Supplementary

Experimental Section

General Procedures. All procedures were carried out under a dry argon atmosphere using standard Schlenk and glovebox techniques. Aromatic, aliphatic hydrocarbon solvents and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves prior to use. Isopropyl alcohol was dried and distilled from magnesium and stored over 4 Å molecular sieves prior to use.

$(Me_3Si)_2NPNSiMe_3$ (I), $(Me_3Si)_2NPS(N^tBu)$ (II) and $(Me_3Si)_2NP(NSiMe_3)_2$ (III) were prepared according to previously published procedures [37-39]. $W_2(O\text{-}^iPr)_6$ was prepared from the reaction of $W_2(NMe_2)_6$ with 2-propanol in hexane and subsequent addition of NMe_3 [35], while $Mo_2(O\text{-}^iPr)_6$ was prepared by the exchange reaction of $Mo_2(NMe_2)_6$ with isopropyl alcohol in pentane [36].

CHN-analyses were performed with Perkin-Elmer 2400 Analyser. ^1H, ^{13}C, ^{31}P NMR spectra were recorded at 400, 100 and 162 MHz, respectively, using a Varian "Mercury" spectrometer. Benzene-d_6 was used as an internal reference for proton (7.16 ppm) and carbon (128.06 ppm) spectra, while 85% H_3PO_4 was used as an external standard for ^{31}P NMR spectra.

Preparation of $[(Me_3Si)_2N\text{-}P(NSiMe_3)(O\text{-}^iPr)]\{(^iPrO)_2W{\equiv}W(O\text{-}^iPr)_3\}$ (1)
In a Schlenk flask, 1.01 g (1.40 mmol) of $W_2(O\text{-}^iPr)_6$ was dissolved in 2.5 mL of benzene, and the solution was cooled to 10 ˚C. A solution of (I) 0.39 g (1.40 mmol) in 1.5 mL of benzene was slowly added dropwise. The mixture was stirred for 24 h at room temperature resulting in a dark brown solution. The solvent was removed in vacuo, producing a dark brown solid. The residue was dissolved in 3 mL of hexane and kept at -30 ˚C for crystallization.
Yield: 0.99 g, (71%) of dark brown crystals.

^1H NMR (400 MHz, benzene-d_6, 26 ˚C) δ = 0.31 (s, 9H, $NSiMe_3$), 0.42 (s, 9H, $N(SiMe_3)_2$), 0.71 (s, 9H, $N(SiMe_3)_2$), 1.14 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.21 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.42 (d, 3H, $^3J_{HH}$= 6.0 Hz, POCH*(Me)$_2$*), 1.43 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.44 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.45 (d, 3H, $^3J_{HH}$= 6.0 Hz, POCH*(Me)$_2$*), 1.48 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.53 (d, 9H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.54 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.60 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 4.95 (doublet of septets (dsept), 1H, $^3J_{HH}$= 6.0 Hz, $^3J_{PH}$= 2.4 Hz, OC*H*$(Me)_2$), 5.04 (dsept, 1H, $^3J_{HH}$= 6.0 Hz, $^3J_{PH}$= 1.2 Hz, OC*H*$(Me)_2$), 5.51 (dsept, 1H, $^3J_{HH}$= 6.0 Hz, $^3J_{PH}$= 5.2 Hz, OC*H*$(Me)_2$), 5.96 (dsept, 1H, $^3J_{HH}$= 6.0 Hz, $^3J_{PH}$= 6.4 Hz, POC*H*$(Me)_2$), 6.07 (sept, 1H, $^3J_{HH}$= 6.0 Hz, OC*H*$(Me)_2$), 6.50 (sept, 1H, $^3J_{HH}$= 6.0 Hz, OC*H*$(Me)_2$).

$^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6, 26 ˚C) δ = 3.85 (d, $^3J_{PC}$= 2.0 Hz, $NSiMe_3$), 7.03 (s, $N(SiMe_3)_2$), 7.43 (d, $^3J_{PC}$= 1.0 Hz, $N(SiMe_3)_2$), 25.53 (d, J_{PC}= 7.0 Hz, OCH*(Me)$_2$*), 25.72 (s, OCH*(Me)$_2$*), 25.93 (s, OCH*(Me)$_2$*), 26.68 (s, OCH*(Me)$_2$*), 27.02 (s, OCH*(Me)$_2$*), 27.12 (s, OCH*(Me)$_2$*), 27.22 (s, OCH*(Me)$_2$*), 27.52 (s, OCH*(Me)$_2$*), 27.84 (d, $^3J_{PC}$= 1.0 Hz, POCH*(Me)$_2$*), 28.07 (d, $^3J_{PC}$= 1.0 Hz, POCH*(Me)$_2$*), 29.25 (s, OCH*(Me)$_2$*), 30.15 (s, OCH*(Me)$_2$*), 70.57 (d, J_{PC}= 1.5 Hz, O*C*H$(Me)_2$), 74.25 (s, O*C*H$(Me)_2$), 74.63 (s, O*C*H$(Me)_2$), 80.24 (s, O*C*H$(Me)_2$), 82.79 (d, J_{PC}= 1.5 Hz, O*C*H$(Me)_2$), 83.37 (d, $^2J_{PC}$= 2.0 Hz, PO*C*H$(Me)_2$).

$^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 26 ˚C) δ = 106.0 (s, satellite $^1J_{WP}$= 509 Hz).

Anal. Calcd for $C_{27}H_{69}N_2O_6PSi_3W_2$: C, 32.40; H, 6.95; N, 2.80. Found: C, 32.31; H, 6.86; N, 2.85.

Preparation of $[(Me_3Si)_2N\text{-}P(NSiMe_3)(O\text{-}^iPr)]\{(^iPrO)_2Mo{\equiv}Mo(O\text{-}^iPr)_3\}$ (2)
Compound 2 was prepared by the same procedure as that reported for 1 by reacting 1.15 g (2.1 mmol) of $Mo_2(OPr\text{-}i)_6$ with 0.59 g (2.1 mmol) of (I).
Yield: 0.94 g, (54%) of red crystals.

^1H NMR (400 MHz, benzene-d_6, 26 ˚C) δ = 0.26 (s, 9H, $NSiMe_3$), 0.48 (br. s, 9H, $N(SiMe_3)_2$), 0.71 (br. s, 9H, $N(SiMe_3)_2$), 0.99 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.11 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.45 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.45 (d, 3H, $^3J_{HH}$= 6.0 Hz, POCH*(Me)$_2$*), 1.47 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.49 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.51 (d, 3H, $^3J_{HH}$= 6.0 Hz, POCH*(Me)$_2$*), 1.54 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.55 (d, 6H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.63 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.64 (d, 3H, $^3J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 4.73 (multiplet, 2H, OC*H*$(Me)_2$), 5.55 (dsept, 1H, $^3J_{HH}$= 6.0 Hz, $^3J_{PH}$= 5.6 Hz, OC*H*$(Me)_2$), 5.98 (dsept, 1H, $^3J_{HH}$= 6.0 Hz, $^3J_{PH}$= 6.4 Hz, POC*H*$(Me)_2$), 6.24 (sept, 1H, $^3J_{HH}$= 6.0 Hz, OC*H*$(Me)_2$), 6.83 (sept, 1H, $^3J_{HH}$= 6.0 Hz, OC*H*$(Me)_2$).

$^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6, 26 ˚C) δ = 3.73 (d, $^3J_{PC}$= 2.0 Hz, $NSiMe_3$), 7.13 (br. s, $N(SiMe_3)_2$), 25.57 (d, J_{PC}= 6.0 Hz, OCH*(Me)$_2$*), 25.95 (s, OCH*(Me)$_2$*), 26.09 (s, OCH*(Me)$_2$*), 26.72 (s, OCH*(Me)$_2$*), 26.76 (s, OCH*(Me)$_2$*), 27.36 (s, OCH*(Me)$_2$*), 27.70 (s, OCH*(Me)$_2$*), 28.09 (d, $^3J_{PC}$= 1.0 Hz, POCH*(Me)$_2$*), 28.30 (d, $^3J_{PC}$= 1.0 Hz, POCH*(Me)$_2$*), 28.53 (s, OCH*(Me)$_2$*), 29.37 (s, OCH*(Me)$_2$*), 70.47 (s, O*C*H$(Me)_2$), 74.81 (s, O*C*H$(Me)_2$), 74.87 (s, O*C*H$(Me)_2$), 78.16 (s, O*C*H$(Me)_2$), 80.29 (d, $^2J_{PC}$= 2.0 Hz, PO*C*H$(Me)_2$), 80.72 (d, J_{PC}= 1.2 Hz, O*C*H$(Me)_2$).

$^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 26 ˚C) δ = 97.7 (s).

Anal. Calcd for $C_{27}H_{69}Mo_2N_2O_6PSi_3$: C, 39.31; H, 8.43; N, 3.40. Found: C, 38.99; H, 8.25; N, 3.21.

Preparation of $[(Me_3Si)_2N\text{-}PS(N^tBu)(O\text{-}^iPr)]\{(^iPrO)_2Mo{\equiv}Mo(O\text{-}^iPr)_3\}$ (3)
In a Schlenk flask, $Mo_2(O\text{-}^iPr)_6$ (0.85 g, 1.56 mmol) was dissolved in 2 mL of benzene, and the solution was cooled to 10 ˚C. 0.46 g (1.56 mmol) of (II) was dissolved in 1.5 mL of benzene thereafter slowly added dropwise. The mixture was

stirred for three days at room temperature, resulting in a dark-brown solution. The solvent was removed in vacuo, yielding a dark brown solid. This solid was dissolved in 2.5 mL of hexane and cooled to -30 ˚C in order to induce further crystallization.
Yield: 0.58 g, (44%) of red crystals.

^{1}H NMR (400 MHz, benzene-d_6, 26 ˚C) δ = 0.40 (s, 9H, $SiMe_3$), 0.64 (s, 9H, $SiMe_3$), 1.11 (s, 9H, N^{t}Bu), 1.34 (d, 9H, $^{3}J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.39 (d, 9H, $^{3}J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.49 (d, 12H, $^{3}J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.52 (d, 3H, $^{3}J_{HH}$= 6.0 Hz, POCH*(Me)$_2$*), 1.55 (d, 3H, $^{3}J_{HH}$= 6.0 Hz, POCH*(Me)$_2$*), 4.85 (sept, 3H, $^{3}J_{HH}$= 6.0 Hz, OC*H*(Me)$_2$), 5.61 (multiplet, 2H, OC*H*(Me)$_2$), 5.82 (sept, 1H, $^{3}J_{HH}$= 6.0 Hz, POC*H*(Me)$_2$).

^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 26 ˚C) δ = 5.41 (d, $^{3}J_{PC}$= 2.0 Hz, $SiMe_3$), 5.54 (d, $^{3}J_{PC}$= 2.0 Hz, $SiMe_3$), 24.83 (d, $^{3}J_{PC}$= 4.0 Hz, POCH*(Me)$_2$*), 25.02 (d, $^{3}J_{PC}$= 4.0 Hz, POCH*(Me)$_2$*), 26.76 (s, OCH*(Me)$_2$*), 27.10 (s, OCH*(Me)$_2$*), 27.41 (s, OCH*(Me)$_2$*), 33.49 (d, $^{3}J_{PC}$= 6.0 Hz, NC*Me$_3$*), 57.87 (d, $^{2}J_{PC}$= 6.0 Hz, N*C*Me$_3$), 72.43 (d, $^{2}J_{PC}$= 4.7 Hz, PO*C*H(Me)$_2$), 72.91 (s, O*C*H(Me)$_2$), 78.16 (s, O*C*H(Me)$_2$).

^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 26 ˚C) δ = 85.7 (s).

Anal. Calcd for $C_{28}H_{69}Mo_2N_2O_6PSi_2$: C, 39.99; H, 8.27; N, 3.33. Found: C, 39.87; H, 8.13; N, 3.24.

Preparation of [$(Me_3Si)_2$N-P$(NSiMe_3)_2$(O-^{i}Pr)]{$(^{i}PrO)_2$Mo≡Mo(O-^{i}Pr)$_3$} (4)
Solution of (III) 0.54 g (1.48 mmol) in 1 mL of benzene was slowly added to solution of Mo_2(OPr-i)$_6$ 0.81 g (1.48 mmol) in 2 mL of benzene. The reaction mixture was stirred at room temperature for 24 h, then the solvent was removed in vacuo and the residue was dissolved in 2.5 mL of hexane. Upon standing at – 30 ˚C the crystals of 4 were formed.
Yield: 0.62 g, (46%) of violet-red crystals.

^{1}H NMR (400 MHz, benzene-d_6, 26 ˚C) δ = 0.04 (s, 9H, $NSiMe_3$), 0.51 (s, 9H, $NSiMe_3$), 0.76 (s, 18H, N$(SiMe_3)_2$), 1.30 (d, 18H, $^{3}J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.37 (br. s, 6H, POCH*(Me)$_2$*),1.56 (d, 6H, $^{3}J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 1.59 (d, 6H, $^{3}J_{HH}$= 6.0 Hz, OCH*(Me)$_2$*), 4.74 (sept, 3H, $^{3}J_{HH}$= 6.0 Hz, OC*H*(Me)$_2$), 5.60 (sept, 1H, $^{3}J_{HH}$= 6.0 Hz, OC*H*(Me)$_2$), 5.61 (sept, 1H, $^{3}J_{HH}$= 6.0 Hz, OC*H*(Me)$_2$), 6.08 (multiplet, POC*H*(Me)$_2$).

^{13}C{^{1}H} NMR (100 MHz, benzene-d_6, 26 ˚C) δ = 5.94 (d, $^{3}J_{PC}$= 2.0 Hz, $NSiMe_3$), 6.37 (d, $^{3}J_{PC}$= 4.0 Hz, N$(SiMe_3)_2$), 7.07 (d, $^{3}J_{PC}$= 1.5 Hz, $NSiMe_3$), 25.18 (s, POCH*(Me)$_2$*), 25.20(s, POCH*(Me)$_2$*), 26.22 (s, OCH*(Me)$_2$*), 26.84 (s, OCH*(Me)$_2$*), 27.54 (s, OCH*(Me)$_2$*), 71.05 (s, O*C*H(Me)$_2$), 76.39 (s, O*C*H(Me)$_2$), 77.67 (d, $^{2}J_{PC}$= 1.0 Hz, PO*C*H(Me)$_2$).

^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 26 ˚C) δ = 6.5 (d, $^{3}J_{HP}$= 7 Hz).

Anal. Calcd for $C_{30}H_{78}Mo_2N_3O_6PSi_4$: C, 39.50; H, 8.62; N, 4.61. Found: C, 39.23; H, 8.48; N, 4.52.

Table S1 Crystal data for (**1**), (**2**), (**3**) and (**4**)

	(1)	**(2)**	**(3)**	**(4)**
Formula	$C_{27}H_{69}N_2O_6PSi_3W_2$	$C_{27}H_{69}Mo_2N_2O_6PSi_3$	$C_{28}H_{69}Mo_2N_2O_6PSSi_2$	$C_{30}H_{78}Mo_2N_3O_6PSi_4$
F_w	1000.78	824.96	840.94	912.16
space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	P-1
T, K	100(2)	100(2)	100(2)	100(2)
a, Å	11.679(3)	11.643(3)	9.439(3)	11.760(3)
b, Å	16.861(4)	16.741(4)	17.008(5)	13.424(4)
c, Å	21.651(6)	21.756(6)	25.776(7)	16.339(5)
α, °				88.52(3)
β, °	99.88(3)	99.96(3)		86.50(3)
γ, °				64.50(3)
V, Å^3	4200(2)	4177(2)	4138(2)	2323.8(12)
Z	4	4	4	2
λ, Å	0.71073	0.71073	0.71073	0.71073
ρ_{calc}, g cm^{-3}	1.583	1.312	1.350	1.304
μ, mm^{-1}	5.631	0.759	0.789	0.714
R_1 [$I>2\sigma(I)$]	0.0196	0.0807	0.0451	0.0448
wR_2 [all data]	0.0448	0.1238	0.0470	0.0558

[a] Footnote text.

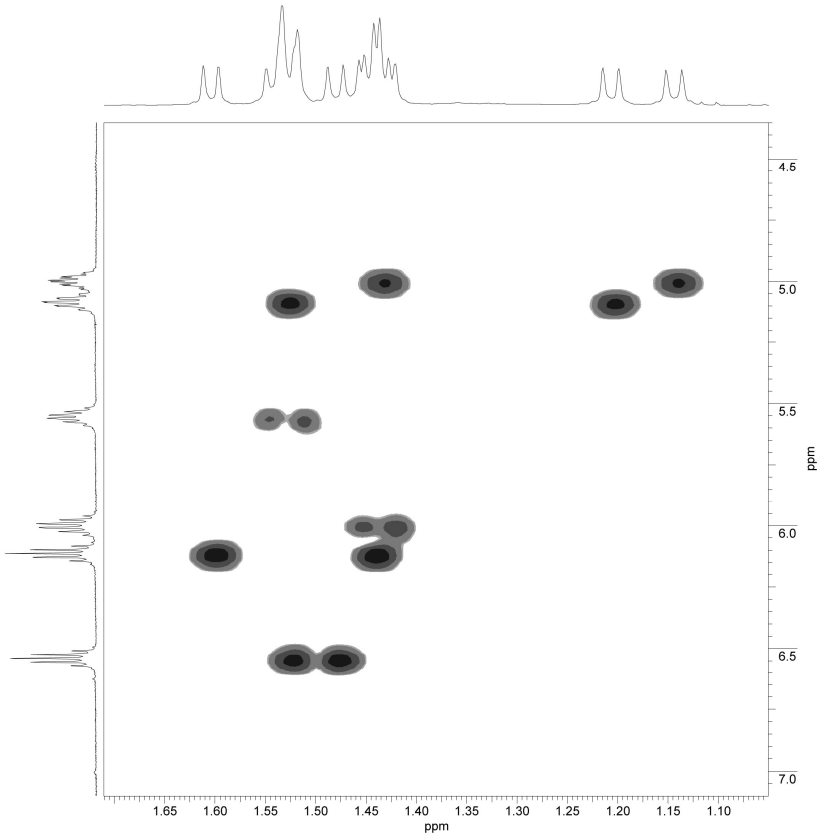

Fig. S2 A 2D ^{1}H NMR chemical shift correlated contour plot (COSY) for (**1**) recorded in benzene-d_6 at 400 MHz and 26 ˚C.

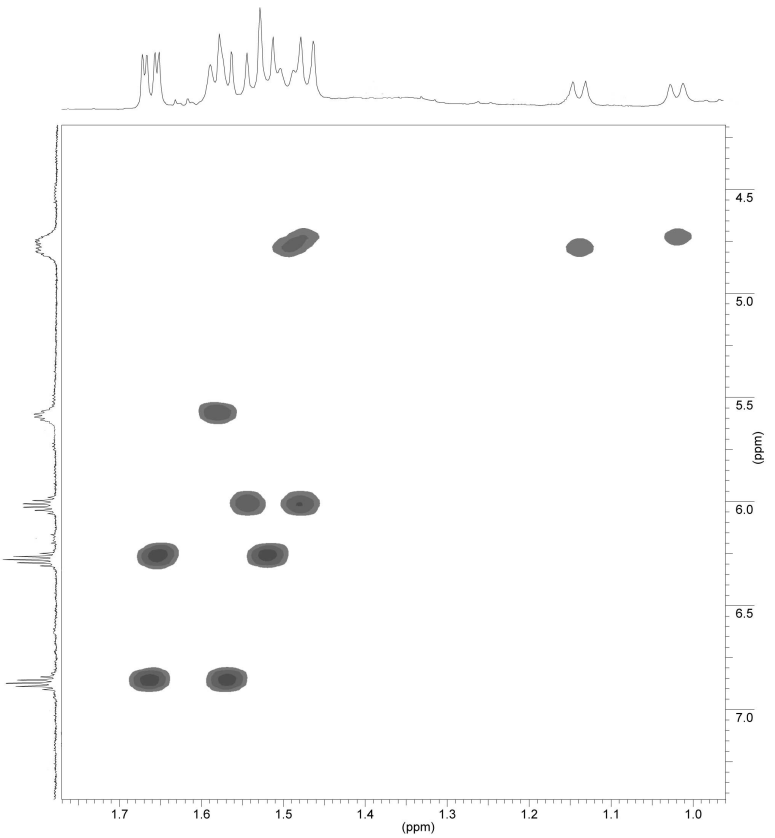

Fig. S3 A 2D ^{1}H NMR chemical shift correlated contour plot (COSY) for (**2**) recorded in benzene-d_6 at 400 MHz and 26 ˚C.

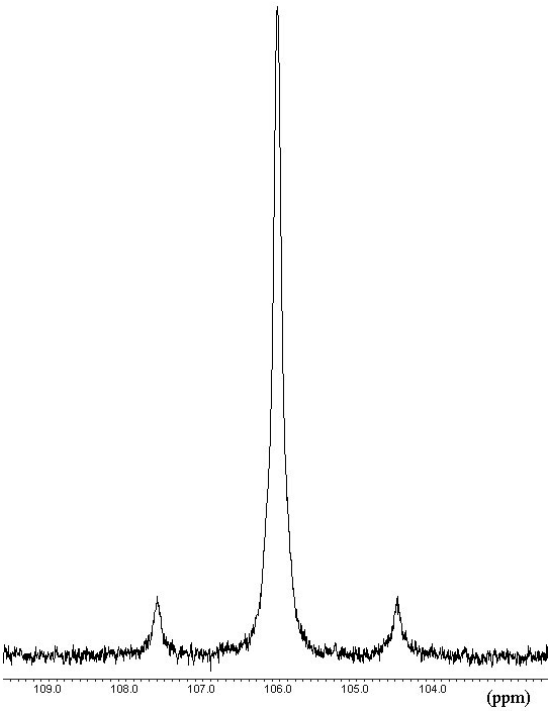

Fig. S4 The ^{31}P NMR spectrum of (**1**)

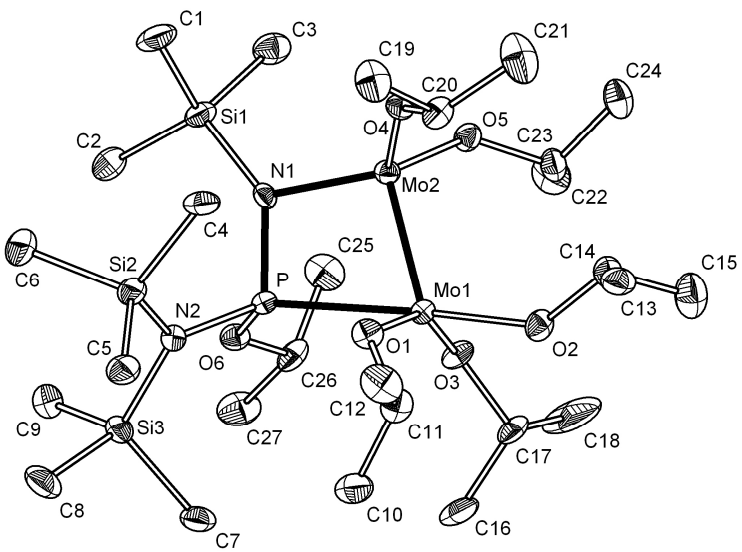

Fig. S5 The molecular structure of (2).