

Electronic Supporting Information

Preparation and reactivity of dinitrogen-bridged dimolybdenum-dichloride complex

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Experimental Section

General. ^1H NMR (270 MHz) and $^{31}\text{P}\{^1\text{H}\}$ NMR (109 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvent, and spectra were referenced to residual solvent (^1H) or external standard ($^{31}\text{P}\{^1\text{H}\}$: 85% H_3PO_4). IR spectra were recorded on a JASCO FT/IR 4100 Fourier Transform infrared spectrometer. Absorption spectra were recorded on a Shimadzu MultiSpec-1500. Mass spectra were recorded on a JEOL Accu TOF JMS-T100LP. Evolved dihydrogen was quantified by a gas chromatography using a Shimadzu GC-8A with a TCD detector and a SHINCARBON ST (6 m x 3 mm). Elemental analyses were performed at Microanalytical Center of The University of Tokyo. Cyclic voltammograms were recorded on an ALS/Chi model 610C electrochemical analyzer with platinum working electrode at a scan rate of 200 mV/s in THF containing 0.1 M [Bu_4N]ClO₄ and 1 mM sample at room temperature.

All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques or glovebox techniques unless otherwise stated. Solvents were dried by the usual methods, then distilled and degassed before use. $[\text{MoCl}_3(\text{PNP})]_2$ (**1**, **PNP** = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) was prepared according to the literature methods.

Preparation of $[\text{MoCl}_2(\text{PNP})]_2(\mu\text{-N}_2)\cdot 0.5\text{C}_6\text{H}_{14}$ (2**·**0.5C₆H₁₄**).** A mixture of $[\text{MoCl}_3(\text{PNP})]$ (605 mg, 1.0 mmol) and KC_8 (144 mg, 1.1 mmol) in THF (25 mL) was stirred at room temperature for 20 h under N_2 . The resultant dark blue-green solution was filtered and extracted with THF (2 mL x 3).

The combined extract was concentrated in *vacuo* to about 15 mL. Slow addition of hexane to the obtained solution afforded $2 \cdot C_6H_{14}$ as purple crystals, which were collected by filtration and dried in *vacuo* to afford $2 \cdot 0.5C_6H_{14}$ as a dark brown crystalline solid (385 mg, 0.32 mmol, 64% yield). Magnetic susceptibility (Evans method): $\mu_{\text{eff}} = 3.2 \mu_B$ in THF-*d*₈ at 296 K. Anal Calcd for C₄₉H₉₃Cl₄Mo₂N₄P₄: C, 49.21; H, 7.84; N, 4.69. Found: C, 49.02; H, 7.75; N, 3.98.

Reaction of 2 with LiBHEt₃ under N₂. To a solution of $2 \cdot 0.5C_6H_{14}$ (54 mg, 0.045 mmol) in THF (5 mL) was added 1.09 M THF solution of LiBHEt₃ (0.4 mL, 0.436 mmol), and then the mixture was stirred at room temperature for 20 h under N₂. The resultant dark green solution was concentrated under reduced pressure. To the residue was added benzene (4 mL), and the solution was filtered. Slow addition of hexane (15 mL) afforded [Mo(N₂)₂(PNP)]₂(μ-N₂) (**3**) as dark green crystals (22 mg, 0.020 mmol, 43% yield).

Protonolysis of 2. To a solution of $2 \cdot 0.5C_6H_{14}$ (47.7 mg, 0.040 mmol) in THF (5 mL) was added concentrated sulfuric acid (50 μL) under Ar atmosphere, and the mixture was stirred at room temperature for 20 h. The reaction mixture was stirred at room temperature for 24 h. Potassium hydroxide aqueous solution (30 wt%; 5 mL) was added, and the mixture was distilled into dilute H₂SO₄ solution (0.5 M, 10 mL) under reduced pressure. No ammonia and hydrazine were detected by the indophenol² and the *p*-(dimethylamino)benzaldehyde methods³.

X-ray Crystallography. Crystallographic data of $2 \cdot C_6H_{14}$ is summarized in Table 1. Diffraction data was collected at -100 °C ($2 \cdot C_6H_{14}$) on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71075 \text{ \AA}$). Reflections were collected for the 2θ range of 5° to 55°. Intensity data were collected for Lorenz-polarization effects and for empirical absorption (REQAB). The structure solution and refinements were carried out by using the *CrystalStructure* crystallographic software package.⁴ The positions of the non-hydrogen atoms were

determined by direct methods (SIR-97)⁵, and subsequent Fourier syntheses (DIRDIF-99⁶) and were refined F_o^2 using all unique reflections by full-matrix least-squares with anisotropic thermal parameters except for the solvated molecules (C47–C52 for $2 \cdot C_6H_{14}$), which were refined isotropically. All the other hydrogen atoms were placed at the calculated positions with fixed isotropic parameter.

CCDC 953144 ($2 \cdot C_6H_{14}$) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

References and Notes

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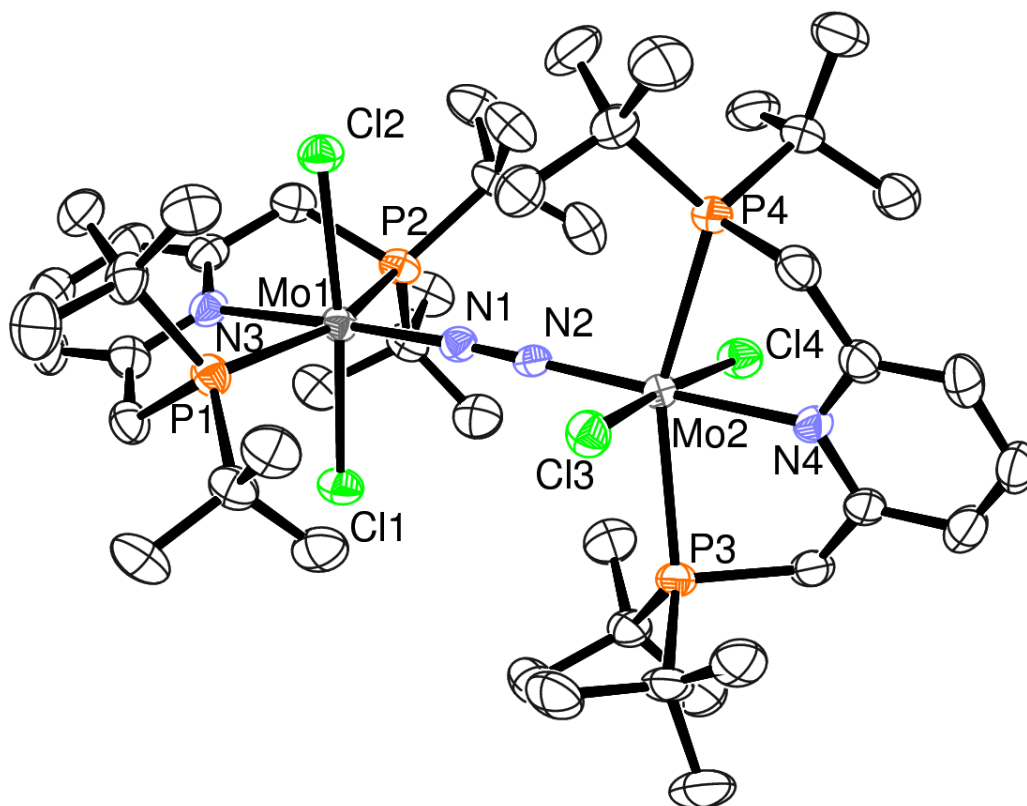


Figure 1. ORTEP drawing of **2**·C₆H₁₄. Thermal ellipsoids are shown at the 50% probability level.

All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1–N1 1.925(2), Mo2–N2 1.927(2), Mo1–N3 2.192(2), Mo2–N4 2.197(2), N1–N2 1.169(3), Mo1–N1–N2 177.1 (2), Mo2–N2–N1 177.9(2), P1–Mo1–P2 157.59(3), P3–Mo2–P4 156.94(3), Cl1–Mo1–Cl2 173.41(3), Cl3–Mo2–Cl4 174.64(3).

Table 1. X-ray Crystallographic Data for **2**·C₆H₁₄.

2 ·C ₆ H ₁₄	
chemical formula	C ₅₂ H ₁₀₀ Cl ₄ Mo ₂ N ₄ P ₄
formula weight	1238.98
dimensions of crystals	0.35 × 0.30 × 0.20
crystal system	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	12.335(2)
<i>b</i> , Å	12.716(2)
<i>c</i> , Å	20.165(2)
α , deg	88.584(4)
β , deg	86.511(3)
γ , deg	87.074(3)
<i>V</i> , Å ³	3151.9(7)
<i>Z</i>	2
ρ_{calcd} , g cm ⁻³	1.305
<i>F</i> (000)	1304
μ , cm ⁻¹	7.028
trans. factors range	0.743–0.869
no. reflections measured	30283
no. unique reflections	14181 (<i>R</i> _{int} = 0.049)
no. parameters refined	665
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0478
<i>wR</i> 2 (all data) ^b	0.1210
GOF (all data) ^c	1.000
max diff peak / hole, e Å ⁻³	1.15/–0.90

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$,

$w = 4F_o^2 / 1.7\sigma(F_o^2)$. ^c $GOF = [\sum w(F_o^2 - F_c^2)^2 / (N_o - N_{\text{params}})]^{1/2}$.