Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Structural Characterization of Molybdenum-Dinitrogen Complex as Key Species toward Ammonia Formation by Dispersive XAFS Spectroscopy

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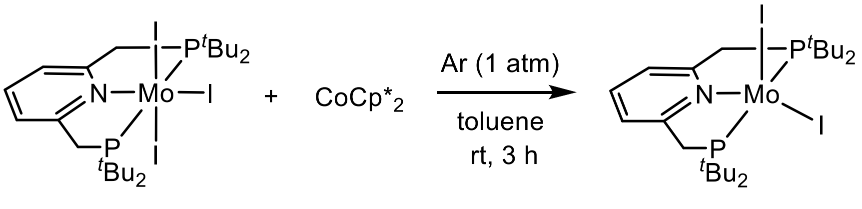
Contents

General methods

All manipulations were carried out under an atmosphere of nitrogen or argon by using standard Schlenk techniques or glovebox techniques unless otherwise stated. Toluene was distilled from dark-blue Na/benzophenone ketyl solution, degassed, and stored over molecular sieves 4Å in a nitrogen-filled glove box. Other solvents were dried by general methods, and degassed before use. [MoI_3(**PNP**)] (**2**, **PNP** = $C_5NH_3(CH_2P^tBu_2)_2$)[1], [Mo(≡N)I(PNP)] (**3**)[1], $CoCp^*_2$ (Cp* = η^5-C_5Me_5)[2], [$Mo(N_2)_2$(**PNP**)]$_2$(μ-N_2)[3], and [$MoCl_2$(**PNP**)]$_2$(μ-N_2)[4] were prepared according to the literature methods. Other reagents were purchased commercially and used as received.

^1H NMR (400 MHz) and $^{31}P\{^1H\}$ NMR (162 MHz) spectra were recorded on a JEOL ECS400 spectrometer in suitable solvents, and spectra were referenced to residual solvent (^1H) or external standard ($^{31}P\{^1H\}$: 85% H_3PO_4). Magnetic susceptibility was measured in THF-d_8 using the Evans method[5]. Elemental analyses were performed at Microanalytical Center of The University of Tokyo.

Preparation of [MoI_2(PNP)] (6)



2 **6**

All manipulations were carried out under argon. A mixture of **2** (136 mg, 0.16 mmol) and $CoCp^*_2$ (57 mg, 0.17 mmol) in toluene (15 mL) was stirred at room temperature for 3 h. Volatiles were removed in vacuo, and THF (10 mL) was added to the residue. The THF solution was filtered through Celite, and the filter cake was washed with THF (2 mL x 3). After the combined filtrate was concentrated to about 8 mL, slow addition of hexane (15 ml) afforded **6** as dark brown crystals, which were collected by filtration, washed with hexane (1 mL x 3), and dried in vacuo (55 mg, 0.070 mmol, 45% yield). Magnetic susceptibility (Evans method): μ_{eff} = 3.19 μ_B in THF-d_8 at 294 K. Anal Calcd for $C_{23}H_{43}I_2MoNP_2 \cdot 0.5C_6H_{14}$: C, 39.61; H, 6.39; N, 1.78. Found: C, 40.01; H, 6.04; N, 1.99. The amount of hexane in this sample was determined by ^1H NMR in THF-d_8.

Set-up of dispersive XAFS (DXAFS) experiment and data analysis

In-situ DXAFS spectra of Mo K-edge were measured at the BL28B2 beamline of the SPring-8 (Japan). The DXAFS measurement system consists of a polychromator (Laue configuration) with a Si(422) net plane and a position sensitive detector (PSD) mounted on a θ–2θ diffractometer. The energy calibration was carried out using a spectrum of Mo foil. The reaction of **2** with $CoCp^*_2$ was carried out under a nitrogen atmosphere using a Schlenk tube. A solution of $CoCp^*_2$ (13.2 mg, 40 μmol, 2.0 eq. to the Mo complex) in THF (0.5 mL) was added to a solution of **2** (17.4 mg, 20 μmol) in THF (2 mL) at 298 K or 198 K, and then the DXAFS measurements were performed. The DXAFS spectra were recorded with a time resolution of 298 ms. We confirmed that the spectra of **2** did not change in the initial 100 shots (29.8 ms) under X-ray irradiation. Thus, to improve the signal-to-noise ratio of the spectra, 100 spectra were accumulated into one spectrum before the analysis. XAFS data were analysed using the Athena and Artemis programs with the theoretical standards calculated using FEFF[6].

Standard XAFS measurements

XAFS spectra of several reference samples were measured by a transmission mode at the NW10A beamline of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF, Japan), and BL01B1 beamline of the SPring-8 (Japan).

Comparison of the selected XANES spectra in Fig. 1 (Fig. S1)

The selected XANES spectra in **Fig. 1** were compared with the several reference samples (**Fig. S1**). After introduction of $CoCp^*_2$ at 198 K, the spectrum of **2** (a, blue) changed to the light blue one (b), and it was stable for 22 min (c). On the other hand, after removing the cooling bath, the spectrum shape changed to the red one (d) at room temperature, and the shape of spectrum (d) was similar to that of the reference sample of **3** dissolved in THF solution. These results mean that the formed Mo species (**A**) is unstable around room temperature and easily decomposes to **3**.

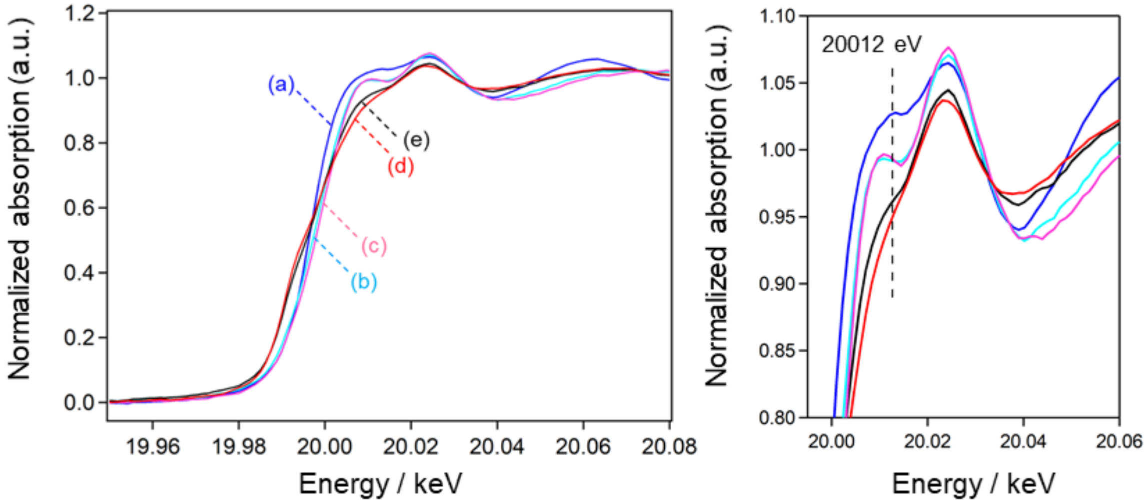


Fig. S1 Comparison of the selected XANES spectra in **Fig. 1**. (a, blue): **2** in THF (before addition of $CoCp^*_2$), (b, light blue): after 1 min, (c, pink): after 22 min, (d, red) after 60 min at 298 K, and (e, black): **3** in THF measured at 298 K. The XANES spectra were recorded at 198 K unless otherwise stated.

Effect of temperature on the shape of XANES spectra (Fig. S2)

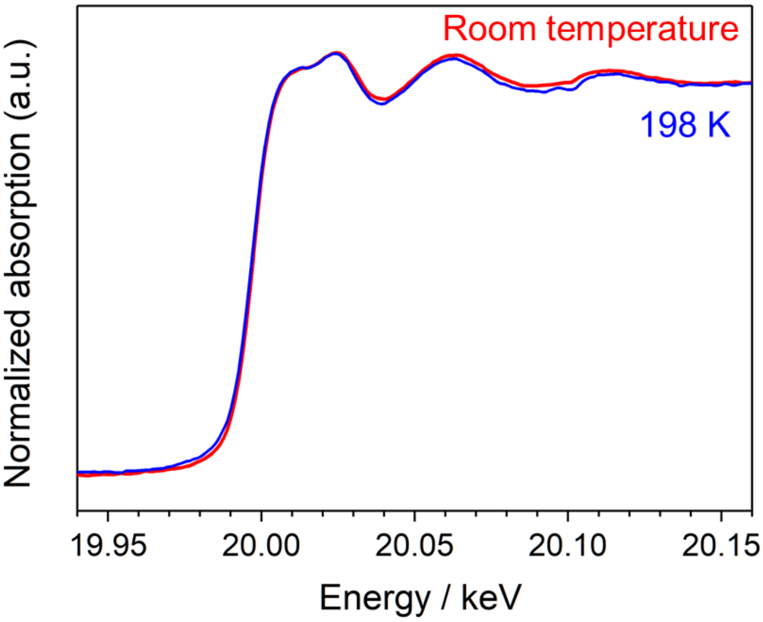


Fig. S2 XANES spectra of **2** in THF measured at room temperature and 198 K.

XANES calculation and structure model used for the calculation (Table S1 and S2)

FDMNES program was used for Mo K-edge XANES calculation. Self-consistent calculation was carried out using full multiple scattering (FMS) approach and muffin-tin (MT) potential because it produced the similar spectrum to that by finite-deference method (FDM) using full potential which is computationally more expensive. The cluster size was fixed to 6 Å for the calculation. In the XANES calculation of the Mo complexes, crystallographic data were used for Mo metal, **2**, and **3**. For dimolybdenum candidates, $[MoI(N_2)(PNP)]_2(\mu\text{-}N_2)$ (**4**) and $[MoI(PNP)]_2(\mu\text{-}N_2)$ (**1**), structural data were taken from optimized structures calculated with the Gaussian 09 program.[7] DFT calculations were performed at the B3LYP-D3 level of theory.[8-12] We employed the SDD (Stuttgart/Dresden pseudopotentials) basis set[13,14] for Mo and I atoms, and the 6-31G(d) basis set[15-18] for the others. Cartesian coordinates of **4** and $[MoI(PNP)]_2(\mu\text{-}N_2)$ **1** are listed in **Table S1** and **S2**.

Table S1. Cartesian coordinate of $[MoI(N_2)(\mathbf{PNP})]_2(\mu\text{-}N_2)$ (**4**) in the triplet state. Units are presented in Å.

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SCF Energy = -3767.93050126 hartree
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Atom       Coordinates (Angstroms)
           X             Y             Z
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 Mo     2.699470   -0.134964    0.112840
 Mo    -2.682400   -0.169145   -0.117543
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  C     4.755889    4.533439    1.386609
  C     5.603417    2.299482    2.159443
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  N    -5.736179   -0.876821   -0.118460
---------------------------------------------
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Table S2. Cartesian coordinate of [MoI(**PNP**)]$_2$(μ-N$_2$) (**1**) in the triplet state. Units are presented in Å.

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SCF Energy = -3548.83343700 hartree
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Atom       Coordinates (Angstroms)
           X             Y             Z
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 Mo     2.519538   -0.097157   -0.055223
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  H    -4.553525   -4.157098    2.189947
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  H    -5.658994   -2.180355    4.176321
  H    -4.322361   -1.043216    4.380233
  H    -5.002267    0.170885    2.276328
  H    -6.350398   -0.962847    2.126635
  H    -5.259708   -0.729697    0.760171
  H     0.103190   -2.240751    1.190217
  H     0.480267   -3.812266    1.879577
  H     0.207126   -2.442795    2.939711
  H    -2.925163   -4.616531    0.834597
  H    -1.234417   -5.119281    0.941343
  H    -1.701269   -3.751829   -0.088453
  H    -1.725062   -3.405918    4.254545
  H    -1.179036   -4.889058    3.465843
  H    -2.893432   -4.469838    3.443122
  H    -3.474409    2.360853   -4.211315
  H    -5.047719    1.586309   -4.426591
  H    -3.714580    0.670879   -3.704667
  H    -5.348322    0.132854   -1.767719
  H    -6.565700    1.145121   -2.547040
  H    -6.126192    1.454137   -0.868374
  H    -5.616806    3.928357   -1.513316
  H    -6.238188    3.411475   -3.079259
  H    -4.700183    4.259140   -2.991272
  H    -0.313277    1.642741   -2.108995
  H    -0.045991    3.117302   -3.041242
  H    -1.342110    2.000174   -3.499531
  H    -2.660886    4.321197   -3.398221
  H    -1.345735    5.162681   -2.576393
  H    -2.941234    5.085250   -1.818863
  H    -1.563223    4.288986    0.204042
  H    -0.076230    4.156924   -0.743164
  H    -0.699816    2.740074    0.129607
---------------------------------------------
```

Comparison of experimental and simulated XANES spectra of Mo foil (Fig. S3)

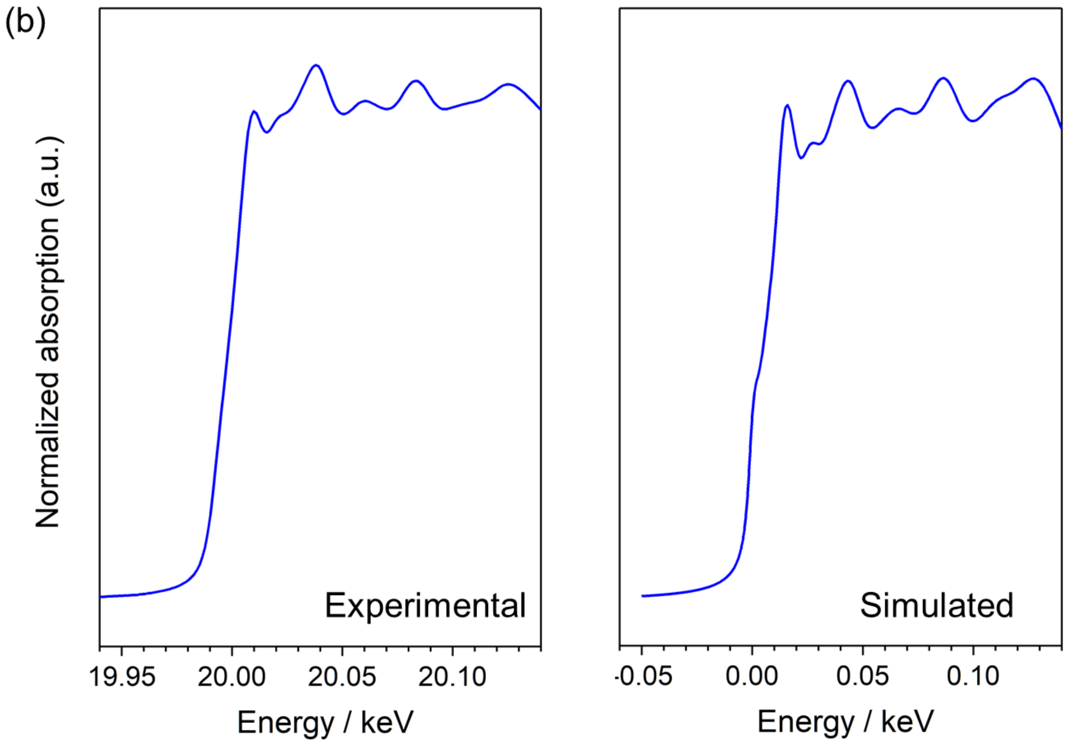

Fig. S3 Comparison of experimental and simulated XANES spectra of Mo foil with the body-centered cubic (bcc) structure.

Simulated XANES spectra of the isomers of [MoI(N_2)(PNP)]$_2$(μ-N_2) (Fig. S4)

We simulated the XANES spectra using the molecular structures in **Fig. S4**. No clear difference was observed among these three complexes in both the XANES spectra (A) and its derivative spectra (B). We previously proposed that **3** is formed from **1**, having a five-coordinated Mo center, via a dissociation of its N≡N bond based on the DFT calculation results^1. When considering the coordination geometry of **3**, a simple coordination of two nitrogen molecules gave (b) leading to **3** after N_2 dissociation from molybdenum atoms. In other words, the structure (b) is the closest coordination geometry to **1** in terms of the formation of **3** among these three structures. Thus, we proposed that the structure (b) is the most possible one among these three structures.

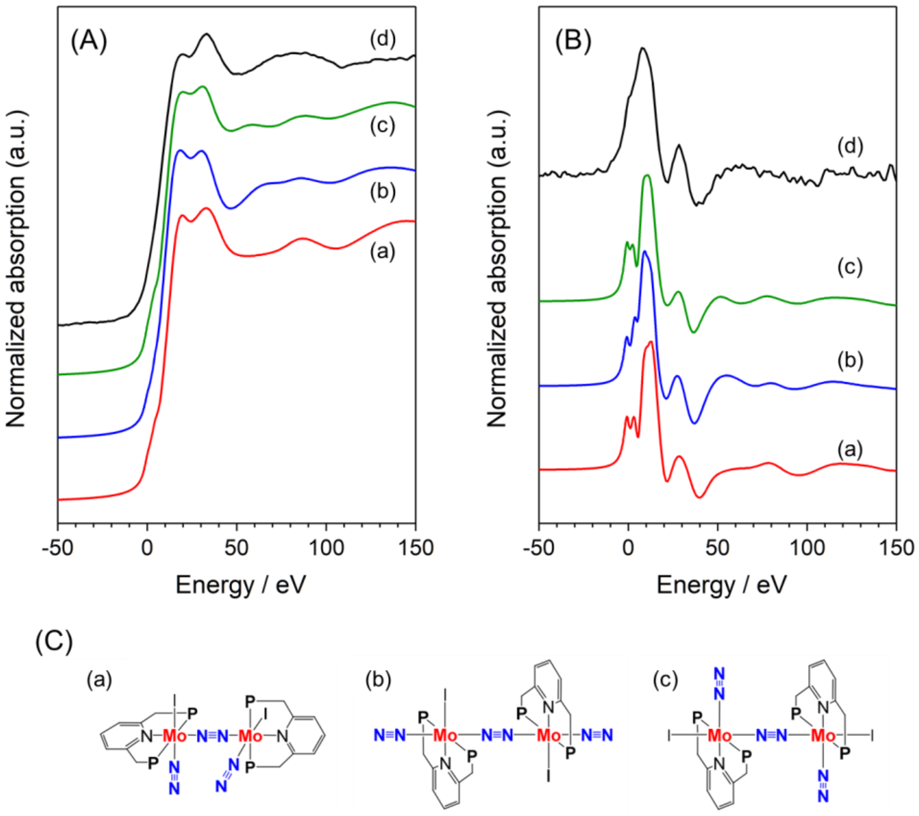

Fig. S4 Simulated XANES spectra of the isomers (a–c) of [MoI(N_2)(**PNP**)]$_2$(μ-N_2) (**4**) (A) and the first derivative (B), and structure used for the simulation (C). (d): experimental spectrum of **A**.

EXAFS data analysis and curve fitting results of 2 (Fig. S5 and Table S3)

For the curve fitting analysis of the EXAFS spectra, we first started the data analysis of the spectrum of **2** in THF solution measured by a conventional XAFS (NW10A, KEK-PF, Quick-XAFS mode). For the analysis, coordination numbers (CNs) of N, P, and I were fixed to 1, 2, and 3, respectively, based on the crystallographic data[1]. As shown in **Fig. S5** and **Table S3**, the atomic distances (*r*) of Mo–N, Mo–P, and Mo–I were estimated to be 2.23, 2.72, and 2.76 Å, respectively, by the curve-fitting analysis, and these values were closed to the crystallographic data[1] (distances of Mo–N, Mo–P, and Mo–I were 2.21, 2.67–2.68, and 2.77–2.78 Å, respectively). The result supports the validity of the curve-fitting analysis in our reaction system.

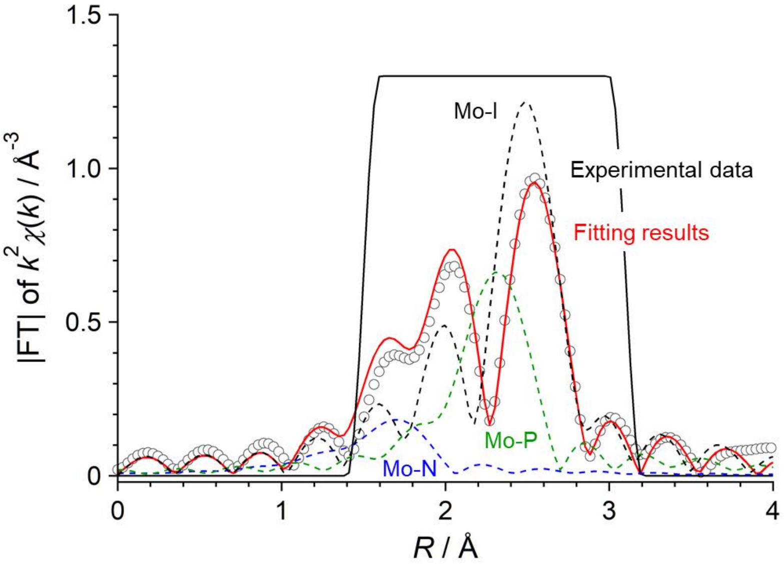

Fig. S5 Curve-fitting result of the EXAFS spectrum of **2** in THF.

Table S3. Results of the curve-fitting analysis of the EXAFS spectrum of **2** in THF.[a]

Shell	C.N. [b]	*r* [c] / Å	σ^2 [d]	ΔE [e]	R [f] (%)
Mo–N	1 [g]	2.23	0.0026	–3.2	0.72
Mo–P	2 [g]	2.72	0.0024	17.4	
Mo–I	3 [g]	2.76	0.0038	–1.4	

[a] XAFS data were analyzed with IFEFFIT (Athena and Arthemis). Analysis condition: *k* weight: 2, *k* range: 3.0–12 $Å^{-1}$, *r* range: 1.5–3.1 Å. [b] Coordination number. [c] Atomic distance. [d] Debye–Waller factor. [e] Edge shift. [f] R factor. [g] These values were fixed in the curve-fitting analysis.

EXAFS data of reference dimolybdenum complexes (Fig. S6)

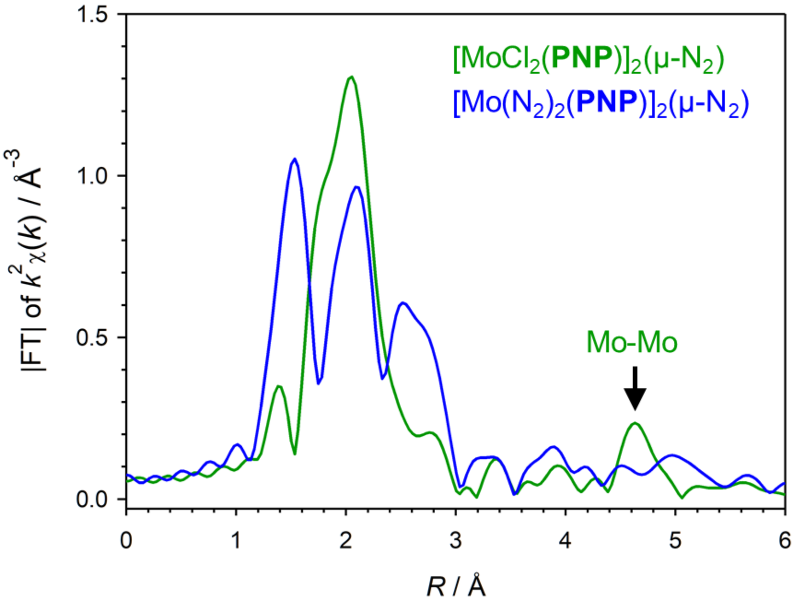

Fig. S6 Fourier transformed EXAFS spectra of [MoCl$_2$(**PNP**)]$_2$(μ-N$_2$) and [Mo(N$_2$)$_2$(**PNP**)]$_2$(μ-N$_2$). The spectra were obtained by a conventional XAFS (NW10A, KEK-PF, Quick-XAFS mode). k range: 3.1–15.8 Å^{-1}.

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