)	52(2)	10(1)	-5(1)	-3(1)
C(20)	19(1)	26(1)	37(1)	1(1)	-2(1)	-5(1)
C(21)	44(1)	41(1)	20(1)	-4(1)	2(1)	-6(1)
C(22)	31(1)	69(2)	61(2)	40(2)	-7(1)	-6(1)
C(23)	31(1)	31(1)	46(1)	-7(1)	-2(1)	8(1)
C(24)	22(1)	33(1)	29(1)	-1(1)	2(1)	0(1)
C(25)	24(1)	41(1)	49(2)	-5(1)	-2(1)	5(1)
C(26)	25(1)	57(2)	53(2)	-19(1)	11(1)	1(1)

C(27)	35(1)	59(2)	42(2)	−5(1)	19(1)	−8(1)
C(28)	33(1)	37(1)	30(1)	1(1)	11(1)	−4(1)
C(29)	22(1)	50(1)	27(1)	1(1)	2(1)	−7(1)
C(30)	29(1)	36(1)	36(1)	5(1)	3(1)	−12(1)
C(31)	30(1)	38(1)	26(1)	−5(1)	0(1)	−14(1)
C(32)	22(1)	37(1)	31(1)	6(1)	−2(1)	−8(1)
C(33)	19(1)	38(1)	39(1)	−4(1)	3(1)	−5(1)
C(34)	33(1)	89(2)	35(1)	2(1)	10(1)	−6(1)
C(35)	59(2)	42(2)	68(2)	14(1)	6(1)	−21(1)
C(36)	55(2)	54(2)	41(2)	−16(1)	0(1)	−19(1)
C(37)	30(1)	58(2)	49(2)	24(1)	−5(1)	−8(1)
C(38)	26(1)	49(2)	74(2)	−19(1)	6(1)	6(1)

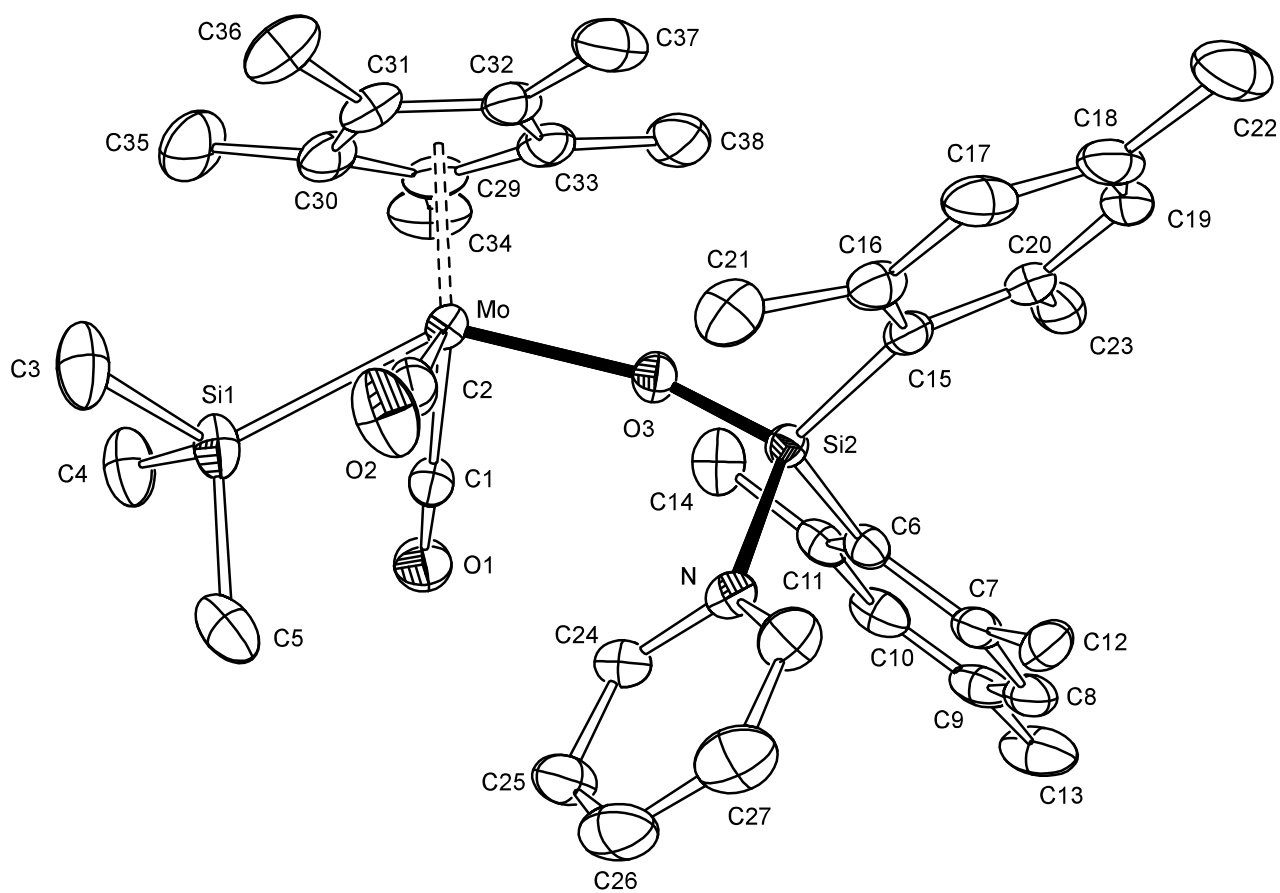


Figure S1. ORTEP drawing of **2b**. (thermal ellipsoids at the 50% probability level).

Table S5. Crystal data and structure refinement for complex **6**.

Complex	Cp*(OC)Mo{=C(SiMe ₃)OSiMe ₃ O}(PMe ₃) (6)
Empirical formula	C ₃₆ H ₅₅ MoO ₃ PSi ₂
Formula weight	718.89
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	<i>P</i> -42 ₁ <i>c</i>
Unit cell dimensions	<i>a</i> = 28.053(3) Å <i>b</i> = 28.053(3) Å <i>c</i> = 9.4610(13) Å
Volume (Å ³)	7445.5(19)
<i>Z</i>	8
<i>D</i> _{calc} (Mg / m ³)	1.283
Absorption coefficient (mm ⁻¹)	0.492
<i>F</i> (000)	3034
Crystal Size (mm ³)	0.13 × 0.04 × 0.03
Theta Range for data collection (°)	2.696 – 27.539
Index ranges	–36 ≤ <i>h</i> ≤ 36, –36 ≤ <i>k</i> ≤ 36, –12 ≤ <i>l</i> ≤ 12
Reflections collected	130137
Independent reflections [<i>R</i> (int)]	8562 [0.1246]
Absorption correction	Multi-scan
Maximum and minimum transmission	1.000 and 0.868
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	8562 / 0 / 405
Goodness-of-fit on <i>F</i> ²	1.046
Final <i>R</i> indices ^a [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0363, <i>wR</i> 2 = 0.0855
<i>R</i> indices ^a (all data)	<i>R</i> 1 = 0.0442, <i>wR</i> 2 = 0.0887
Largest difference in peak and hole (eÅ ⁻³)	1.156 and -0.439

^a*R*1 = Σ||*F*_o| - |*F*_c|| / Σ|*F*_o|.

*wR*2 = [Σ[*w* (*F*_o² - *F*_c²)²] / Σ[*w* (*F*_o²)²]]^{0.5},

calc *w* = 1 / [σ² (*F*_o²) + (0.0497*P*)² + 1.7469*P*] where *P* = (*F*_o² + 2*F*_c²) / 3.

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U(\text{eq})^{\text{a)}$
Mo	2179(1)	4799(1)	1447(1)	20(1)
P	2629(1)	4176(1)	151(1)	23(1)
Si(1)	2851(1)	5585(1)	83(1)	19(1)
Si(2)	1495(1)	5193(1)	−1582(1)	28(1)
O(1)	1326(1)	4168(1)	437(4)	39(1)
O(2)	2855(1)	5137(1)	1135(3)	22(1)
O(3)	2362(1)	5500(1)	−912(3)	23(1)
C(1)	1638(2)	4414(2)	783(5)	28(1)
C(2)	2025(1)	5191(2)	−305(4)	22(1)
C(3)	2866(2)	4379(1)	−1538(5)	27(1)
C(4)	3146(2)	3918(2)	1005(5)	36(1)
C(5)	2312(2)	3639(2)	−395(6)	37(1)
C(6)	2810(2)	6172(1)	1107(4)	23(1)
C(7)	3193(2)	6284(1)	2008(5)	26(1)
C(8)	3173(2)	6680(2)	2895(5)	33(1)
C(9)	2782(2)	6986(2)	2903(5)	37(1)
C(10)	2415(2)	6885(2)	2009(5)	35(1)
C(11)	2413(2)	6487(1)	1105(5)	29(1)
C(12)	3637(2)	5977(2)	2082(5)	31(1)
C(13)	2771(2)	7424(2)	3848(7)	57(2)
C(14)	1978(2)	6417(2)	194(5)	34(1)
C(15)	3366(1)	5621(1)	−1240(4)	22(1)
C(16)	3324(1)	5936(1)	−2409(5)	25(1)
C(17)	3687(2)	5966(1)	−3403(5)	29(1)
C(18)	4102(2)	5701(2)	−3288(5)	33(1)
C(19)	4144(2)	5397(2)	−2157(5)	33(1)
C(20)	3786(1)	5348(1)	−1129(5)	27(1)
C(21)	2897(2)	6256(2)	−2607(5)	29(1)

C(22)	4502(2)	5758(2)	−4343(6)	49(1)
C(23)	3892(2)	5005(2)	56(5)	34(1)
C(24)	910(2)	5216(2)	−646(6)	40(1)
C(25)	1526(2)	4654(2)	−2759(6)	41(1)
C(26)	1527(2)	5721(2)	−2787(6)	40(1)
C(27)	1621(2)	4791(2)	3257(5)	33(1)
C(28)	1940(1)	4397(1)	3508(5)	28(1)
C(29)	2391(2)	4585(2)	3830(5)	30(1)
C(30)	2349(2)	5091(2)	3828(5)	36(1)
C(31)	1886(2)	5220(2)	3433(5)	37(1)
C(32)	1081(2)	4761(3)	3187(6)	57(2)
C(33)	1800(2)	3884(2)	3637(7)	48(1)
C(34)	2818(2)	4308(3)	4327(6)	56(2)
C(35)	2748(2)	5418(2)	4257(6)	66(2)
C(36)	1679(3)	5716(2)	3375(7)	73(2)

Table S7. Bond lengths [Å] and angles [deg] for **6**.

Mo-C(1)	1.965(4)	C(7)-C(12)	1.515(6)
Mo-C(2)	2.036(4)	C(8)-C(9)	1.393(7)
Mo-O(2)	2.141(2)	C(9)-C(10)	1.362(7)
Mo-C(27)	2.319(4)	C(9)-C(13)	1.519(6)
Mo-C(28)	2.350(5)	C(10)-C(11)	1.406(6)
Mo-C(31)	2.367(5)	C(11)-C(14)	1.505(6)
Mo-C(29)	2.408(5)	C(15)-C(20)	1.409(5)
Mo-C(30)	2.444(4)	C(15)-C(16)	1.421(6)
Mo-P	2.4791(11)	C(16)-C(17)	1.388(6)
P-C(4)	1.811(5)	C(16)-C(21)	1.509(6)
P-C(5)	1.822(4)	C(17)-C(18)	1.387(6)
P-C(3)	1.823(5)	C(18)-C(19)	1.373(7)
Si(1)-O(2)	1.604(3)	C(18)-C(22)	1.510(6)
Si(1)-O(3)	1.681(3)	C(19)-C(20)	1.404(6)
Si(1)-C(6)	1.913(4)	C(20)-C(23)	1.507(6)
Si(1)-C(15)	1.914(4)	C(27)-C(31)	1.423(7)
Si(2)-C(24)	1.866(4)	C(27)-C(28)	1.441(6)
Si(2)-C(26)	1.872(5)	C(27)-C(32)	1.518(6)
Si(2)-C(25)	1.879(5)	C(28)-C(29)	1.404(6)
Si(2)-C(2)	1.915(4)	C(28)-C(33)	1.497(6)
O(1)-C(1)	1.162(5)	C(29)-C(30)	1.425(6)
O(3)-C(2)	1.407(5)	C(29)-C(34)	1.504(7)
C(6)-C(7)	1.408(6)	C(30)-C(31)	1.398(7)
C(6)-C(11)	1.422(6)	C(30)-C(35)	1.503(7)
C(7)-C(8)	1.393(6)	C(31)-C(36)	1.508(7)
C(1)-Mo-C(2)	82.67(17)	C(2)-Mo-C(27)	117.56(15)
C(1)-Mo-O(2)	152.05(15)	O(2)-Mo-C(27)	134.66(14)
C(2)-Mo-O(2)	80.58(13)	C(1)-Mo-C(28)	77.41(17)
C(1)-Mo-C(27)	73.17(18)	C(2)-Mo-C(28)	150.95(15)

O(2)-Mo-C(28)	125.41(13)	C(5)-P-Mo	118.31(16)
C(27)-Mo-C(28)	35.96(14)	C(3)-P-Mo	113.55(13)
C(1)-Mo-C(31)	105.06(18)	O(2)-Si(1)-O(3)	104.00(14)
C(2)-Mo-C(31)	107.60(16)	O(2)-Si(1)-C(6)	111.15(16)
O(2)-Mo-C(31)	101.27(15)	O(3)-Si(1)-C(6)	110.92(16)
C(27)-Mo-C(31)	35.34(16)	O(2)-Si(1)-C(15)	116.20(16)
C(28)-Mo-C(31)	58.78(15)	O(3)-Si(1)-C(15)	104.88(16)
C(1)-Mo-C(29)	110.72(17)	C(6)-Si(1)-C(15)	109.37(16)
C(2)-Mo-C(29)	161.67(16)	C(24)-Si(2)-C(26)	107.6(2)
O(2)-Mo-C(29)	91.17(12)	C(24)-Si(2)-C(25)	110.5(2)
C(27)-Mo-C(29)	58.18(15)	C(26)-Si(2)-C(25)	105.9(2)
C(28)-Mo-C(29)	34.31(15)	C(24)-Si(2)-C(2)	112.5(2)
C(31)-Mo-C(29)	57.76(16)	C(26)-Si(2)-C(2)	110.4(2)
C(1)-Mo-C(30)	129.02(17)	C(25)-Si(2)-C(2)	109.6(2)
C(2)-Mo-C(30)	127.58(17)	Si(1)-O(2)-Mo	115.29(14)
O(2)-Mo-C(30)	78.78(13)	C(2)-O(3)-Si(1)	114.0(2)
C(27)-Mo-C(30)	56.91(16)	O(1)-C(1)-Mo	176.4(4)
C(28)-Mo-C(30)	56.77(15)	O(3)-C(2)-Si(2)	105.2(3)
C(31)-Mo-C(30)	33.74(18)	O(3)-C(2)-Mo	121.6(3)
C(29)-Mo-C(30)	34.14(15)	Si(2)-C(2)-Mo	132.8(2)
C(1)-Mo-P	81.28(13)	C(7)-C(6)-C(11)	117.4(4)
C(2)-Mo-P	94.94(12)	C(7)-C(6)-Si(1)	116.9(3)
O(2)-Mo-P	78.06(7)	C(11)-C(6)-Si(1)	125.5(3)
C(27)-Mo-P	134.61(12)	C(8)-C(7)-C(6)	120.7(4)
C(28)-Mo-P	102.60(10)	C(11)-C(6)-Si(1)	117.3(4)
C(31)-Mo-P	157.10(13)	C(8)-C(7)-C(6)	121.9(4)
C(29)-Mo-P	99.35(11)	C(8)-C(7)-C(12)	118.31(16)
C(30)-Mo-P	126.39(13)	C(6)-C(7)-C(12)	113.55(13)
C(4)-P-C(5)	100.8(2)	C(9)-C(8)-C(7)	121.9(4)
C(4)-P-C(3)	102.9(2)	C(10)-C(9)-C(8)	117.5(4)
C(5)-P-C(3)	100.9(2)	C(10)-C(9)-C(13)	121.3(5)
C(4)-P-Mo	117.91(17)	C(8)-C(9)-C(13)	121.2(5)

C(9)-C(10)-C(11)	123.2(4)	C(27)-C(28)-C(33)	126.1(4)
C(10)-C(11)-C(6)	119.2(4)	C(29)-C(28)-Mo	75.1(3)
C(10)-C(11)-C(14)	117.1(4)	C(27)-C(28)-Mo	70.8(2)
C(6)-C(11)-C(14)	123.7(4)	C(33)-C(28)-Mo	127.1(4)
C(20)-C(15)-C(16)	117.7(4)	C(28)-C(29)-C(30)	107.4(4)
C(20)-C(15)-Si(1)	123.7(3)	C(28)-C(29)-C(34)	126.3(5)
C(16)-C(15)-Si(1)	118.6(3)	C(30)-C(29)-C(34)	125.5(5)
C(17)-C(16)-C(15)	120.3(4)	C(28)-C(29)-Mo	70.6(3)
C(17)-C(16)-C(21)	117.5(4)	C(30)-C(29)-Mo	74.3(3)
C(15)-C(16)-C(21)	122.2(4)	C(34)-C(29)-Mo	128.2(3)
C(16)-C(17)-C(18)	122.0(4)	C(31)-C(30)-C(29)	109.6(4)
C(19)-C(18)-C(17)	117.8(4)	C(31)-C(30)-C(35)	127.4(5)
C(19)-C(18)-C(22)	121.2(4)	C(29)-C(30)-C(35)	123.0(5)
C(17)-C(18)-C(22)	121.0(4)	C(31)-C(30)-Mo	70.1(3)
C(19)-C(20)-C(15)	122.7(4)	C(29)-C(30)-Mo	71.5(3)
C(19)-C(20)-C(23)	119.5(4)	C(35)-C(30)-Mo	126.8(3)
C(15)-C(20)-C(23)	115.9(4)	C(30)-C(31)-C(27)	107.3(4)
C(28)-C(27)-C(32)	124.6(4)	C(30)-C(31)-C(36)	127.3(5)
C(31)-C(27)-Mo	107.8(4)	C(27)-C(31)-C(36)	125.1(5)
C(28)-C(27)-Mo	73.2(2)	C(30)-C(31)-Mo	76.2(3)
C(32)-C(27)-Mo	129.9(3)	C(27)-C(31)-Mo	70.5(3)
C(29)-C(28)-C(27)	107.8(4)	C(36)-C(31)-Mo	124.4(4)
C(29)-C(28)-C(33)	125.5(4)		

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	20(1)	16(1)	23(1)	0(1)	2(1)	-1(1)
P	23(1)	17(1)	29(1)	-1(1)	0(1)	1(1)
Si(1)	19(1)	17(1)	23(1)	0(1)	0(1)	-2(1)
Si(2)	21(1)	32(1)	31(1)	0(1)	-3(1)	0(1)
O(1)	31(2)	38(2)	46(2)	-5(2)	0(2)	-11(1)
O(2)	19(1)	20(1)	27(2)	1(1)	-2(1)	-2(1)
O(3)	22(1)	23(1)	26(2)	3(1)	-2(1)	-4(1)
C(1)	25(2)	27(2)	31(2)	-1(2)	-1(2)	1(2)
C(2)	21(2)	21(2)	22(2)	-2(2)	-1(1)	2(2)
C(3)	30(2)	27(2)	24(2)	-2(2)	5(2)	3(2)
C(4)	31(2)	36(2)	41(3)	5(2)	0(2)	14(2)
C(5)	41(3)	22(2)	49(3)	-8(2)	4(2)	-5(2)
C(6)	28(2)	16(2)	25(2)	1(1)	6(2)	-3(1)
C(7)	29(2)	25(2)	25(2)	1(2)	7(2)	-7(2)
C(8)	37(2)	32(2)	32(2)	-6(2)	6(2)	-16(2)
C(9)	46(3)	26(2)	39(3)	-8(2)	20(2)	-12(2)
C(10)	40(2)	23(2)	41(3)	-3(2)	16(2)	2(2)
C(11)	28(2)	22(2)	37(3)	0(2)	8(2)	-1(2)
C(12)	30(2)	31(2)	31(2)	-2(2)	-6(2)	-5(2)
C(13)	66(4)	42(3)	63(4)	-25(3)	23(3)	-12(3)
C(14)	31(2)	29(2)	41(3)	1(2)	3(2)	9(2)
C(15)	21(2)	18(2)	27(2)	-6(2)	0(2)	-3(1)
C(16)	27(2)	20(2)	26(2)	-5(2)	0(2)	-5(2)
C(17)	34(2)	27(2)	27(2)	-5(2)	4(2)	-10(2)
C(18)	32(2)	31(2)	36(3)	-12(2)	7(2)	-8(2)
C(19)	22(2)	30(2)	48(3)	-12(2)	3(2)	-1(2)
C(20)	22(2)	21(2)	39(3)	-6(2)	2(2)	-3(1)
C(21)	31(2)	27(2)	29(2)	7(2)	1(2)	-4(2)
C(22)	43(3)	45(3)	57(4)	-8(3)	23(3)	-2(2)

C(23)	26(2)	30(2)	47(3)	6(2)	−4(2)	3(2)
C(24)	22(2)	51(3)	48(3)	5(3)	0(2)	6(2)
C(25)	42(3)	43(3)	38(3)	−8(2)	−10(2)	0(2)
C(26)	32(2)	48(3)	39(3)	9(2)	−11(2)	5(2)
C(27)	30(2)	43(2)	26(3)	1(2)	7(2)	9(2)
C(28)	30(2)	26(2)	27(2)	4(2)	5(2)	−2(2)
C(29)	27(2)	40(2)	24(2)	2(2)	3(2)	2(2)
C(30)	50(3)	40(2)	18(2)	−3(2)	7(2)	−19(2)
C(31)	57(3)	30(2)	25(2)	2(2)	10(2)	4(2)
C(32)	29(2)	99(5)	43(3)	−5(3)	10(2)	13(3)
C(33)	57(3)	35(2)	52(3)	14(3)	10(3)	−12(2)
C(34)	44(3)	91(5)	33(3)	4(3)	1(2)	28(3)
C(35)	91(5)	79(4)	30(3)	−7(3)	9(3)	−55(4)
C(36)	139(6)	40(3)	41(4)	1(3)	31(4)	35(4)



1.4 X-ray Crystal Structure Analysis of $\text{Cp}^*(\text{OC})_2\text{Mo}\{\text{OSiMe}_2\text{OC}(\text{Me})=\text{CH}_2\}$ (8**)** A single crystal suitable for X-ray crystal structure analysis was obtained by recrystallization from toluene/hexane solution of **8**. The final residue $R1$ and the weighted $wR2$ were 0.0575 and 0.1545, 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 **8** with atomic numbering schemes is shown in Figure S3.

1.5 X-ray Crystal Structure Analysis of $\text{Cp}^*(\text{OC})_2\text{W}\{\text{OSiMe}_2\text{OC}(\text{Me})=\text{CH}_2\}$ (9**)** A single crystal suitable for X-ray crystal structure analysis was obtained by recrystallization from hexane solution of **9**. The final residue $R1$ and the weighted $wR2$ were 0.0232 and 0.0579, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters are listed in Tables S13, S14, S15, and S16, respectively. ORTEP drawing of **9** with atomic numbering schemes is shown in Figure S4.

Table S9. Crystal data and structure refinement for complex **8**.

Complex	Cp*(OC) ₂ Mo{OSiMes ₂ OC(Me)=CH ₂ } (8)
Empirical formula	C ₃₃ H ₄₂ MoO ₄ Si
Formula weight	626.69
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 12.343(3) Å <i>b</i> = 14.711(4) Å <i>β</i> = 96.300(5)° <i>c</i> = 16.766(4) Å
Volume (Å ³)	3025.9(13)
<i>Z</i>	4
<i>D</i> _{calc} (Mg / m ³)	1.376
Absorption coefficient (mm ⁻¹)	0.508
<i>F</i> (000)	1312
Crystal Size (mm ³)	0.10 × 0.05 × 0.03
Theta Range for data collection (°)	2.769 – 27.526
Index ranges	–16 ≤ <i>h</i> ≤ 16, –19 ≤ <i>k</i> ≤ 19, –21 ≤ <i>l</i> ≤ 21
Reflections collected	48919
Independent reflections [<i>R</i> (int)]	6932 [0.1298]
Absorption correction	Multi-scan
Maximum and minimum transmission	1.000 and 0.826
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6932 / 0 / 364
Goodness-of-fit on <i>F</i> ²	1.019
Final <i>R</i> indices ^a [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0575, <i>wR</i> 2 = 0.1415
<i>R</i> indices ^a (all data)	<i>R</i> 1 = 0.0809, <i>wR</i> 2 = 0.1544
Largest difference in peak and hole (eÅ ⁻³)	1.622 and -0.760

^a*R*1 = Σ||*F*_o| - |*F*_c|| / Σ|*F*_o|.

*wR*2 = [Σ[*w* (*F*_o² - *F*_c²)²] / Σ[*w* (*F*_o²)²]]^{0.5},

calc *w* = 1 / [σ²(*F*_o²) + (0.0765*P*)²] where *P* = (*F*_o² + 2*F*_c²) / 3.

Table S10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U(\text{eq})^{\text{a}}$
Mo	5546(1)	1792(1)	1774(1)	28(1)
Si	6695(1)	1887(1)	135(1)	31(1)
O(1)	5556(3)	3892(2)	1525(2)	58(1)
O(2)	3149(3)	2487(2)	1750(2)	62(1)
O(3)	6846(2)	1610(2)	1058(2)	33(1)
O(4)	5360(2)	1722(2)	-176(2)	35(1)
C(1)	5579(3)	3103(3)	1549(2)	39(1)
C(2)	4022(3)	2201(3)	1756(2)	43(1)
C(3)	4906(3)	670(2)	850(2)	34(1)
C(4)	4661(3)	1378(3)	327(2)	34(1)
C(5)	3511(3)	1679(3)	73(3)	43(1)
C(6)	6734(3)	1946(3)	2910(2)	37(1)
C(7)	5654(3)	2058(3)	3117(2)	38(1)
C(8)	5104(3)	1207(3)	2974(2)	38(1)
C(9)	5866(3)	568(2)	2718(2)	38(1)
C(10)	6861(3)	1008(3)	2706(2)	37(1)
C(11)	7653(4)	2621(3)	2997(3)	54(1)
C(12)	5225(4)	2881(3)	3509(3)	52(1)
C(13)	3972(4)	970(4)	3185(3)	55(1)
C(14)	5638(4)	-433(3)	2557(3)	52(1)
C(15)	7917(4)	593(3)	2530(3)	54(1)
C(16)	7418(3)	1149(2)	-573(2)	34(1)
C(17)	7229(3)	1303(2)	-1407(2)	35(1)
C(18)	7731(3)	764(3)	-1938(2)	39(1)
C(19)	8417(3)	53(3)	-1689(3)	42(1)
C(20)	8593(3)	-105(3)	-877(3)	41(1)
C(21)	8116(3)	423(3)	-305(2)	37(1)
C(22)	6484(3)	2057(3)	-1754(2)	40(1)
C(23)	8971(4)	-507(3)	-2288(3)	52(1)
C(24)	8369(3)	165(3)	565(3)	45(1)
C(25)	7075(3)	3129(2)	7(2)	32(1)
C(26)	6370(3)	3845(2)	-296(2)	35(1)
C(27)	6766(3)	4727(3)	-310(2)	38(1)

C(28)	7816(3)	4961(3)	-16(2)	39(1)
C(29)	8506(3)	4268(3)	286(2)	37(1)
C(30)	8155(3)	3365(2)	295(2)	35(1)
C(31)	5188(3)	3705(3)	-591(3)	44(1)
C(32)	8210(4)	5937(3)	-27(3)	53(1)
C(33)	8978(3)	2667(3)	646(2)	41(1)

Table S11. Bond lengths [$\text{\AA}$] and angles [deg] for **8**.

Mo-C(1)	1.967(4)	C(8)-C(13)	1.519(6)
Mo-C(2)	1.972(4)	C(9)-C(10)	1.390(5)
Mo-O(3)	2.124(2)	C(9)-C(14)	1.517(5)
Mo-C(7)	2.274(4)	C(10)-C(6)	1.436(5)
Mo-C(6)	2.284(4)	C(10)-C(15)	1.497(6)
Mo-C(8)	2.307(4)	C(16)-C(17)	1.410(5)
Mo-C(3)	2.341(4)	C(16)-C(21)	1.415(5)
Mo-C(9)	2.400(4)	C(17)-C(22)	1.516(6)
Mo-C(10)	2.419(4)	C(18)-C(17)	1.388(5)
Mo-C(4)	2.620(4)	C(19)-C(18)	1.382(6)
Si-O(3)	1.592(3)	C(19)-C(23)	1.518(5)
Si-O(4)	1.691(3)	C(20)-C(19)	1.374(6)
Si-C(16)	1.901(4)	C(21)-C(20)	1.412(5)
Si-C(25)	1.904(4)	C(21)-C(24)	1.505(6)
O(1)-C(1)	1.162(4)	C(25)-C(30)	1.411(5)
O(2)-C(2)	1.156(5)	C(25)-C(26)	1.424(5)
O(4)-C(4)	1.368(4)	C(26)-C(31)	1.502(6)
C(3)-C(4)	1.373(5)	C(27)-C(26)	1.388(5)
C(4)-C(5)	1.503(5)	C(28)-C(27)	1.379(6)
C(6)-C(11)	1.503(6)	C(28)-C(32)	1.516(6)
C(7)-C(6)	1.423(6)	C(29)-C(28)	1.387(5)
C(7)-C(8)	1.431(5)	C(30)-C(29)	1.398(5)
C(7)-C(12)	1.502(5)	C(30)-C(33)	1.517(5)
C(8)-C(9)	1.428(5)		
C(1)-Mo-C(2)	74.78(18)	O(3)-Mo-C(7)	128.00(13)
C(1)-Mo-O(3)	88.96(14)	C(1)-Mo-C(6)	92.15(15)
C(2)-Mo-O(3)	143.89(14)	C(2)-Mo-C(6)	120.44(15)
C(1)-Mo-C(7)	91.23(16)	O(3)-Mo-C(6)	91.64(12)
C(2)-Mo-C(7)	85.14(16)	C(7)-Mo-C(6)	36.39(14)

C(1)-Mo-C(8)	123.05(15)	C(3)-Mo-C(4)	31.49(12)
C(2)-Mo-C(8)	79.13(16)	C(9)-Mo-C(4)	117.25(12)
O(3)-Mo-C(8)	135.35(12)	C(10)-Mo-C(4)	132.01(12)
C(7)-Mo-C(8)	36.41(14)	O(3)-Si-O(4)	105.56(13)
C(6)-Mo-C(8)	60.12(14)	O(3)-Si-C(16)	116.56(16)
C(1)-Mo-C(3)	125.19(15)	O(4)-Si-C(16)	103.55(15)
C(2)-Mo-C(3)	87.30(15)	O(3)-Si-C(25)	110.58(16)
O(3)-Mo-C(3)	75.96(11)	O(4)-Si-C(25)	110.32(15)
C(7)-Mo-C(3)	139.08(13)	C(16)-Si-C(25)	109.88(16)
C(6)-Mo-C(3)	139.60(13)	Si-O(3)-Mo	120.18(14)
C(8)-Mo-C(3)	102.68(13)	C(4)-O(4)-Si	121.5(2)
C(1)-Mo-C(9)	148.96(15)	O(1)-C(1)-Mo	170.2(4)
C(2)-Mo-C(9)	109.09(16)	O(2)-C(2)-Mo	176.4(4)
O(3)-Mo-C(9)	101.44(12)	C(4)-C(3)-Mo	85.5(2)
C(7)-Mo-C(9)	59.28(13)	O(4)-C(4)-Mo	105.0(2)
C(6)-Mo-C(9)	58.74(13)	C(3)-C(4)-Mo	63.0(2)
C(8)-Mo-C(9)	35.25(13)	C(5)-C(4)-Mo	118.6(2)
C(3)-Mo-C(9)	85.82(13)	O(4)-C(4)-C(3)	124.4(3)
C(1)-Mo-C(10)	124.42(16)	O(4)-C(4)-C(5)	110.8(3)
C(2)-Mo-C(10)	136.66(15)	C(3)-C(4)-C(5)	122.6(3)
O(3)-Mo-C(10)	79.06(11)	C(7)-C(6)-Mo	71.4(2)
C(7)-Mo-C(10)	58.70(13)	C(10)-C(6)-Mo	77.4(2)
C(6)-Mo-C(10)	35.41(13)	C(11)-C(6)-Mo	123.8(3)
C(8)-Mo-C(10)	57.67(13)	C(7)-C(6)-C(10)	107.4(3)
C(3)-Mo-C(10)	104.21(13)	C(7)-C(6)-C(11)	128.2(4)
C(9)-Mo-C(10)	33.53(13)	C(10)-C(6)-C(11)	123.9(4)
C(1)-Mo-C(4)	93.72(15)	C(6)-C(7)-Mo	72.2(2)
C(2)-Mo-C(4)	75.90(14)	C(8)-C(7)-Mo	73.0(2)
O(3)-Mo-C(4)	73.20(11)	C(12)-C(7)-Mo	125.9(3)
C(7)-Mo-C(4)	158.35(13)	C(6)-C(7)-C(8)	107.3(3)
C(6)-Mo-C(4)	163.61(13)	C(6)-C(7)-C(12)	125.7(4)
C(8)-Mo-C(4)	127.31(13)	C(8)-C(7)-C(12)	126.6(4)

C(9)-C(8)-Mo	75.9(2)	C(16)-C(17)-C(22)	121.7(3)
C(7)-C(8)-Mo	70.6(2)	C(19)-C(18)-C(17)	122.7(4)
C(13)-C(8)-Mo	126.9(3)	C(20)-C(19)-C(18)	116.9(3)
C(9)-C(8)-C(7)	108.1(3)	C(20)-C(19)-C(23)	122.0(4)
C(9)-C(8)-C(13)	124.9(4)	C(18)-C(19)-C(23)	121.1(4)
C(7)-C(8)-C(13)	126.4(4)	C(19)-C(20)-C(21)	123.3(4)
C(10)-C(9)-Mo	74.0(2)	C(20)-C(21)-C(16)	118.9(4)
C(8)-C(9)-Mo	68.8(2)	C(20)-C(21)-C(24)	117.6(4)
C(14)-C(9)-Mo	126.6(3)	C(16)-C(21)-C(24)	123.5(3)
C(10)-C(9)-C(8)	108.1(3)	C(30)-C(25)-Si	115.6(3)
C(10)-C(9)-C(14)	126.5(4)	C(26)-C(25)-Si	126.9(3)
C(8)-C(9)-C(14)	125.2(4)	C(30)-C(25)-C(26)	117.3(3)
C(9)-C(10)-Mo	72.5(2)	C(27)-C(26)-C(25)	119.6(4)
C(6)-C(10)-Mo	67.2(2)	C(27)-C(26)-C(31)	117.0(3)
C(15)-C(10)-Mo	127.2(3)	C(25)-C(26)-C(31)	123.3(3)
C(9)-C(10)-C(6)	108.9(3)	C(28)-C(27)-C(26)	123.2(4)
C(9)-C(10)-C(15)	127.1(4)	C(27)-C(28)-C(29)	117.5(4)
C(6)-C(10)-C(15)	124.0(4)	C(27)-C(28)-C(32)	121.4(4)
C(17)-C(16)-Si	119.3(3)	C(29)-C(28)-C(32)	121.1(4)
C(21)-C(16)-Si	123.0(3)	C(28)-C(29)-C(30)	121.6(4)
C(17)-C(16)-C(21)	117.7(3)	C(29)-C(30)-C(25)	120.8(3)
C(18)-C(17)-C(16)	120.5(4)	C(29)-C(30)-C(33)	116.9(3)
C(18)-C(17)-C(22)	117.8(4)	C(25)-C(30)-C(33)	122.3(3)

Symmetry transformations used to generate equivalent atoms:

Table S12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	36(1)	25(1)	26(1)	-1(1)	9(1)	1(1)
Si	36(1)	29(1)	30(1)	1(1)	11(1)	1(1)
O(1)	95(2)	30(2)	50(2)	1(1)	22(2)	5(2)
O(2)	48(2)	81(2)	59(2)	-18(2)	8(2)	19(2)
O(3)	36(1)	34(1)	31(1)	1(1)	12(1)	2(1)
O(4)	39(1)	41(2)	28(1)	1(1)	11(1)	-3(1)
C(1)	56(2)	30(2)	32(2)	2(2)	11(2)	4(2)
C(2)	43(2)	46(2)	40(2)	-10(2)	6(2)	6(2)
C(3)	46(2)	31(2)	28(2)	-3(1)	14(2)	-4(2)
C(4)	39(2)	37(2)	29(2)	-3(2)	11(2)	-2(2)
C(5)	37(2)	58(3)	35(2)	0(2)	8(2)	-9(2)
C(6)	47(2)	34(2)	30(2)	-2(2)	2(2)	-1(2)
C(7)	54(2)	33(2)	27(2)	-4(2)	6(2)	4(2)
C(8)	49(2)	40(2)	27(2)	-1(2)	11(2)	-3(2)
C(9)	59(2)	29(2)	27(2)	1(1)	6(2)	0(2)
C(10)	47(2)	40(2)	25(2)	4(2)	6(2)	7(2)
C(11)	59(3)	47(3)	52(3)	-3(2)	0(2)	-12(2)
C(12)	70(3)	45(2)	40(2)	-13(2)	6(2)	14(2)
C(13)	54(3)	71(3)	43(3)	4(2)	21(2)	-9(2)
C(14)	86(3)	29(2)	41(2)	4(2)	8(2)	-4(2)
C(15)	57(3)	61(3)	44(3)	1(2)	6(2)	22(2)
C(16)	39(2)	27(2)	40(2)	-3(2)	16(2)	-5(1)
C(17)	39(2)	31(2)	37(2)	0(2)	14(2)	-9(2)
C(18)	48(2)	37(2)	35(2)	-9(2)	19(2)	-12(2)
C(19)	42(2)	39(2)	47(2)	-11(2)	19(2)	-9(2)
C(20)	40(2)	32(2)	55(3)	-1(2)	17(2)	-1(2)
C(21)	38(2)	33(2)	43(2)	1(2)	16(2)	-4(2)
C(22)	53(2)	36(2)	32(2)	0(2)	12(2)	-3(2)

C(23)	54(3)	50(3)	55(3)	-16(2)	20(2)	-1(2)
C(24)	53(2)	39(2)	48(2)	4(2)	18(2)	8(2)
C(25)	40(2)	30(2)	28(2)	-1(1)	12(2)	2(1)
C(26)	47(2)	35(2)	25(2)	1(2)	11(2)	5(2)
C(27)	52(2)	33(2)	33(2)	1(2)	18(2)	7(2)
C(28)	55(2)	33(2)	31(2)	0(2)	16(2)	1(2)
C(29)	45(2)	40(2)	27(2)	-4(2)	10(2)	-5(2)
C(30)	45(2)	32(2)	29(2)	0(1)	15(2)	3(2)
C(31)	49(2)	37(2)	45(2)	4(2)	6(2)	7(2)
C(32)	69(3)	32(2)	59(3)	-1(2)	14(2)	-2(2)
C(33)	44(2)	36(2)	43(2)	1(2)	7(2)	-1(2)

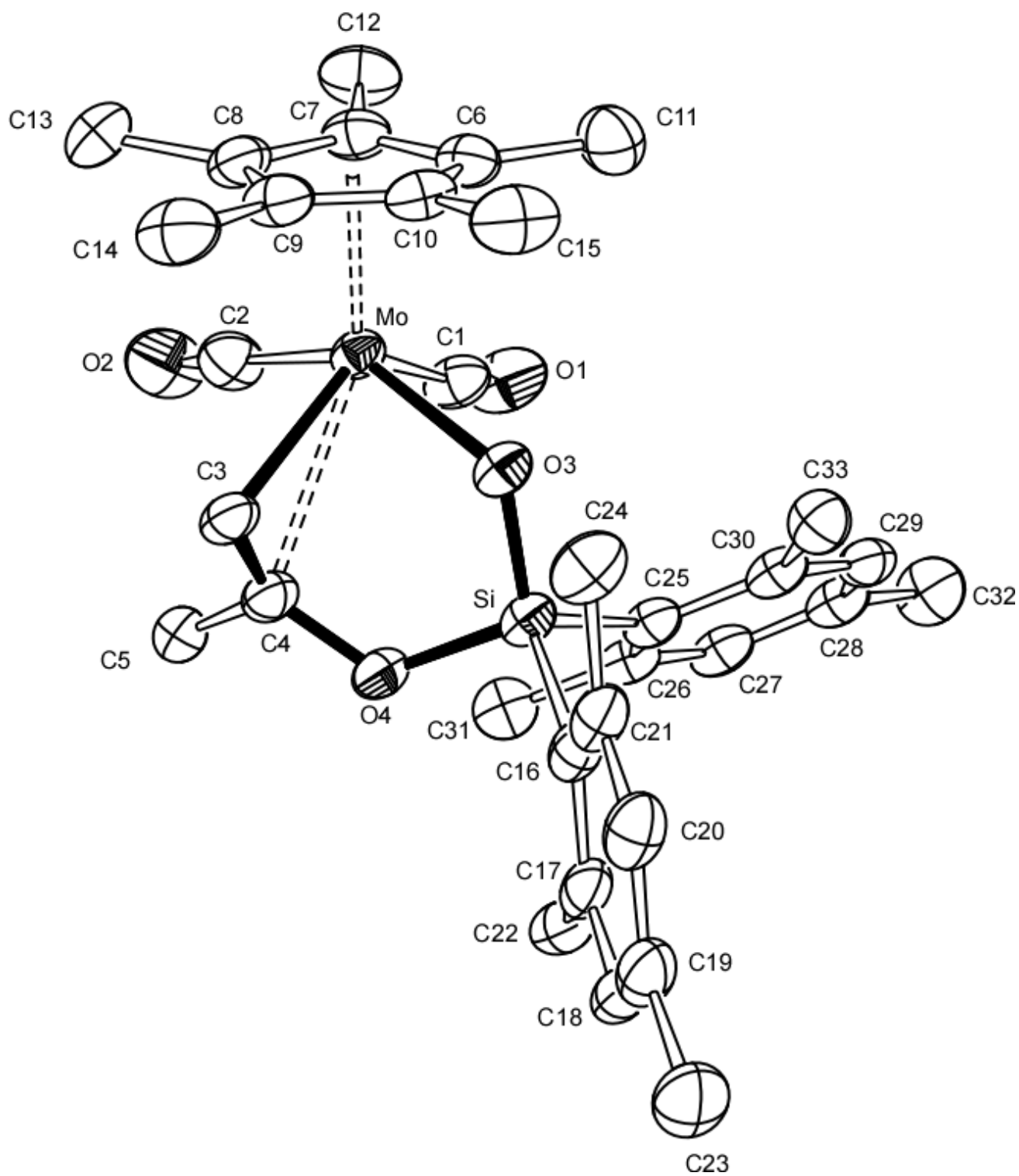


Figure S3. ORTEP drawing of **8**. (thermal ellipsoids at the 50% probability level).

Table S13. Crystal data and structure refinement for complex **9**.

Complex	Cp*(OC) ₂ W{OSiMes ₂ OC(Me)=CH ₂ } (9)
Empirical formula	C ₃₃ H ₄₂ O ₄ SiW
Formula weight	714.60
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 11.3269(17) Å <i>b</i> = 20.581(3) Å <i>β</i> = 105.485(4)° <i>c</i> = 13.585(2) Å
Volume (Å ³)	3052.0(8)
<i>Z</i>	4
<i>D</i> _{calc} (Mg / m ³)	1.555
Absorption coefficient (mm ⁻¹)	3.859
<i>F</i> (000)	1440
Crystal Size (mm ³)	0.07 × 0.04 × 0.03
Theta Range for data collection (°)	2.720 – 27.534
Index ranges	–14 ≤ <i>h</i> ≤ 14, –25 ≤ <i>k</i> ≤ 26, –17 ≤ <i>l</i> ≤ 17
Reflections collected	50978
Independent reflections [<i>R</i> (int)]	7031 [0.0761]
Absorption correction	Multi-scan
Maximum and minimum transmission	1.000 and 0.890
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	7031 / 0 / 364
Goodness-of-fit on <i>F</i> ²	1.043
Final <i>R</i> indices ^a [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0232, <i>wR</i> 2 = 0.0559
<i>R</i> indices ^a (all data)	<i>R</i> 1 = 0.0280, <i>wR</i> 2 = 0.0579
Largest difference in peak and hole (eÅ ⁻³)	1.392 and -0.513

^a*R*1 = Σ||*F*_o| - |*F*_c|| / Σ|*F*_o|.

*wR*2 = [Σ[*w* (*F*_o² - *F*_c²)²] / Σ[*w* (*F*_o²)²]]^{0.5},

calc *w* = 1 / [σ²(*F*_o²) + (0.0261*P*)² + 2.0861*P*] where *P* = (*F*_o² + 2*F*_c²) / 3.

Table S14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U(\text{eq})^{\text{a)}$
W	5575(1)	1371(1)	2396(1)	19(1)
Si	2673(1)	1509(1)	2443(1)	21(1)
O(1)	4728(2)	1367(1)	13(2)	40(1)
O(2)	6976(2)	2453(1)	1544(2)	39(1)
O(3)	3850(2)	1070(1)	2494(1)	24(1)
O(4)	3188(2)	2275(1)	2378(1)	24(1)
C(1)	4940(3)	1380(1)	893(2)	26(1)
C(2)	6468(2)	2066(1)	1903(2)	27(1)
C(3)	5175(2)	2119(1)	3547(2)	26(1)
C(4)	4408(2)	2417(1)	2697(2)	25(1)
C(5)	4693(2)	3051(1)	2269(2)	32(1)
C(6)	6291(2)	325(1)	2349(2)	22(1)
C(7)	7259(2)	776(1)	2382(2)	24(1)
C(8)	7529(2)	1107(1)	3345(2)	26(1)
C(9)	6739(2)	842(1)	3913(2)	26(1)
C(10)	6022(2)	352(1)	3315(2)	24(1)
C(11)	5801(3)	−161(1)	1520(2)	31(1)
C(12)	7995(3)	821(2)	1610(2)	35(1)
C(13)	8576(3)	1564(2)	3761(3)	39(1)
C(14)	6761(3)	1008(2)	4998(2)	40(1)
C(15)	5114(3)	−70(1)	3634(2)	34(1)
C(16)	2140(2)	1355(1)	3632(2)	22(1)
C(17)	2206(2)	1797(1)	4438(2)	25(1)
C(18)	1911(2)	1595(1)	5322(2)	26(1)
C(19)	1538(2)	965(1)	5451(2)	26(1)
C(20)	1440(2)	534(1)	4645(2)	25(1)
C(21)	1728(2)	713(1)	3747(2)	22(1)
C(22)	2572(3)	2504(1)	4417(2)	34(1)
C(23)	1212(3)	763(2)	6413(2)	36(1)
C(24)	1569(2)	215(1)	2911(2)	26(1)
C(25)	1352(2)	1453(1)	1258(2)	24(1)
C(26)	372(2)	1904(1)	1137(2)	27(1)
C(27)	−611(3)	1883(1)	272(2)	34(1)

C(28)	−690(3)	1433(2)	−499(3)	41(1)
C(29)	264(3)	993(2)	−382(2)	35(1)
C(30)	1273(2)	993(1)	472(2)	27(1)
C(31)	340(2)	2405(1)	1941(2)	30(1)
C(32)	−1794(4)	1417(2)	−1418(3)	62(1)
C(33)	2234(3)	477(2)	495(2)	35(1)

Table S15. Bond lengths [Å] and angles [deg] for **9**.

W-C(2)	1.970(3)	C(8)-C(9)	1.436(4)
W-C(1)	1.977(3)	C(8)-C(13)	1.502(4)
W-O(3)	2.0877(18)	C(9)-C(10)	1.409(4)
W-C(7)	2.270(3)	C(9)-C(14)	1.507(4)
W-C(6)	2.308(2)	C(10)-C(15)	1.495(4)
W-C(8)	2.309(3)	C(16)-C(17)	1.410(4)
W-C(3)	2.324(3)	C(16)-C(21)	1.424(4)
W-C(9)	2.392(3)	C(17)-C(18)	1.393(4)
W-C(10)	2.424(3)	C(17)-C(22)	1.517(4)
W-C(4)	2.616(3)	C(18)-C(19)	1.388(4)
Si-O(3)	1.5968(19)	C(19)-C(20)	1.391(4)
Si-O(4)	1.6907(19)	C(19)-C(23)	1.509(4)
Si-C(25)	1.886(3)	C(20)-C(21)	1.395(4)
Si-C(16)	1.896(3)	C(21)-C(24)	1.503(3)
O(1)-C(1)	1.154(3)	C(25)-C(30)	1.412(4)
O(2)-C(2)	1.163(3)	C(25)-C(26)	1.423(4)
O(4)-C(4)	1.365(3)	C(26)-C(27)	1.387(4)
C(3)-C(4)	1.389(4)	C(26)-C(31)	1.508(4)
C(4)-C(5)	1.499(4)	C(27)-C(28)	1.383(5)
C(6)-C(10)	1.426(3)	C(28)-C(29)	1.385(5)
C(6)-C(7)	1.429(4)	C(28)-C(32)	1.514(5)
C(6)-C(11)	1.497(4)	C(29)-C(30)	1.395(4)
C(7)-C(8)	1.432(4)	C(30)-C(33)	1.514(4)
C(7)-C(12)	1.507(4)		
C(2)-W-C(1)	73.71(11)	O(3)-W-C(7)	130.01(8)
C(2)-W-O(3)	144.25(9)	C(2)-W-C(6)	116.85(10)
C(1)-W-O(3)	88.83(10)	C(1)-W-C(6)	90.78(10)
C(2)-W-C(7)	83.08(10)	O(3)-W-C(6)	93.81(8)
C(1)-W-C(7)	94.07(10)	C(7)-W-C(6)	36.36(9)

C(2)-W-C(8)	73.71(11)	C(3)-W-C(4)	31.98(8)
C(1)-W-C(8)	144.25(9)	C(9)-W-C(4)	115.22(8)
O(3)-W-C(8)	88.83(10)	C(10)-W-C(4)	132.58(8)
C(7)-W-C(8)	83.08(10)	O(3)-Si-O(4)	103.59(9)
C(6)-W-C(8)	94.07(10)	O(3)-Si-C(25)	117.69(11)
C(2)-W-C(3)	130.01(8)	O(4)-Si-C(25)	102.64(10)
C(1)-W-C(3)	116.85(10)	O(3)-Si-C(16)	108.71(11)
O(3)-W-C(3)	90.78(10)	O(4)-Si-C(16)	113.15(10)
C(7)-W-C(3)	93.81(8)	C(25)-Si-C(16)	110.84(11)
C(6)-W-C(3)	36.36(9)	Si-O(3)-W	127.84(10)
C(8)-W-C(3)	81.86(10)	C(4)-O(4)-Si	121.16(17)
C(2)-W-C(9)	127.53(11)	O(1)-C(1)-W	170.8(3)
C(1)-W-C(9)	131.96(9)	O(2)-C(2)-W	175.1(2)
O(3)-W-C(9)	36.45(9)	C(4)-C(3)-W	85.66(16)
C(7)-W-C(9)	60.27(9)	O(4)-C(4)-C(3)	121.6(2)
C(6)-W-C(9)	87.60(10)	O(4)-C(4)-C(5)	111.6(2)
C(8)-W-C(9)	127.34(10)	C(3)-C(4)-C(5)	123.7(2)
C(3)-W-C(9)	78.48(8)	O(4)-C(4)-W	106.55(16)
C(2)-W-C(10)	132.71(9)	C(3)-C(4)-W	62.37(14)
C(1)-W-C(10)	140.38(9)	C(5)-C(4)-W	119.06(17)
O(3)-W-C(10)	96.37(9)	C(10)-C(6)-C(7)	107.2(2)
C(7)-W-C(10)	114.14(10)	C(10)-C(6)-C(11)	126.2(2)
C(6)-W-C(10)	149.26(10)	C(7)-C(6)-C(11)	125.9(2)
C(8)-W-C(10)	58.11(9)	C(10)-C(6)-W	76.97(15)
C(3)-W-C(10)	106.16(9)	C(7)-C(6)-W	70.38(14)
C(9)-W-C(10)	34.01(9)	C(11)-C(6)-W	125.57(18)
C(2)-W-C(4)	77.44(10)	C(6)-C(7)-C(8)	108.2(2)
C(1)-W-C(4)	95.38(9)	C(6)-C(7)-C(12)	125.5(2)
O(3)-W-C(4)	73.38(7)	C(8)-C(7)-C(12)	125.7(2)
C(7)-W-C(4)	154.96(9)	C(6)-C(7)-W	73.26(14)
C(6)-W-C(4)	165.60(9)	C(8)-C(7)-W	73.23(14)
C(8)-W-C(4)	123.79(9)	C(12)-C(7)-W	126.53(19)

C(7)-C(8)-C(9)	107.4(2)	C(16)-C(17)-C(22)	124.3(2)
C(7)-C(8)-C(13)	126.6(3)	C(19)-C(18)-C(17)	122.6(2)
C(9)-C(8)-C(13)	125.3(3)	C(18)-C(19)-C(20)	117.4(2)
C(7)-C(8)-W	70.32(14)	C(18)-C(19)-C(23)	121.3(2)
C(9)-C(8)-W	75.40(15)	C(20)-C(19)-C(23)	121.3(3)
C(13)-C(8)-W	127.24(19)	C(19)-C(20)-C(21)	122.1(2)
C(10)-C(9)-C(8)	108.0(2)	C(20)-C(21)-C(16)	120.1(2)
C(10)-C(9)-C(14)	125.6(3)	C(20)-C(21)-C(24)	118.2(2)
C(8)-C(9)-C(14)	126.1(3)	C(16)-C(21)-C(24)	121.8(2)
C(10)-C(9)-W	74.28(14)	C(30)-C(25)-C(26)	117.4(2)
C(8)-C(9)-W	69.09(14)	C(30)-C(25)-Si	124.2(2)
C(14)-C(9)-W	126.86(18)	C(26)-C(25)-Si	118.4(2)
C(9)-C(10)-C(6)	109.0(2)	C(27)-C(26)-C(25)	120.1(3)
C(9)-C(10)-C(15)	125.7(2)	C(27)-C(26)-C(31)	117.8(3)
C(6)-C(10)-C(15)	125.3(2)	C(25)-C(26)-C(31)	122.1(2)
C(9)-C(10)-W	71.72(15)	C(28)-C(27)-C(26)	122.6(3)
C(6)-C(10)-W	68.06(14)	C(27)-C(28)-C(29)	117.3(3)
C(15)-C(10)-W	125.87(18)	C(27)-C(28)-C(32)	120.8(3)
C(17)-C(16)-C(21)	117.7(2)	C(29)-C(28)-C(32)	121.9(3)
C(17)-C(16)-Si	126.18(19)	C(28)-C(29)-C(30)	122.5(3)
C(21)-C(16)-Si	115.90(18)	C(29)-C(30)-C(25)	120.1(3)
C(18)-C(17)-C(16)	120.1(2)	C(29)-C(30)-C(33)	116.3(3)
C(18)-C(17)-C(22)	115.6(2)	C(25)-C(30)-C(33)	123.6(2)

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W	16(1)	20(1)	22(1)	0(1)	6(1)	1(1)
Si	17(1)	22(1)	27(1)	−3(1)	10(1)	−1(1)
O(1)	52(2)	39(1)	25(1)	−1(1)	6(1)	5(1)
O(2)	39(1)	33(1)	50(1)	6(1)	20(1)	−5(1)
O(3)	18(1)	23(1)	33(1)	−1(1)	11(1)	−1(1)
O(4)	16(1)	23(1)	35(1)	−1(1)	10(1)	−1(1)
C(1)	25(1)	22(1)	31(1)	−2(1)	5(1)	2(1)
C(2)	25(1)	24(1)	33(1)	−2(1)	11(1)	−1(1)
C(3)	23(1)	27(1)	30(1)	−5(1)	10(1)	2(1)
C(4)	20(1)	25(1)	31(1)	−8(1)	8(1)	−1(1)
C(5)	22(1)	25(1)	48(2)	1(1)	6(1)	−2(1)
C(6)	21(1)	23(1)	26(1)	3(1)	10(1)	4(1)
C(7)	21(1)	23(1)	29(1)	1(1)	9(1)	3(1)
C(8)	19(1)	25(1)	32(1)	1(1)	4(1)	5(1)
C(9)	27(1)	26(1)	25(1)	2(1)	6(1)	9(1)
C(10)	22(1)	26(1)	27(1)	6(1)	10(1)	6(1)
C(11)	34(2)	27(1)	32(1)	−2(1)	10(1)	0(1)
C(12)	32(2)	38(2)	44(2)	1(1)	23(1)	2(1)
C(13)	24(2)	35(2)	50(2)	−6(1)	−1(1)	0(1)
C(14)	49(2)	44(2)	26(1)	0(1)	6(1)	14(1)
C(15)	36(2)	32(2)	41(2)	9(1)	21(1)	3(1)
C(16)	16(1)	25(1)	27(1)	−2(1)	7(1)	0(1)
C(17)	19(1)	28(1)	30(1)	−4(1)	11(1)	−1(1)
C(18)	18(1)	34(1)	26(1)	−6(1)	7(1)	2(1)
C(19)	19(1)	35(1)	25(1)	2(1)	6(1)	6(1)
C(20)	18(1)	24(1)	33(1)	3(1)	8(1)	2(1)
C(21)	14(1)	26(1)	27(1)	0(1)	5(1)	2(1)
C(22)	38(2)	30(2)	39(2)	−11(1)	20(1)	−6(1)

C(23)	38(2)	42(2)	31(1)	4(1)	13(1)	4(1)
C(24)	26(1)	23(1)	32(1)	−3(1)	11(1)	−4(1)
C(25)	21(1)	26(1)	26(1)	3(1)	10(1)	−5(1)
C(26)	24(1)	25(1)	33(1)	7(1)	10(1)	−2(1)
C(27)	29(1)	30(2)	41(2)	13(1)	4(1)	−1(1)
C(28)	40(2)	36(2)	39(2)	9(1)	−2(1)	−8(1)
C(29)	39(2)	34(2)	30(1)	1(1)	4(1)	−11(1)
C(30)	27(1)	29(1)	26(1)	1(1)	11(1)	−8(1)
C(31)	23(1)	30(1)	40(2)	5(1)	15(1)	6(1)
C(32)	61(3)	50(2)	54(2)	8(2)	−24(2)	2(2)
C(33)	30(2)	39(2)	36(2)	−13(1)	11(1)	−3(1)

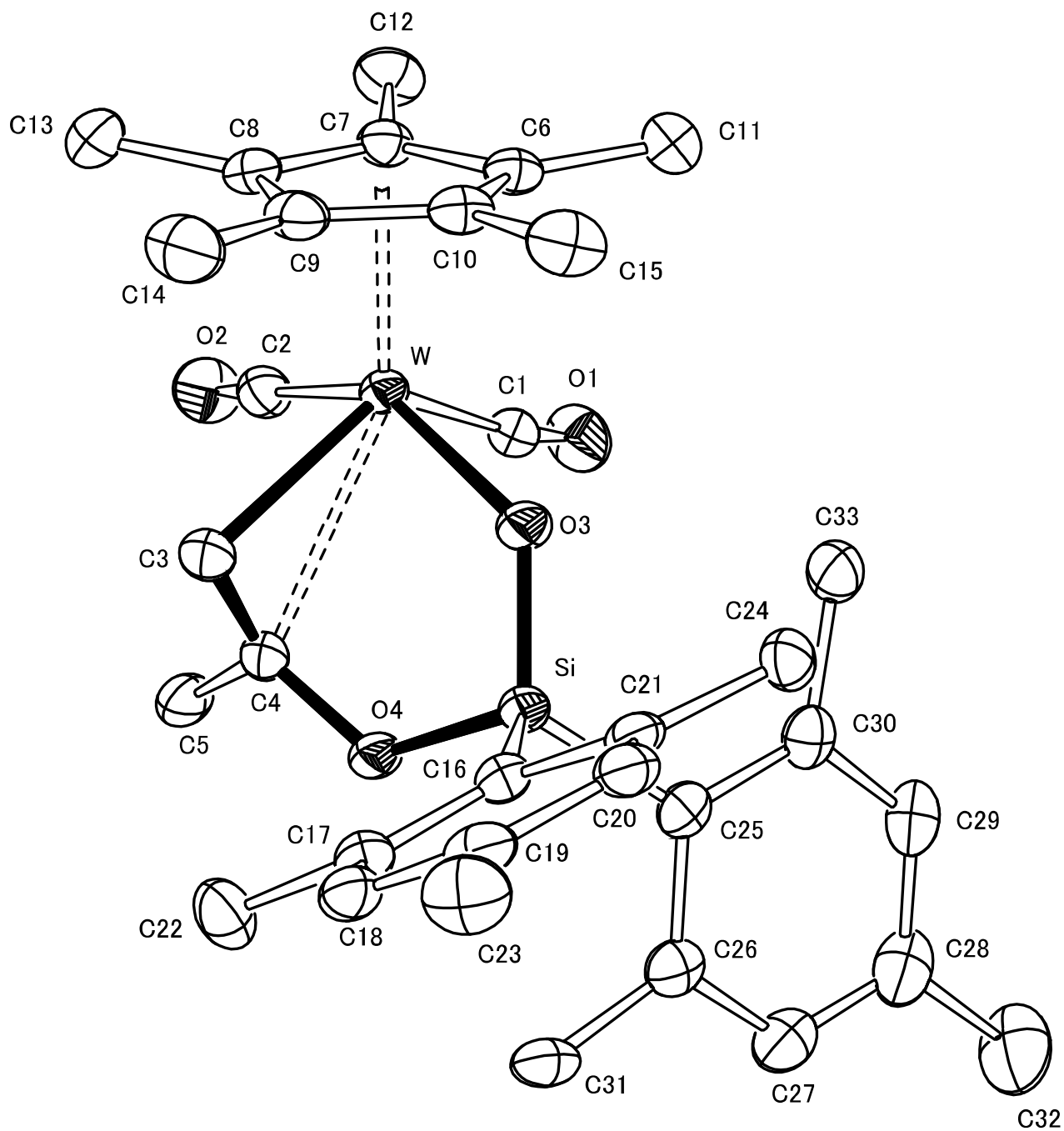


Figure S4. ORTEP drawing of **9**. (thermal ellipsoids at the 50% probability level).

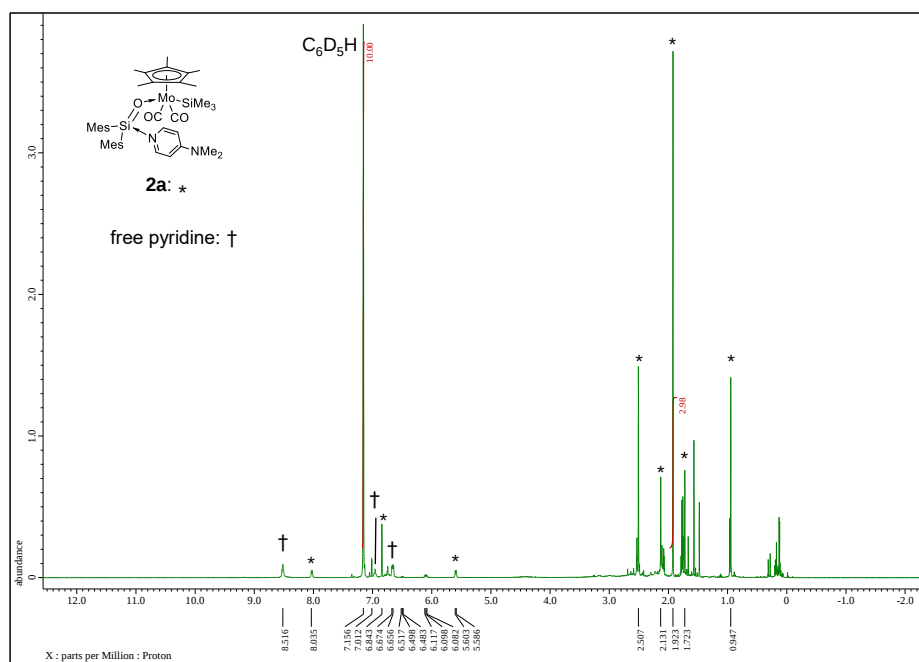


Figure S5. ¹H NMR spectrum of the reaction of **2b** with 1 equiv. of DMAP (400 MHz, C₆D₆).

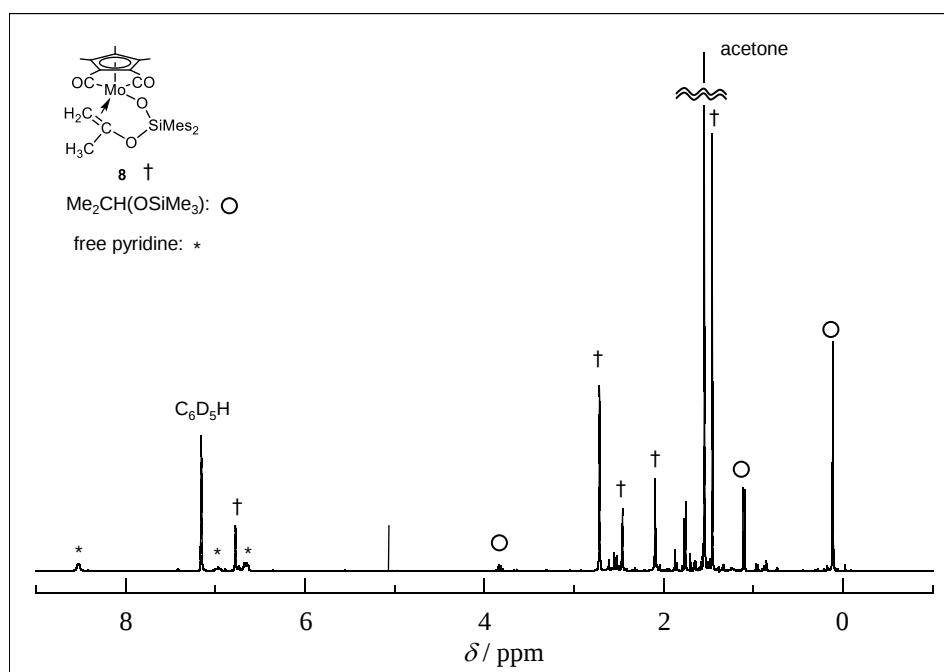


Figure S6. ¹H NMR spectrum of the reaction of **2b** with excess acetone (300 MHz, C₆D₆).

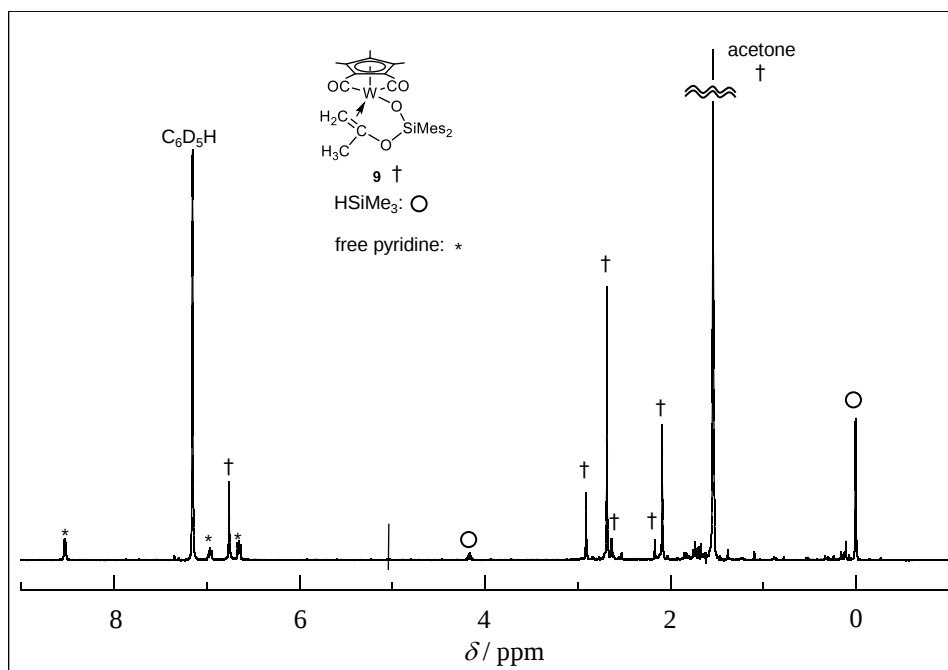


Figure S7. ¹H NMR spectrum of the reaction of **1b** with excess acetone (400 MHz, C₆D₆).

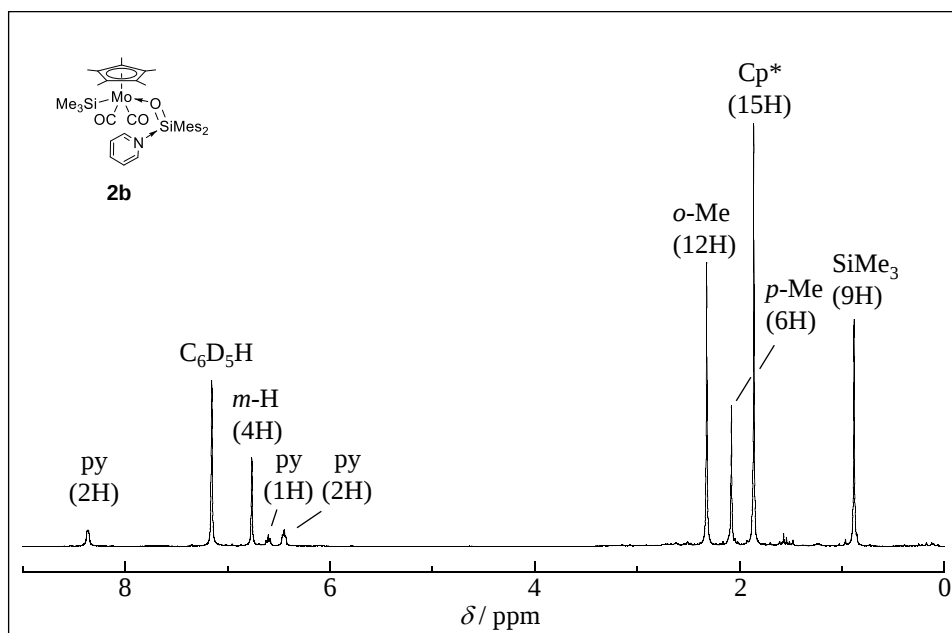


Figure S8. ¹H NMR spectrum of **2b** (400 MHz, C₆D₆).

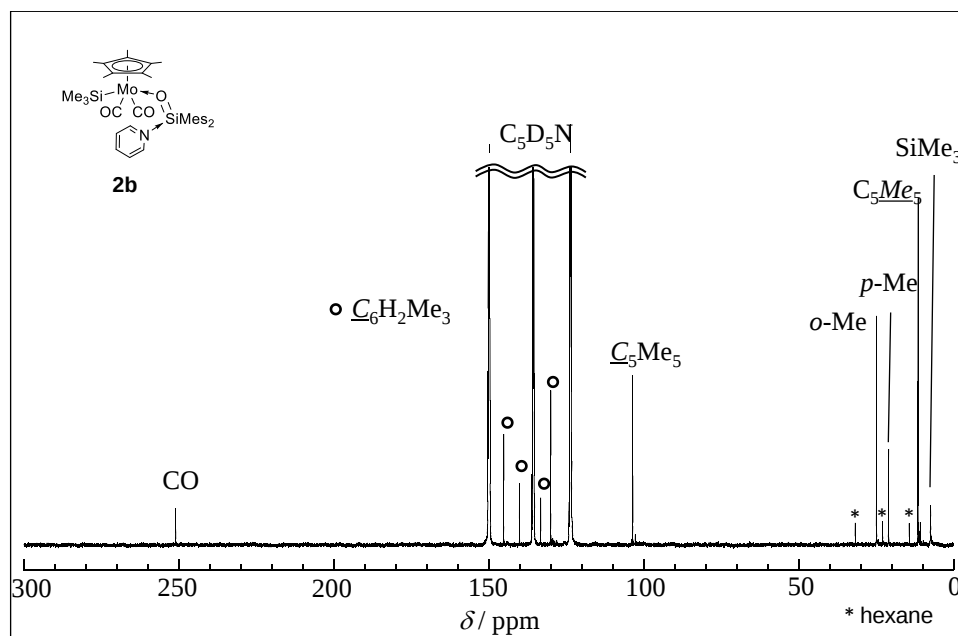


Figure S9. ^{13}C NMR spectrum of **2b** (150.9 MHz, $\text{C}_6\text{D}_5\text{N}$, -20°C).

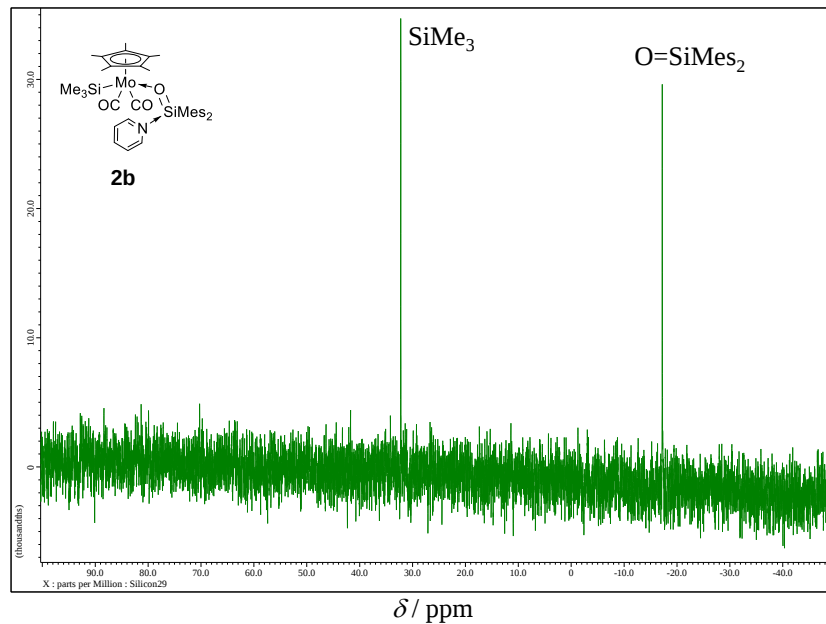


Figure S10. ^{29}Si NMR spectrum of **2b** (119.2 MHz, $\text{C}_6\text{D}_5\text{N}$, -20°C).

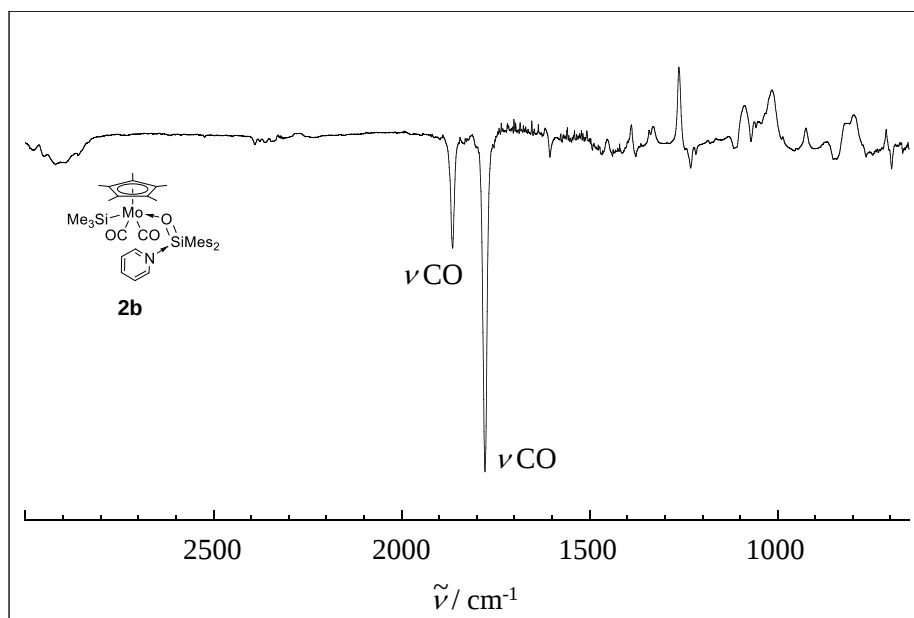


Figure S11. IR spectrum of **2b** (C_6D_6).

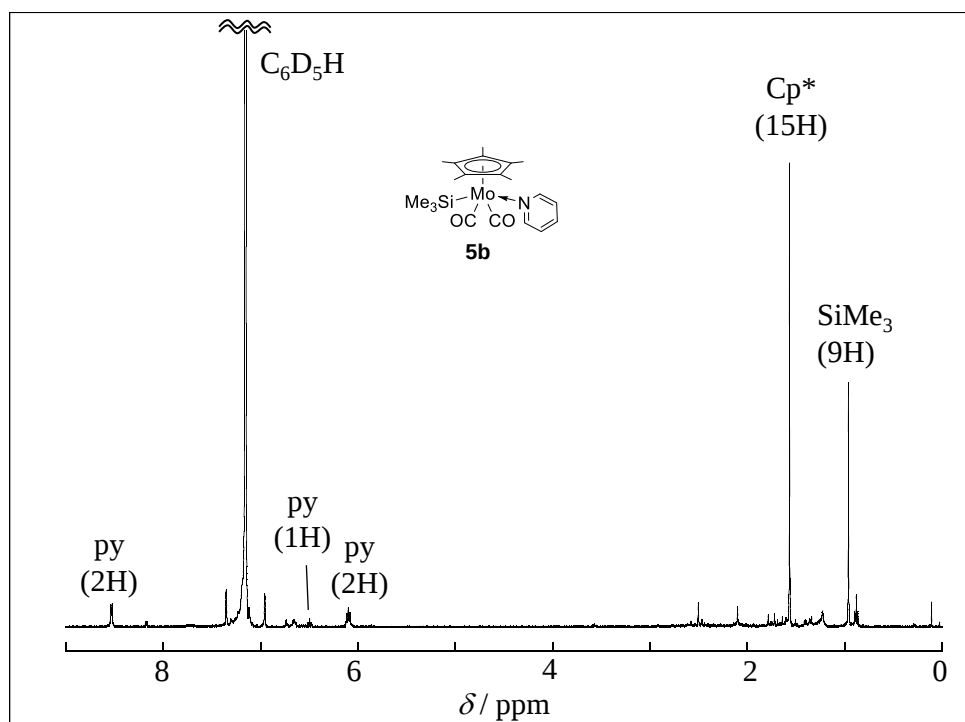


Figure S12. ^1H NMR spectrum of **5b** (400 MHz, C_6D_6).

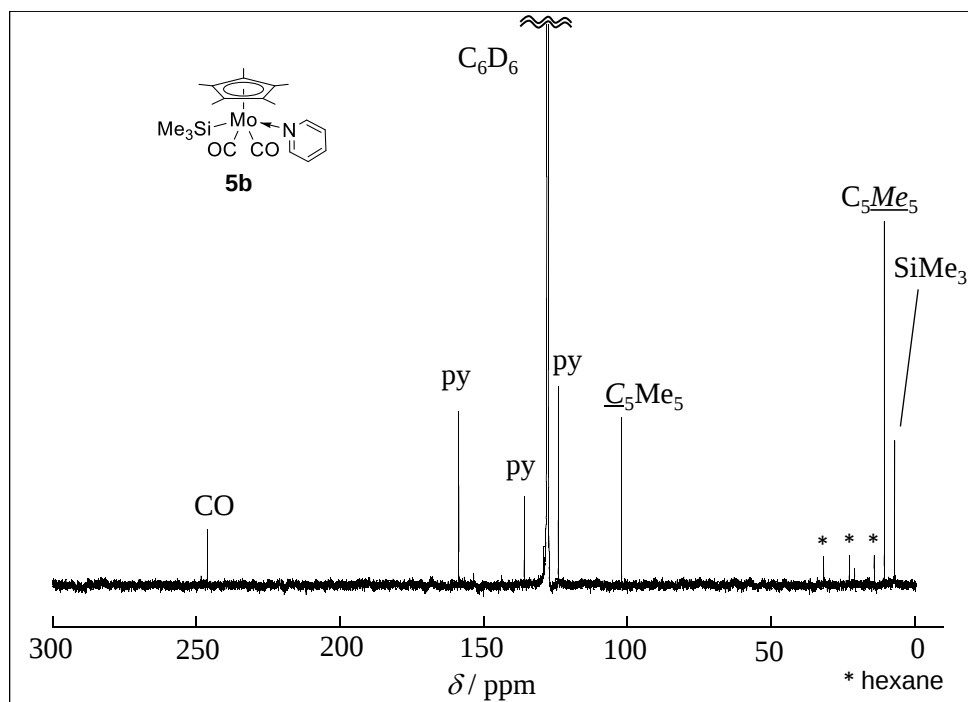


Figure S13. ^{13}C NMR spectrum of **5b** (150.6 MHz, C_6D_6).

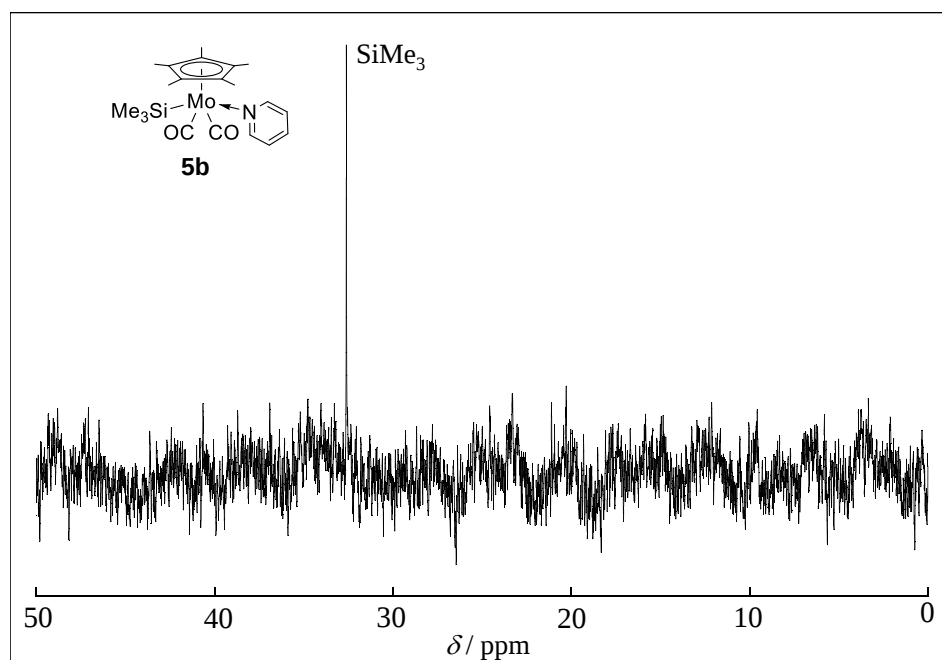


Figure S14. ^{29}Si NMR spectrum of **5b** (119.2 MHz, C_6D_6).

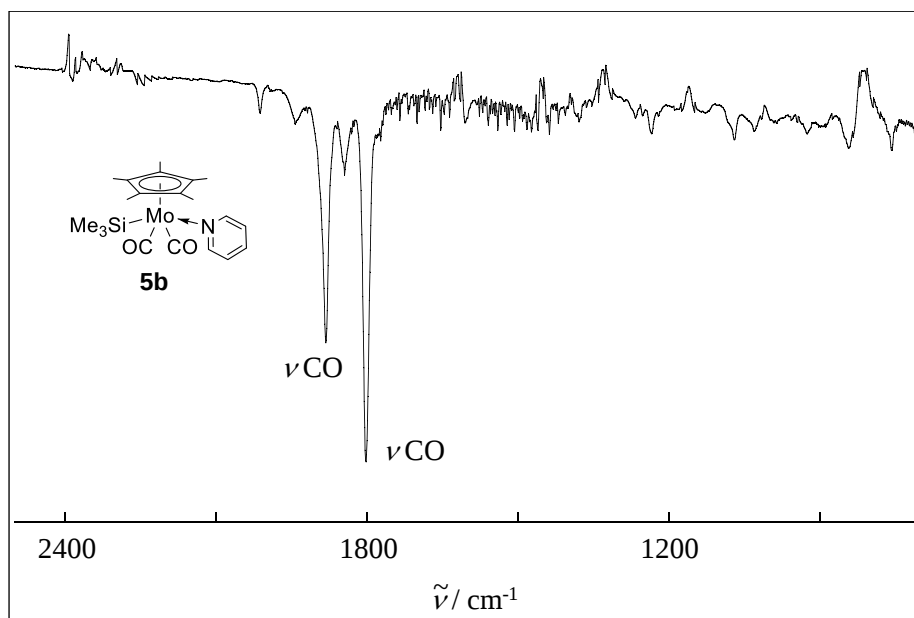


Figure S15. IR spectrum of **5b** (C_6D_6).

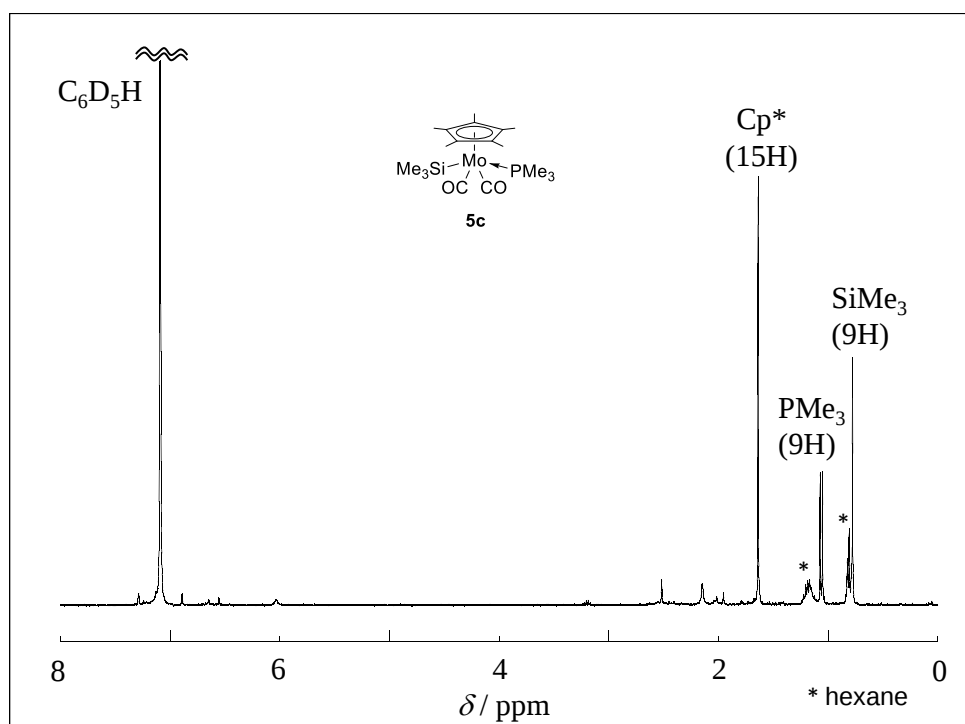


Figure S16. ^1H NMR spectrum of **5c** (400 MHz, C_6D_6).

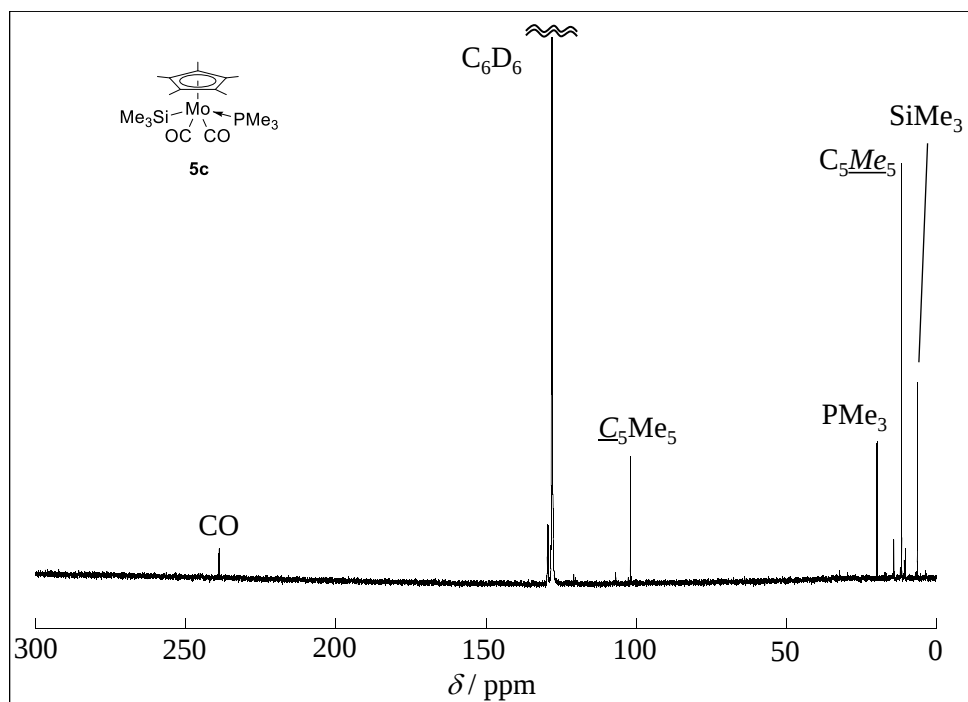


Figure S17. ^{13}C NMR spectrum of **5c** (150.6 MHz, C_6D_6).

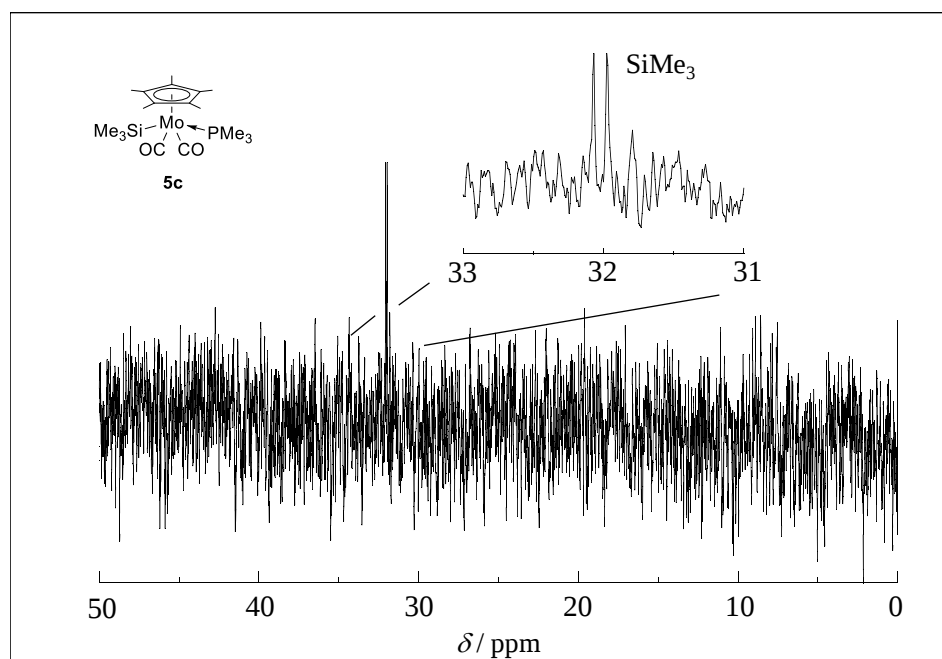


Figure S18. ^{29}Si NMR spectrum of **5c** (119.2 MHz, C_6D_6).

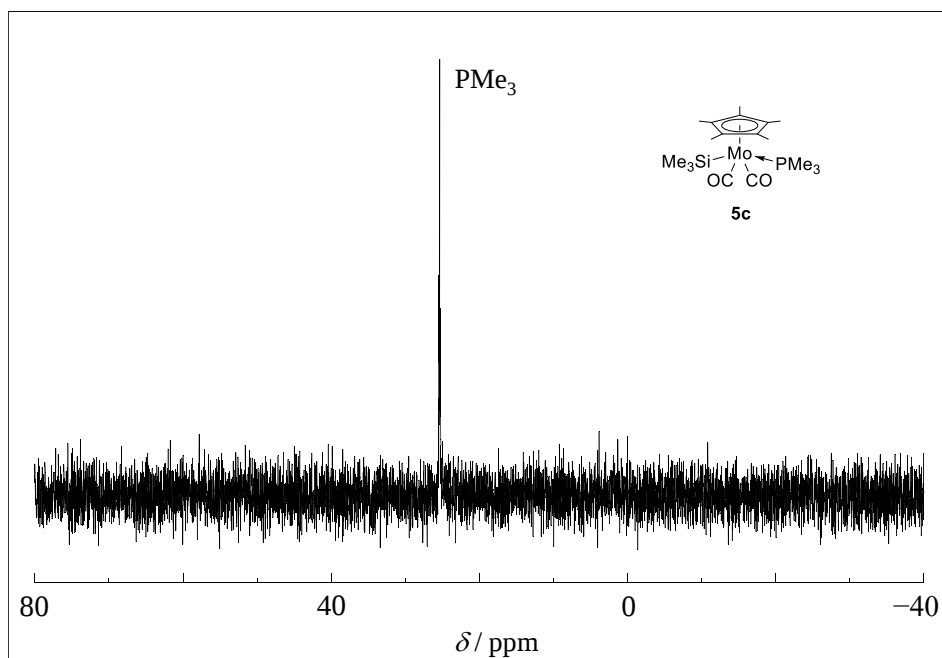


Figure S19. ^{31}P NMR spectrum of **5c** (161.9 MHz, C_6D_6).

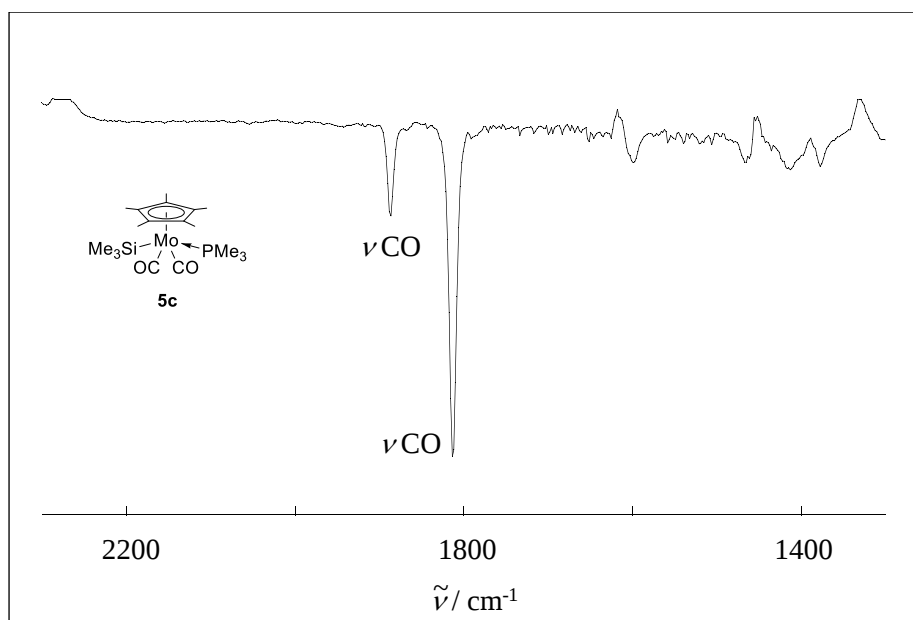


Figure S20. IR spectrum of **5c** (C_6D_6).

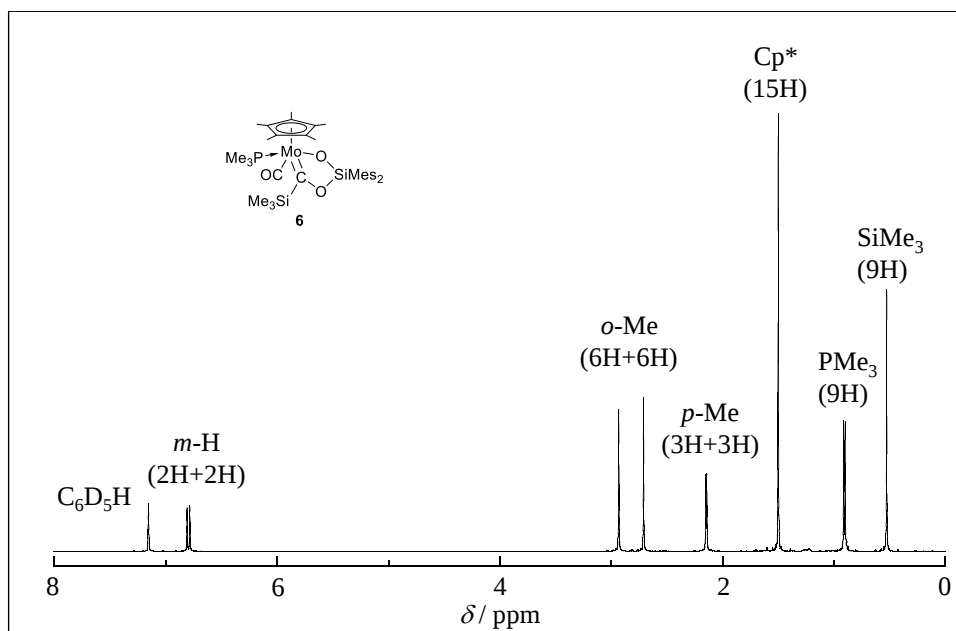


Figure S21. ¹H NMR spectrum of **6** (600 MHz, C₆D₆).

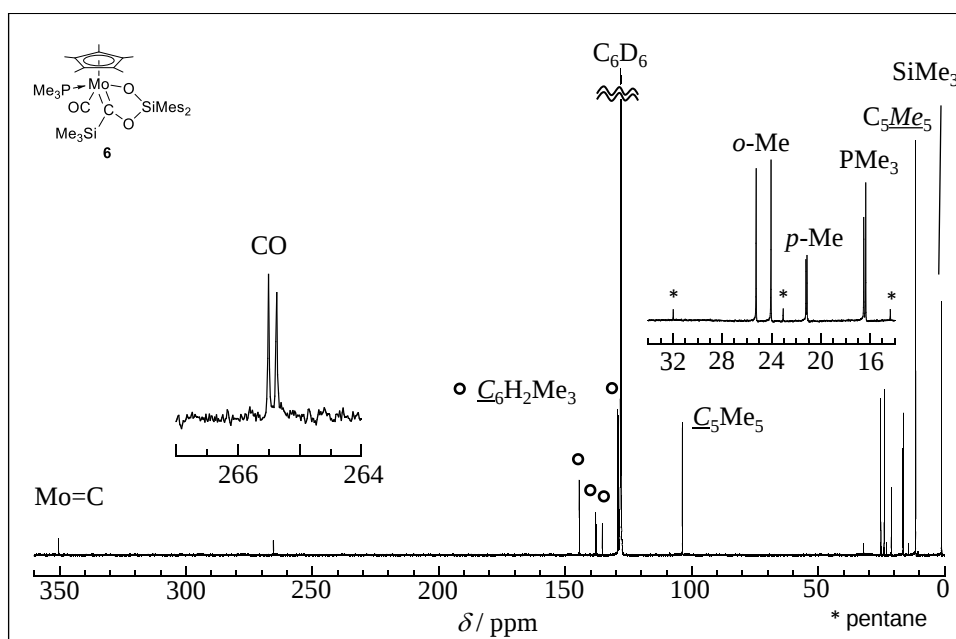


Figure S22. ¹³C NMR spectrum of **6** (150.9 MHz, C₆D₆).

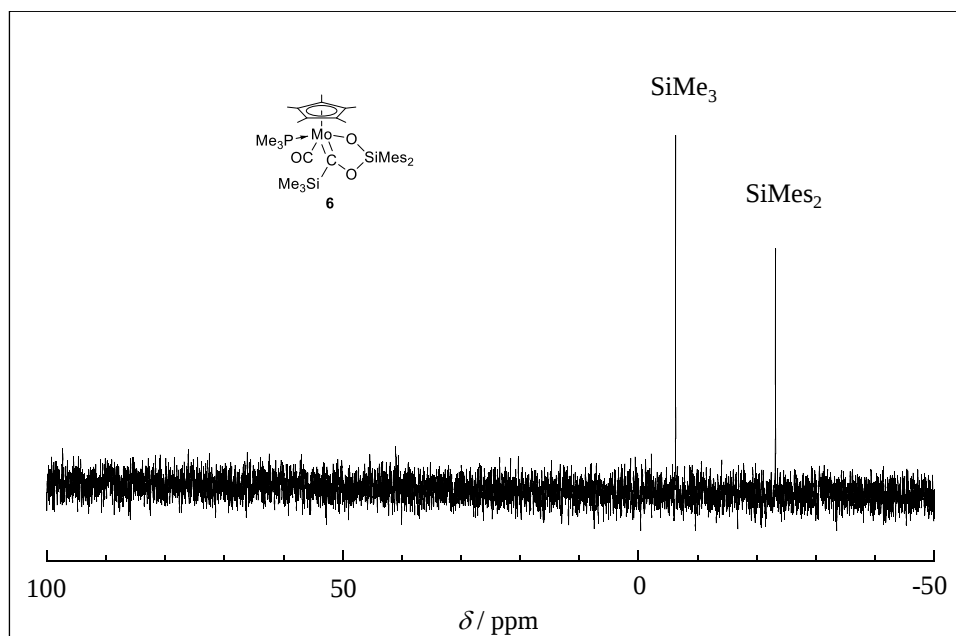


Figure S23. ^{29}Si NMR spectrum of **6** (119.2 MHz, C_6D_6).

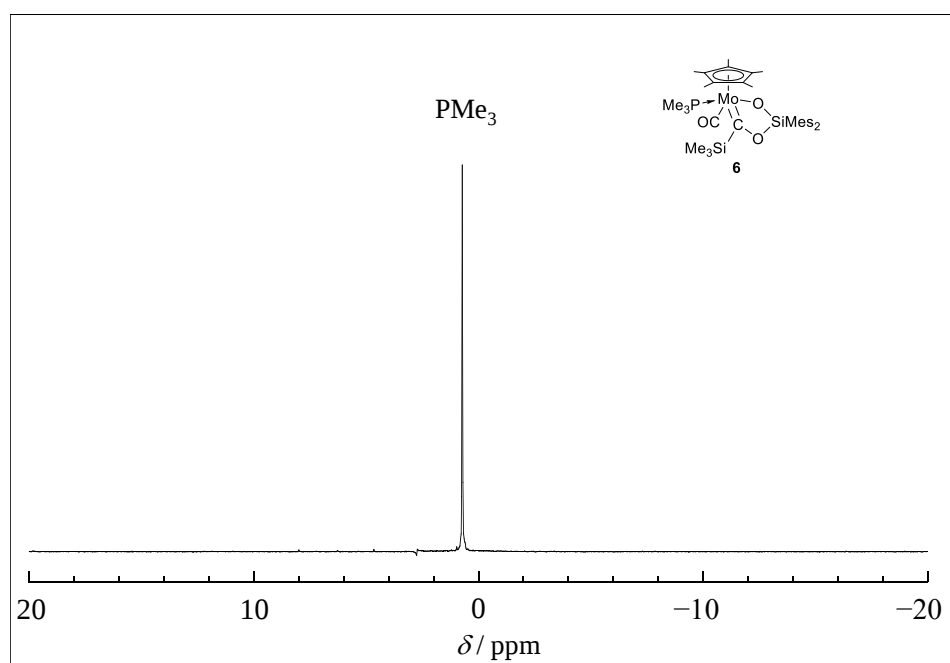


Figure S24. ^{31}P NMR spectrum of **6** (121.7 MHz, C_6D_6).

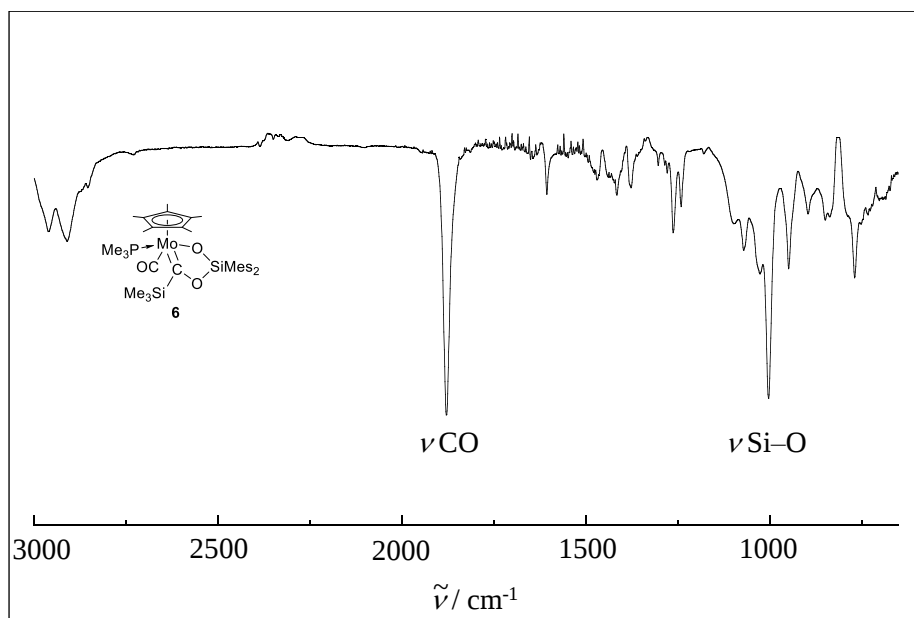


Figure S25. IR spectrum of **6** (C_6D_6).

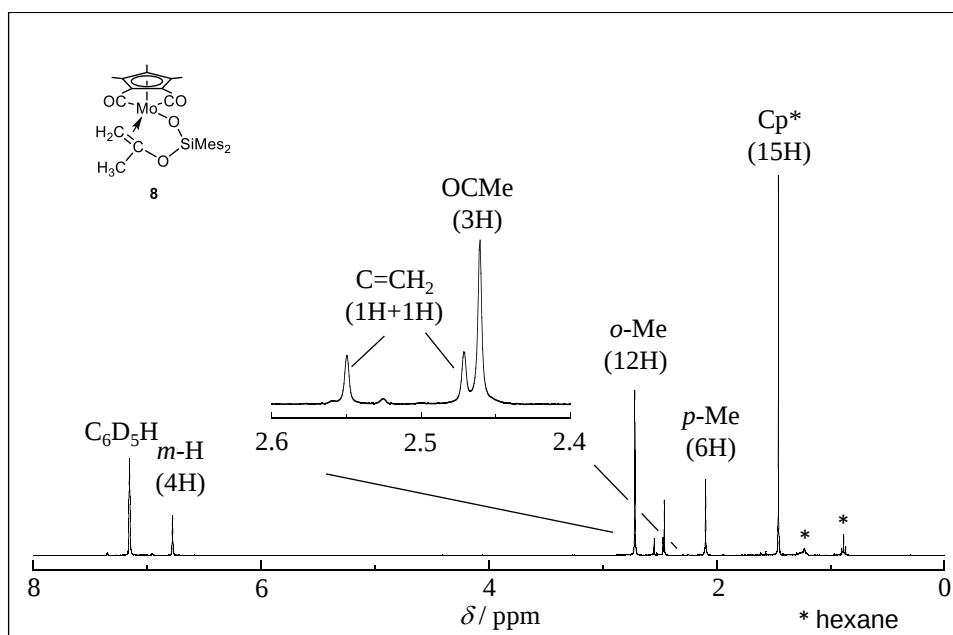


Figure S26. ^1H NMR spectrum of **8** (400 MHz, C_6D_6).

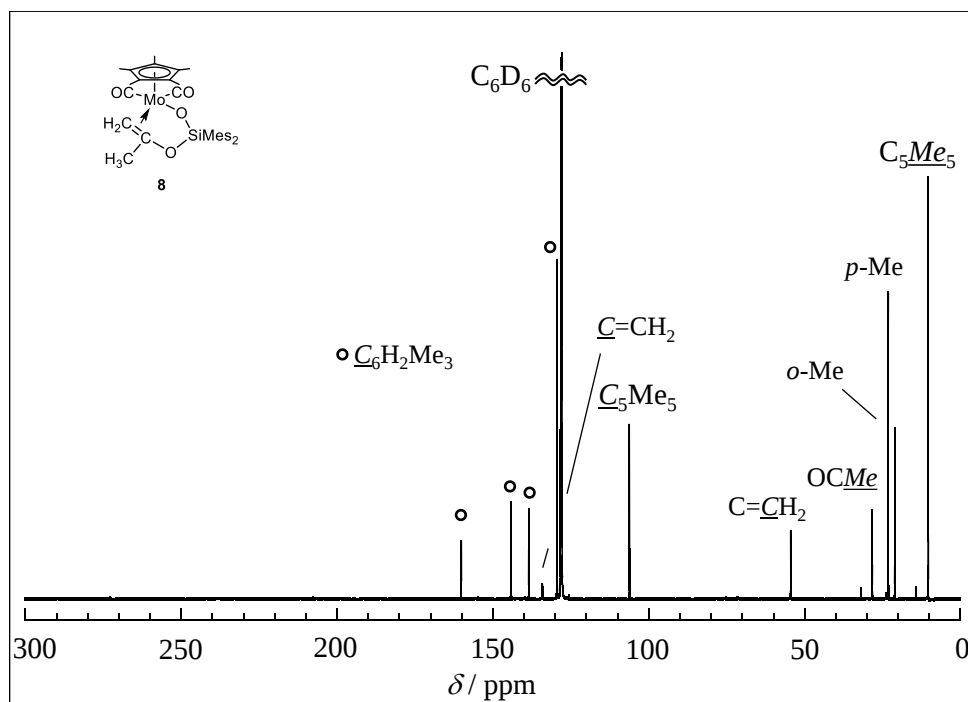


Figure S27. ^{13}C NMR spectrum of **8** (150.9 MHz, C_6D_6).

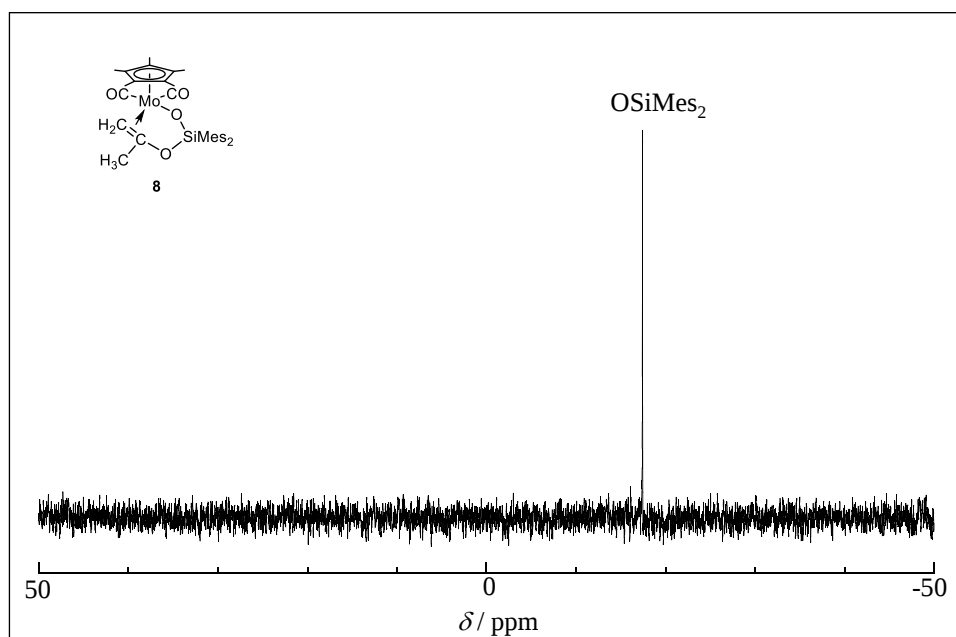


Figure S28. ^{29}Si NMR spectrum of **8** (119.2 MHz, C_6D_6).

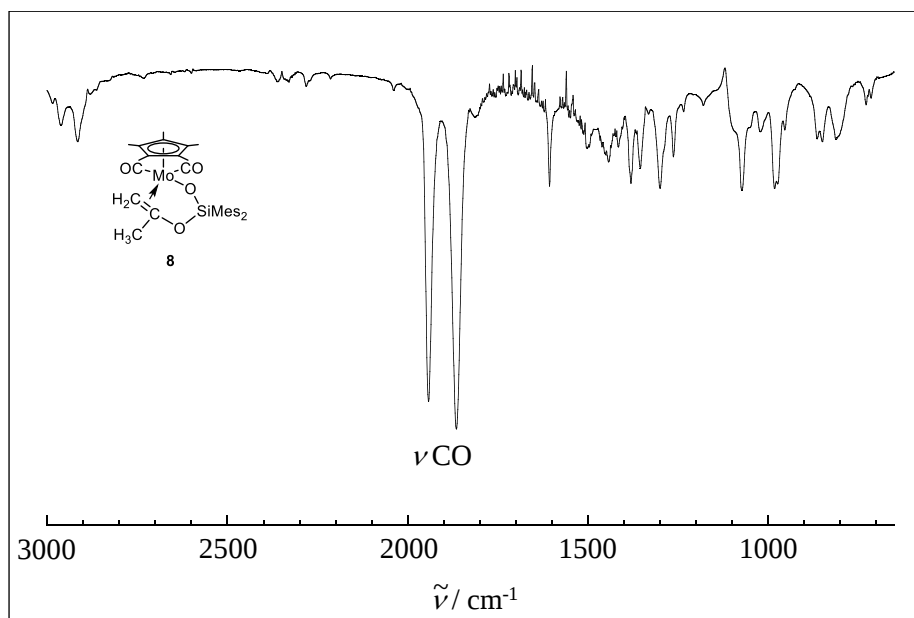


Figure S29. IR spectrum of **8** (C_6D_6).

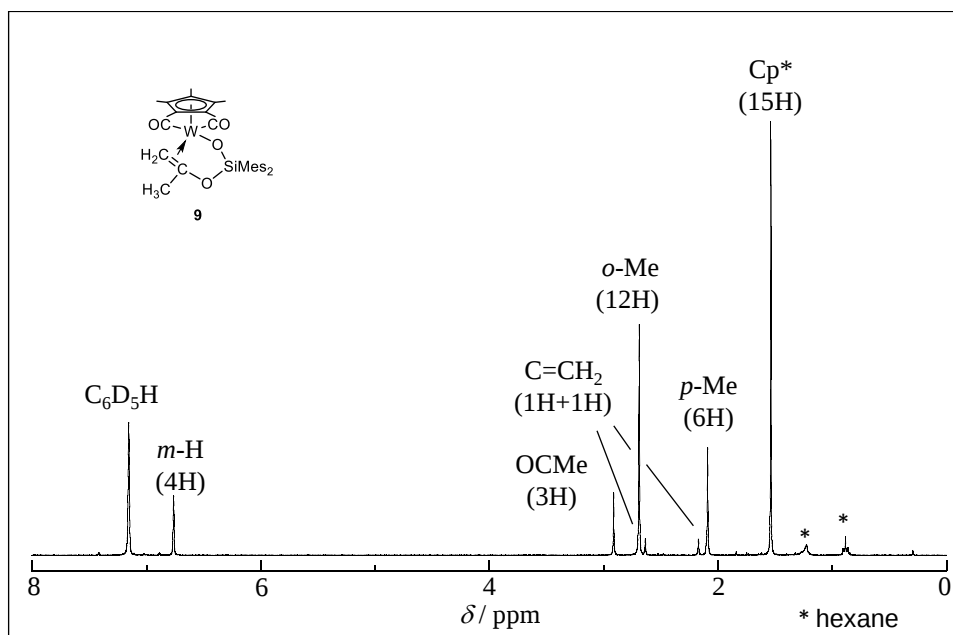


Figure S30. ^1H NMR spectrum of **9** (300 MHz, C_6D_6).

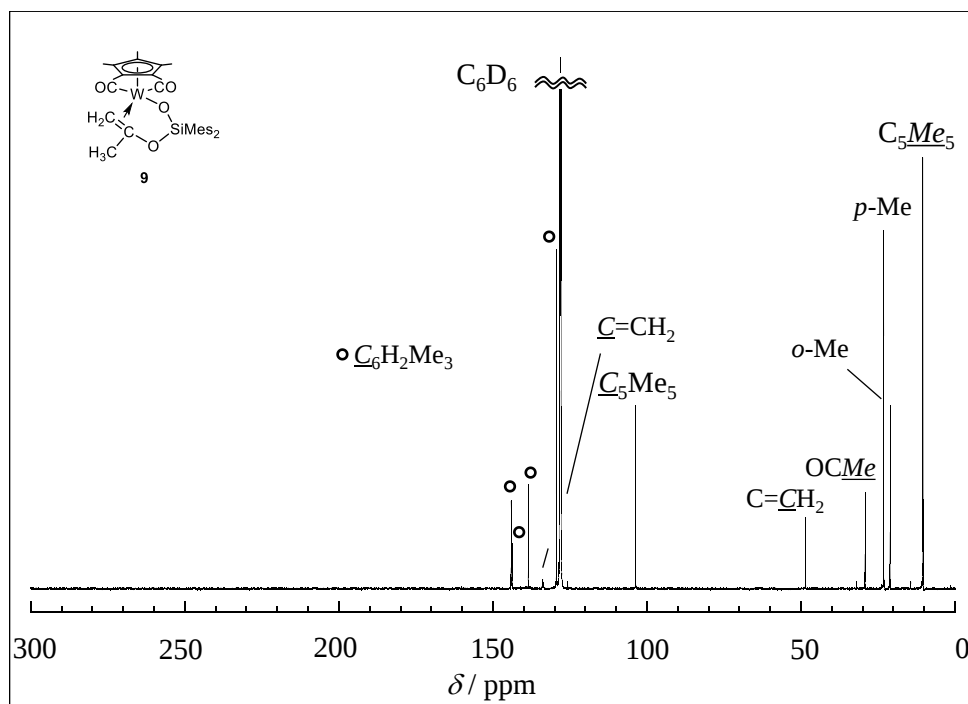


Figure S31. ^{13}C NMR spectrum of **9** (150.9 MHz, C_6D_6).

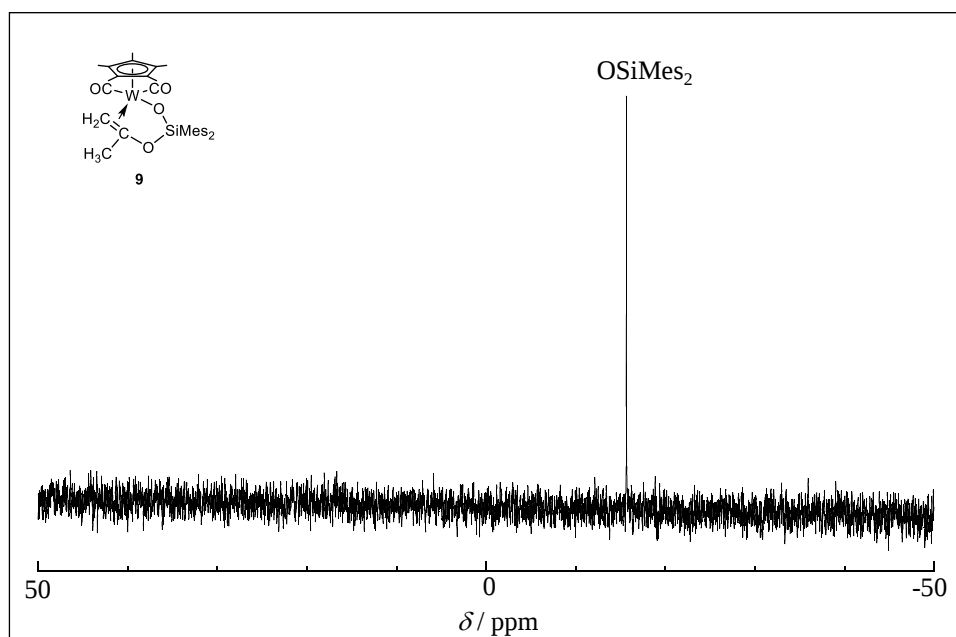


Figure S32. ^{29}Si NMR spectrum of **9** (119.2 MHz, C_6D_6).

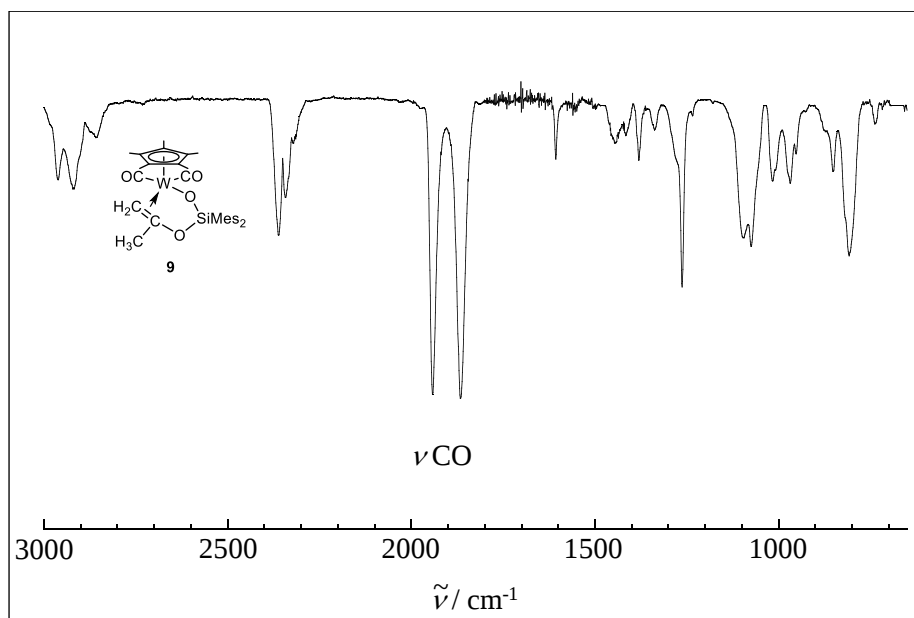


Figure S33. IR spectrum of **9** (C_6D_6).

References

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