

Electronic Supporting Information

Preparation and reactivity of molybdenum–dinitrogen complexes bearing arsenic-containing ANA-type pincer ligand

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General Methods. All manipulations were carried out under an atmosphere of dry dinitrogen in a VAC glovebox or using standard Schlenk techniques. THF, diethyl ether, and hexane were purified by passing through a purification system (Glass Contour). tBu_2AsCl ,¹ $[\text{MoCl}_3(\text{thf})_3]$,² and $[\text{nBu}_4\text{N}][\text{BAr}^{\text{F}}_4]$ ($\text{BAr}^{\text{F}}_4 = \text{tetrakis}[3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}]\text{borate}$)³ were prepared according to the literature procedures. All the other dry solvents and reagents were obtained from commercial sources and used without further purification.

^1H , ^{13}C , and ^{31}P NMR spectra were recorded on a JEOL Excalibur 270 spectrometer (^1H , 270 MHz; ^{13}C , 67.8 MHz; ^{31}P , 109 MHz) in $\text{THF-}d_8$ at room temperature and were referenced to residual solvents (for ^1H and ^{13}C NMR) or an external standard (85% H_3PO_4 for ^{31}P NMR). Elemental analyses were performed at the Microanalytical Center of The University of Tokyo or on an Exeter Analytical CE-440 Elemental Analyzer. IR spectra were recorded on a JASCO FT/IR 4100 Fourier Transform Infrared Spectrophotometer. Raman spectra were recorded on a JASCO NRS-2000. Absorption spectra were recorded on a Shimadzu MultiSpec-1500. Evolved dihydrogen was quantified by a gas chromatography using a Shimadzu GC-8A with a TCD detector and a SHINCARBON ST (6 m \times 3 mm). Cyclic voltammograms were recorded on an ALS/Chi model 610C electrochemical analyzer with platinum working electrode at a scan rate of 100 mV/s in THF containing 0.1 M $[\text{nBu}_4\text{N}][\text{BAr}^{\text{F}}_4]$ and 1 mM sample at 25 °C.

Preparation of 2,6-Bis[(di-*tert*-butylarsino)methyl]pyridine (tBuANA, 2b). To a solution of 2,6-lutidine (419 mg, 3.91 mmol) in diethyl ether (30 mL) was added nBuLi (1.64 M in hexane, 5.8 mL, 9.51 mmol) at 0 °C. The reaction mixture was heated under reflux for 15 h and

then cooled to $-78\text{ }^{\circ}\text{C}$. Diethyl ether solution (20 mL) of $t\text{Bu}_2\text{AsCl}$ (2.17 g, 9.66 mmol) was added dropwise, and the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, which was then gradually warmed to room temperature and stirred at room temperature for additional 3 h. The reaction was quenched with degassed water to form a colorless suspension, and the ethereal solution was collected by filtration, dried with anhydrous MgSO_4 , collected by filtration again, and dried in vacuo to remove solvents. The colorless residue was further extracted with pentane and desiccated in vacuo to give 2,6-bis[(di-*tert*-butylarsino)methyl]pyridine ($t\text{BuANA}$, **2b**) as a colorless solid (1.715 g, 3.54 mmol, 91% isolated yield). $^1\text{H NMR}$ ($\text{C}_4\text{D}_8\text{O}$, δ): 7.37 (t, $J = 7.7\text{ Hz}$, 1H, 4-H of $\text{C}_5\text{H}_3\text{N}$), 6.97 (d, $J = 7.7\text{ Hz}$, 2H, 3-H of $\text{C}_5\text{H}_3\text{N}$), 2.97 (s, 4H, CH_2), 1.18 (s, 36H, $t\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, δ): 162.4 (4-C of $\text{C}_5\text{H}_3\text{N}$), 136.5 (2-C of $\text{C}_5\text{H}_3\text{N}$), 120.3 (3-C of $\text{C}_5\text{H}_3\text{N}$), 33.7 ($\text{C}(\text{CH}_3)_3$), 31.9 (CH_2), 30.4 (CH_3). Anal. Calcd for $\text{C}_{23}\text{H}_{43}\text{As}_2\text{N}$: C, 57.14; H, 8.97; N, 2.90. Found: C, 56.85; H, 9.03; N, 2.52.

Preparation of $[\text{MoCl}_3(t\text{BuANA})]$ (3b**).** A mixture of $[\text{MoCl}_3(\text{thf})_3]$ (840 mg, 2.01 mmol) and **2b** (1.039 g, 2.15 mmol) in THF (20 mL) was stirred at $55\text{ }^{\circ}\text{C}$ for 20 h. The resultant red solution was dried in vacuo and washed with hexane, and the residue was recrystallized from dichloromethane–hexane to afford $[\text{MoCl}_3(t\text{BuANA})]$ (**3b**) as paramagnetic orange block crystals (1.044 g, 1.52 mmol, 76% isolated yield). Anal. Calcd for $\text{C}_{23}\text{H}_{43}\text{As}_2\text{Cl}_3\text{MoN}$: C, 40.28; H, 6.32; N, 2.04. Found: C, 39.94; H, 6.35; N, 1.90.

Preparation of *trans,cis*- $[\{\text{Mo}(\text{N}_2)_2(t\text{BuANA})\}_2(\mu\text{-N}_2)]$ (4b**).** To a solution of **3b** (68.5 mg, 0.100 mmol) in THF (5 mL) was added Na–Hg (0.5 wt%, 2.76 g, 0.600 mmol), and the reaction mixture was stirred at room temperature for 6 h under an atmospheric pressure of dinitrogen. The resultant dark purple solution was collected by decantation and concentrated in vacuo. To the dark brown residue was added THF (1 mL) and pentane (5 mL) to give a suspension, which was further filtered through a pad of Celite. The filtrate was dried in vacuo to give a brown residue, which was crystallized from THF–pentane at $-35\text{ }^{\circ}\text{C}$ to give efflorescent dark purple plate crystals of *trans,cis*- $[\{\text{Mo}(\text{N}_2)_2(t\text{BuANA})\}_2(\mu\text{-N}_2)]\cdot\text{C}_4\text{H}_8\text{O}$ (**4b**· $\text{C}_4\text{H}_8\text{O}$), which lost THF of crystallization in vacuo to give a brown powder of **4b** (38.1 mg, 0.0293 mmol, 59% isolated yield). Brown block crystals of **4b**· C_6H_{14} suitable for X-ray crystallography were further obtained by layering hexane onto a THF solution of **4b**, which was then kept cooled at $-35\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$

(C₄D₈O, δ): 7.33–7.08 (m, 6H, C₅H₃N), 3.48 (br, 2H, CH₂), 3.43 (br, 2H, CH₂), 3.39–3.28 (m, 4H, m), 1.32–1.23 (m, 54H, 'Bu), 1.17 (br, 18H, 'Bu). IR (KBr, cm⁻¹): 1955 (vs), 1870 (s). Raman (THF, cm⁻¹): 1904. Anal. Calcd for C₄₆H₈₆As₄Mo₂N₁₂: C, 42.54; H, 6.67; N, 12.94. Found: C, 42.97; H, 6.96; N, 8.86.

Preparation of *trans*-[Mo(N₂)₂(PMe₃)('BuANA)] (5b). To a solution of **3b** (100.0 mg, 0.146 mmol) in THF (5 mL) were added Na–Hg (0.5 wt%, 4.14 g, 0.900 mmol) and PMe₃ (1 M toluene solution, 0.2 mL, 0.2 mmol), and the reaction mixture was stirred at room temperature for 12 h under an atmospheric pressure of dinitrogen. The resultant purple solution was collected by decantation, and was concentrated in vacuo. To the purple residue was added THF (1 mL) and pentane (5 mL), and the solution was filtered through a pad of Celite. The filtrate was dried in vacuo to give a purple residue, which was further crystallized from THF–pentane at –35 °C to give red platelet crystals of *trans*-[Mo(N₂)₂(PMe₃)('BuANA)] (**5b**) (31.8 mg, 0.045 mmol, 31% isolated yield). ¹H NMR (C₄D₈O, δ): 7.34 (d, *J* = 7.4 Hz, 2H, 3-H of C₅H₃N), 7.24 (t, *J* = 7.4 Hz, 1H, 2-H of C₅H₃N), 3.47 (s, 4H, CH₂), 1.63 (d, *J* = 5.4 Hz, 9H, PMe₃), 1.24 (s, 36H, 'Bu). ³¹P{¹H} NMR (C₄D₈O, δ): +13.6 (s). IR (KBr, cm⁻¹): 1915 (vs). Anal. Calcd for C₂₆H₅₂As₂MoN₅P: C, 43.89; H, 7.37; N, 9.84. Found: C, 43.25; H, 7.46; N, 5.29.

Protonolysis of Molybdenum–Dinitrogen Complexes. A typical experimental procedure⁴ for the protonolysis of dinitrogen complex into ammonia using the dinitrogen complex **4b** is described below. To a solution of **4b** (52.0 mg, 0.040 mmol) in THF (5 mL) was added concentrated sulfuric acid (50 μ L). The mixture was stirred at room temperature for 24 h. The reaction mixture was evaporated under reduced pressure. Aqueous solution of potassium hydroxide (30 wt%; 5 mL) was added to the residue, and the mixture was distilled into dilute sulfuric acid solution (0.5 M, 10 mL) under reduced pressure. The amount of ammonia or hydrazine was determined by the indophenol⁵ or *p*-(dimethylamino)benzaldehyde method.⁶ Detailed results are summarized in Table S1.

Catalytic Reduction of Dinitrogen to Ammonia. A typical experimental procedure⁷ for the catalytic reduction of dinitrogen into ammonia using the dinitrogen complex **4b** is described below. In a 50 mL Schlenk flask were placed **4b** (13.0 mg, 0.010 mmol) and 2,6-lutidinium trifluoromethanesulfonate (246.8 mg, 0.960 mmol). Toluene (2.5 mL) was added under an

atmospheric pressure of dinitrogen, and then a solution of cobaltocene (136.1 mg, 0.720 mmol) in toluene (2.5 mL) was slowly added to the stirred suspension in the Schlenk flask with a syringe pump at a rate of 2.5 mL per hour. After the addition of cobaltocene for an hour, the mixture was further stirred at room temperature for additional 19 hours. The amount of dihydrogen of the catalytic reaction was determined by gas chromatography. The reaction mixture was evaporated under reduced pressure, and the distillate was trapped in dilute sulfuric acid solution (0.5 M, 10 mL). Aqueous solution of potassium hydroxide (30 wt %; 5 mL) was added to the residue, and the mixture was distilled into another dilute sulfuric acid solution (0.5 M, 10 mL). The amount of ammonia in each of the sulfuric acid solutions was determined by the indophenol method.⁶ Detailed results are summarized in [Table S2](#).

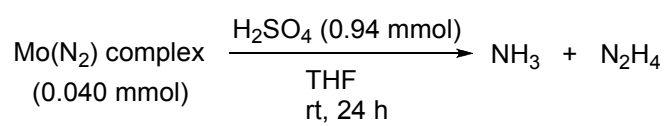
X-ray Crystallography. Diffraction data for [MoCl₃(^tBuANA)] (**3b**), *trans,cis*-[Mo(N₂)₂(^tBuANA)₂(μ-N₂)]·C₆H₁₄ (**4b**·C₆H₁₄), and [Mo(N₂)₂(PMe₃)(^tBuANA)] (**5b**) were collected on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo-Kα radiation (λ = 0.71075 Å) with Varimax optics. Reflections were collected for the 2θ range of 5° to 55°. Intensity data were corrected for empirical (ABSCOR for **3b** and **5b**) or numerical (NUMABS for **4b**·C₆H₁₄) absorptions, for Lorentz and polarization effects.⁸ Flack parameter was refined to be 0.030(5) for **3b**.⁹ The structure solution and refinements were carried out by using CrystalStructure package.¹⁰ The positions of non-hydrogen atoms were determined by direct methods (SIR97¹¹ for **3b** and **4b**·C₆H₁₄; SHELX97¹² for **5b**) and subsequent Fourier syntheses, and were refined on F_o² with all the unique reflections by full-matrix least squares with anisotropic thermal parameters except for the hexane carbons in **4b**·C₆H₁₄ which were solved isotropically. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Goodness of fit indicator [Σw(|F_o| - |F_c|)² / (N_{obs} - N_{params})]^{1/2} were all refined to the value of 1.000. The atomic scattering factors were taken from ref. [13](#), and anomalous dispersion effects were included.¹⁴ The values of Δf' and Δf'' were taken from ref. [15](#). Details of the crystals and data collection parameters are summarized in [Table S3](#). ORTEP drawings and important structural parameters of **3b**, **4b**·C₆H₁₄, and **5b** are depicted in [Figures S1–S3](#) and summarized in [Tables S4–S6](#). CCDC 949577 (**3b**), 949578 (**4b**·C₆H₁₄), and 949579 (**5b**) contain

the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Examples of Arsine-Ligated Transition Metal–Dinitrogen Complexes. For the previous examples of transition metal–dinitrogen complexes with arsines as auxiliary ligands, see ref. 16.

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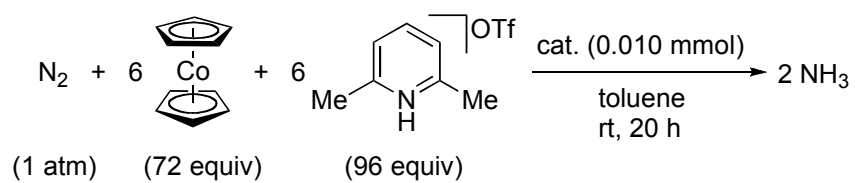
Table S1. Protonolysis of Molybdenum–Dinitrogen Complexes



run	Mo(N ₂) complex	NH ₃ (mmol)	NH ₃ (equiv/Mo) ^a	N ₂ H ₄ (mmol)	N ₂ H ₄ (equiv/Mo) ^a
1	4b	0.048	0.60	0	0
2	5b	0.013	0.33	0	0
3 ^b	1a	0.049	0.61	0.005	0.06
4 ^b	5a	0.034	0.85	0.003	0.08

^aEquiv based on the molybdenum atom. ^bRef 4.

Table S2. Molybdenum-Catalyzed Reduction of Molecular Dinitrogen



run	catalyst	Cp_2Co (equiv)	NH_3 (mmol)	NH_3 (equiv) ^a	H_2 (mmol)	H_2 (equiv) ^a
1	4b	72	0.02	2	0.16	16
2	4b	0	0.01	1	0.01	1
3 ^b	1a	72	0.12	12	0.10	10
4 ^b	4e	72	0.03	3	0.21	21
5 ^b	4f	72	0.01	1	0.22	22

^aEquiv based on the catalyst. ^bRef 7.

Table S3. X-ray Crystallographic Data for **3b**, **4b**·C₆H₁₄, and **5b**

	3b	4b ·C ₆ H ₁₄	5b
chemical formula	C ₂₃ H ₄₃ As ₂ Cl ₃ MoN	C ₅₂ H ₁₀₀ As ₄ Cl ₄ Mo ₂ N ₁₂	C ₂₆ H ₅₂ As ₂ MoN ₅ P
formula weight	685.74	1385.01	711.49
crystal size (mm ³)	0.41 × 0.31 × 0.17	0.33 × 0.11 × 0.09	0.13 × 0.07 × 0.02
color, habit	orange, block	brown, block	red, platelet
crystal system	orthorhombic	monoclinic	triclinic
space group	C222 ₁ (#20)	P2 ₁ /c (#14)	P1 (#2)
<i>a</i> (Å)	16.6959(3)	18.4671(5)	10.6374(10)
<i>b</i> (Å)	25.6652(5)	13.9179(4)	11.4503(10)
<i>c</i> (Å)	13.6023(3)	25.7755(8)	15.0424(12)
α (deg)	90	90	107.8606(18)
β (deg)	90	104.8817(8)	99.1578(17)
γ (deg)	90	90	105.823(2)
<i>V</i> (Å ³)	5828.64(19)	6402.7(3)	1617.8(3)
<i>Z</i>	8	4	2
<i>d</i> _{calcd} (g cm ⁻³)	1.563	1.437	1.460
<i>F</i> (000)	2776	2848	732
μ (cm ⁻¹)	29.897	24.850	25.072
transmission factors	0.409–0.602	0.542–0.800	0.509–0.951
temperature (°C)	–75	–90	–75
measured reflections	27848	56538	15254
unique reflections	6582	14514	7273
<i>R</i> _{int}	0.0322	0.0660	0.0596
refined parameters	324	701	368
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0191	0.0603	0.0559
<i>wR</i> 2 (all data) ^b	0.0395	0.0973	0.0782
residual peaks (e Å ⁻³)	+1.32/–0.778	+2.08/–1.21	+1.13/–1.45
CCDC number	949577	949578	949579

^a*R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b*wR*2 = $[\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$, $w = 4F_o^2 / \{q\sigma(F_o^2)\}$ [$q = 1.64$ (**3b**), 3.405 (**4b**·C₆H₁₄), 2.11 (**5b**)].

Table S4. Selected Bond Lengths (Å) and Angles (deg) for **3b**

Mo(1)–As(1)	2.65796(16)	Mo(2)–As(2)	2.6447(3)
Mo(1)–Cl(1)	2.3982(7)	Mo(2)–Cl(3)	2.3969(9)
Mo(1)–Cl(2)	2.4148(6)	Mo(2)–Cl(4)	2.4157(5)
Mo(1)–N(1)	2.239(3)	Mo(1)–N(1)	2.207(3)
As(1)–C(4)	1.948(3)	As(2)–C(16)	1.957(3)
As(1)–C(5)	2.013(3)	As(2)–C(17)	2.021(3)
As(1)–C(9)	2.022(3)	As(2)–C(21)	2.016(3)
As(1)–Mo(1)–As(1)*	155.034(9)	As(2)–Mo(2)–As(2) [#]	159.360(14)
As(1)–Mo(1)–Cl(1)	102.483(5)	As(2)–Mo(2)–Cl(3)	100.320(8)
As(1)–Mo(1)–Cl(2)	89.102(15)	As(2)–Mo(2)–Cl(4)	89.300(14)
As(1)–Mo(1)–Cl(2)*	90.409(15)	As(2)–Mo(2)–Cl(4) [#]	89.993(14)
As(1)–Mo(1)–N(1)	77.517(5)	As(2)–Mo(2)–N(2)	79.680(8)
Cl(1)–Mo(1)–Cl(2)	91.133(17)	Cl(3)–Mo(2)–Cl(4)	91.97(2)
Cl(1)–Mo(1)–N(1)	180	Cl(3)–Mo(2)–N(2)	180
Cl(2)–Mo(1)–Cl(2)*	177.73(3)	Cl(4)–Mo(2)–Cl(4) [#]	176.05(3)
Cl(2)–Mo(1)–N(1)	88.867(17)	Cl(4)–Mo(2)–N(2)	88.03(2)

Symmetry Operators, *: X, –Y+1, –Z+2; #: –X+1, Y, –Z+1/2+1.

Table S5. Selected Bond Lengths (Å) and Angles (deg) for **4b**·C₆H₁₄

Mo(1)–As(1)	2.5484(5)	Mo(2)–As(3)	2.5343(6)
Mo(1)–As(2)	2.5646(6)	Mo(2)–As(4)	2.5192(6)
Mo(1)–N(1)	2.002(4)	Mo(2)–N(2)	2.110(4)
Mo(1)–N(3)	2.026(4)	Mo(2)–N(7)	1.999(4)
Mo(1)–N(5)	2.007(4)	Mo(2)–N(9)	1.969(4)
Mo(1)–N(11)	2.240(4)	Mo(2)–N(12)	2.194(4)
N(1)–N(2)	1.142(6)		
N(3)–N(4)	1.115(6)	N(7)–N(8)	1.123(6)
N(5)–N(6)	1.125(6)	N(9)–N(10)	1.129(6)
As(1)–Mo(1)–As(2)	155.41(3)	As(3)–Mo(2)–As(4)	158.84(2)
As(1)–Mo(1)–N(1)	99.51(10)	As(3)–Mo(2)–N(2)	89.73(9)
As(1)–Mo(1)–N(3)	90.99(10)	As(3)–Mo(2)–N(7)	102.86(11)
As(1)–Mo(1)–N(5)	88.46(10)	As(3)–Mo(2)–N(9)	88.81(11)
As(1)–Mo(1)–N(11)	77.46(9)	As(3)–Mo(2)–N(12)	78.73(9)
As(2)–Mo(1)–N(1)	105.08(10)	As(4)–Mo(2)–N(2)	93.08(10)
As(2)–Mo(1)–N(3)	88.60(11)	As(4)–Mo(2)–N(7)	98.01(11)
As(2)–Mo(1)–N(5)	90.38(11)	As(4)–Mo(2)–N(9)	87.14(11)
As(2)–Mo(1)–N(11)	77.95(9)	As(4)–Mo(2)–N(12)	80.46(9)
N(1)–Mo(1)–N(3)	91.81(15)	N(2)–Mo(2)–N(7)	91.67(15)
N(1)–Mo(1)–N(5)	91.87(16)	N(2)–Mo(2)–N(9)	176.46(14)
N(1)–Mo(1)–N(11)	176.09(15)	N(2)–Mo(2)–N(12)	87.25(13)
N(3)–Mo(1)–N(5)	176.31(16)	N(7)–Mo(2)–N(9)	91.80(16)
N(3)–Mo(1)–N(11)	90.72(15)	N(7)–Mo(2)–N(12)	178.08(15)
N(5)–Mo(1)–N(11)	85.61(15)	N(9)–Mo(2)–N(12)	89.30(15)
Mo(1)–N(1)–N(2)	177.5(4)	Mo(2)–N(2)–N(1)	178.2(3)
Mo(1)–N(3)–N(4)	176.7(4)	Mo(2)–N(7)–N(8)	177.1(5)
Mo(1)–N(5)–N(6)	175.7(4)	Mo(2)–N(9)–N(10)	177.0(4)

Table S6. Selected Bond Lengths (Å) and Angles (deg) for **5b**

Mo(1)–As(1)	2.5506(8)	Mo(1)–As(2)	2.5533(7)
Mo(1)–P(1)	2.4177(18)	Mo(1)–N(1)	2.268(5)
Mo(1)–N(2)	2.004(4)	Mo(1)–N(3)	2.041(4)
N(2)–N(3)	1.077(6)	N(4)–N(5)	1.069(6)
As(1)–Mo(1)–As(2)	154.93(3)	As(1)–Mo(1)–P(1)	104.07(4)
As(1)–Mo(1)–N(1)	77.42(11)	As(1)–Mo(1)–N(2)	92.41(13)
As(1)–Mo(1)–N(4)	88.59(13)	As(2)–Mo(1)–P(1)	100.95(5)
As(2)–Mo(1)–N(1)	77.54(11)	As(2)–Mo(1)–N(2)	86.46(13)
As(2)–Mo(1)–N(4)	93.85(13)	P(1)–Mo(1)–N(1)	178.29(12)
P(1)–Mo(1)–N(2)	88.97(15)	P(1)–Mo(1)–N(4)	88.01(15)
N(1)–Mo(1)–N(2)	90.13(17)	N(1)–Mo(1)–N(4)	92.89(17)
N(2)–Mo(1)–N(4)	177.0(2)		
Mo(1)–N(2)–N(3)	178.1(5)	Mo(1)–N(4)–N(5)	177.9(5)

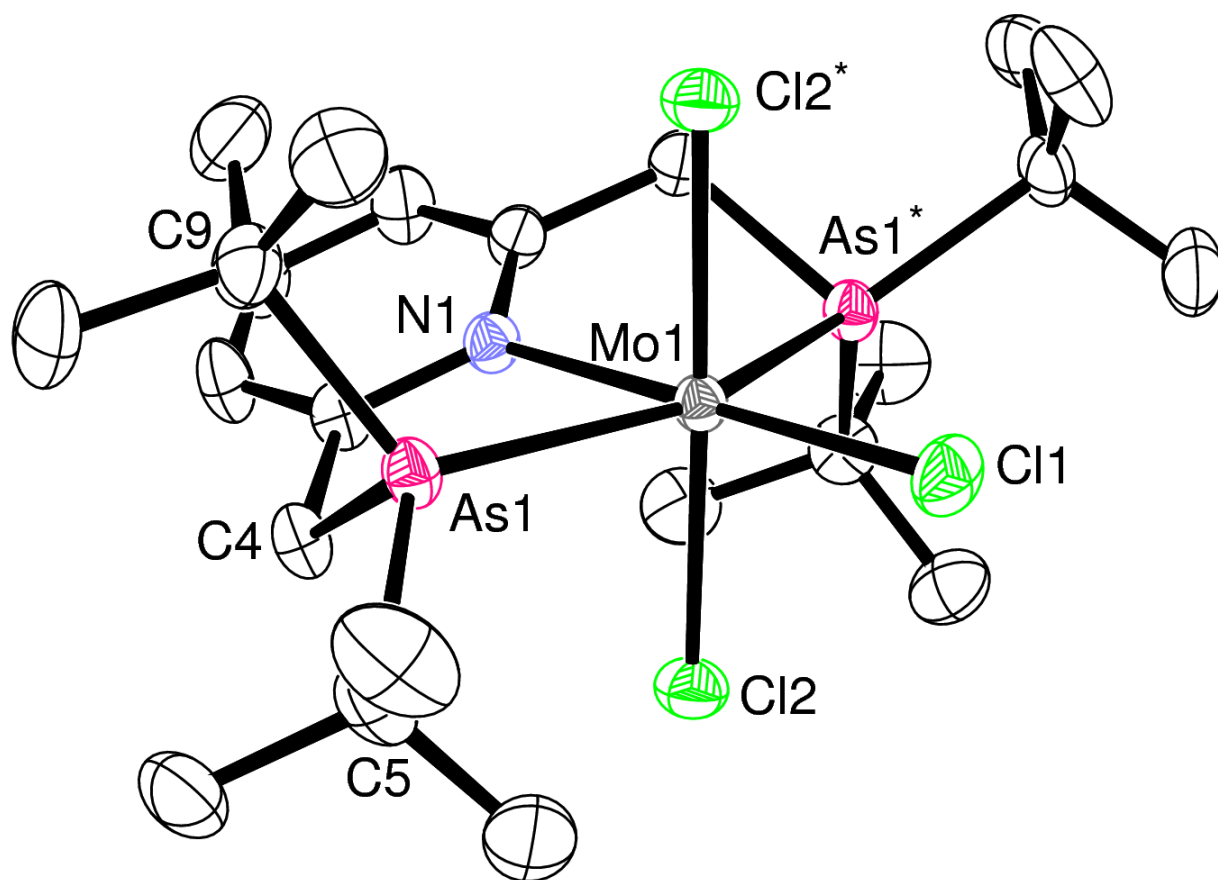


Figure S1. ORTEP drawing of **3b**, where only one of the two crystallographically independent structures is shown. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry Operators, *: $+X, -Y+1, -Z+2$.

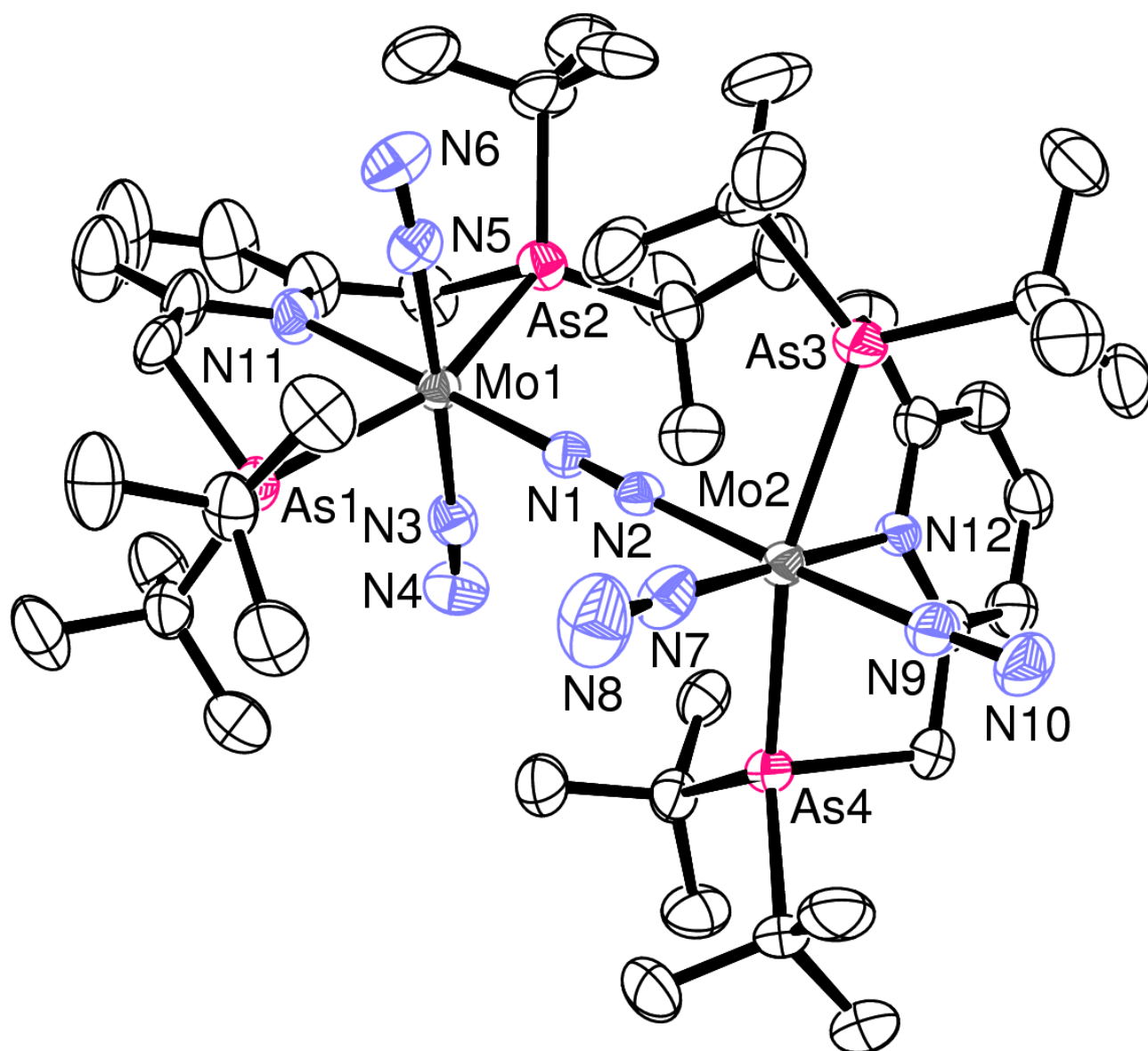


Figure S2. ORTEP drawing of **4b**. Thermal ellipsoids are shown at the 50% probability level.

Hydrogen atoms and hexane molecule are omitted for clarity.

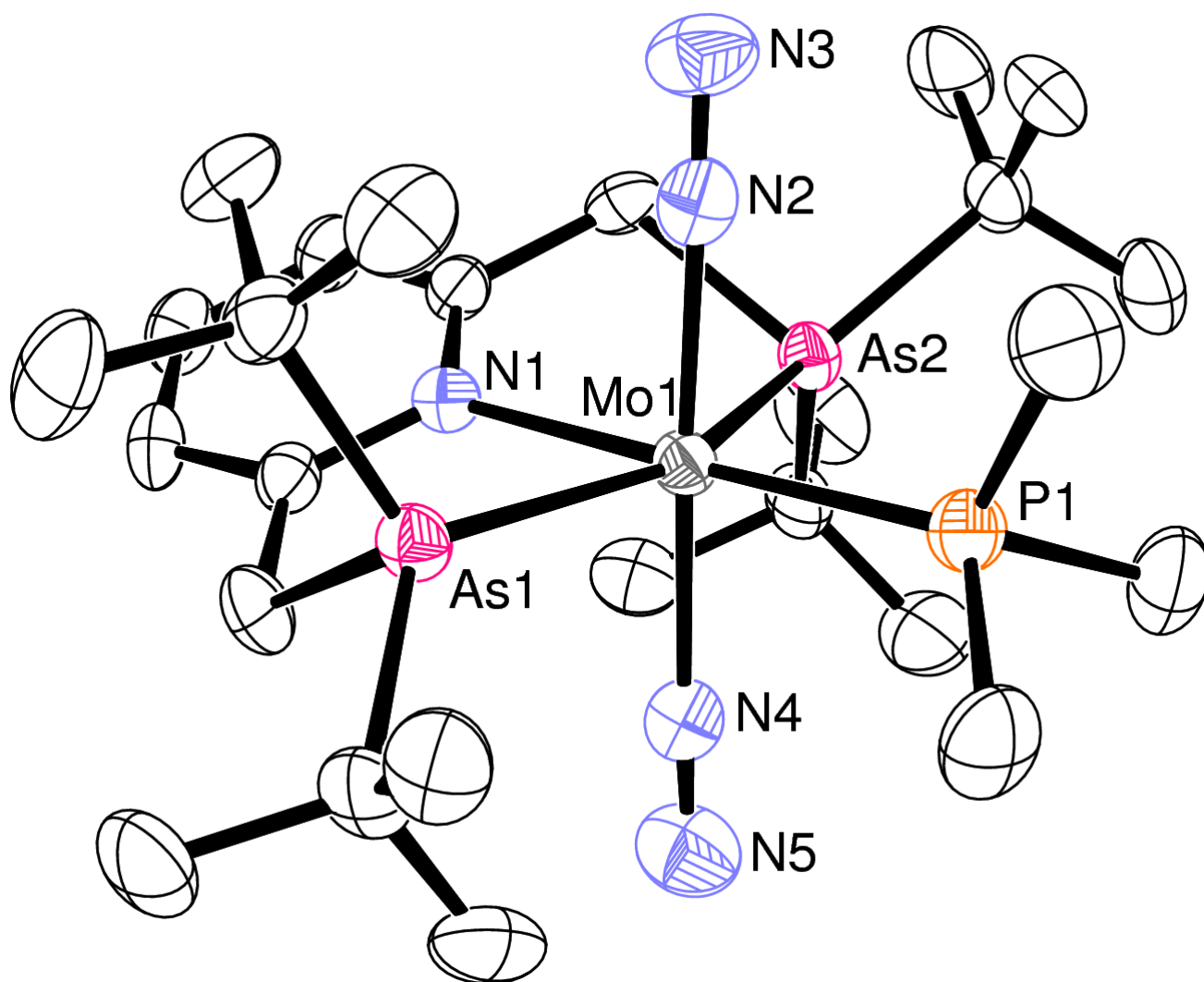


Figure S3. ORTEP drawing of **5b**. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms are omitted for clarity.

References and Notes

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