Supplementary Material for:

Synthesis of Planar Macrocyclic Tetradentate Phosphine - Mo Complexes

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■ General considerations:

All manipulation and reactions described below were carried out in a glovebox under N_2. NMR spectra were measured on a Bruker 400 MHz spectrometer. ^{31}P chemical shifts were referenced to a phosphoric acid external standard. MALDI-TOF spectra were measured by a Bruker ultraflextreme. EA were measured on Thermo Flash Smart from Thermo Scientific. 1,5-diphosphabicyclo[3.3.0]octane,[1] $Mo(O)(Cl)_2(PPh_2Me)_3$,[2] 1,1-bis(iodomethyl)cyclopropane,[3] 3,3-bis(iodomethyl)-oxetane,[3] were prepared according to the corresponding literature. Other reagents were commercially purchased and were dried and degassed prior to use. THF and Et_2O were distilled from sodium and other extra dry solvents were commercially available and used without further purification.

X-Ray diffraction: The crystal data of complexes **Mo1** and **Mo4** were collected using MoKα radiation (wavelength = 0.71073 Å) on a Bruker D8 Venture diffractometer. The crystal data of complex **P2** was collected using CuKα radiation (wavelength = 1.54178 Å) on a Bruker D8 Quest diffractometer. The crystal data of complexes **Mo2** and **Mo3** were collected using GaKα radiation (wavelength = 1.34139 Å) on a Bruker D8 Venture diffractometer. Crystals were mounted in inert oil and crystal structure determinations were conducted at low temperature. An empirical absorption correction with SADABS[4] was applied. The structures were solved using intrinsic phasing method (ShelXT)[5] and refined using the least-squares method on F^2 (ShelXL).[6] All non-H atoms were refined with anisotropic displacement parameters. The cation of **Mo2** and **Mo3** disordered in

two directions, several restrains (DFIX, SADI, SIMU, DELU) were used in order to improve the refinement stability. Restrains (DFIX, DANG, SADI, SIMU, DELU) were also used for the refinement of the PF_6^-, if disordered. X-ray crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/) with reference numbers: 2433616 (**P2**), 2433617 (**Mo1**), 2433618 (**Mo2**), 2433619 (**Mo3**), 2433620 (**Mo4**).

■ Experimental procedure:

Synthesis of [PP^{Cpr}PP]I$_2$ (P2) (PP^{Cpr}PP = 4-{[(octahydro[1,2]diphospholo[1,2-a][1,2]diphosphol-4-ium-4-ylmethyl)cyclopropyl]methyl}-octahydro-[1,2]diphospholo-[1,2-a][1,2]diphosphol-4-ium)

To a DMF solution (5 mL) of 1,5-diphosphabicyclo[3.3.0]octane (277 mg, 1.9 mmol) in a Schlenk tube was added 1,1-bis(iodomethyl)cyclopropane (306 mg, 0.95 mmol). The mixture was heated to 50 ℃ and stirred for 20 minutes, with the precipitation of a white solid of **P2**. The white solid was isolated and dried under vacuum. Compound **P2** was recrystallized from its concentrated methanol solution. Isolated yield: 408 mg, 70%. **^{1}H{P} NMR (400 MHz, CD$_3$OD)**: δ = 3.08 (s, 4H), 2.80 (dt, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 5.2 Hz, 4H), 2.65~2.58 (m, 4H), 2.45~2.33 (m, 8H), 2.21~2.13 (m, 8H), 0.99 (s, 4H) ppm (**Figure S1**); **^{31}P{H} NMR (162 MHz, DMF)**: δ = 79.6 (dt, $^1J_{PP}$ = 251.8 Hz, $^4J_{PP}$ = 13.6 Hz, 2P), -50.0 (dt, $^1J_{PP}$ = 252.0 Hz, $^4J_{PP}$ = 14.3 Hz, 2P) ppm (**Figure S2**). Anal: calcd for $C_{17}H_{32}P_4I_2$: C 33.25; H 5.25; found: C 33.48, H 5.03.

Synthesis of 1-{[(1,5-diphosphocan-1-ylmethyl)cyclopropyl]methyl}-1,5-diphosphocane (HPP^{Cpr}PPH, P3)

To a suspension of **P2** (122.8 mg, 0.2 mmol) in THF (5 mL) was added sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) (86 μL, 3.5 M in toluene, 0.3 mmol) at ambient temperature over 5 minutes. The white solid of **P2** gradually dissolved, resulting in a clear solution. Several drops of methanol were added to quench the remaining Red-Al. The solvent was removed under reduced pressure, and *n*-hexane was added to extract the product. The extraction was combined and taken to dryness, yielding **P3** as colorless oil. **P3** was directly used as a calibrated solution, for the following reactions without further purification. Isolated yield: 65.2 mg, 90% (calculated via the concentration). **^{1}H NMR (400 MHz, Toluene-*d*$_8$)**: δ = 3.30 (d, $^1J_{PH}$ = 196.4 Hz, 2H), 1.85 (br s, 8H), 1.61~1.58 (m, 14H), 1.32~1.30 (m, 6H), 0.35 (s, 4H) ppm (**Figure S3**); **^{1}H{P} NMR (400 MHz, Toluene-*d*$_8$)**: δ = 3.30 (s, 2H), 1.85 (br s,

8H), 1.60~1.57 (m, 14H), 1.33~1.28 (m, 6H), 0.35 (s, 4H) ppm (**Figure S4**); **^{31}P{H} NMR (162 MHz, THF)**: δ = -34.9 (d, $^{4}J_{PP}$ = 22.7 Hz, 2P), -73.6 (d, $^{4}J_{PP}$ = 24.5 Hz, 2P) ppm (**Figure S5**); **^{31}P NMR (162 MHz, THF)**: δ = -35.0 (br s, 2P), -73.6 (pseudo d, $^{1}J_{PH}$ = 199.1 Hz, 2P) ppm (**Figure S6**).

Synthesis of [(HPP^{Cpr}PPH)Mo(O)(OMe)][PF$_6$] (Mo1)

Mo(O)(Cl)$_2$(PPh$_2$Me)$_3$ (117.5 mg, 0.15 mmol), **P3** (54.3 mg, 0.15 mmol) and MeOLi (5.7 mg, 0.15 mmol) were mixed in 5 mL of methanol and stirred at ambient temperature for 2 h, resulting in a clear dark brownish-yellow solution. The solvent was removed under reduced pressure and acetonitrile was added to the residues. Then $NaPF_6$ (25.2 mg, 0.15 mmol) was added to the extraction. After removal of insoluble materials by filtration, yellow crystals of **Mo1** were obtained by layering *n*-hexane on top of the dichloromethane solution. Isolated yield: 46.8 mg, 48%. **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)**: 5.88 (d, $^{1}J_{PH}$ = 316.3 Hz, 2H), 3.15 (s, 3H), 2.41~1.73 (m, 28H), 0.64~0.53 (m, AA'BB', 4H) ppm (**Figure S7**); **^{1}H{P} NMR (400 MHz, CD$_2$Cl$_2$):** δ = 5.88 (s, 2H), 3.15 (s, 3H), 2.40~1.73 (m, 28H), 0.64~0.54 (m, AA'BB', 4H) ppm (**Figure S8**); **^{31}P NMR (162 MHz, CD$_2$Cl$_2$)**: δ = 0.0 (pseudo d, $^{2}J_{PP}$ = 203.0 Hz, 2P), -36.1 (pseudo dd, $^{1}J_{PH}$ = 314.8 Hz, $^{2}J_{PP}$ = 201.6 Hz, 2P), -144.5 (heptet, $^{1}J_{PF}$ = 710.4 Hz, 1P) ppm (**Figure S9**); **^{31}P{H} NMR (162 MHz, CD$_2$Cl$_2$)**: δ = 0.9~-1.0 (m, AA'BB', 2P), -34.5~-36.3 (m, AA'BB', 2P), -144.5 (heptet, $^{1}J_{PF}$ = 710.4 Hz, 1P) ppm (**Figure S10**). MS (MALDI-TOF, *m/z*): 507.1 [cation]$^+$. Anal: calcd for $C_{18}H_{37}F_6MoO_2P_5$: C 33.24, H 5.73; found: 33.19, H 5.63.

Synthesis of [(PP^{Cpr}PP^{Cpr})Mo(O)(OMe)][PF$_6$] (Mo2) (PP^{Cpr}PP^{Cpr} = dispiro-[cyclopropane-1,11'-1,5,9,13-tetraphosphatricyclo-[11.3.3.3^{5,9}]docosane-3',1''-cyclopropane])

KHMDS (60 μL, 1.0 M in THF, 0.06 mmol) was added dropwise into the THF (2 mL) suspension of **Mo1** (19.5 mg, 0.03 mmol) at -60 °C, and the reaction mixture gradually turned into a deep green solution. 1,1-bis(iodomethyl)cyclopropane (9.7 mg, 0.03mmol) was added, resulting in a color change to a dark brown. As the temperature slowly warmed to room temperature, the yellow solid of **Mo2** precipitated. Crystals of **Mo2** were obtained by vapor diffusion of diethyl ether into the dichloromethane solution. Isolated yield: 10.7 mg, 50%. **^{1}H{P} NMR (400 MHz, CD$_2$Cl$_2$)**: δ = 3.12 (s, 3H), 2.45~1.83 (m, 32H), 0.59 (br s, 4H), 0.54 (br s, 4H) ppm (**Figure S11**); **^{31}P{H} NMR (162 MHz, CD$_2$Cl$_2$)**: δ = 5.0 (s, 4P), -144.5 (heptet, $^{1}J_{PF}$ = 710.4 Hz, 1P) ppm (**Figure S12**). MS (MALDI-TOF, *m/z*): 573.1 [cation]$^+$. Anal: calcd for $C_{23}H_{43}F_6MoO_2P_5$: C

38.56, H 6.05; found: 38.44, H 6.05. **Figure S13** is the $^{13}C\{H\}$ NMR, however, besides some small signals of minor impurities, only broad peaks are observed in the spectra. Many adverse factors lead to this phenomenon. First, many C nuclei are close in chemical shift. Second, the coupling between P nuclei splits those signals of C nuclei. Last, fluxional ring-flipping processes occurring on the NMR timescale broadens the signals. Lowering the testing temperature does not significantly improve this issue. Overall, the $^{13}C\{H\}$ NMR are not very informative for the structure identification. Variable temperature $^{31}P\{H\}$ NMR (**Figure S14**) and $^{1}H\{P\}$ NMR (**Figure S15**) spectra were also recorded.

Synthesis of [($PP^{Cpr}PP^{Oxt}$)Mo(O)(OMe)][PF_6] (Mo3) ($PP^{Cpr}PP^{Oxt}$ = dispiro-[oxetane-3,11'-1,5,9,13-tetraphosphatricyclo[11.3.3.3^{5,9}]-docosane-3',1''-cyclopropane])

Following the procedure of **Mo2**, **Mo3** was prepared by using 3,3-bis(iodomethyl)oxetane (10.1 mg, 0.03 mmol) instead of 1,1-bis(iodomethyl)cyclopropane. Yellow crystals of **Mo3** were obtained by vapor diffusion of diethyl ether into the dichloromethane solution. Isolated yield: 10.5 mg, 48%. **$^{1}H\{P\}$ NMR (400 MHz, CD_2Cl_2)**: δ = 4.52 (s, 2H), 4.48 (br s, 2H), 3.03 (s, 3H), 2.42~1.62 (m, 32H), 0.59 (br s, 2H), 0.54 (br s, 2H) ppm (**Figure S16**); **$^{31}P\{H\}$ NMR (162 MHz, CD_2Cl_2)**: δ = 9.2~5.4 (br m, 2P), 5.4~1.6 (br m, 2P), -144.5 (heptet, $^{1}J_{PF}$ = 710.4 Hz, 1P) ppm (**Figure S17**). MS (MALDI-TOF, *m/z*): 589.1 [cation]$^{+}$. Anal: calcd for $C_{23}H_{43}F_6MoO_3P_5$: C 37.72, H 5.92; found: 37.72, H 6.05.

Synthesis of [($PP^{Cpr}PP^{Xy}$)Mo(O)(OMe)][PF_6] (Mo4) ($PP^{Cpr}PP^{Xy}$ = spiro[1,5,9,18-tetraphosphatetracyclo[16.3.3.3^{5,9}.0^{11,16}]heptacosa-11(12),13,15-triene-3,1'-cyclopropane])

Following the procedure of **Mo2**, **Mo4** was prepared by using *α*,*α*'-dibromo-*o*-xylene (7.9 mg, 0.03 mmol) instead of 1,1-bis(iodomethyl)cyclopropane. Yellow crystals of **Mo4** were obtained by vapor diffusion of diethyl ether into the *N*,*N*-dimethylformamide (DMF) solution. Isolated yield: 9.5 mg, 42%. **$^{1}H\{P\}$ NMR (400 MHz, CD_2Cl_2)**: δ = 7.21~7.14 (m, AA'BB', 4H), 4.00 (d, $^{2}J_{HH}$ = 13.0 Hz, 2H), 3.53 (d, $^{2}J_{HH}$ = 13.0 Hz, 2H), 2.46~2.09 (m, 21H), 1.93~1.88 (m, 6H), 1.72~1.57 (m, 4H), 0.53 (br s, 2H), 0.42 (br s, 2H) ppm (**Figure S18**); **$^{31}P\{H\}$ NMR (162 MHz, CD_2Cl_2)**: δ = 3.3~1.6 (m, 2P), 1.6~-0.1 (m, 2P), -144.5 (heptet, $^{1}J_{PF}$ = 710.4 Hz, 1P) ppm (**Figure S19**). MS (MALDI-TOF, *m/z*): 609.1 [cation]$^{+}$. Anal: calcd for $C_{26}H_{43}F_6MoO_2P_5 \cdot 2C_3H_7NO$: C 42.77, H 6.39;

found: 42.66, H 6.71.

References:

1 K. Issleib and P. Thorausch, *Phosphorus Sulfur*, 1978, **4**, 137.

2 A. V. Butcher and J. Chatt, *J. Chem. Soc. A*, 1970, 2652.

3 Q. Ma, K. Lei, J. Ding, L. Yu and J. Ding, *Polym. Chem.*, 2017, **8**, 6665.

4 SAINT, Program for data correction (Bruker-AXS).

5 G. M. Sheldrick ShelXT, University of Göttingen, *Acta Crystallogr. Sect. A*, 2015, **71**, 3-8.

6 G. M. Sheldrick ShelXT, University of Göttingen, *Acta Crystallogr. Sect. C*, 2015, **71**, 3-8.

■ NMR spectra

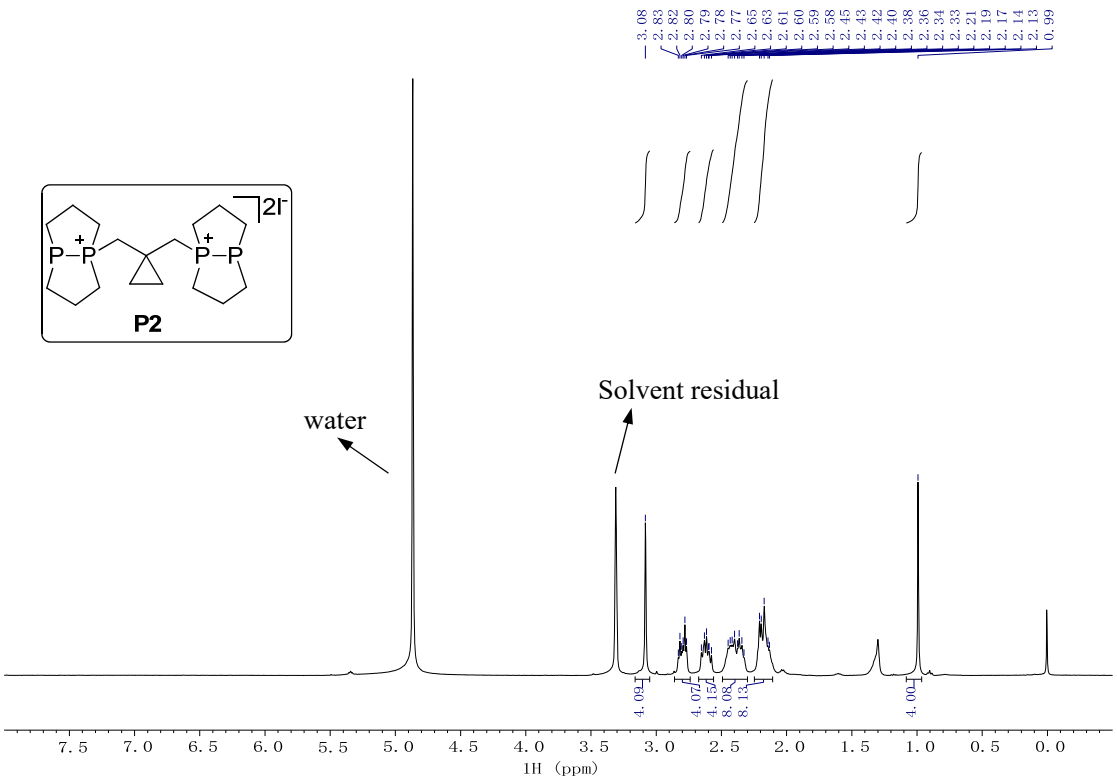


Figure S1. $^{1}H\{P\}$ NMR spectrum of $[PP^{Cpr}PP]I_2$ (**P2**) in CD_3OD.

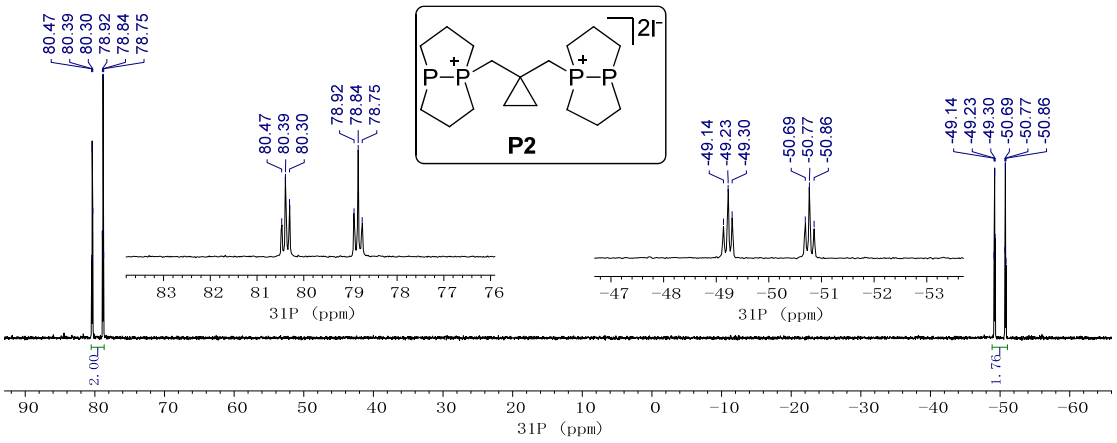


Figure S2. $^{31}P\{H\}$ NMR spectrum of $[PP^{Cpr}PP]I_2$ (**P2**) in DMF.

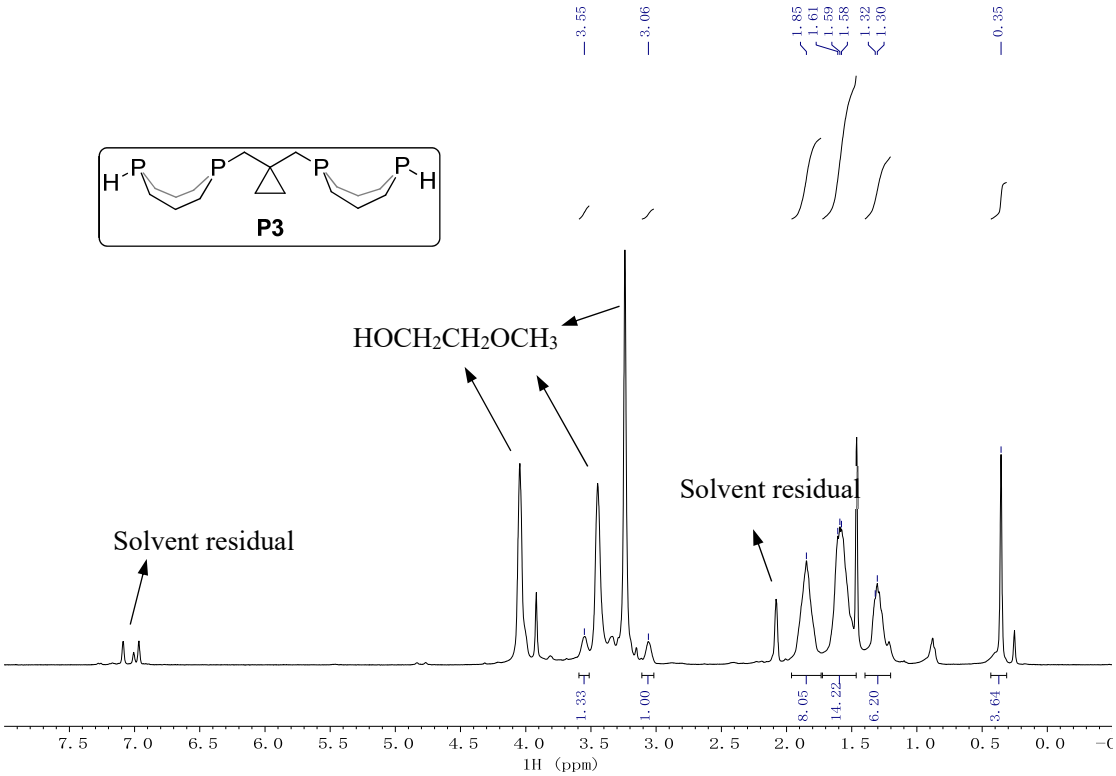


Figure S3. ^{1}H NMR spectrum of HPP^{Cpr}PPH (**P3**) (crude product) in toluene-d_8.

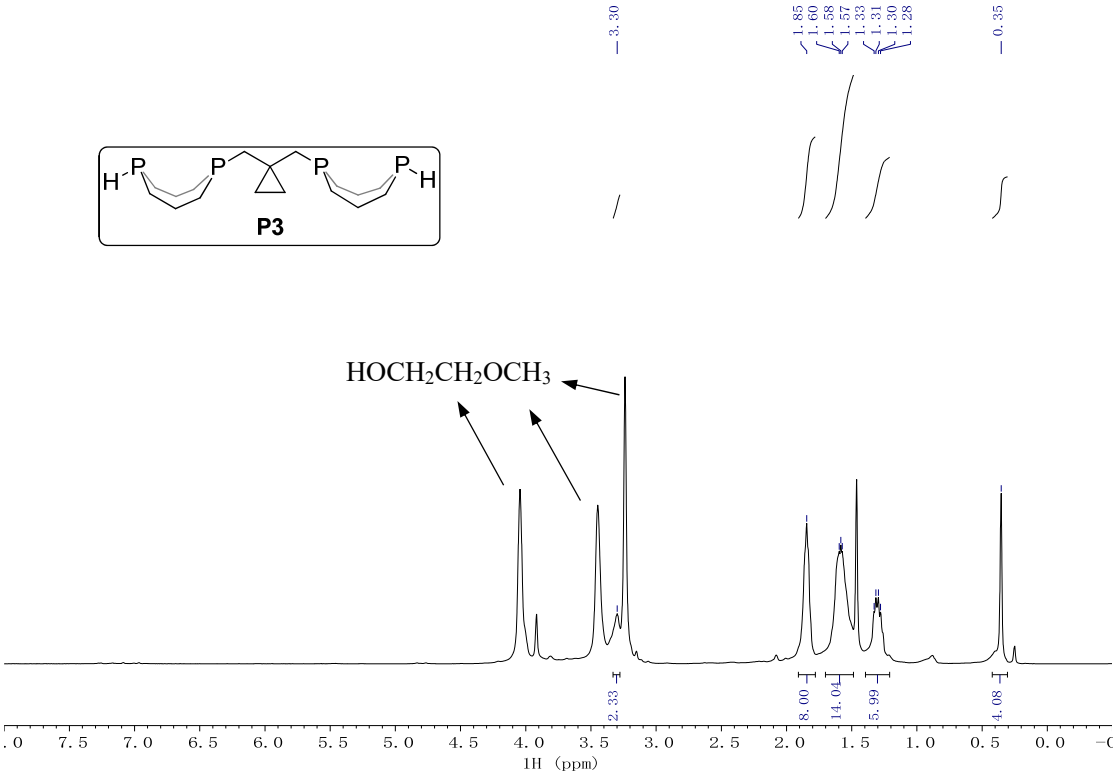


Figure S4. ^{1}H{P} NMR spectrum of HPP^{Cpr}PPH (**P3**) (crude product) in toluene-d_8.

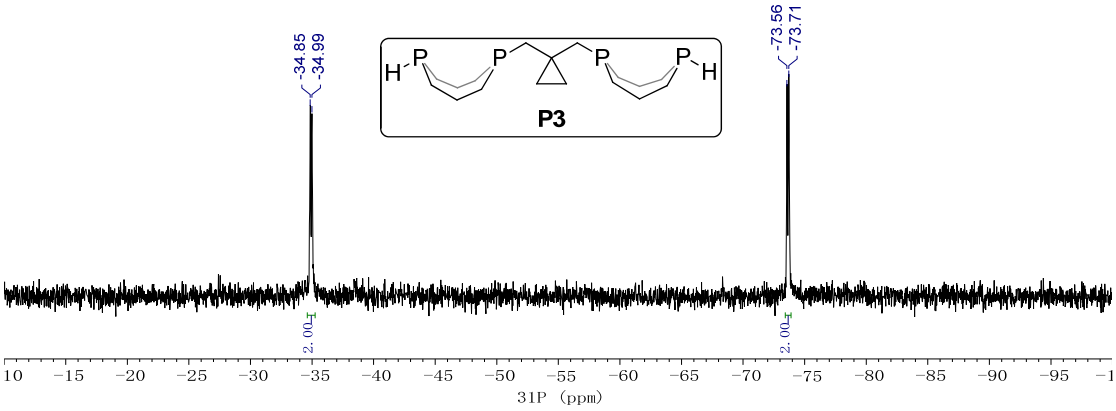


Figure S5. $^{31}P\{H\}$ NMR spectrum of HPP^{Cpr}PPH (**P3**) in THF.

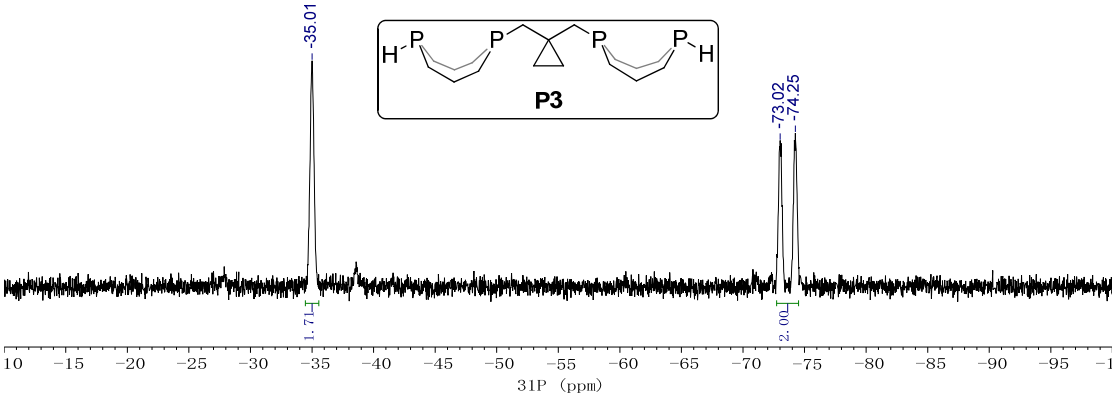


Figure S6. ^{31}P NMR spectrum of HPP^{Cpr}PPH (**P3**) in THF.

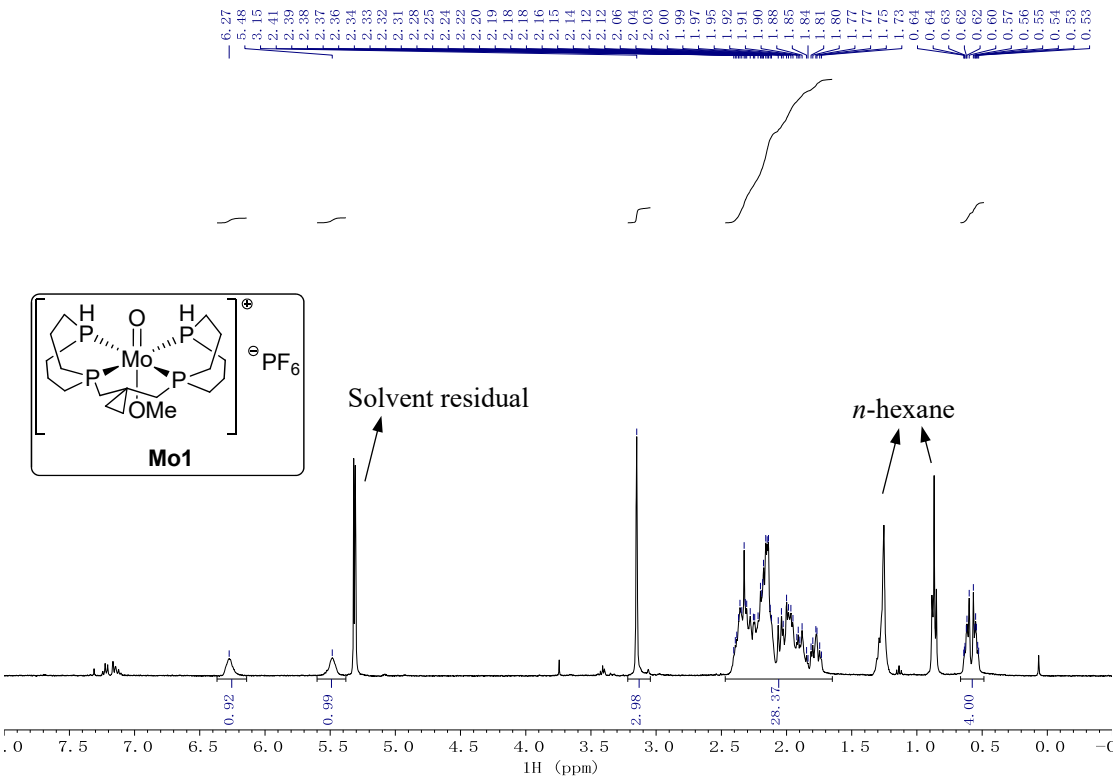


Figure S7. ^{1}H NMR spectrum of [(HPP^{Cpr}PPH)Mo(O)(OMe)][PF_6] (**Mo1**) in CD_2Cl_2.

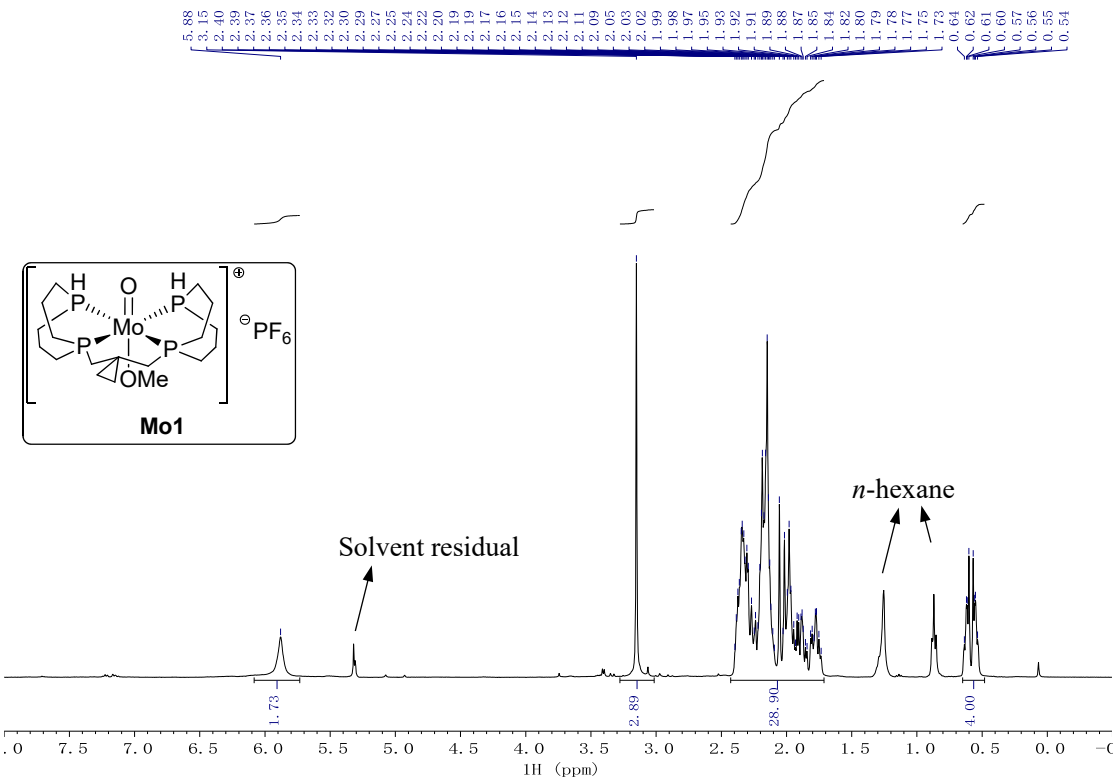


Figure S8. ^{1}H{P} NMR spectrum of [(HPP^{Cpr}PPH)Mo(O)(OMe)][PF_6] (**Mo1**) in CD_2Cl_2.

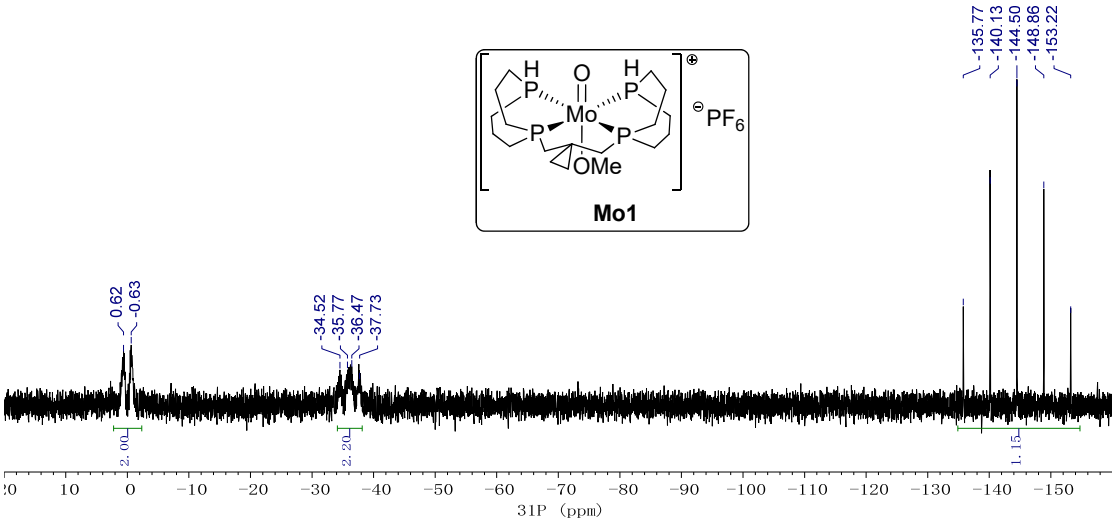


Figure S9. ^{31}P NMR spectrum of [(HPP^{Cpr}PPH)Mo(O)(OMe)][PF_6] (**Mo1**) in CD_2Cl_2.

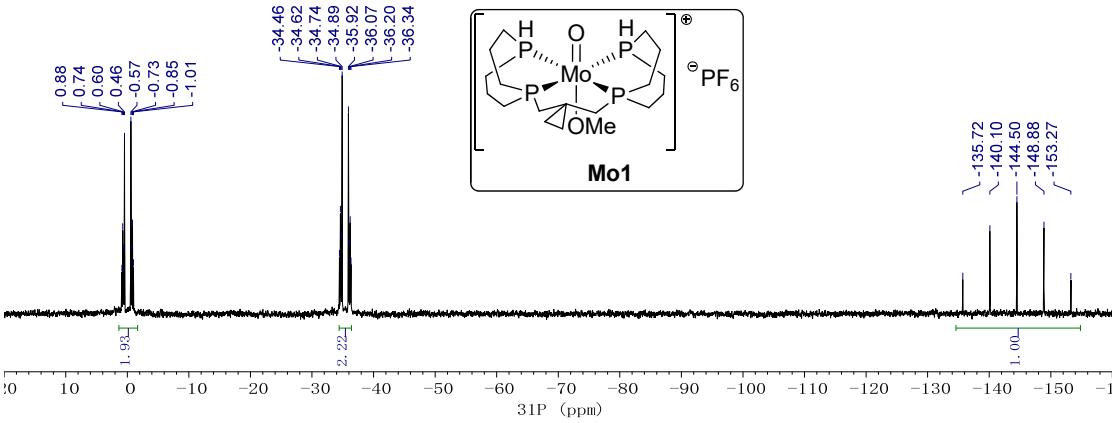


Figure S10. $^{31}P\{H\}$ NMR spectrum of [(HPP^{Cpr}PPH)Mo(O)(OMe)][PF_6] (**Mo1**) in CD_2Cl_2.

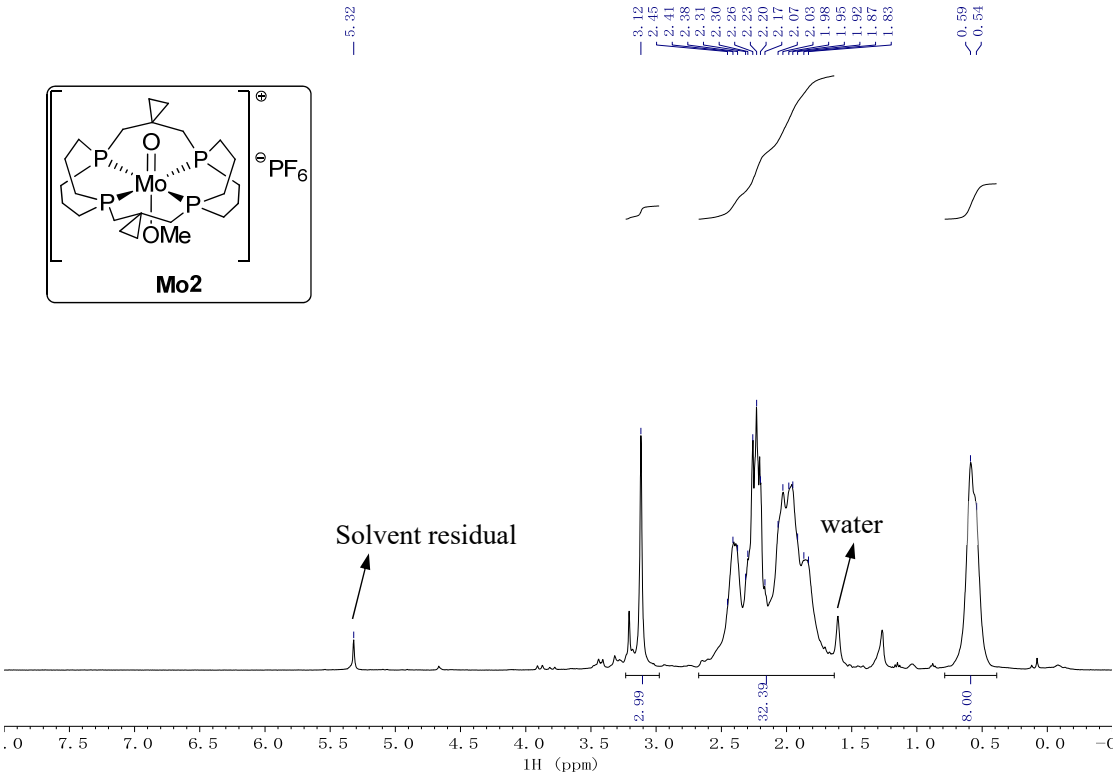


Figure S11. $^{1}H\{P\}$ NMR spectrum of $[(PP^{Cpr}PP^{Cpr})Mo(O)(OMe)][PF_6]$ (**Mo2**) in CD_2Cl_2.

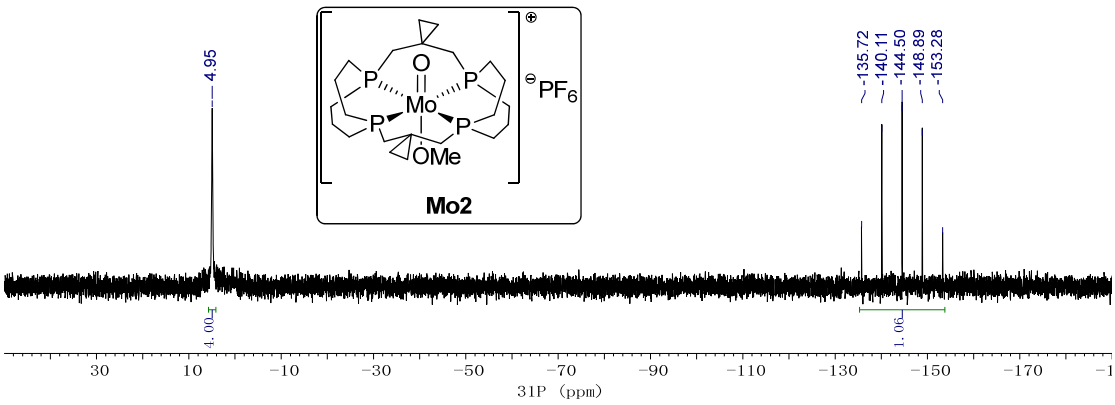


Figure S12. $^{31}P\{H\}$ NMR spectrum of $[(PP^{Cpr}PP^{Cpr})Mo(O)(OMe)][PF_6]$ (**Mo2**) in CD_2Cl_2.

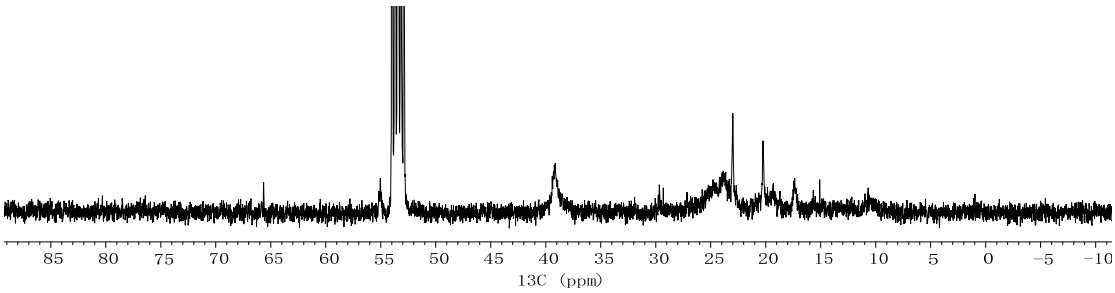


Figure S13. $^{13}C\{H\}$ NMR spectrum of $[(PP^{Cpr}PP^{Cpr})Mo(O)(OMe)][PF_6]$ (**Mo2**) in CD_2Cl_2 (8000 scans).

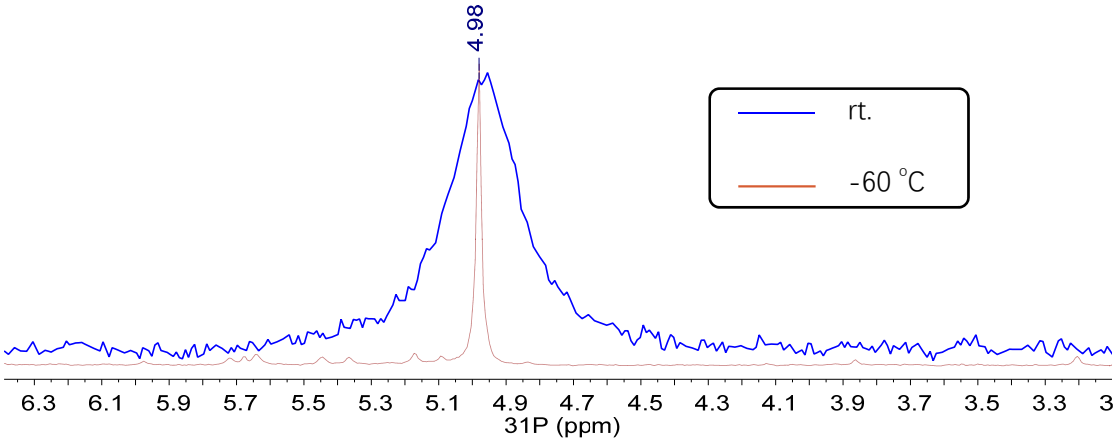


Figure S14. Variable temperature $^{31}P\{H\}$ NMR of $[(PP^{Cpr}PP^{Cpr})Mo(O)(OMe)][PF_6]$ (**Mo2**) in CD_2Cl_2.

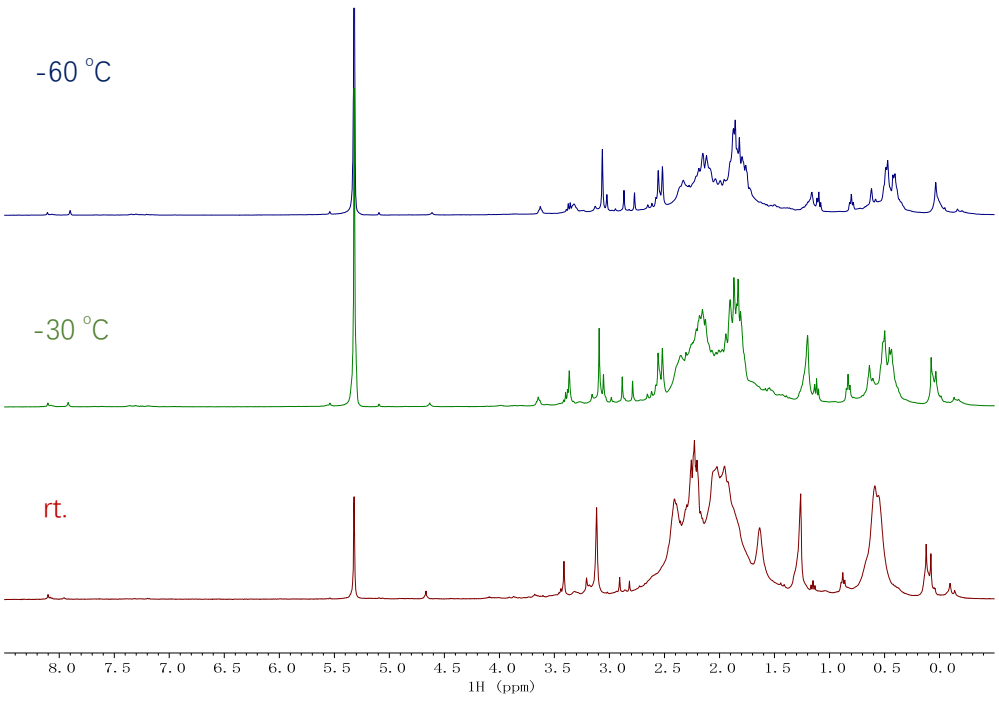


Figure S15. Variable temperature $^{1}H\{P\}$ NMR of $[(PP^{Cpr}PP^{Cpr})Mo(O)(OMe)][PF_6]$ (**Mo2**) in CD_2Cl_2.

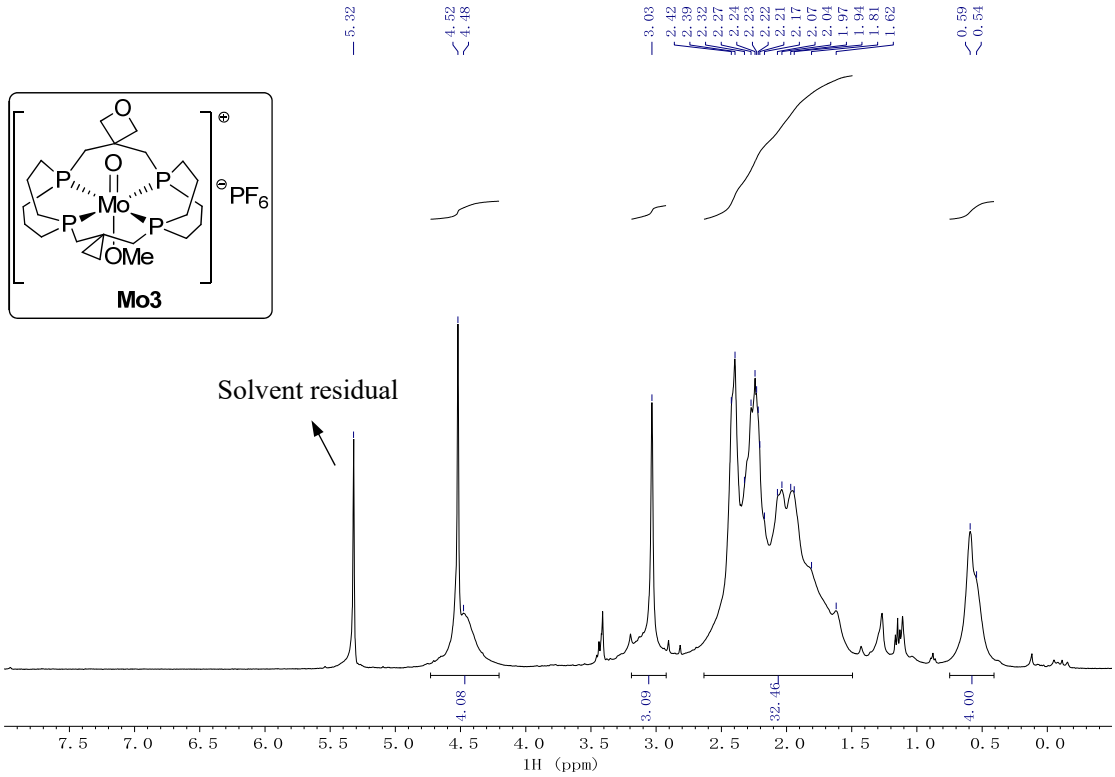


Figure S16. $^{1}H\{P\}$ NMR spectrum of $[(PP^{Cpr}PP^{Oxt})Mo(O)(OMe)][PF_6]$ (**Mo3**) in CD_2Cl_2.

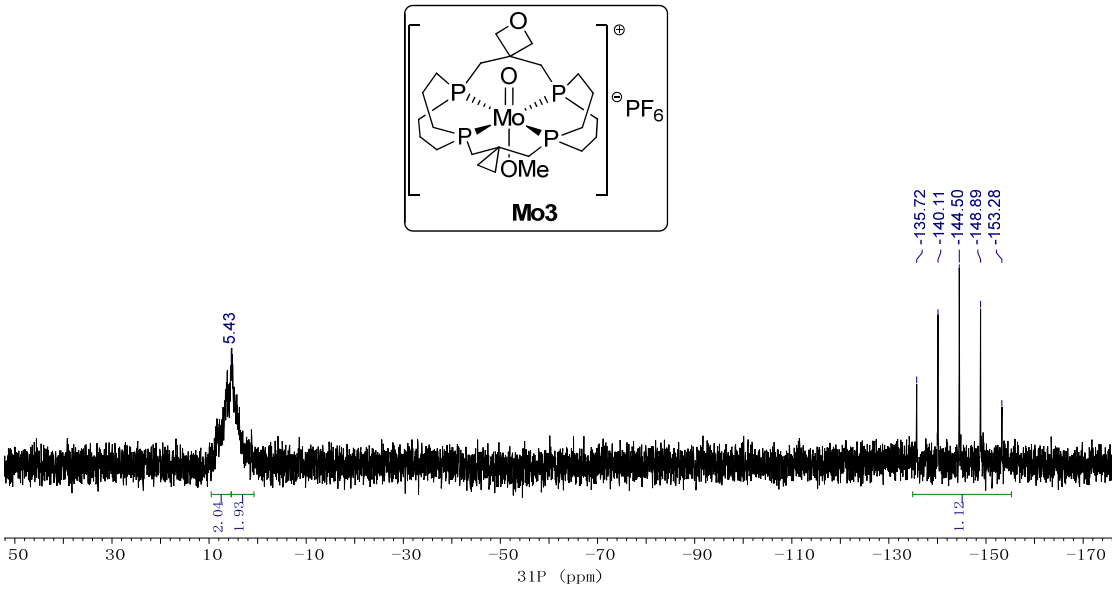


Figure S17. $^{31}P\{H\}$ NMR spectrum of $[(PP^{Cpr}PP^{Oxt})Mo(O)(OMe)][PF_6]$ (**Mo3**) in CD_2Cl_2.

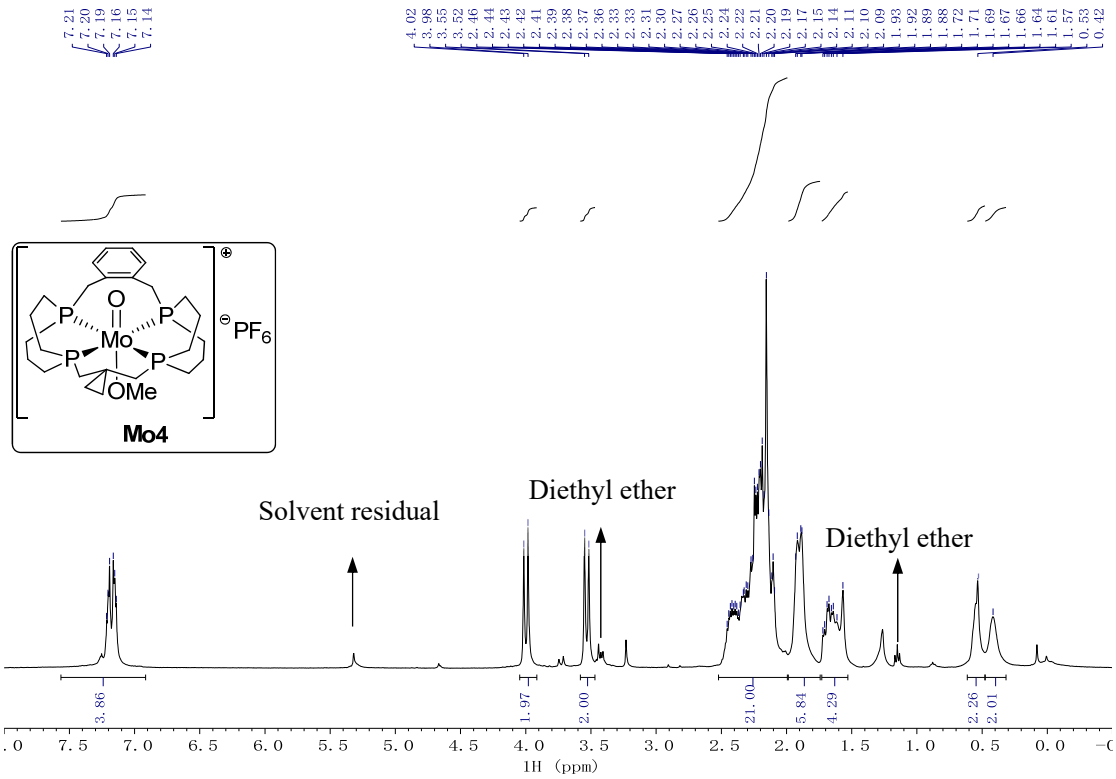


Figure S18. $^{1}H\{P\}$ NMR spectrum of $[(PP^{Cpr}PP^{Xy})Mo(O)(OMe)][PF_6]$ (**Mo4**) in CD_2Cl_2.

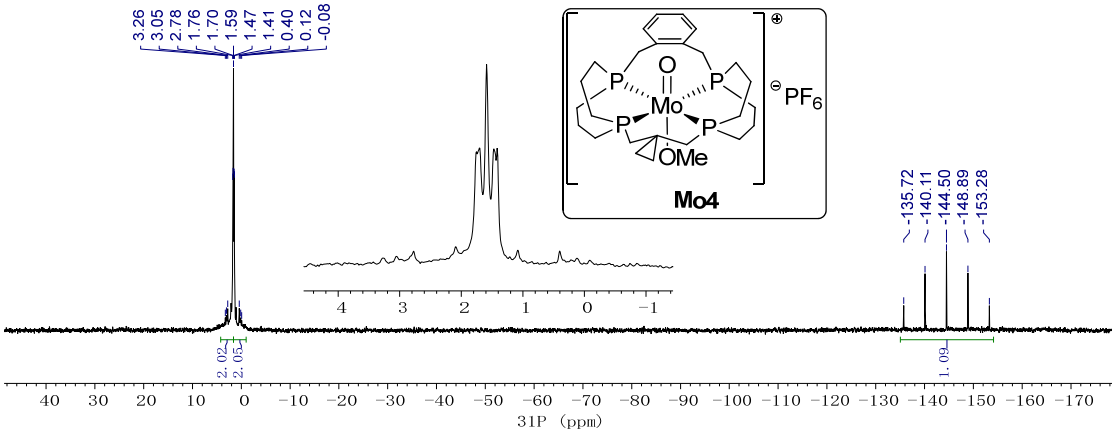
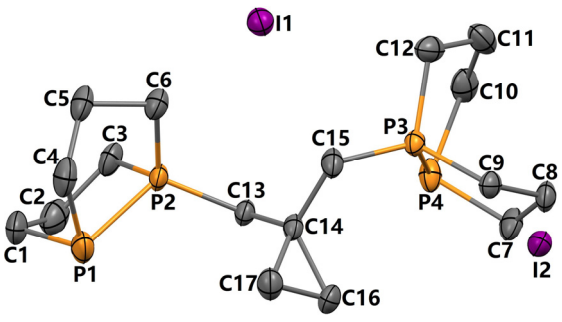


Figure S19. $^{31}P\{H\}$ NMR spectrum of $[(PP^{Cpr}PP^{Xy})Mo(O)(OMe)][PF_6]$ (**Mo4**) in CD_2Cl_2.

■ X-ray diffraction data

Table S1. [PP^{Cpr}PP]I_2 (P2)

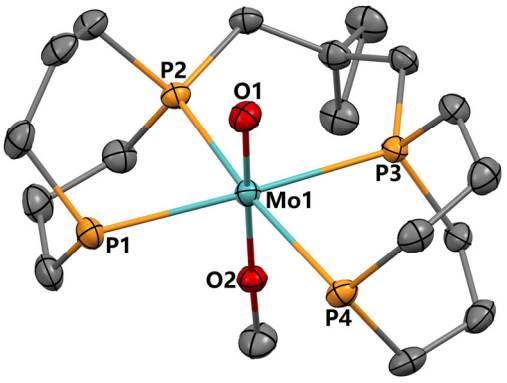
Molecular formula	$C_{17}H_{32}I_2P_4$	
Formula weight	614.10	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.261 × 0.126 × 0.115 mm^3	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell parameters	a = 25.0082(10) Å	α = 90°
	b = 7.2516(3) Å	β = 107.782(2)°
	c = 13.3724(5) Å	γ = 90°
	V = 2309.22(16) Å^3	
Z	4	
F(000)	1200	
Density (calcd)	1.766 g/cm^3	
Absorption coefficient	23.985 mm^{-1}	
Theta range for data collection	6.811 to 70.048°	
Limiting indices	-30<=h<=30, -8<=k<=8, -16<=l<=15	
Reflections collected / unique	33796 / 4176 [R(int) = 0.0634]	
Completeness to theta = 67.679°	99.7%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4176 / 2 / 209	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0795	
R indices (all data)	R1 = 0.0317, wR2 = 0.0796	
Largest diff. peak and hole	1.142 and -0.835 eÅ^{-3}	



Selected bond lengths (Å) and angles (°): P1-P2 2.193(2), P3-P4 2.186(2), P3-C12 1.811(7), P4-C7 1.863(7), C14-C17 1.509(9), P3-C9 1.810(6), C9-C8 1.522(9), C9-P3-C12 109.9(3), C9-P3-C15 112.9(3), C12-P3-C15 111.9(4), C9-P3-P4 100.2(2), C12-P3-P4 100.9(3), C15-P3-P4 119.9(2), C13-P2-C6 116.4(3), C13-P2-C3 109.6(3), C6-P2-C3 112.2(3), C13-P2-P1 118.3(2).

Table S2. [(HPP^{Cpr}PPH)Mo(O)(OMe)][PF_6] (Mo1)

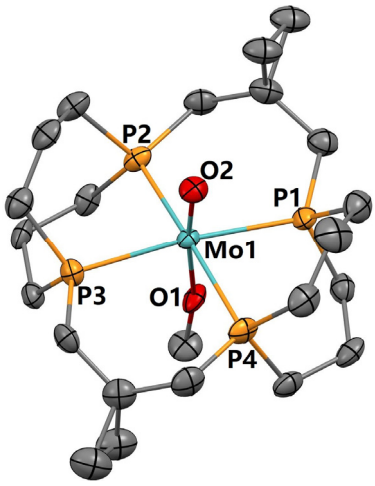
Molecular formula	$C_{18}H_{37}F_6MoO_2P_5$	
Formula weight	650.26	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.472 × 0.137 × 0.076 mm^3	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell parameters	a = 11.2715(6) Å	α = 90°
	b = 9.0595(4) Å	β = 102.768(2)°
	c = 25.2626(14) Å	γ = 90°
	V = 2515.9(2) $Å^3$	
Z	4	
F(000)	1328	
Density (calcd)	1.717 g/cm^3	
Absorption coefficient	0.899 mm^{-1}	
Theta range for data collection	2.248 to 30.557°	
Limiting indices	-14<=h<=16, -12<=k<=12, -35<=l<=32	
Reflections collected / unique	23192 / 7183 [R(int) = 0.0589]	
Completeness to theta = 25.242°	98.2%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7183 / 0 / 299	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1005	
R indices (all data)	R1 = 0.0564, wR2 = 0.1069	
Largest diff. peak and hole	0.927 and -0.879 $eÅ^{-3}$	



Selected bond lengths (Å) and angles (°): Mo1-O1 1.719(2), Mo1-O2 1.9487(19), Mo1-P1 2.5203(8), Mo1-P2 2.4863(7), Mo1-P3 2.4609(7), Mo1-P4 2.5086(8), O1-Mo1-O2 179.06(9), O1-Mo1-P1 94.44(7), O1-Mo(1)-P2 93.07(7), O1-Mo1-P3 91.58(7), O1-Mo1-P4 93.17(7), O2-Mo1-P1 86.50(6), O2-Mo1-P2 87.16(6), O2-Mo1-P3 87.49(6), O2-Mo1-P4 86.46(6), P1-Mo1-P2 77.42(3), P1-Mo1-P3 169.74(3), P1-Mo1-P4 111.01(3), P2-Mo1-P3 93.99(3), P2-Mo1-P4 169.07(3), P3-Mo1-P4 76.88(3).

Table S3. [(PP^{Cpr}PP^{Cpr})Mo(O)(OMe)][PF$_6$] (Mo2)

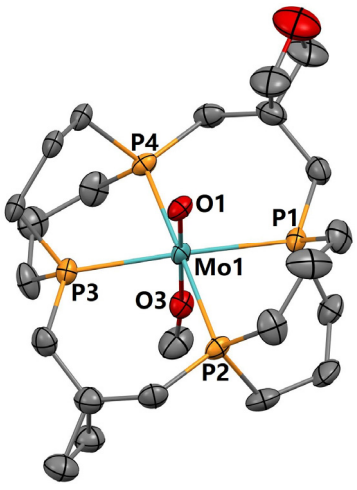
Molecular formula	$C_{23}H_{43}F_6MoO_2P_5$
Formula weight	716.36
Temperature	170(2) K
Wavelength	1.34139 Å
Crystal size	0.108 × 0.062 × 0.052 mm^3
Crystal system	Monoclinic
Space group	C2/c
Unit cell parameters	a = 19.4121(6) Å α = 90°
	b = 9.7496(3) Å β = 107.8730(10)°
	c = 16.2388(5) Å γ = 90°
	V = 2925.03(16) Å^3
Z	4
F(000)	1472
Density (calcd)	1.627 g/cm^3
Absorption coefficient	4.525 mm^{-1}
Theta range for data collection	4.164 to 53.855°
Limiting indices	-22<=h<=23, -11<=k<=11, -19<=l<=19
Reflections collected / unique	21393 / 2664 [R(int) = 0.0868]
Completeness to theta = 53.594°	99.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2664 / 369 / 331
Goodness-of-fit on F^2	1.173
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1027
R indices (all data)	R1 = 0.0552, wR2 = 0.1046
Largest diff. peak and hole	0.654 and -0.575 eÅ^{-3}



Selected bond lengths (Å) and angles (°): Mo1-O1 1.712(13), Mo1-O2 1.971(12), Mo1-P1 2.438(6), Mo1-P2 2.437(5), Mo1-P3 2.437(6), Mo1-P4 2.436(5), O1-Mo1-O2 178.2(9), O1-Mo1-P1 95.2(6), O1-Mo1-P2 95.2(6), O1-Mo1-P3 94.7(6), O1-Mo1-P4 95.3(5), O2-Mo1-P1 84.0(6), O2-Mo1-P2 83.3(5), O2-Mo1-P3 86.1(6), O2-Mo1-P4 86.2(5), P1-Mo1-P2 97.6(5), P1-Mo1-P3 170.1(7), P1-Mo1-P4 79.5(6), P2-Mo1-P3 81.8(5), P2-Mo1-P4 169.4(6), P3-Mo1-P4 99.4(6).

Table S4. [(PP^{Cpr}PP^{Oxt})Mo(O)(OMe)][PF$_6$] (Mo3)

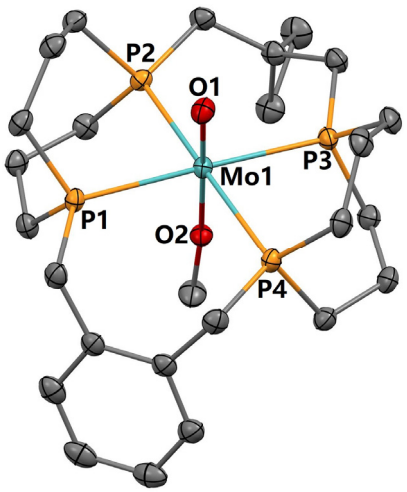
Molecular formula	$C_{23}H_{43}F_6MoO_3P_5$
Formula weight	732.36
Temperature	170(2) K
Wavelength	1.34139 Å
Crystal size	0.306 × 0.059 × 0.057 mm^3
Crystal system	Monoclinic
Space group	C2
Unit cell parameters	a = 19.4237(7) Å α = 90°
	b = 9.6183(4) Å β = 107.8221(11)°
	c = 16.5169(6) Å γ = 90°
	V = 2937.66(19) Å^3
Z	4
F(000)	1504
Density (calcd)	1.656 mg/m^3
Absorption coefficient	4.532 mm^{-1}
Theta range for data collection	2.445 to 63.438°
Limiting indices	-25<=h<=23, -12<=k<=12, -21<=l<=21
Reflections collected / unique	26021 / 6980 [R(int) = 0.0467]
Completeness to theta = 53.594°	97.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6980 / 434 / 474
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1085
R indices (all data)	R1 = 0.0421, wR2 = 0.1087
Largest diff. peak and hole	1.044 and -0.884 eÅ^{-3}



Selected bond lengths (Å) and angles (°): Mo1-O1 1.764(4), Mo1-O3 1.925(4), Mo1-P1 2.4433(13), Mo1-P2 2.4293(15), Mo1-P3 2.4227(15), Mo1-P4 2.4251(15), O1-Mo1-O3 179.5(2), O1-Mo1-P1 92.96(14), O1-Mo1-P2 91.87(14), O1-Mo1-P3 91.36(14), O1-Mo1-P4 91.77(14), O3-Mo1-P1 87.32(13), O3-Mo1-P2 87.74(14), O3-Mo1-P3 88.36(13), O3-Mo1-P4 88.62(13), P1-Mo1-P2 81.20(6), P1-Mo1-P3 175.67(7), P1-Mo1-P4 98.73(6), P2-Mo1-P3 98.83(5), P2-Mo1-P4 176.36(7), P3-Mo1-P4 80.97(5).

Table S5. [(PP^{Cpr}PP^{Xy})Mo(O)(OMe)][PF$_6$] (Mo4)

Molecular formula	$2C_{26}H_{43}F_6MoO_2P_5 \cdot C_3H_7NO$
Formula weight	1577.88
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal size	0.250 × 0.220 × 0.180 mm^3
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell parameters	a = 15.5120(8) Å α = 90°
	b = 14.9330(10) Å β = 101.467(2)°
	c = 14.2680 (9) Å γ = 90°
	V = 3239.1(3) Å^3
Z	2
F(000)	1624
Density (calcd)	1.618 mg/m^3
Absorption coefficient	0.716 mm^{-1}
Theta range for data collection	2.728 to 34.275°
Limiting indices	-24<=h<=19, -18<=k<=23, -22<=l<=19
Reflections collected / unique	83295 / 11863 [R(int) = 0.0568]
Completeness to theta = 25.242°	99.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11863 / 0 / 409
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0876
R indices (all data)	R1 = 0.0461, wR2 = 0.0954
Largest diff. peak and hole	2.285 and -0.974 eÅ^{-3}



Selected bond lengths (Å) and angles (°): Mo1-O1 1.7142(13), Mo1-O2 1.9696(12), Mo1-P1 2.4616(5), Mo1-P2 2.4627(5), Mo1-P3 2.4611(5), Mo1-P4 2.4670(5), O1-Mo1-O2 177.80(6), O1-Mo1-P1 91.69(5), O1-Mo1-P2 95.01(5), O1-Mo1-P3 95.44(5), O1-Mo1-P4 91.59(5), O2-Mo1-P1 87.00(4), O2-Mo1-P2 86.48(4), O2-Mo1-P3 85.98(4), O2-Mo1-P4 87.01(4), P1-Mo1-P2 79.101(15), P1-Mo1-P3 172.039(16), P1-Mo1-P4 103.944(15), P2-Mo1-P3 96.715(15), P2-Mo1-P4 172.662(16), P3-Mo1-P4 79.436(15).