Supporting Information

Reactive Coordinatively Saturated Mo(III) Complex: Exploiting the Hemilability of tris(*tert*-butoxy)silanolate Ligands.

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General Considerations

All experiments were carried out under an inert argon atmosphere using Schlenk techniques and a MBraun glovebox equipped with a purifier unit. Water and oxygen levels were always kept below 0.1 ppm. Toluene was purified using double MBraun SPS alumina columns. Benzene, Diethyl Ether and benzene-d_6 were distilled from Na/benzophenone. Pentane was de-olefinated by treatment with sulfuric acid (two cycles, then neutralized with sodium bicarbonate, filtered through Celite® and dried over magnesium sulphate), then distilled from K/benzophenone. All the solvents were degassed by three consecutive freeze-pump-thaw cycles. $(^tBuO)_3SiOH$ was purchased from Aldrich and sublimed prior to use. Elemental Analyses were performed in Mikroelementaranalytisches Laboratorium, ETH, Zurich. All infrared (IR) spectra were recorded using a Bruker FT- IR Alpha spectrometer placed in the glovebox, equipped with OPUS software. The IR spectrometer presents a total spectral range of 275-7500 cm^{-1} with a resolution < 2 cm^{-1}. The interferometer is RockSolid, and the detector is a DTGS (triglycine sulfate) and the source is a SiC globar source. The solid samples were investigated in a magnetic pellet holder. A typical experiment consisted of the measurement of transmission in 32 scans in the region from 4000 to 400 cm^{-1}. Solution ^{1}H-NMR spectra were obtained on Bruker DRX 300 and Bruker DRX 400 spectrometers. The ^{1}H chemical shifts are referenced relative to the residual solvent peak and reported relative to tetramethylsilane (δ= 0 ppm). Magnetic susceptibility was measured using Evans Method[1] using a sealed glass capillary coaxial with a J-young NMR tube. VT-NMR was measured on

a Bruker DRX 400 spectrometer in benzene-d_6 at 298.15 K. Ethylene and N_2 were stored on Cu-catalyst (R3-11 from BASF) and 4-Å molecular sieves before use. Isobutene, CO, CO_2 and N_2O were dried on 4-Å molecular sieves before use. But-2-yne was distilled over Na and degassed by three consecutive freeze-pump-thaw cycles.

Synthesis of Molecular Precursors and Reactivity

Synthesis of [Mo(OSi(OtBu)$_3$)$_3$], 1.

A solution of HOSi(O^{t}Bu)$_3$ (465 mg, 1.758 mmol, 2.98 equiv.) in diethyl ether (10 mL, –40 °C) was added dropwise to a slurry of Mo(N(^{t}Bu)Ar)$_3$[2] (371 mg, 0.593 mmol, 1 equiv.) in diethyl ether (10 mL, –80 °C). The reaction mixture initially red turned brown. After stirring for 2h at –80 °C, the volatiles were removed *in vacuo* to afford a brown solid, before being extracted with cold toluene (–40°C). Removal of the volatiles at -40°C under high vacuum (10^{-5} mbar) afforded a brown solid. Recrystallization from cold pentane (–40°C) afforded dark purple crystals of **1** (187 mg, combined yield: 35%).

^{1}H NMR (300 MHz, C_6D_6): δ = 3.82 (br), $\nu_{½}$ = 164 Hz.

μ_{eff} = 3.74 μ_B

IR (in KBr): v = 2975m, 1473w, 1390w, 1365w, 1240m, 1187w, 1127w, 1066w, 1026w, 983w, 940w, 828w, 814w, 694w, 625w, 568w, 514w.

Anal.Calcd. for $C_{36}H_{81}MoO_{12}Si_3$: C, 48.61 (48.79% expected); H, 9.45 (9.21% expected); N, 0.14 (0% expected).

Reaction of $Mo(TBOS)_3$, 1 with ethylene, synthesis of [C_2H_4-$Mo(OSi(OtBu)_3)_3$], 1-(ethylene).

A solution of $Mo(TBOS)_3$ (22.3 mg, 0.025 mmol, 1 equiv.) in C_6D_6 (2 mL) was loaded in a J-Young NMR tube and contacted with isobutene (700 mbar, 0.99 mmol, 40 equiv.). The reaction mixture initially amber turned green. Volatiles were removed *in vacuo* and the solid was extracted in pentane (0.4 mL). Green crystals of **1-(ethylene)** were obtained by slow evaporation at –40 °C (11 mg, 48% yield).

^1H NMR (300 MHz, C_6D_6, ppm): δ = 1.69 (br), $\nu_{½}$ = 73 Hz.

μ_{eff} = 1.6 μ_B

IR (in KBr): v = 2976m, 2932w, 1473w, 1389w, 1365m, 1244m, 1193m, 1063s, 1026m, 901m, 829m, 700m, 660w, 513w, 471w.

Anal.Calcd. for $C_{38}H_{85}MoO_{12}Si_3$: C, 47.16 (49.92% expected); H, 8.75 (9.37% expected); N, 0.01 (0% expected). Variable lower values were found for carbon and hydrogen through the analysis of multiple samples. This is probably due to the loss of ethylene and to the partial decomposition of the TBOS ligand in volatile products (isobutene) during the transfer of the product at room temperature to elemental analysis as previously observed for reduced complexes bearing TBOS ligand.[3]

Reaction of $Mo(TBOS)_3$, 1 with isobutene, synthesis of [C_4H_9-$Mo(OSi(OtBu)_3)_3$],1-(isobutene).

A solution of $Mo(TBOS)_3$ (9.6 mg, 0.01 mmol, 1 equiv.) in C_6D_6 (2 mL) was loaded in a J-Young NMR tube and contacted with isobutene (76 mbar, 0.108 mmol, 10 equiv.). The reaction mixture initially amber turned green. Volatiles

were removed *in vacuo* and the solid was extracted in pentane (0.3 mL). Green crystals of **1-(isobutene)** were obtained by slow evaporation at –40 °C) (5 mg, 48% yield).

^{1}H NMR (300 MHz, C_6D_6, ppm): δ = 1.69 (br), $\nu_{½}$ = 73 Hz.

Reaction of Mo(TBOS)$_3$, 1 with but-2-yneyne, synthesis of [C_4H_6-Mo(OSi(OtBu)$_3$)$_3$], 1-(but-2-yne).

A solution of Mo(TBOS)$_3$ (8 mg, 0.008 mmol, 1 equiv.) in C_6D_6 (2 mL) was loaded in a J-Young NMR tube and contacted with but-2-yne (30 µL, 0.36 mmol, 40 equiv.). The reaction mixture initially amber turned green/yellow; this change being accompanied with the formation of a white solid (possibly being polymerized butyne). Filtration, removal of the volatiles *in vacuo* and crystallization in pentane by slow evaporation (0.3 mL, –40 °C) afforded **1-(but-2-yne)** (5 mg, 48% yield) as bright green crystals.

^{1}H NMR (300 MHz, C_6D_6, ppm): δ = 1.59 (br) $\nu_{½}$ = 46 Hz, 1.51 (s, C*H*$_3$–C≡C–C*H*$_3$).

Reaction of Mo(TBOS)$_3$, 1 with N_2, synthesis of [Mo(N)(OSi(OtBu)$_3$)$_3$], 2.

A solution of Mo(TBOS)$_3$ (41 mg, 0.046 mmol, 1 equiv.) in C_6D_6 (2 mL) was loaded in a J-Young NMR tube and contacted with N_2 (1 atm, 0.10 mmol, 2.5 equiv.). The reaction mixture initially amber first turned to dark blue, before gradually turning colorless over a period of 1.5 h. Volatiles were removed *in vacuo* and the solid was extracted in pentane (0.4 mL). Colorless crystals of **2** were obtained by slow evaporation at –40 °C (15 mg, 40% yield).

^{1}H NMR (300 MHz, C_6D_6, ppm): δ = 1.49 (br), $\nu_{½}$ = 1.81 Hz.

IR (in KBr): v = 2976m, 1765w, 1473w, 1390w, 1366m, 1244m, 1192m, 1067m, 1027w, 893m, 831w, 702m, 657w, 544w, 473w.

Anal.Calcd. for $C_{36}H_{81}MoNO_{12}Si_3$: C, 48.16 (48.03% expected); H, 9.06 (9.07% expected); N, 1.75 (1.56% expected).

Reaction of $Mo(TBOS)_3$, 1 with N_2O, synthesis of $[Mo(N)(OSi(OtBu)_3)_3]$, 2, and $[Mo(NO)(OSi(OtBu)_3)_3]$, 1-NO.

A solution of $Mo(TBOS)_3$ (50 mg, 0.056 mmol, 1 equiv.) in C_6D_6 (2 mL) was loaded in a J-Young NMR tube and contacted with N_2O (300 mbar, 0.42 mmol,8 equiv.). The reaction mixture initially amber turned to green. Volatiles were removed *in vacuo* and the solid was extracted in pentane (0.5 mL). A mixture of **2** and **1-NO** (colorless and yellow crystals) was obtained by slow evaporation at –40 °C (30 mg).

^{1}H NMR (300 MHz, C_6D_6 ppm): δ = 1.51 (**1-NO**), $\nu_{½}$ = 1.5 Hz, 1.50 ppm, (**2**) $\nu_{½}$ = 1.49 Hz.

IR (in KBr): v = 2976m, 2932w, 1677w, 1473w, 1389w, 1366m, 1243m, 1191m, 1067s, 1027w, 983w, 886m, 830w, 702m, 667w, 554w, 472w.

Reaction of $Mo(TBOS)_3$, 1 with CO_2, synthesis of $[Mo(O)(OSi(OtBu)_3)_3]$, 4, and $[Mo(CO)(OSi(OtBu)_3)_3]$, 1-CO.

A solution of $Mo(TBOS)_3$ (45.3 mg, 0.0511 mmol, 1 equiv.) in C_6D_6 (2 mL) was loaded in a J-Young NMR tube and contacted with CO_2 (900 mbar, 1.25 mmol, 25 equiv.). The reaction mixture initially amber turned to dark red. Volatiles were removed *in vacuo* and the solid was extracted in pentane (0.5 mL). A mixture of **4** and **1-CO** (red crystals) was obtained by slow evaporation at –40 °C (35 mg).

^{1}H NMR (300 MHz, C_6D_6, ppm): δ = 1.83 (br), $\nu_{½}$ = 88 Hz, 1.44 (br), $\nu_{½}$ = 17 Hz.

IR (in KBr): v = 2975m, 2931w, 1865m, 1473w, 1389w, 1365m, 1242s, 1192m, 1066s, 1027w, 982w, 938w, 880m, 828w, 700m, 642w, 595w, 469w.

Reaction of $Mo(TBOS)_3$with CO: synthesis of $[Mo(CO)(OSi(OtBu)_3)_3]$, 1-CO.

1-CO can be independently obtained contacting **1** with CO. A solution of $Mo(TBOS)_3$ (17.6 mg, 0.0198 mmol, 1 equiv.) in C_6D_6 (2 mL) was loaded in a J-Young NMR tube and contacted with isobutene (300 mbar, 0.42 mmol, 21 equiv.). The reaction mixture initially amber turned to red. Volatiles were removed *in vacuo* and the solid was extracted in pentane (0.2 mL) Red crystals of **1-CO** were obtained by slow evaporation at –40 °C) (9 mg, 59% yield).

^1H NMR (300 MHz, C_6D_6 ppm): δ = 1.56 (br). $\nu_{½}$ = 105 Hz

The complex does not show loss of CO upon exposure to vacuum (10^{-3} mbar). Anal.Calc. for $C_{37}H_{81}MoO_{17}Si_3$: C, 48.18 (49.61% expected); H, 9.00 (9.29% expected). The lower value found for carbon and hydrogen is probably due to the partial decomposition of the TBOS ligand in volatile products (isobutene) during the transfer of product at room temperature to elemental analysis as previously observed for reduced complexes bearing TBOS ligand.[4]

Solution NMR-Spectroscopy

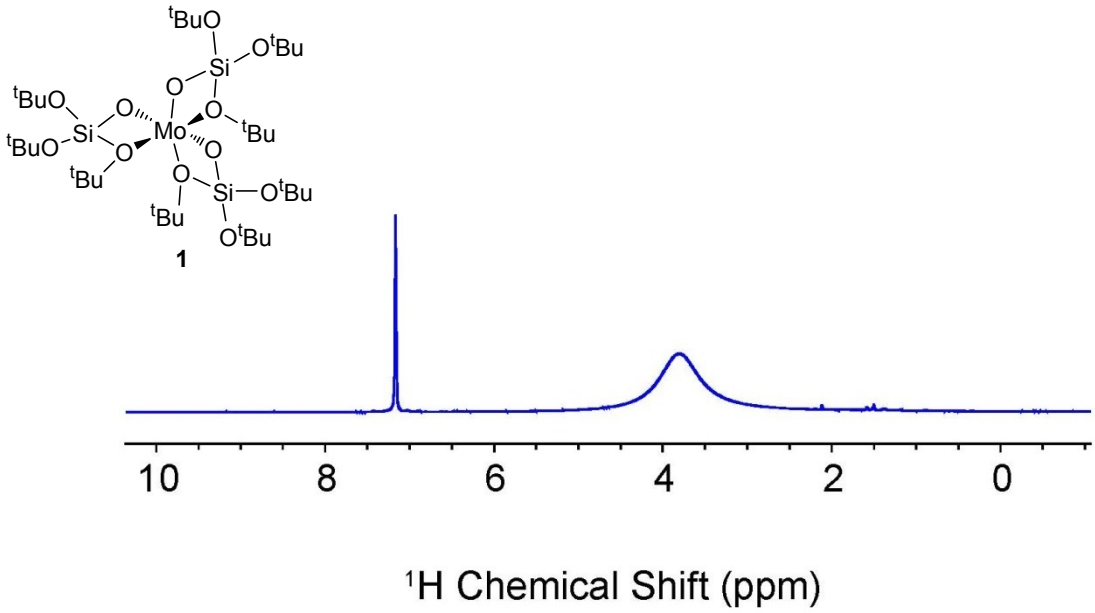


Figure S1 ^{1}H NMR spectrum (300MHz, C_6D_6, 25°C) of [Mo(OSi(OtBu)$_3$)$_3$], **1**.

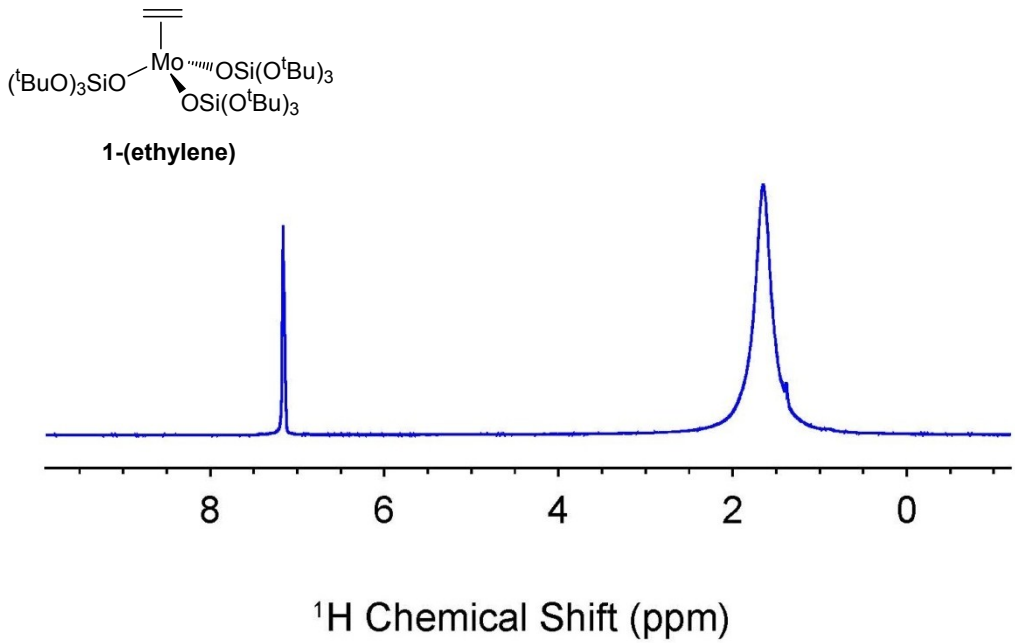


Figure S2. ^{1}H NMR spectrum (300MHz, C_6D_6, 25°C) of [C_2H_4-Mo(OSi(OtBu)$_3$)$_3$], **1-(ethylene)**.

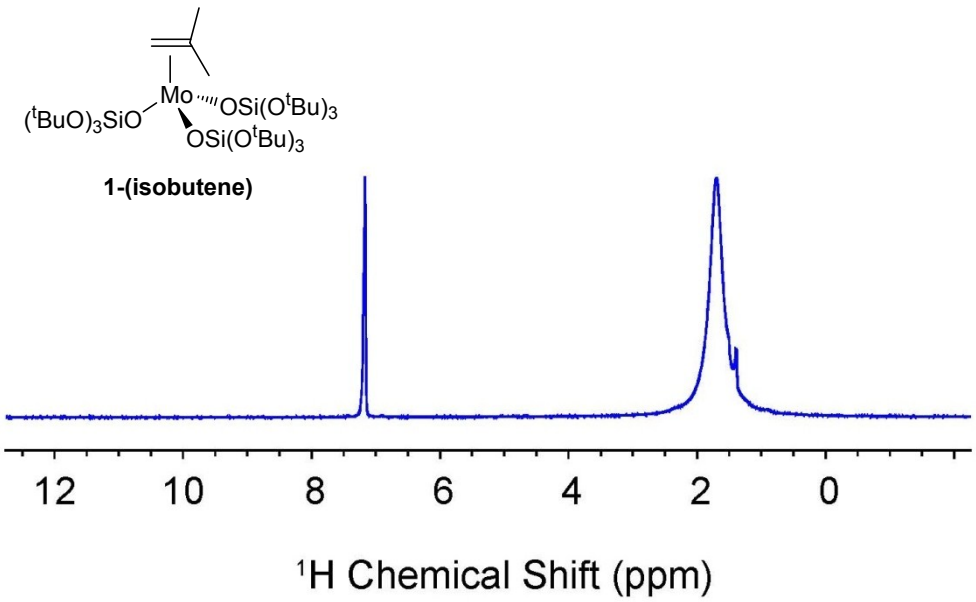


Figure S3. ^{1}H NMR spectrum (300MHz, C_6D_6, 25°C) of [C_4H_9-Mo(OSi(OtBu)$_3$)$_3$], **1-(isobutene)**.

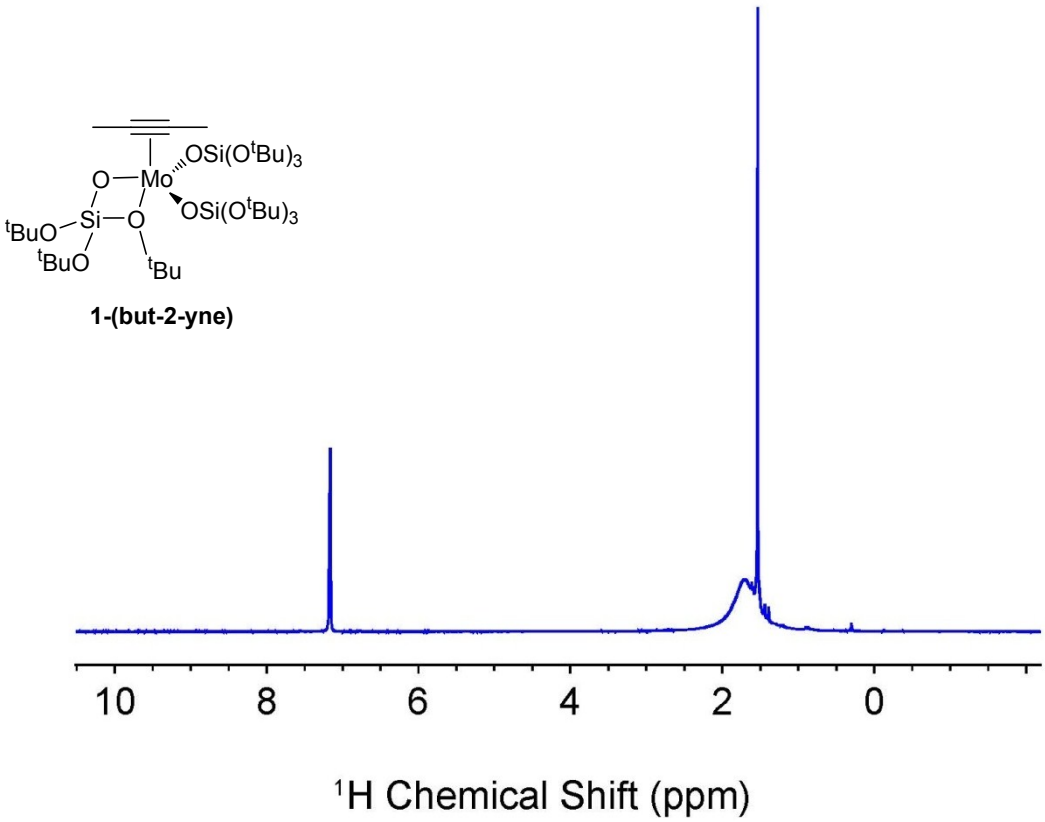


Figure S4. ^{1}H NMR spectrum (300MHz, C_6D_6, 25°C) of [C_4H_6-Mo(OSi(OtBu)$_3$)$_3$], **1-(but-2-yne)**.

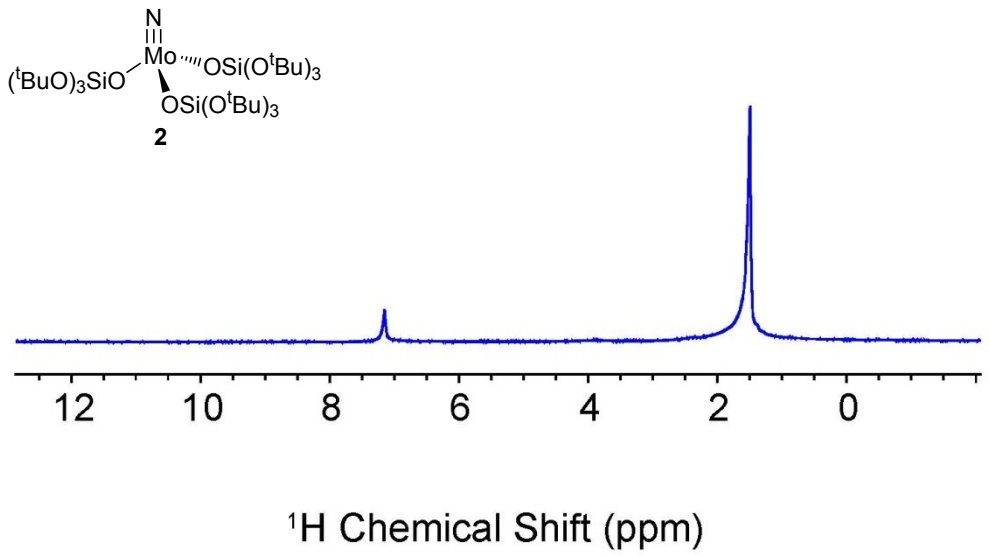


Figure S5. ^{1}H NMR spectrum (300MHz, C_6D_6, 25°C) of [Mo(N)(OSi(OtBu)$_3$)$_3$], **2**

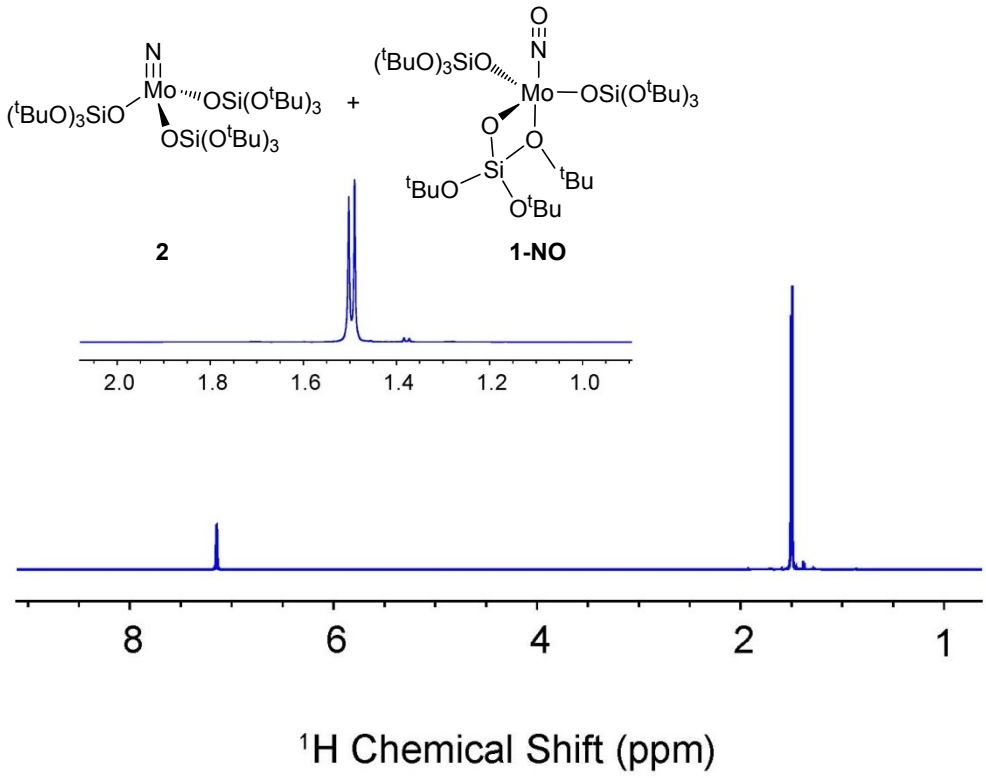


Figure S6. ^{1}H NMR spectrum (300MHz, C_6D_6, 25°C) of the mixture of [Mo(N)(OSi(OtBu)$_3$)$_3$], **2**, and [Mo(NO)(OSi(OtBu)$_3$)$_3$], **1-NO**.

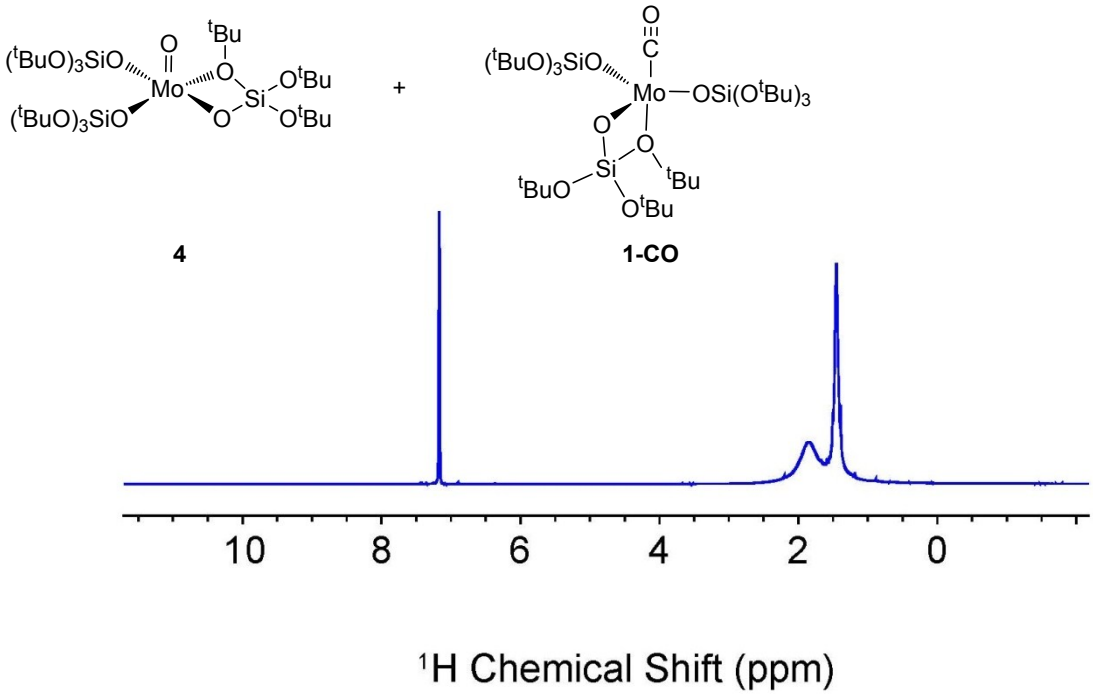


Figure S7. ^{1}H NMR spectrum (300MHz, C_6D_6, 25°C) of [Mo(CO)(OSi(OtBu)$_3$)$_3$], **4**, and [Mo(O)(OSi(OtBu)$_3$)$_3$], **1-CO**.

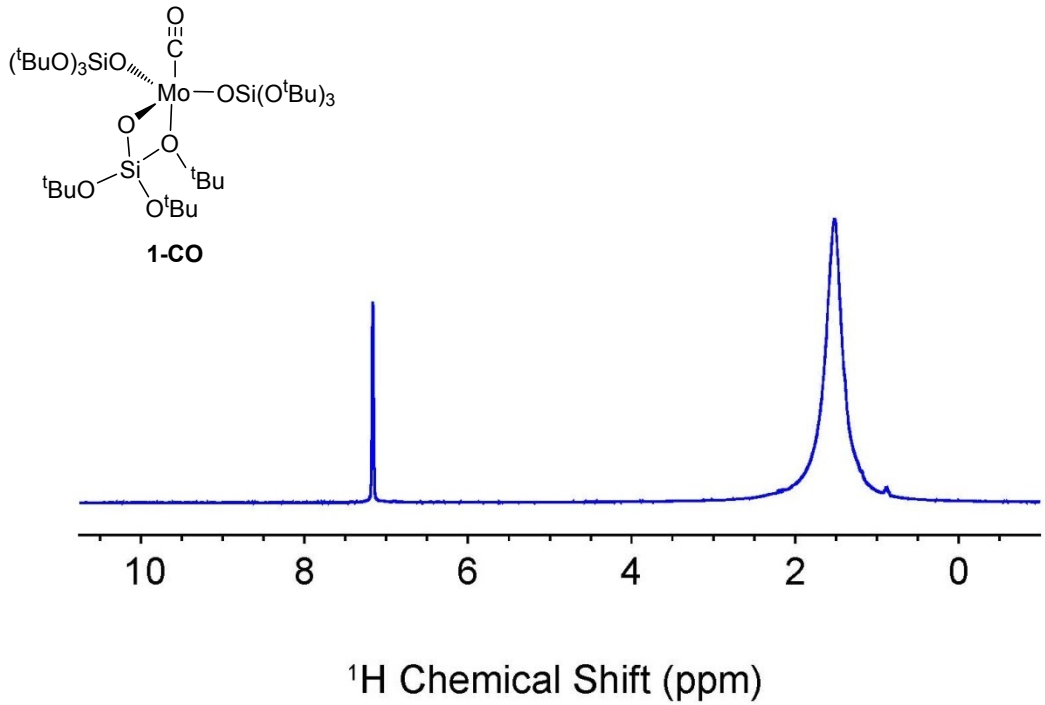


Figure S8. ^{1}H NMR spectrum (300MHz, C_6D_6, 25°C) of [Mo(CO)(OSi(OtBu)$_3$)$_3$], **1-CO**.

Solution NMR, Variable Temperature Experiment

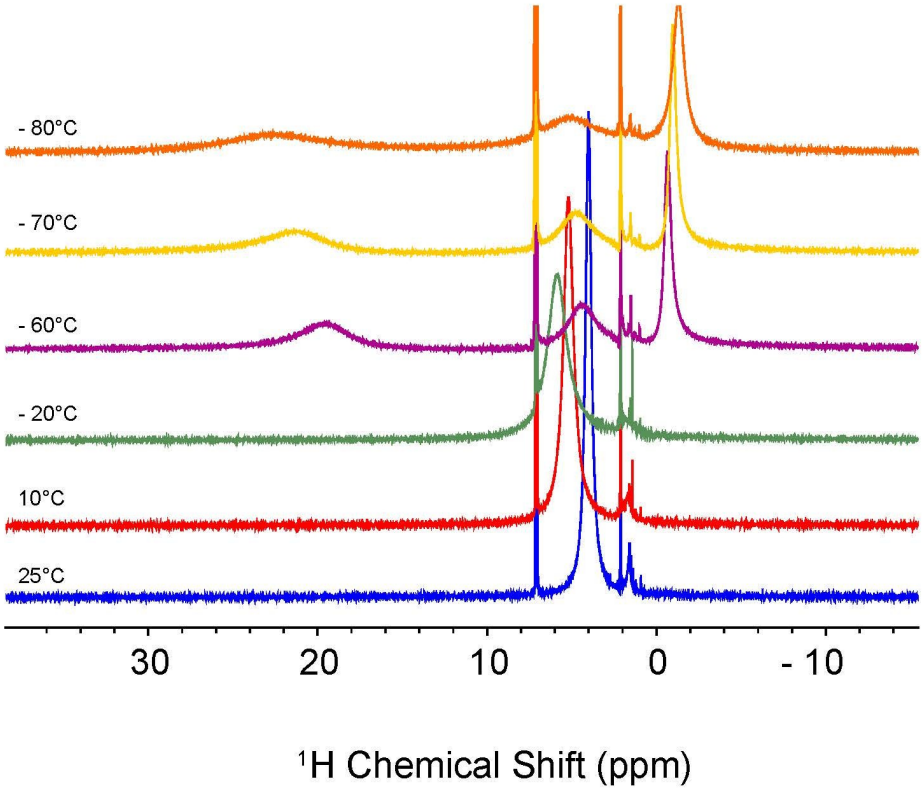


Figure S9. 1H NMR spectrum (400MHz, toluene-d8) of $[Mo(OSi(OtBu)_3)_3]$, **1**.

IR spectra

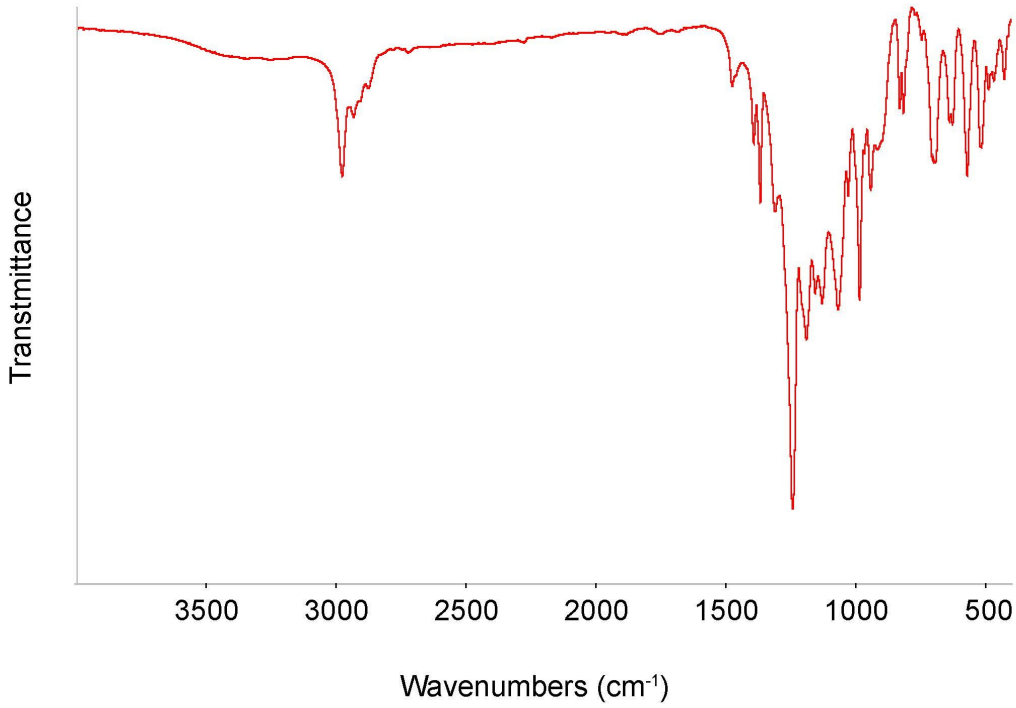


Figure S10. IR transmittance spectrum of **1**, powder, r.t

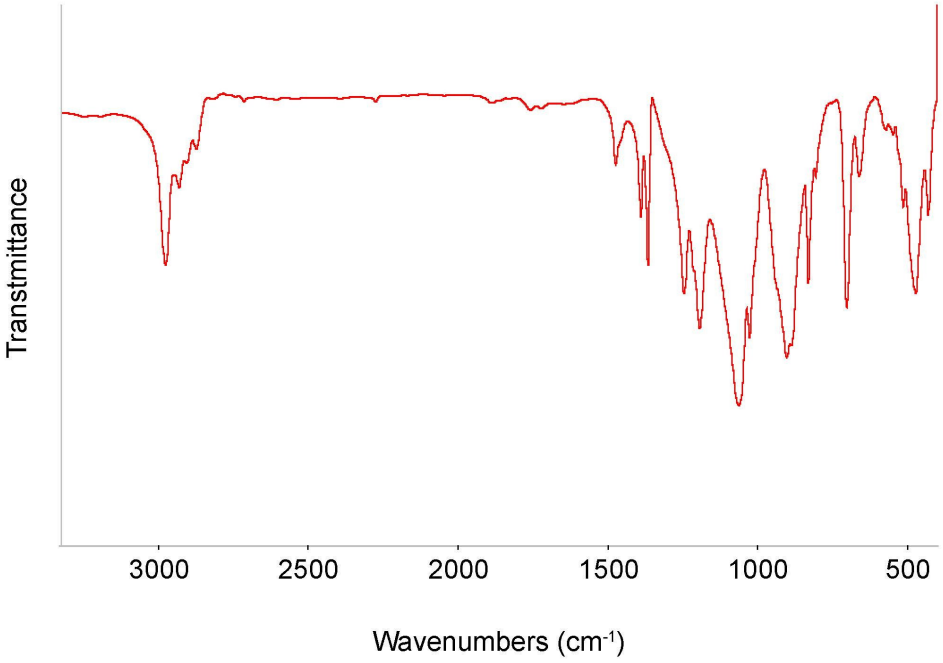


Figure S11. IR transmittance spectrum of **1-(ethylene)**, powder, r.t

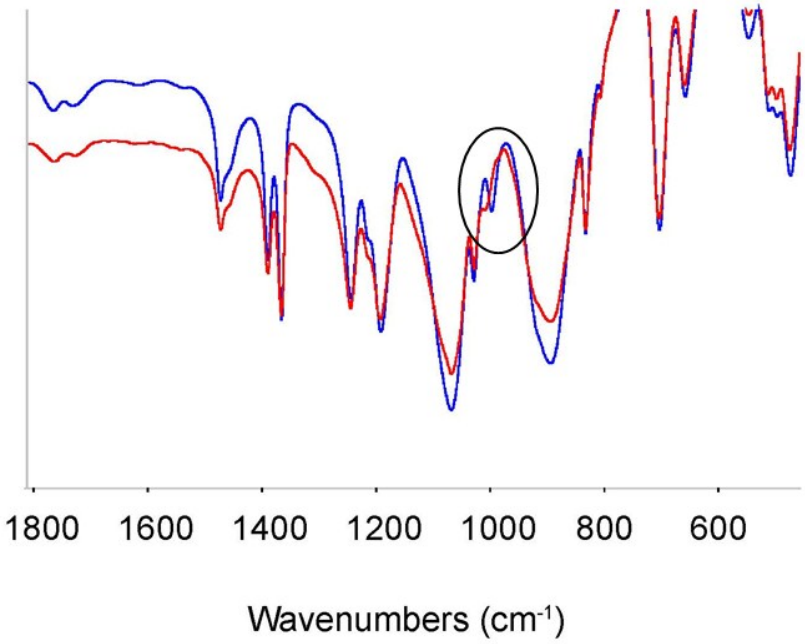


Figure S12. IR transmittance spectrum of **2**-14N (red) and **2**-15N (blue), powder, r.t

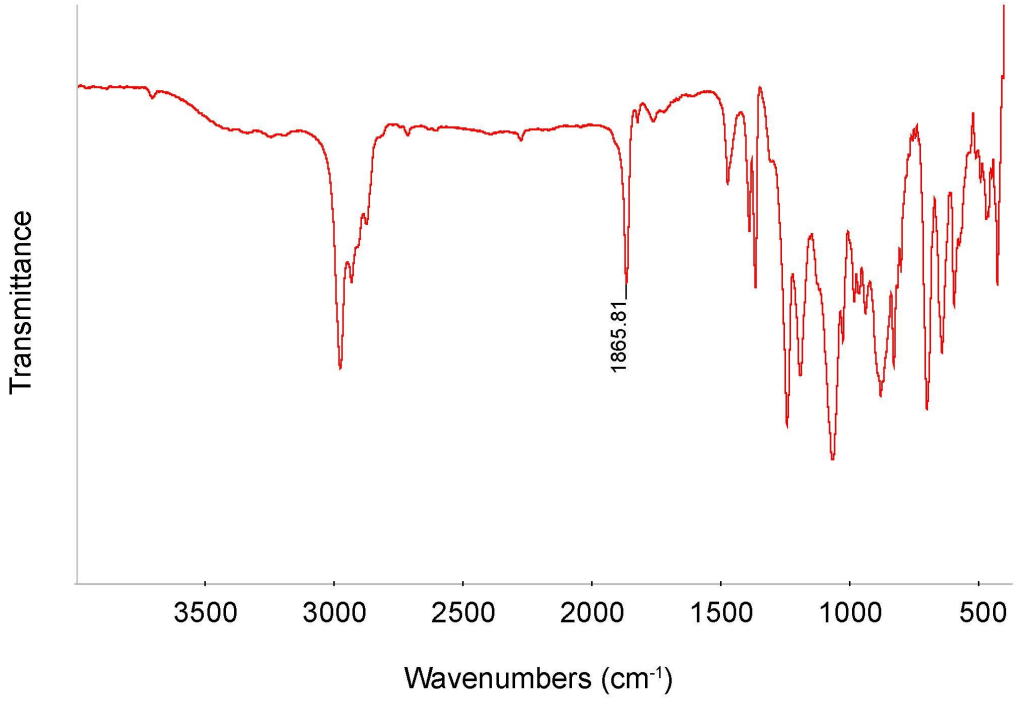
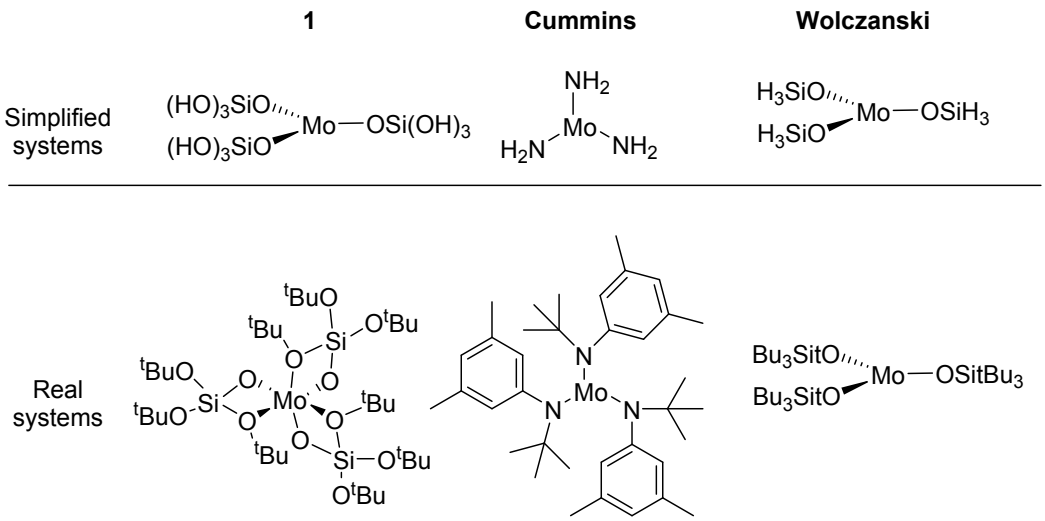
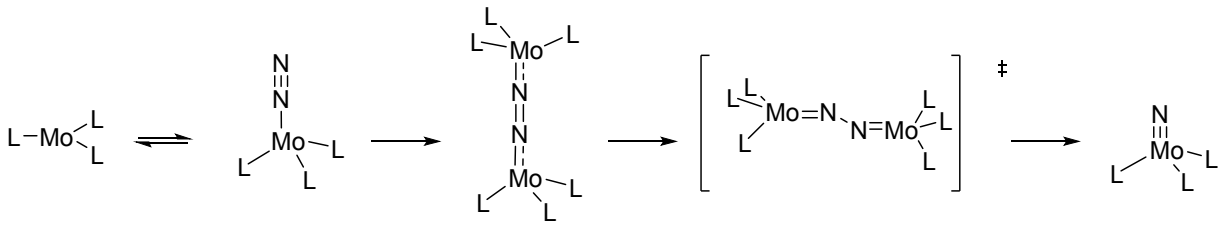


Figure S13. IR transmittance spectrum of **1-CO**, powder, r.t

Computational details

DFT calculations were carried out with the gaussian09 program[4], using the unrestricted b3lyp functional[5] in combination with a lanl2dz core potential and the associated basis set on Mo[6], and a 6-31g(d) basis set on all other atoms.[7] Enthalpies and Gibbs energies were calculated at 298.15 K. The spin-states of the various intermediates and transition states of lowest energy are in accordance with previous literature reports.[8]





a **b** **c** **d** **e**

S = 4 S = 2 S = 3 S = 1 S = 1

Table S1 ΔH and ΔG values in kcal/mol for the calculate structures of simplified systems and real systems

	ΔH kcal/mol					**ΔG kcal/mol**				
Simplified systems	**$1X_i$**	**$1\text{-}N_2X_i$**	**$3X_i$**	**TS ($3X_i$ – $2X_i$)**	**$2X_i$**	**$1X_i$**	**$1\text{-}N_2X_i$**	**$3X_i$**	**TS ($3X_i$ – $2X_i$)**	**$2X_i$**
Complex 1	0.0	-13.7	-46.8	-11.7	-44.2	0	2.8	-6.5	27.4	-18.6
Cummins	0.0	-7.0	-30.6	-9.7	-50.7	0	5.2	-7.3	17.2	-32.9
Wolczanski	0.0	2.5	-26.2	0.2	-37.1	0	13.3	-1.6	30.9	-19.6
	ΔH kcal/mol					**ΔG kcal/mol**				
Real systems	**$1X_i$**	**$1\text{-}N_2X_i$**	**$3X_i$**	**TS ($3X_i$ – $2X_i$)**	**$2X_i$**	**$1X_i$**	**$1\text{-}N_2X_i$**	**$3X_i$**	**TS ($3X_i$ – $2X_i$)**	**$2X_i$**
Complex 1	0.0	4.2	-7.8	-	-26.3	0	6.3	12.9	-	-27.3
Cummins	0.0	2.9	-3.6	-	-32.4	0	15.3	32.7	-	-13.3
Wolczanski	0.0	3.7	-0.7	-	-28.6	0	13.5	27.2	-	-15.6

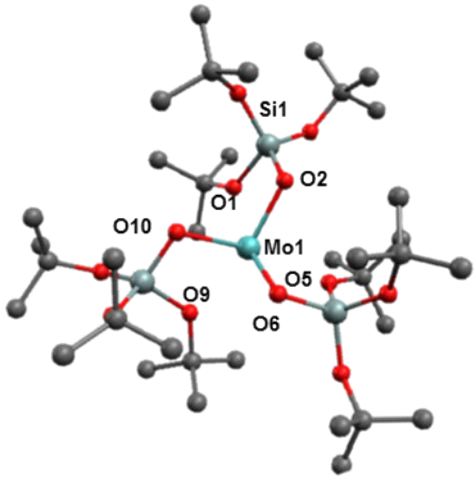


Figure S14 Calculated structure of Mo[(TBOS)$_3$], **1T$_L$**. Hydrogen atoms and methyl groups of *t*Bu have been omitted for clarity.

Table S2. Selected bonds for calculated **Mo(TBOS)$_3$,** compared to experimental data (distances are given in Å)

	Exp	Calc
Mo1 – O1	2.302(4)	2.410
Mo1 – O2	2.020(4)	2.042
Mo1 – O5	2.329(4)	2.414
Mo1 – O6	2.046(4)	2.043
Mo1 – O9	2.336(4)	2.431
Mo1 – O10	2.020(4)	2.040
Si1 – O1	1.677(5)	1.707
Si1 – O2	1.608(4)	1.624

Table S3. Selected angles for calculated **Mo(TBOS)$_3$, 1T$_L$** compared to experimental data (given in °)

	Exp	Calc
O2-Mo-O1	68.33(16)	67.2
O2-Mo-O5	85.58(15)	87.6
O6-Mo-O5	67.73(14)	67.2
O6-Mo-O9	82.85(15)	87.8
O10- Mo-O1	85.63(15)	88.1
O10-Mo-O9	67.29(16)	66.9

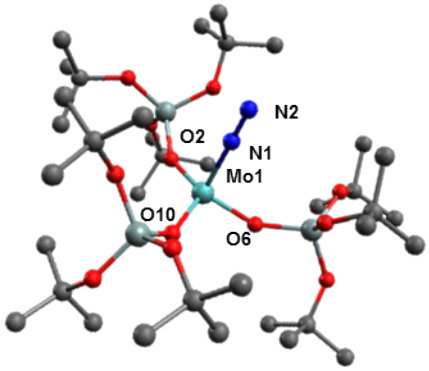


Figure S15 Calculated structure of [N2-Mo(TBOS)$_3$], **1-N2T$_L$**. Hydrogen atoms and methyl groups of *t*Bu have been omitted for clarity.

Table S4. Selected bonds for calculated **Mo(TBOS)$_3$,** (distances are given in Å)

Mo1 – O6	1.950
Mo1 – O2	1.912
Mo1 – O10	1.919
Mo1 – N1	1.951
N1 – N2	1.133

Table S5. Selected angles for calculated **Mo(TBOS)$_3$,** (given in °)

O10-Mo-O6	109.6
O10-Mo-O2	124.4
O6-Mo-O5	111.9

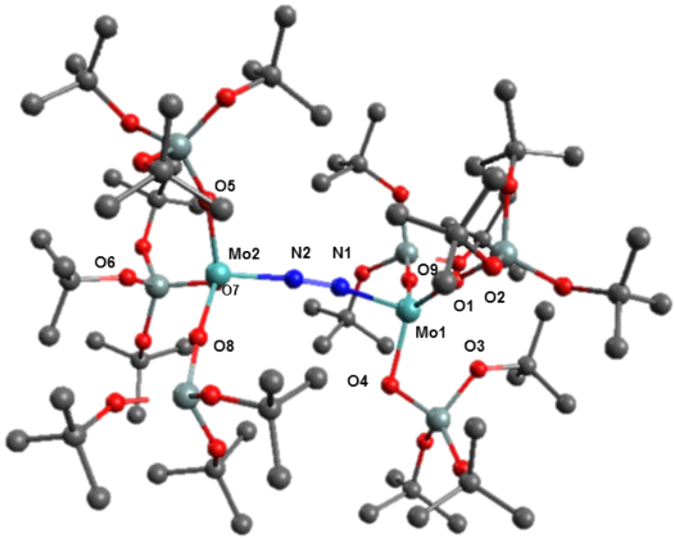


Figure S16 Calculated structure of (μ-N_2)[Mo(TBOS)]$_2$, **3T$_L$** Hydrogen atoms and methyl groups of *t*Bu have been omitted for clarity.

Table S6. Selected bonds for **(μ-N_2)[Mo(OSi(OtBu)$_3$)$_3$], 3T$_L$** compared to experimental data (distances are given in Å)

	Exp	Calc
Mo1 – O1	1.936	1.936
Mo1 – O2	1.972	1.972
Mo1 – O3	2.510	2.510
Mo1 – O4	1.972	1.972
Mo1 – N1	1.865(4)	1.899
Mo2 – O5	1.911(3)	1.942
Mo2 – O6	2.334(3)	2.500
Mo2 – O7	1.947(3)	1.973
Mo2 – O8	1.905(3)	1.924
Mo2 – N2	1.859(3)	1.900
N2 – N1	1.209(5)	1.187

Table S7. Selected angles for **(μ-N_2)[Mo(OSi(OtBu)$_3$)$_3$],3T$_L$** compared to experimental data (given in °)

	Exp	Calc
N1-Mo1-O4	92.90(13)	93.7
O5-Mo2-O7	116.92(12)	116.9
O8-Mo2-O5	121.26(12)	120.2
O8-Mo2-O7	116.19(12)	117.5
N2-Mo2-O5	98.69(13)	99.7
N2-Mo2-O8	99.99(13)	99.4
N1-N2-Mo2	172.5(3)	170.9
N2-N1-Mo1	169.0(3)	170.0

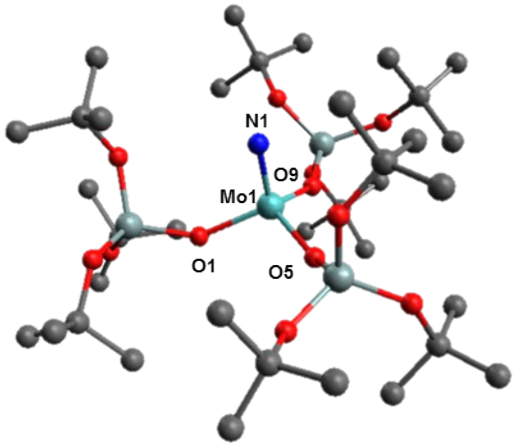


Figure S17. Calculated structure for [Mo(N)(TBOS)$_3$], **2T$_L$**. Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S8. Selected bonds for **[Mo(N)(OSi(OtBu)$_3$)$_3$], 2T$_L$** (distances are given in Å)

	Exp	Calc
Mo1 – O1	1.880(9)	1.894
Mo1 – O5	1.884(9)	1.904
Mo1 – O9	1.877(9)	1.907
Mo1 – N1	1.582(13)	1.656

Table S9. Selected angles for **[Mo(N)(OSi(OtBu)$_3$)$_3$], 2T$_L$** compared to experimental data (given in °)

	Exp	Calc
O9-Mo1-O1	112.6(4)	112.6
O9-Mo-O5	111.4(4)	111.1
N1-Mo1-O1	106.3(5)	107.1
N1-Mo1-O5	107.5(5)	107.0
N1-Mo1-O9	104.8(5)	106.8

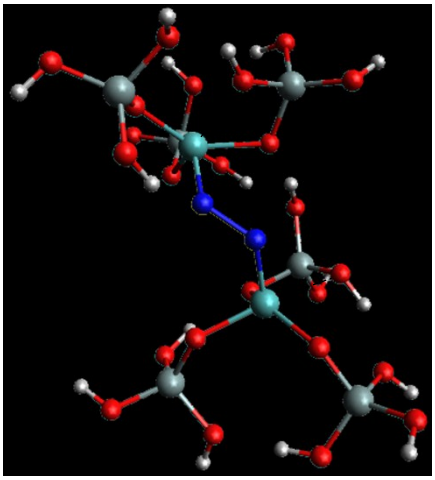


Figure S18. Calculated structure for **(μ-N_2)[Mo(OSi(OtBu)$_3$)$_3$], TS $3T_s$-$2T_s$**.

Table S10. Selected bonds for **[Mo(N)(OSi(OtBu)$_3$)$_3$], 2** (distances are given in Å)

Mo1 --- $O_{\kappa 2}$	2.428
Mo2 --- $O_{\kappa 2}$	2.235
Mo1 – N1	1.740
Mo2 – N2	1.749
N1-N2	1.546

X-Ray Crystallography

$[Mo(OSi(OtBu)_3)_3]$, 1.

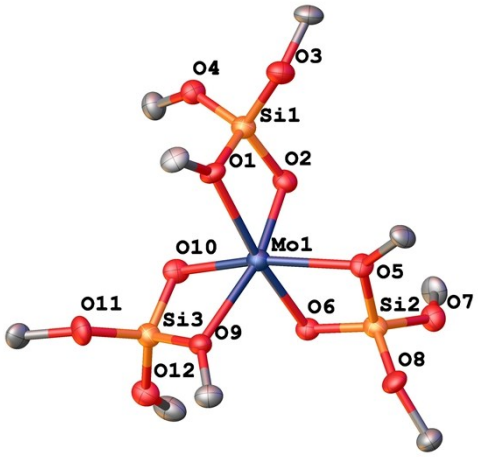


Figure S19 Thermal ellipsoid plot at the 50% probability of Mo[$(TBOS)_3$], **1**. Hydrogen atoms and methyl groups of *t*Bu have been omitted for clarity.

Table S11. Selected bonds for **$Mo(TBOS)_3$, 1,** (distances are given in Å)

Mo1 – O1	2.302(4)
Mo1 – O2	2.020(4)
Mo1 – O5	2.329(4)
Mo1 – O6	2.046(4)
Mo1 – O9	2.336(4)
Mo1 – O10	2.020(4)
Si1 – O1	1.677(5)
Si1 – O2	1.608(4)

Table S12. Selected angles for **Mo(TBOS)$_3$,1,** (given in °)

O2-Mo-O1	68.33(16)
O2-Mo-O5	85.58(15)
O6-Mo-O5	67.73(14)
O6-Mo-O9	82.85(15)
O10- Mo-O1	85.63(15)
O10-Mo-O9	67.29(16)

Table S13. Crystallographic data for **Mo(TBOS)$_3$**

Empirical formula	$C_{36}H_{81}MoO_{12}Si_3$
Formula weight	886.21
Temperature/K	103(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	14.2373(7)
b/Å	17.8493(7)
c/Å	19.9245(9)
α/°	100.521(4)
β/°	95.866(4)
γ/°	93.602(3)
Volume/Å^3	4934.9(4)
Z	4
ρ_{calc}g/cm^3	1.193
μ/mm^{-1}	0.388
F(000)	1908.0
Crystal size/mm^3	0.1884 × 0.153 × 0.1038
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.576 to 50.054
Index ranges	-16 ≤ h ≤ 16, -21 ≤ k ≤ 21, -23 ≤ l ≤ 23
Reflections collected	38942
Independent reflections	17217 [R_{int} = 0.1114, R_{sigma} = 0.1829]
Data/restraints/parameters	17217/0/991
Goodness-of-fit on F^2	0.970
Final R indexes [I>=2σ (I)]	R_1 = 0.0818, wR_2 = 0.1564
Final R indexes [all data]	R_1 = 0.1447, wR_2 = 0.1899
Largest diff. peak/hole / e Å^{-3}	1.68/-1.21

$[C_2H_4\text{-}Mo(OSi(OtBu)_3)_3]$, 1-(ethylene).

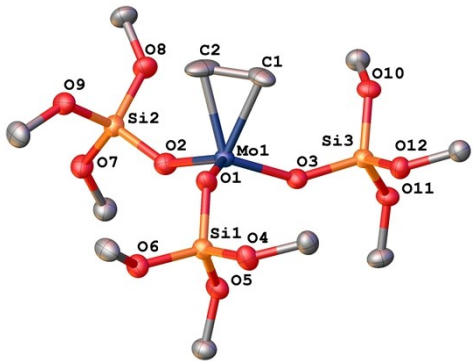


Figure S20. Thermal ellipsoid plot at the 50% probability of $[Mo(C_2H_4)(TBOS)_3]$, **2**. Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S14. Selected bonds for **$[C_2H_4\text{-}Mo(OSi(OtBu)_3)_3]$, 1-(ethylene)** (distances are given in Å)

Mo1 – O1	1.899(3)
Mo1 – O2	1.903(3)
Mo1 – O3	1.898(3)
Mo1 – C1	2.132(4)
Mo1 – C2	2.120(5)
C1 – C2	1.406(7)

Table S15. Selected angles for **[C_2H_4-Mo(OSi(OtBu)$_3$)$_3$], 1-(ethylene)** (given in °)

O1-Mo1-O2	119.96(13)
O1-Mo1-C1	91.35(16)
O1-Mo1-C2	94.37(18)
O2-Mo1-C1	124.42(17)
O2-Mo1-C2	90.59(17)
O3-Mo1-O1	121.47(13
O3-Mo1-O2	106.08(12)
O3-Mo1-C1	90.61(16)
O3-Mo1-C2	120.53(19)
C2-Mo1-C1	38.62(19)

Table S16. Crystallographic data for **[C_2H_4-Mo(OSi(OtBu)$_3$)$_3$], 1-(ethylene)**

Empirical formula	$C_{38}H_{85}MoO_{12}Si_3$
Formula weight	914.26
Temperature/K	102(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.1924(4)
b/Å	22.5596(8)
c/Å	24.6615(8)
α/°	90
β/°	90.745(3)
γ/°	90
Volume/Å^3	5113.8(3)
Z	4
ρ_{calc}g/cm^3	1.188
μ/mm^{-1}	0.376
F(000)	1972.0
Crystal size/mm^3	0.493 × 0.246 × 0.173
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.764 to 54.2
Index ranges	-11 ≤ h ≤ 11, -28 ≤ k ≤ 28, -31 ≤ l ≤ 31
Reflections collected	44057
Independent reflections	11276 [R_{int} = 0.0703, R_{sigma} = 0.0833]
Data/restraints/parameters	11276/0/514
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0770, wR_2 = 0.1233
Final R indexes [all data]	R_1 = 0.1138, wR_2 = 0.1353
Largest diff. peak/hole / e Å^{-3}	1.45/-0.83

$[C_4H_8\text{-}Mo(OSi(OtBu)_3)_3]$, 1-(isobutene).

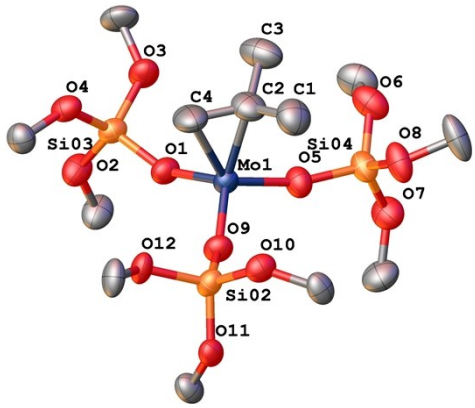


Figure S21. Thermal ellipsoid plot at the 50% probability of $[Mo(C_4H_6)(TBOS)_3]$, **3.** Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S17. Selected bonds for **$[C_4H_6\text{-}Mo(OSi(OtBu)_3)_3]$, 1-(isobutene)** (distances are given in Å)

Mo1 – O1	1.885(3)
Mo1 – O5	1.905(4)
Mo1 – O9	1.889(4)
Mo1 –C2	2.091(6)
Mo1 – C4	2.148(6)
C2-C4	1.391(9)

Table S18. Selected angles for **[C_4H_6-Mo(OSi(OtBu)$_3$)$_3$], 1-(isobutene)** (given in °)

O1-Mo1-O5	108.84(16)
O1-Mo1-09	114.58(16)
O1-Mo1-C2	115.1(2)
O1-Mo1-C4	93.7(2)
O9-Mo1-O5	110.41(16)
O5-Mo1-C2	92.5(2)
O5-Mo1-C4	130.5(2)
O9-Mo1-C2	113.1(2)
O9-Mo1-C4	98.2(2)
C2-C4-Mo1	68.6(4)
C2-Mo1-C4	38.3(2)

Table S19. Crystallographic data for **[C_4H_6-Mo(OSi(OtBu)$_3$)$_3$], 1-(isobutene)**

Empirical formula	$C_{40}H_{89}MoO_{12}Si_3$
Formula weight	942.32
Temperature/K	110(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.9560(13)
b/Å	22.695(3)
c/Å	18.4102(19)
β/°	108.778(10)
Volume/Å^3	5520.8(11)
Z	4
ρ_{calc}g/cm^3	1.134
μ/mm^{-1}	0.350
F(000)	2036.0
Crystal size/mm^3	0.25 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.68 to 50.698
Index ranges	-16 ≤ h ≤ 16, -24 ≤ k ≤ 27, -20 ≤ l ≤ 22
Reflections collected	21963
Independent reflections	9993 [R_{int} = 0.0714, R_{sigma} = 0.1144]
Data/restraints/parameters	9993/654/608
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0743, wR_2 = 0.1479
Final R indexes [all data]	R_1 = 0.1268, wR_2 = 0.1748
Largest diff. peak/hole / e Å^{-3}	1.06/-0.51

[C_4H_9-Mo(OSi(OtBu)$_3$)$_3$], 1-(but-2-yne).

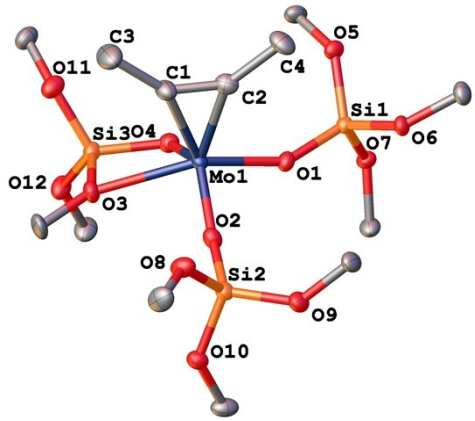


Figure S22. Thermal ellipsoid plot at the 50% probability of [Mo(C_4H_8)(TBOS)$_3$], **4**. Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S20. Selected bonds for **[C_4H_9-Mo(OSi(OtBu)$_3$)$_3$], 1-(but-2-yne)** (distances are given in Å)

Mo1 – O1	1.977(2)
Mo1 – O2	1.904(2)
Mo1 – O3	2.375(2
Mo1 – O4	1.968(3)
Mo1 – C1	2.007(4)
Mo1 – C2	1.997(4
C1-C2	1.283(5)

Table S21. Selected angles for **[C_4H_9-Mo(OSi(OtBu)$_3$)$_3$], 1-(but-2-yne)** (given in °)

O1-Mo1-O3	145.31(10)
O1-Mo1-C1	123.06(13)
O1-Mo1-C2	86.42(13)
O2-Mo1-O1	93.73(10)
O2-Mo1-C1	112.29(14)
O2-Mo-C2	112.17(13)
O1-Mo-O4	86.44(10)
O4-Mo1-O3	67.19(10)
O4-Mo1-C1	106.08(14)
O4-Mo1-C2	114.26(13)
C1-Mo1-O3	87.03(13)
O2-Mo1-O3	124.19(13)
C2-Mo1-C1	37.36(15)
C3-C1-Mo1	148.0(3)
C1-C2-Mo1	71.7(2)

Table S22. Crystallographic data for **[C_4H_9-Mo(OSi(OtBu)$_3$)$_3$], 1-(but-2-yne)**

Empirical formula	$C_{40}H_{87}MoO_{12}Si_3$
Formula weight	940.30
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.5671(15)
b/Å	21.407(2)
c/Å	19.204(2)
α/°	90
β/°	108.995(2)
γ/°	90
Volume/Å^3	5273.8(10)
Z	4
ρ_{calc}g/cm^3	1.184
μ/mm^{-1}	0.367
F(000)	2028.0
Crystal size/mm^3	0.25 × 0.22 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.942 to 50.182
Index ranges	-14 ≤ h ≤ 16, -25 ≤ k ≤ 25, -22 ≤ l ≤ 22
Reflections collected	33034
Independent reflections	9365 [Rint = 0.0632, Rsigma = 0.0651]
Data/restraints/parameters	9365/0/534
Goodness-of-fit on F2	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0500, wR2 = 0.1145
Final R indexes [all data]	R1 = 0.0795, wR2 = 0.1287
Largest diff. peak/hole / e Å-3	1.19/-0.66

[Mo(N)(OSi(OtBu)$_3$)$_3$], 2.

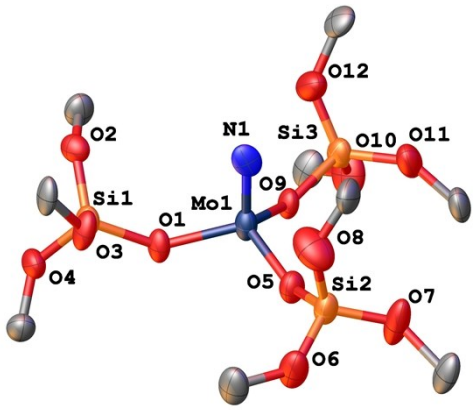


Figure S23. Thermal ellipsoid plot at the 50% probability of ([Mo(N)(TBOS)$_3$], **5**. Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S23. Selected bonds for **[Mo(N)(OSi(OtBu)$_3$)$_3$], 2** (distances are given in Å)

Mo1 – O1	1.880(9)
Mo1 – O5	1.884(9)
Mo1 – O9	1.877(9)
Mo1 – N1	1.582(13)

Table S24. Selected angles for **[Mo(N)(OSi(OtBu)$_3$)$_3$], 2** (given in °)

O1-Mo1-O5	113.6(4)
O9-Mo1-O1	112.6(4)
O9-Mo-O5	111.4(4)
N1-Mo1-O1	106.3(5)
N1-Mo1-O5	107.5(5)
N1-Mo1-O9	104.8(5)

Table S25. Crystallographic data for **[Mo(N)(OSi(OtBu)$_3$)$_3$], 2**

Empirical formula	$C_{36}H_{81}MoNO_{12}Si_3$
Formula weight	900.22
Temperature/K	103(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	13.8010(7)
b/Å	23.8385(14)
c/Å	31.3507(18)
α/°	81.022(5)
β/°	85.122(5)
γ/°	89.856(5)
Volume/Å^3	10150.4(10)
Z	8
ρ_{calc}g/cm^3	1.178
μ/mm^{-1}	0.379
F(000)	3872.0
Crystal size/mm^3	0.277 × 0.191 × 0.133
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.344 to 50.7
Index ranges	-16 ≤ h ≤ 16, -28 ≤ k ≤ 28, -37 ≤ l ≤ 37
Reflections collected	76710
Independent reflections	37052 [R_{int} = 0.1526, R_{sigma} = 0.3252]
Data/restraints/parameters	37052/2290/1903
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.1434, wR_2 = 0.3148
Final R indexes [all data]	R_1 = 0.3258, wR_2 = 0.4225
Largest diff. peak/hole / e Å^{-3}	2.26/-1.30

$[Mo(N_2)(OSi(OtBu)_3)_3]$, 3.

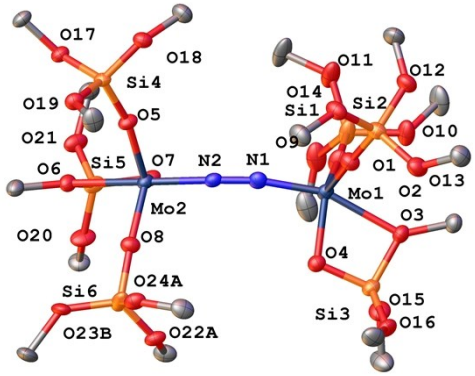


Figure S24. Thermal ellipsoid plot at the 50% probability of (μ-N_2)[Mo(TBOS)]$_2$, **6**. Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S26. Selected bonds for **$[Mo(N_2)(OSi(OtBu)_3)_3]$, 3** (distances are given in Å)

Mo1 – O1	1.893(3)
Mo1 – O2	1.908(3)
Mo1 – O3	2.349(3)
Mo1 – O4	1.940(3)
Mo1 – N1	1.865(4)
Mo2 – O5	1.911(3)
Mo2 – O6	2.334(3)
Mo2 – O7	1.947(3)
Mo2 – O8	1.905(3)
Mo2 – N2	1.859(3)
N2 – N1	1.209(5)

Table S27. Selected angles for **[Mo(N_2)(OSi(OtBu)$_3$)$_3$], 3** (given in °)

O1-Mo1-O2	118.62(14)
O1-Mo1-O3	88.58(12)
O1-Mo1-O4	116.28(13)
O2-Mo1-O3	89.30(11)
O2-Mo1-O4	119.26(12)
O4-Mo1-O3	67.97(11)
N1-Mo1-O1	99.18(14)
N1-Mo1-O2	102.05(14)
N1-Mo1-O3	160.81(13)
N1-Mo1-O4	92.90(13)
O5-Mo2-O6	89.75(11)
O5-Mo2-O7	116.92(12)
O7-Mo2-O6	68.35(11)
O8-Mo2-O5	121.26(12)
O8-Mo2-O6	87.67(11)
O8-Mo2-O7	116.19(12)
N2-Mo2-O5	98.69(13)
N2-Mo2-O6	163.31(12)
N2-Mo2-O7	94.96(13)
N2-Mo2-O8	99.99(13)
N1-N2-Mo2	172.5(3)
N2-N1-Mo1	169.0(3)

Table S28. Crystallographic data for **[Mo(N_2)(OSi(OtBu)$_3$)$_3$], 3**

Empirical formula	$C_{72}H_{162}N_2O_{24}Si_6Mo_2$
Formula weight	1800.45
Temperature/K	103.6
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.3627(10)
b/Å	22.7035(17)
c/Å	30.730(2)
β/°	98.381(2)
Volume/Å^3	9913.4(12)
Z	4
ρ_{calc}g/cm^3	1.206
μ/mm^{-1}	0.388
F(000)	3872.0
Crystal size/mm^3	0.32 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.402 to 52.326
Index ranges	-16 ≤ h ≤ 17, -28 ≤ k ≤ 28, -37 ≤ l ≤ 37
Reflections collected	189789
Independent reflections	19701 [R_{int} = 0.0883, R_{sigma} = 0.0540]
Data/restraints/parameters	19701/1080/1176
Goodness-of-fit on F^2	1.156
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1229
Final R indexes [all data]	R_1 = 0.0998, wR_2 = 0.1503
Largest diff. peak/hole / e Å^{-3}	1.67/-1.11

[Mo(NO)(OSi(OtBu)$_3$)$_3$], 1-NO.

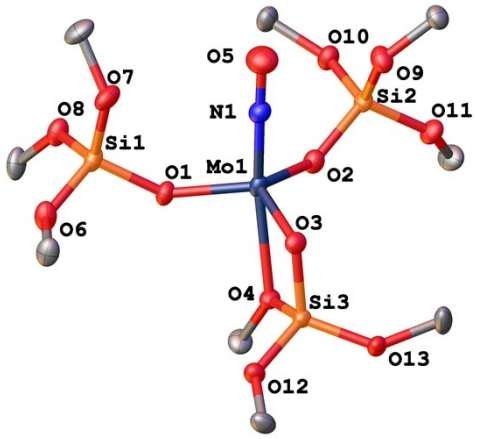


Figure S25. Thermal ellipsoid plot at the 50% probability of [Mo(NO)(TBOS)$_3$], **7**. Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S29. Selected bonds for **[Mo(NO)(OSi(OtBu)$_3$)$_3$], 1-NO** (distances are given in Å)

Mo1 – O1	1.9008(18)
Mo1 – O2	1.9090(19)
Mo1 – O3	1.9454(18)
Mo1 – O4	2.3807(18)
Mo1 – N1	1.715(3)
N1 – O5	1.198(3)

Table S30. Selected angles for **[Mo(NO)(OSi(OtBu)$_3$)$_3$], 1-NO** (given in °)

O1-Mo1-O2	116.23(8)
O1-Mo1-O3	117.76(8)
O1-Mo1-O4	87.86(7)
O2-Mo1-O3	118.43(8)
O2-Mo1-O4	87.39(7)
O3-Mo1-O4	67.58(7)
N1-Mo1-O1	100.63(10)
N1-Mo1-O2	99.63(10)
N1-Mo1-O3	97.48(10)
N1-Mo1-O4	165.03(9)
O5-N1-Mo1	178.6(2)

Table S31. Crystallographic data for **[Mo(NO)(OSi(OtBu)$_3$)$_3$], 1-NO**

Empirical formula	$C_{36}H_{81}MoNO_{13}Si_3$
Formula weight	916.22
Temperature/K	103.66(18)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.11460(10)
b/Å	46.9112(6)
c/Å	23.1165(3)
α/°	90
β/°	90.0070(10)
γ/°	90
Volume/Å^3	15306.2(3)
Z	12
ρ_{calc}g/cm^3	1.193
μ/mm^{-1}	0.379
F(000)	5904.0
Crystal size/mm^3	0.6924 × 0.3017 × 0.0517
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.49 to 52.744
Index ranges	-17 ≤ h ≤ 17, -58 ≤ k ≤ 58, -28 ≤ l ≤ 28
Reflections collected	255717
Independent reflections	31298 [Rint = 0.0663, Rsigma = 0.0503]
Data/restraints/parameters	31298/1368/1571
Goodness-of-fit on F2	1.075
Final R indexes [I>=2σ (I)]	R1 = 0.0497, wR2 = 0.0898
Final R indexes [all data]	R1 = 0.0749, wR2 = 0.0963
Largest diff. peak/hole / e Å-3	1.08/-0.97

[Mo(O)(OSi(OtBu)$_3$)$_3$], 4.

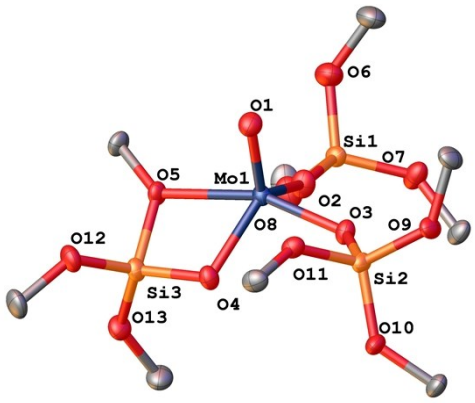


Figure S26. Thermal ellipsoid plot at the 50% probability of [Mo(O)(TBOS)$_3$], **8**. Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S32. Selected bonds for **[Mo(O)(OSi(OtBu)$_3$)$_3$], 4** (distances are given in Å)

Mo1 – O1	1.665(2)
Mo1 – O2	1.907(2)
Mo1 – O3	1.920(2)
Mo1 – O4	1.959(2)
Mo1 – O5	2.251(2)

Table S33. Selected angles for **[Mo(O)(OSi(OtBu)$_3$)$_3$], 4** (given in °)

O1-Mo1-O2	116.40(11)
O1-Mo1-O3	102.77(10)
O1-Mo1-O4	119.05(10)
O1-Mo1-O5	95.58(9)
O2-Mo1-O3	90.67(9)
O2-Mo1-O4	121.91(10)
O2-Mo1-O5	90.11(9)
O3-Mo1-O4	93.04(9)
O3-Mo1-O5	159.07(9)
O4-Mo1-O5	68.99(8)

Table S34. Crystallographic data for **[Mo(O)(OSi(OtBu)$_3$)$_3$], 4**

Empirical formula	$C_{36}H_{81}MoO_{13}Si_3$
Formula weight	902.21
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.0787(5)
b/Å	23.6043(8)
c/Å	36.5549(12)
α/°	90
β/°	103.0700(10)
γ/°	90
Volume/Å^3	15195.1(8)
Z	12
ρ_{calc}g/cm^3	1.183
μ/mm^{-1}	0.380
F(000)	5820.0
Crystal size/mm^3	0.2 × 0.12 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.446 to 50.054
Index ranges	-21 ≤ h ≤ 21, -28 ≤ k ≤ 28, -43 ≤ l ≤ 43
Reflections collected	308685
Independent reflections	26833 [R_{int} = 0.0652, R_{sigma} = 0.0334]
Data/restraints/parameters	26833/1626/1509
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.0946
Final R indexes [all data]	R_1 = 0.0646, wR_2 = 0.1041
Largest diff. peak/hole / e Å^{-3}	2.04/-1.51

[Mo(CO)(OSi(OtBu)$_3$)$_3$], 1-CO.

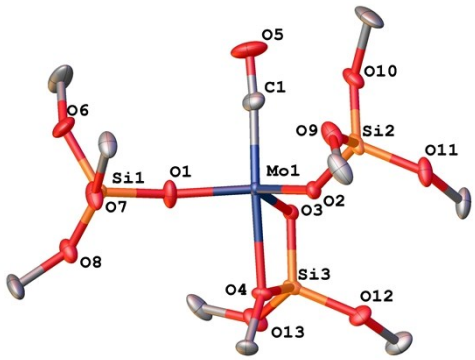


Figure S27. Thermal ellipsoid plot at the 50% probability of [Mo(CO)(TBOS)$_3$], **9**. Hydrogen atoms and methyl groups of *t*Bu groups have been omitted for clarity.

Table S35. Selected bonds for **[Mo(CO)(OSi(OtBu)$_3$)$_3$], 1-CO** (distances are given in Å)

Mo1 – O1	1.8800(19)
Mo1 – O2	1.9087(17)
Mo1 – O3	1.9722(18)
Mo1 – O4	2.3074(17)
Mo1 – C1	1.931(3)
O5-C1	1.156(3)

Table S36. Selected angles for **[Mo(CO)(OSi(OtBu)$_3$)$_3$], 1-CO** (given in °)

O1-Mo1-O2	128.04(8)
O1-Mo1-O3	115.62(8)
O1-Mo1-O4	90.56(8)
O1-Mo1-C1	92.77(11)
O2-Mo1-O3	113.02(8)
O2-Mo1-O4	90.62(7)
O2-Mo1-C1	97.65(10)
O3-Mo1-C4	68.75(7)
C1-Mo1-O3	98.00(10)
C1-Mo1-O4	166.42(9)
O5-C1-Mo1	175.2(3)

Table S37. Crystallographic data for **[Mo(CO)(OSi(OtBu)$_3$)$_3$], 1-CO**

Empirical formula	$C_{37}H_{81}MoO_{13}Si_3$
Formula weight	914.22
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	26.8309(13)
b/Å	15.5455(7)
c/Å	27.4545(13)
α/°	90
β/°	117.032(2)
γ/°	90
Volume/Å^3	10200.2(8)
Z	8
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	0.379
F(000)	3928.0
Crystal size/mm^3	0.24 × 0.16 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.664 to 52.744
Index ranges	-33 ≤ h ≤ 33, -18 ≤ k ≤ 19, -34 ≤ l ≤ 34
Reflections collected	201998
Independent reflections	20874 [R_{int} = 0.0769, R_{sigma} = 0.0392]
Data/restraints/parameters	20874/1694/1136
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.0878
Final R indexes [all data]	R_1 = 0.0687, wR_2 = 0.1016
Largest diff. peak/hole / e Å^{-3}	0.92/-0.88

[1] D. F. Evans, *Journal of the Chemical Society (Resumed)* **1959**, 2003-2005

[2] C. E. Laplaza, C. C. Cummins, *Science* **1995**, *268*, 861-863

[3] C. Camp, C. Kefalidis, J. Pécaut, L. Maron, M.Mazzanti, *Angew. Chem. Int. Ed.,* **2013**, 52, 12646-12650.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.

Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, **2009**.

[5] A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652.

[6] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.

[7] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.*, **1971**, *54*, 724.

[8] D. C. Graham, G. J. O. Beran, M. Head-Gordon, G. Christian, R. Stranger, B. F. Yates, *J. Phys. Chem. A*, **2005**, *109*, 6762-6772.