Electronic Supplementary Information

Dinitrogen activation by penta-pyridyl molybdenum complex

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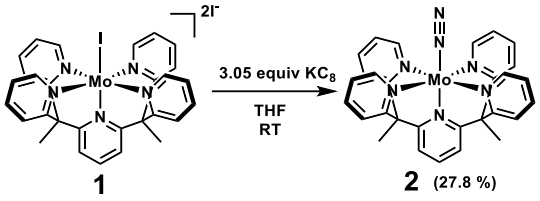
Materials and Methods

All air- and moisture-sensitive manipulations, including basic Schlenk and glovebox techniques, were performed using oven-dried or flame-dried glassware under an N_2 atmosphere. Air- and moisture-insensitive reactions were carried out under ambient conditions and were magnetically stirred. Et_2O, toluene and THF were distilled from deep purple sodium benzophenone ketyl. Acetonitrile was dried over P_2O_5 and vacuum-distilled. THF-d_8 was degassed by freeze-pump thaw and dried over activated 3 Å molecular sieves. All deuterated solvents were purchased from Aldrich (USA) and Cambridge Isotope Laboratories (USA). $Py_5Me_2MoI_3$ (compound **1**)[1] was synthesized following the literature procedure. Potassium graphite (KC_8) was synthesized by heating stoichiometric amounts of potassium and graphite at 140 °C under an N_2 atmosphere.[2] The NMR spectra were recorded on a DRX 500 spectrometer (Bruker, USA) operating at 500 MHz for ^1H and 850 MHz for ^{13}C acquisition, respectively. Chemical shifts were referenced to the residual proton solvent peaks (^1H: / THF-d_8, δ 1.72, 3.58) and ^{13}C solvent signals (THF-d_8, δ 25.31, 67.21).[3] Signals are described as follows: chemical shift in ppm, multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet and m = multiplet; coupling constants in Hz; integration. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Infrared spectra were obtained as thin films formed by evaporation of solutions on KBr windows using a Bruker Alpha system. Electronic absorption spectra were measured with a Cary 6000i ultraviolet–visible–near infrared (UV-VIS-NIR) system (Agilent, USA).

Experimental Section

A common procedure for preparing 2 ($Py_5Me_2MoN_2$)



THF (2 mL) was added by KC_8 (15.68 mg, 7.07 μmol, 3.05 equiv.). The KC_8-THF mixture was added to the suspended THF solution (6 mL) of **1** (35 mg, 0.038 mmol, 1.00 equiv.). The blue mixture was stirred at room temperature for 16 h. The resultant mixture was filtered through a plug of Celite. The blue filtrate was evaporated in vacuo for 24 h affording 6 mg (27.8 %) of the product **2** as a blue powder. The elemental analysis was inhibited by its air sensitivity.

^{1}H NMR (500 MHz, THF-d_8, 23 °C, δ): 8.09 (d, J = 5.9 Hz, 4H), 7.52 (d, J = 8.1 Hz, 4H), 7.35 (d, J = 8.0, 2H), 6.87 (t, J = 7.92 Hz, 1H), 6.79 (m, 4H), 6.58 (m, 4H), 2.41 (s, 6H). ^{13}C NMR (850 MHz, THF-d_8, 23 °C, δ): 170.27, 152.70, 146.74, 125.37, 124.93, 121.49, 119.65, 119.61, 27.31, 26.37. IR (KBr, cm^{-1}): 1849 (s, ν_{14N2}) 1775 (s, ν_{15N2})

Preparation of single crystals of 2 for X-ray single-crystal analaysis

THF (1.5 or 2 mL) was added to KC_8 (6.83 mg, 0.051 mmol, 3.1 equiv.). The KC_8-THF mixture was added to the suspended THF mixture (1 or 2 mL) of **1** (15 mg, 0.016 mmol, 1.00 equiv.). The blue mixture was stirred at room temperature for 8 h. The resultant mixture was filtered through a plug of Celite. The filtrate was added by 2 or 3 mL of Et_2O. This solution was kept in the freezer (−40 °C) to afford tiny blue square-shaped crystals.

Preparation of $^{15}N_2$ enriched 2

The compound **1** (30 mg, 0.038 mmol, 1.00 equiv.) and KC_8 (13.44 mg, 0.099 mmol, 3.05 equiv.) were added to a 100 mL Schlenk flask as solid. The flask was put out from the glove box and evacuated. THF (7 mL) which was degassed and added by $^{15}N_2$ gas was vacuum transferred to the flask equipped with solid reagents. The THF transferred flask was kept frozen, evacuated the headspace. The headspace was backfilled with $^{15}N_2$ gas. The flask was stirred under room temperature for 24 h. Inside a glovebox, the flask was opened. The blue mixture was filtered through a plug of Celite, followed by evaporation in vacuo for 24 h affording 2.2 mg (11.9 %) of the $^{15}N_2$ enriched product **2** as a blue powder.

Procedure for preparing 3

THF (5 mL) was added to **1** (35 mg, 0.038 mmol, 1.00 equiv). The Na metal (20 mg, 0.870 mmol, 22.87 equiv) was added to the suspended THF mixture of **1** (15 mg, 0.016 mmol, 1.00 equiv.). The heterogeneous brown mixture was stirred at room temperature for 2 days. The resultant mixture was filtered through a plug of Celite. The filtrate was dried in vacuo. The resultant brown solid was extracted by Et_2O, filtered through a plug of Celite to afford a red solution. A small portion of this solution was dried and used in 1H NMR analysis. The single crystal of the compound was prepared by keeping the compound dissolved by dimethoxyethane in the freezer (−40 °C).

^{1}H NMR spectrum of 2

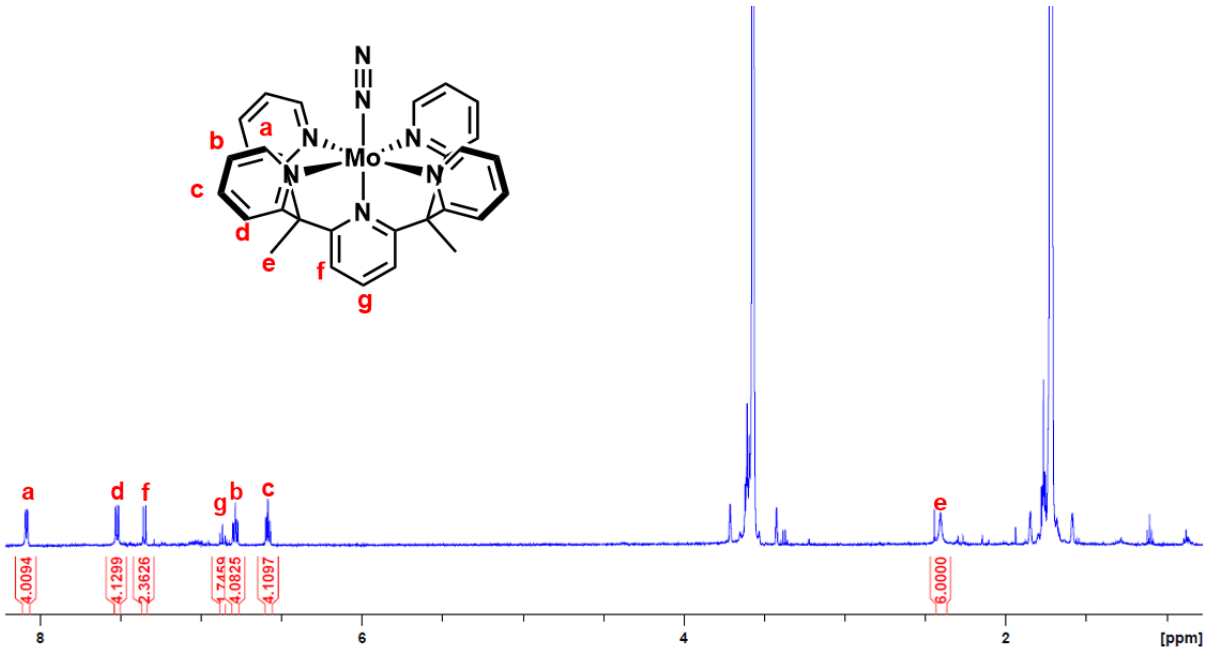


Figure S1. ^{1}H NMR spectrum of **2** in THF-d_8.

^{13}C NMR spectrum of 2

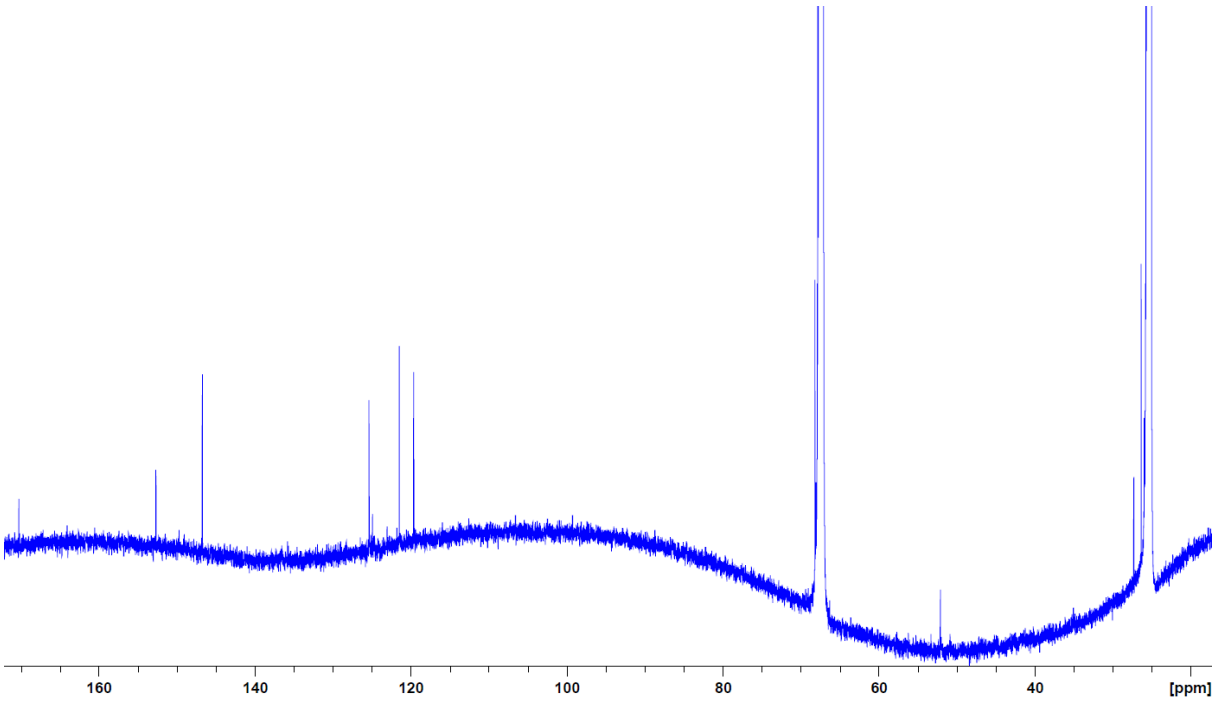


Figure S2. ^{13}C NMR spectrum of **2** in THF-d_8.

UV-vis spectrum of 2

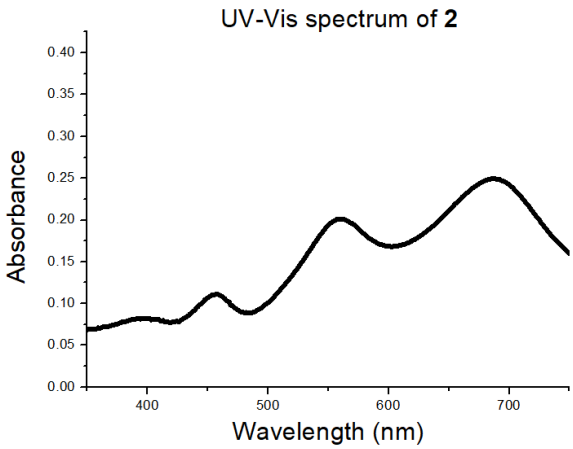


Figure S3. UV/Vis (THF, 25 °C, nm (Absorbance)): λ = 688 (0.249), 560 (0.201), 456 (0.110).

IR spectrum of 2 ($^{14}N_2$)

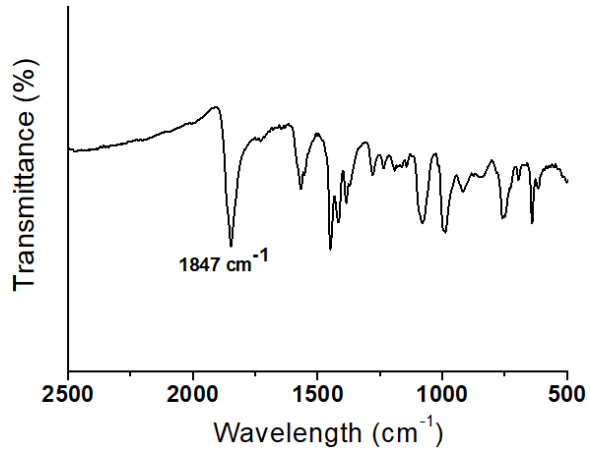


Figure S4. IR spectrum of **2 ($^{14}N_2$)** (a thin film sample formed by evaporation of THF solution on KBr window).

IR spectrum of 2 ($^{15}N_2$)

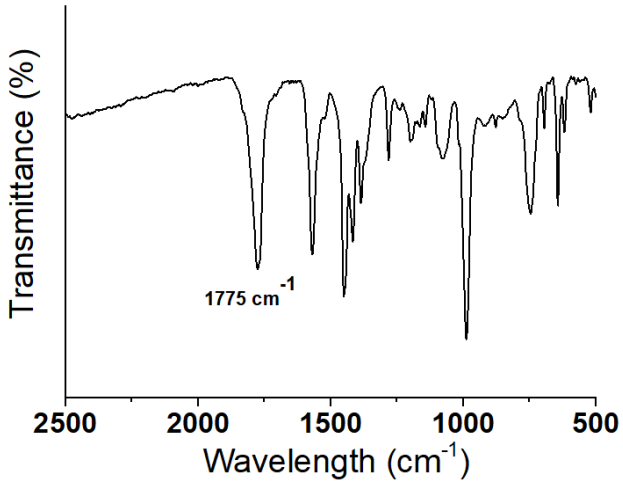


Figure S5. IR spectrum of **2 ($^{15}N_2$)** (a thin film sample formed by evaporation of THF solution on KBr window).

^{1}H-NMR spectrum of excessively reduced 1 compared with the spectrum of 2

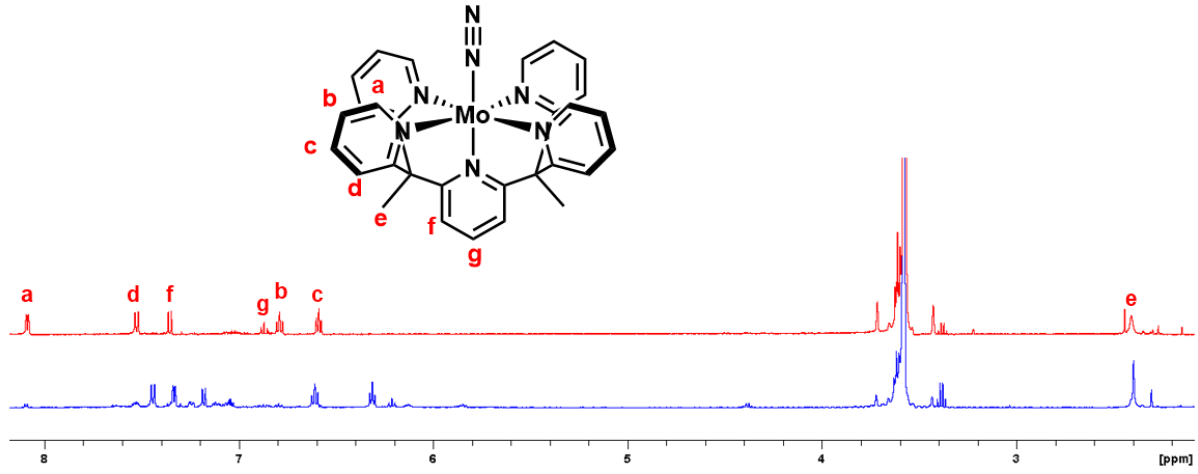


Figure S6. ^{1}H NMR spectrum of unidentified compound formed by adding 4.5 equivalent of KC_8 to **1** (blue spectrum). For comparison, **2** is shown in red spectrum. The experimental procedure followed the Common procedure for preparing **2** ($Py_5Me_2MoN_2$) except for using 4.5 equivalent of KC_8. The spectrum was recorded as a d^8-THF solution. The unidentified compound has peaks (7.43 (d, J = 8.10 Hz), 7.32 (d, J = 5.91 Hz), 7.17 (d, J = 7.08Hz), 6.60 (m), 6.30 (m), 6.87 (t, J = 7.72 Hz), 2.38 (s)).

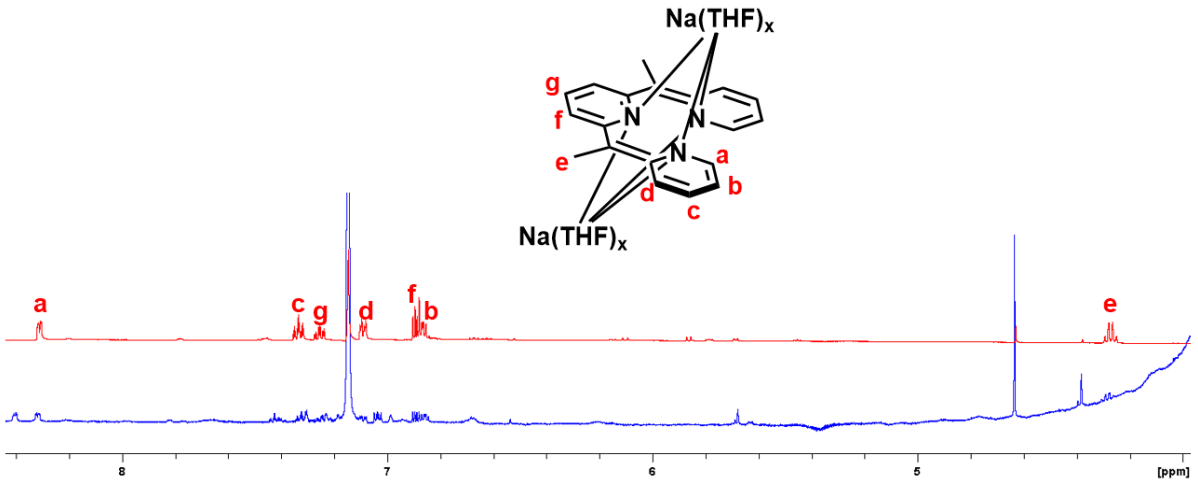


Figure S7. ^{1}H NMR spectrum of **1** which was reduced by 5.2 equivalent of KC_8 (blue spectrum) and an excess amount of sodium metal (red spectrum). For preparing the sample of the blue spectrum, the experimental procedure followed the Common procedure for preparing **2** ($Py_5Me_2MoN_2$) except for the using 5.2 equivalents of KC_8. For preparing the sample of the red spectrum, the experimental procedure followed the procedure for preparing **3**. The spectrum was recorded in a common THF solution added by a small amount of C_6D_6 as an internal standard. The peaks are tentatively assigned. Figure S10 shows the connectivity of this compound in which the THFs are substituted by dimethoxy ethane (see below).

Procedure for NH_3 synthesis

This procedure followed the literature[4] with slight modifications. Inside a glovebox, a mixture of **2** (0.9 ~ 1.2 mg was used), and THF was added to a 100 mL Schlenk flask. The flask was put into a cold well cooled by liquid nitrogen. The flask was kept until the mixture was completely frozen. A mixture of reductant (70 equiv. for **2**) and THF was added to the frozen solution and the flask was shaken in room temperature for 30 seconds. This mixture was again frozen in the cold well. A mixture of proton source (50 equiv. for **1**) and THF was cooled in the cold well and it was slowly added to the frozen solution. The resultant mixture was kept until it was perfectly frozen. The flask was taken out of the glovebox, allowed to stir at room temperature or -78 °C for 3 h.

NH_3 quantification

This procedure also followed the literature[4] with slight modifications. The reaction flask was cooled by liquid nitrogen to allow the solution to be frozen. The flask was opened to the atmosphere and was slowly added a fourfold excess (with respect to proton source) solution of NaO^{t}Bu solution in MeOH over 1 minute. This mixture was frozen and then the headspace of the tube was evacuated. The flask was closed and the mixture was allowed to be stirred at room temperature for 30 minutes. The volatiles of the solution was vacuum transferred into another Schlenk flask charged with HCl (3 to 5 mL of 2.0 M solution in Et_2O). After the transfer, this flask was kept under room temperature for more than 1 h. The solution was evaporated, and the remaining residue was dissolved by distilled water (1 mL). A portion (20 µL) of this resultant solution was analyzed by the indophenol method.[5]

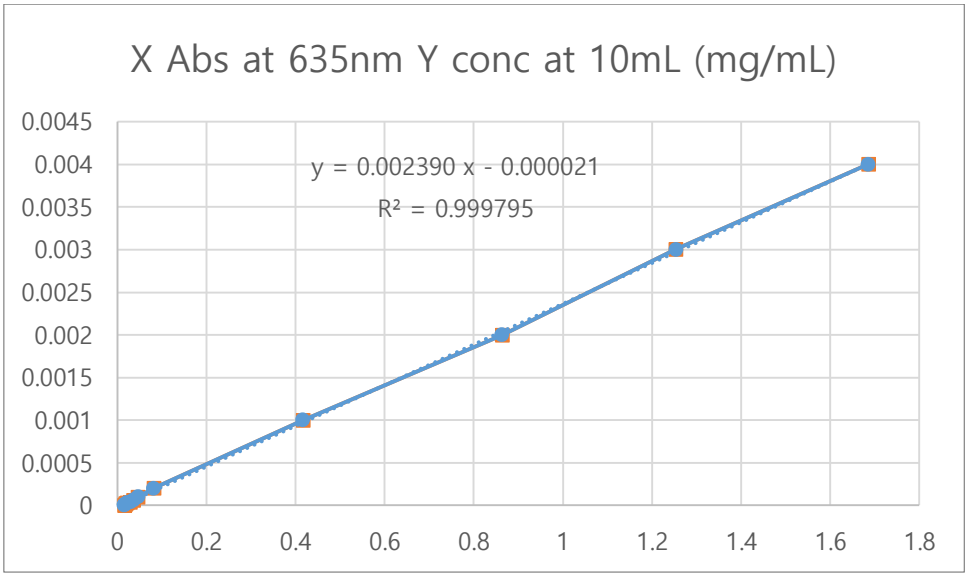


Figure S8. Calibration curve for the indophenol method

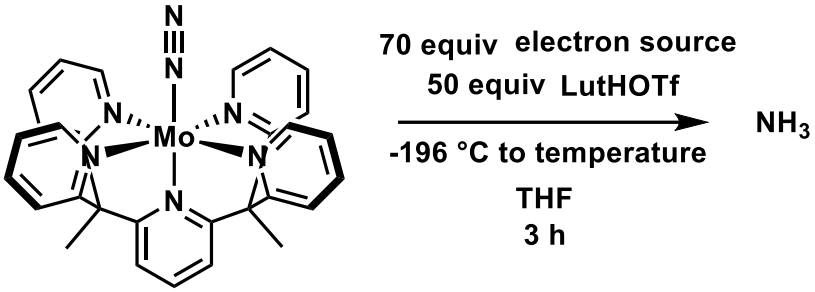


Table S1. Results for the NH_3 synthesis

H^+ source	e^- source	Temperature	NH_3 equiv. per Mo	average
LutHOTf	$CrCp^*_2$	RT	1.33	1.22
LutHOTf	$CrCp^*_2$	RT	1.24	
LutHOTf	$CrCp^*_2$	RT	1.08	
LutHOTf	$CoCp_2$	RT	0.45	0.38
LutHOTf	$CoCp_2$	RT	0.37	
LutHOTf	$CoCp_2$	RT	0.31	
LutHOTf	$CrCp^*_2$	-78 °C	0.22	0.29
LutHOTf	$CrCp^*_2$	-78 °C	0.37	
LutHOTf	$CrCp^*_2$	-78 °C	0.27	
LutHOTf	$CoCp_2$	-78 °C	0.20	0.19
LutHOTf	$CoCp_2$	-78 °C	0.20	
LutHOTf	$CoCp_2$	-78 °C	0.18	

Procedure for $^{15}NH_3$ synthesis

The compound $^{15}N_2$ enriched **2** (1 mg, 0.002 mmol, 1.00 equiv.), $CrCp^*_2$ (45.6 mg, 0.142 mmol, 70 equiv.) and LutHOTf (26.1 mg, 0.142 mmol, 50 equiv.) were added to a 100 mL Schlenk flask as solid. The flask was put out from the glove box and evacuated. THF which was degassed and added by $^{15}N_2$ gas was vacuum transferred to the flask. The flask was kept frozen, evacuated the headspace. The headspace was backfilled with $^{15}N_2$ gas. The flask was stirred under room temperature for 3 h. The procedure for quantification is the same as the procedure for $^{14}NH_3$ synthesis. The overall amount of ammonium salt was determined by the indophenol method (0.64 eq per **2**). The existence of the $^{15}NH_4Cl$ was confirmed by ^{1}H NMR spectrum in d_6-DMSO (Figure S9)

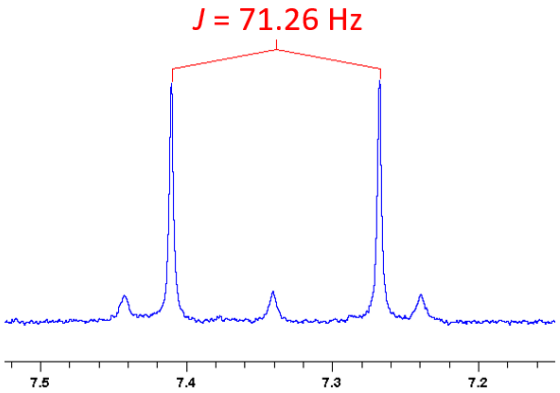


Figure S9. ^{1}H NMR spectrum of [$^{15}NH_4$][Cl] produced from $^{15}N_2$ enriched **2** in d_6-DMSO, J = 71.26 Hz.

X-ray Crystallographic Analysis

CCDC 1971015, 2014521 contain the supplementary crystallographic data for **2** and **3** These data can be obtained free of charge via www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

General information

A suitable crystal was coated with Paratone-N oil and the diffraction data were measured at 100 K using either synchrotron radiation on the 2D beamline at the Pohang Accelerator Laboratory, Korea (for **2**) or using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation on a Bruker Venture CMOS diffractometer (for **3**). Using Olex2 software,[6] the structure was solved by the ShelXT structure solution program[7] using intrinsic phasing, and refined by the ShelXL refinement package[8] using least squares minimisation. All of the nonhydrogen atoms were refined anisotropically and all hydrogen atoms were added to their ideal positions.

A dull violet block-shaped of **2** (0.05 x 0.05 x 0.05 mm3) was picked up with paraton oil and the diffraction data measured at 100 K with synchrotron radiation on a 2D beamline at the Pohang Accelerator Laboratory, Korea.

A clear light red rod-shaped crystal of **3** was picked up with paraton oil and the diffraction data measured on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection.

However, multiple crystallization attempts yielded red crystals suitable for connectivity determination only due to the low completeness. Nevertheless, the crystal structure of **3** clearly shows that two sodium cations were coordinated to one pyridine and two amides, which resulted from the decomposition of penta-pyridyl ligands.

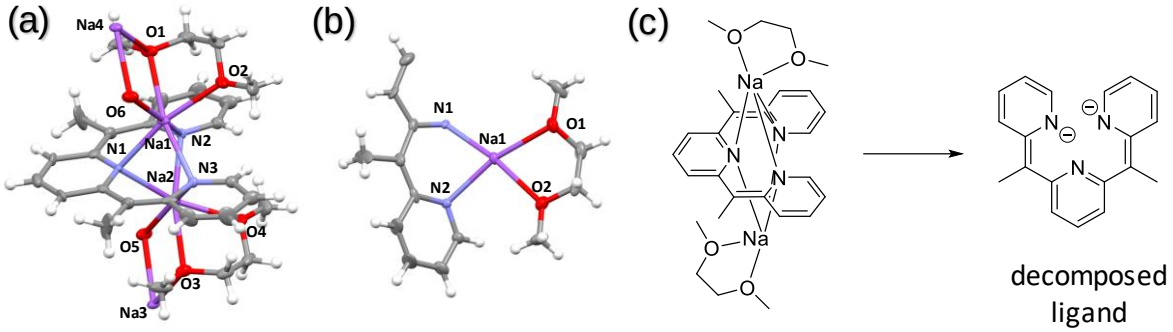


Figure S10. (a) The solid-state structure of **3** as determined using X-ray crystallography (b) asymmetric unit of the solid-state structure of **3**. Selected bond lengths (Å) Na1-N1 2.400(5), Na1-N2 2.454(3), 2.528(3), 2.448(5) (c) Schematic diagram for explaining the connectivity of **3**.

Crystal data and structure refinement for 2

Empirical formula	C29H25MoN7
Formula weight	567.50
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Cmcm
a/Å	14.307(3)
b/Å	11.256(2)
c/Å	20.349(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ^{3}	3277.0(12)
Z	4
ρcalcg/cm^3	1.150
μ/mm^{-1}	0.426
F(000)	1160.0
Crystal size/mm^3	0.05 × 0.05 × 0.05
Radiation	Synchrotron (λ = 0.70000)
2Θ range for data collection/°	5.022 to 52.744
Index ranges	$-17 \leq h \leq 17$, $-14 \leq k \leq 13$, $-25 \leq l \leq 25$
Reflections collected	3254
Independent reflections	1781 [R_{int} = 0.0135, R_{sigma} = 0.0231]
Data/restraints/parameters	1781/54/87
Goodness-of-fit on F^2	1.118
Final R indexes [I>=2σ (I)]	R_1 = 0.0567, wR_2 = 0.1540
Final R indexes [all data]	R_1 = 0.0578, wR_2 = 0.1546
Largest diff. peak/hole / e Å $^{-3}$	1.73/-1.96

Crystal data and structure refinement for 3

Empirical formula	C27H37N3Na2O4
Formula weight	513.57
Temperature/K	100
Crystal system	orthorhombic
Space group	C2/c
a/Å	14.427(5)
b/Å	18.077(10)
c/Å	11.027(4)
α/°	90
β/°	113.285(8)
γ/°	90
Volume/Å ^{3}	2641.5(19)
Z	4
ρcalcg/cm^3	1.291
μ/mm^{-1}	0.114
F(000)	1096.0
Crystal size/mm^3	0.1 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.148 to 56.6
Index ranges	$-15 \leq h \leq 16$, $-23 \leq k \leq 21$, $-13 \leq l \leq 14$
Reflections collected	1939
Independent reflections	1595 [R_{int} = 0.0216, R_{sigma} = 0.0839]
Data/restraints/parameters	1595/0/167
Goodness-of-fit on F^2	0.960
Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1477
Final R indexes [all data]	R_1 = 0.1064, wR_2 = 0.1886
Largest diff. peak/hole / e Å $^{-3}$	0.26/-0.24

DFT Calculations

The resource for calculations was supported by the Korea Institute of Science and Technology Information (KISTI). All the calculations were performed in the DFT method using Gaussian16.[9] Geometries of **2** and **4** were optimized using wB97xD[10] functional and def2-SVP[11] basis set on all atoms. The NBO analysis was augmented by keywords RESONANCE and 3CBOND considering their highly delocalized structures.

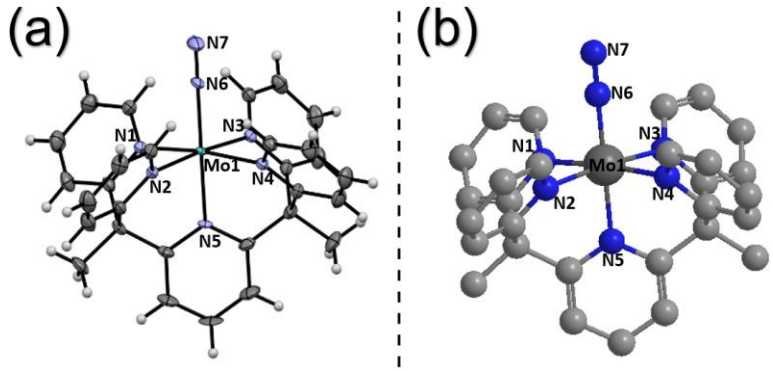


Table S2. (a) Solid-state structure of **2** as determined using X-ray crystallography. (b) Structure of **2** as determined using DFT calculation.

Bond	Lengths and angles from X-ray structure	Lengths and angles from DFT calculation
$Mo_1 – N_6$	1.942(6) Å	1.959 Å
$N_6 – N_7$	1.142(10) Å	1.133 Å
$Mo_1 – N_1$	2.122 Å	2.120 Å
$Mo_1 – N_2$	2.122 Å	2.118 Å
$Mo_1 – N_3$	2.122 Å	2.117 Å
$Mo_1 – N_4$	2.121(3) Å	2.120 Å
$Mo_1 – N_5$	2.096(6) Å	2.115 Å
$Mo_1 – N_6 – N_7$	180.00 °	179.97 °
$N_5 – Mo_1 – N_6$	180.00 °	179.97 °

Coordinates for NBO analysis of 2

C	2.12923300	0.00557800	0.43686100
C	2.87022400	0.85752600	-0.37927900
C	2.78053400	0.74657100	-1.76044600
C	1.94279500	-0.22130100	-2.29799600
C	1.21540500	-1.05838400	-1.45489500
N	1.31666800	-0.93977200	-0.10460700
C	2.20299400	0.09521200	1.97730300
C	0.27346600	-2.14778300	-2.01338400
C	3.16312400	1.22643200	2.36831300
C	0.72341100	-3.54616500	-1.53872200
C	0.30394700	-2.10165300	-3.54680400
N	-0.16575900	-0.55060400	2.38106900
N	0.70457600	-3.79151800	-0.19698700
N	1.94943200	-2.34760700	2.37282500
N	-1.40658500	-1.98781600	-0.18560200
C	2.33043000	-3.49527000	2.99553300
C	3.48472900	-3.62120500	3.73804600
C	4.30881000	-2.50336900	3.89217900
C	3.89670200	-1.30872300	3.31731500
C	2.71363000	-1.23500200	2.57162500
C	-1.17395300	-1.91694400	-1.52772300
C	-2.22583300	-1.67509800	-2.42001300
C	-3.53031800	-1.52828500	-1.96742800
C	-3.76693600	-1.67076500	-0.59791700
C	-2.69658500	-1.90850800	0.23737300
C	0.80920200	0.38365200	2.57564900
C	-1.35659700	-0.36176800	3.01059000
C	-1.66458400	0.75606200	3.75551200
C	-0.69517800	1.75117800	3.90405600
C	0.54740600	1.53931700	3.32218600
C	1.10871900	-4.54679300	-2.43954200
C	1.45541000	-5.81604700	-1.99611900
C	1.36926700	-6.07563200	-0.62590100
C	0.98480200	-5.05611800	0.21799700
Mo	0.21693600	-2.23495000	1.15543800
N	-0.80287300	-3.43648600	2.32020300
N	-1.39632500	-4.13022100	2.99258000
H	3.52458800	1.61435900	0.04482400
H	3.35789200	1.40711600	-2.41052900
H	1.86828400	-0.31070500	-3.37834000
H	2.81875300	2.19015400	1.97202700
H	3.23822000	1.31782100	3.45900500
H	4.17132500	1.04333500	1.97587900
H	-0.02559200	-1.12370200	-3.92021000
H	1.31631800	-2.28340300	-3.92908600
H	-0.35876200	-2.86506300	-3.97298300
H	1.64608600	-4.33701100	2.89094100
H	3.72541200	-4.58132200	4.19818800
H	5.23897100	-2.55554200	4.46127800
H	4.51536100	-0.42544800	3.45835900
H	-2.03579000	-1.59491400	-3.48783300
H	-4.34262600	-1.32729500	-2.66853500
H	-4.77235000	-1.60716500	-0.17759500
H	-2.85286700	-2.06370900	1.30452200
H	-2.07753500	-1.17269100	2.90963300
H	-2.64867400	0.83868600	4.22054400
H	-0.89515800	2.66100100	4.47328100
H	1.31885900	2.29394700	3.45686700
H	1.14401100	-4.34331800	-3.50735600
H	1.76558400	-6.58707800	-2.70388400
H	1.58679400	-7.06192300	-0.21187800
H	0.86909800	-5.23678500	1.28636100

Coordinates for NBO analysis of 4

Mo	5.17013700	4.01436400	15.80436100
N	5.78676600	2.12053500	15.84041700
N	6.12648200	1.04387300	15.85370000
P	5.36927600	4.01484400	13.34458500
C	6.66142400	4.92558000	12.35682200
C	5.37429800	7.50143600	14.47253100
P	4.49191000	6.40169500	15.68154600
C	2.75852000	6.86977000	15.22201300
C	1.32317400	3.80153000	15.63065700
P	2.94768400	2.91223600	15.56958800
C	5.66800100	2.36972600	12.54722700
C	3.91421200	4.64451500	12.36665800
C	2.60286100	1.82939300	14.09632500
C	2.58721300	1.56114400	16.79391300
C	4.65408400	7.52011900	17.15440300
C	5.80690100	5.02285500	19.43206200
P	4.82673400	3.98059200	18.24096500
C	5.12049600	2.35865000	19.08728400
C	3.15942000	4.42836000	18.93271400
C	8.10741700	6.15912100	16.95608600
P	7.53435400	4.56233800	16.20313400
C	8.39555800	3.36217800	17.32498600
C	8.78808800	4.50367100	14.83764500
H	6.36379300	4.97929100	11.29741500
H	6.81394700	5.94495000	12.73396700
H	7.61724300	4.38988100	12.41281300
H	5.12604600	7.20411100	13.44448500
H	5.09309700	8.55840200	14.60359300
H	6.46186100	7.40129700	14.59975400
H	2.06772200	6.51944600	16.00158600
H	2.64403000	7.95993300	15.10987100
H	2.48256900	6.38074700	14.27723700
H	1.27147800	4.42674400	16.53340200
H	1.23062800	4.46217500	14.75678600
H	0.47593300	3.09729700	15.63278500
H	6.62296400	1.97745000	12.92891100
H	4.88880300	1.64747600	12.81418900
H	5.72683100	2.45071300	11.45028000
H	2.96242000	4.34278600	12.82149700
H	3.94223200	4.30429000	11.31888200
H	3.94284500	5.74473000	12.36763700
H	3.34034200	1.01289500	14.09089900
H	2.67748500	2.36985200	13.14494600
H	1.59779900	1.38489100	14.16767600
H	3.42149800	0.84361200	16.77570600
H	1.65957000	1.02856300	16.53227400
H	2.48692800	1.94639100	17.81561300
H	4.04612200	7.14225900	17.98817000
H	5.70270000	7.55491700	17.48013600
H	4.32351900	8.54402900	16.91844800
H	5.68193700	6.08932900	19.20497900
H	5.47666000	4.84434300	20.46761300
H	6.87630100	4.78147700	19.36835300
H	4.89910600	2.40905800	20.16513300
H	6.17547000	2.07917700	18.95133700
H	4.51712100	1.56550100	18.63020100
H	2.36958300	3.80157700	18.50083200
H	2.93192500	5.47108200	18.66571500
H	3.12762200	4.33067600	20.02968200
H	9.19633100	6.15924000	17.12374100
H	7.60227600	6.34012700	17.91333800
H	7.85993800	6.99047800	16.27891400
H	9.46304000	3.60639400	17.44263500
H	8.30418900	2.35239600	16.89817400
H	7.92635100	3.34578400	18.31723900
H	9.81411200	4.55756300	15.23499800
H	8.63560100	5.34449400	14.14825000
H	8.67269900	3.56375200	14.27765500

Selected results of NBO analysis

Summary of Natural Population Analysis of **2**

Atom	No	Charge	Core	Valence	Rydberg	Total
Mo	35	0.01338	35.97647	5.95861	0.05154	41.98662
N	36	0.00246	1.99937	4.93792	0.06026	6.99754
N	37	-0.10926	1.99964	5.08372	0.0259	7.10926

Atom	No	Natural Electron Configuration
Mo	35	[core]5S(0.25)4d(5.26)5p(0.45)5d(0.03)6p(0.01)
N	36	[core]2S(1.34)2p(3.60)3S(0.03)3p(0.03)3d(0.01)
N	37	[core]2S(1.58)2p(3.50)3S(0.01)3p(0.01)3d(0.01)

Summary of Natural Population Analysis of **4**

Atom	No	Charge	Core	Valence	Rydberg	Total
Mo	1	-2.23914	35.97109	8.22662	0.04143	44.23914
N	2	0.07014	1.99934	4.87404	0.05648	6.92986
N	3	-0.10153	1.99962	5.07776	0.02415	7.10153

Atom	No	Natural Electron Configuration
Mo	1	[core]5S(0.41)4d(6.96)5p(0.85)6S(0.01)5d(0.02)6p(0.01)
N	2	[core]2S(1.32)2p(3.55)3S(0.02)3p(0.03)3d(0.01)
N	3	[core]2S(1.56)2p(3.51)3S(0.01)3p(0.01)3d(0.01)

Wiberg bond index matrix in the NAO basis of **2**

	Atom	28	29	30	31	32	33	34	35	36
6	N	0.0004	0.0008	0.0012	0.0012	0.0008	0.0004	0.0014	**0.5978**	0.0320
12	N	0.0142	0.0720	0.0133	0.0006	0.0007	0.0008	0.0020	**0.6417**	0.0073
13	N	0.0008	0.0006	0.0006	0.0133	0.0722	0.0142	1.2348	**0.6404**	0.0073
14	N	0.0002	0.0028	0.0012	0.0002	0.0021	0.0006	0.0033	**0.6399**	0.0073
15	N	0.0006	0.0021	0.0002	0.0012	0.0028	0.0002	0.0037	**0.6394**	0.0073
35	Mo	0.0226	0.0607	0.0121	0.0120	0.0606	0.0226	0.0602	0.0000	1.0003
36	N	0.0007	0.0017	0.0002	0.0002	0.0017	0.0007	0.0029	1.0003	0.0000
37	N	0.0006	0.0069	0.0004	0.0004	0.0069	0.0006	0.0088	0.3488	2.5084

avg N → Mo

0.63184

Wiberg bond index matrix in the NAO basis of 4

	Atom	1	2	3	4	5	6	7	8	9
1	Mo	0.0000	0.9418	0.4215	0.7841	0.0276	0.0225	0.7985	0.0226	0.0226
2	N	0.9418	0.0000	2.5768	0.0141	0.0005	0.002	0.0505	0.0019	0.0029
3	N	0.4215	2.5768	0.0000	0.0107	0.0002	0.0049	0.0094	0.0047	0.0008
4	P	**0.7841**	0.0141	0.0107	0.0000	0.9140	0.0018	0.0228	0.0007	0.0006
7	P	**0.7985**	0.0505	0.0094	0.0228	0.0009	0.9182	0.0000	0.9204	0.0017
10	P	**0.7749**	0.0159	0.0073	0.0218	0.0027	0.0012	0.0181	0.0022	0.9246
17	P	**0.7948**	0.0138	0.0100	0.0748	0.0016	0.0014	0.0210	0.0005	0.0007
21	P	**0.7999**	0.0166	0.0083	0.0213	0.0022	0.0014	0.0194	0.0025	0.0019

avg P → Mo

0.79044

Selected NBOs of 2 that span the input AO space

(Occupancy) Bond orbital/ Coefficients/ Hybrids

15. (1.91073) BD (1) N 6 -Mo 35

85.95% 0.9271* N 6 s(36.34%) p 1.75(63.66%) d 0.00(0.01%)

-0.0002	-0.6023	-0.0233	0.0002	0.4183
0.0219	0.4844	0.0257	-0.4745	-0.0250
0.0005	-0.0048	-0.0055	0.0000	-0.0023

14.05% 0.3748*Mo 35 s(14.15%) p 3.36(47.49%) d 2.69(38.03%) f 0.02(0.33%)

0.0008	-0.3760	-0.0042	-0.0061	0.0073
0.0013	0.0014	-0.0016	-0.3571	-0.0112
0.0019	-0.0019	-0.4231	-0.0137	0.0021
0.0018	0.4098	0.0131	-0.0021	-0.4318
-0.0231	0.2691	-0.0049	0.3220	-0.0052
0.0735	0.0038	-0.1070	-0.0159	-0.0217
-0.0141	-0.0167	-0.0070	0.0422	0.0197
-0.0117				

35. (1.90724) BD (1) N 12 -Mo 35

85.47% 0.9245* N 12 s(37.38%) p 1.68(62.62%) d 0.00(0.01%)

-0.0002	-0.6109	-0.0233	0.0002	-0.1276
-0.0128	0.6279	0.0335	0.4622	0.0252
-0.0028	0.0011	0.0031	-0.0057	0.0013

14.53% 0.3812*Mo 35 s(16.29%) p 2.63(42.86%) d 2.48(40.43%) f 0.03(0.43%)

-0.0001	-0.4035	-0.0069	-0.0030	0.0022
0.0010	0.0002	0.0002	0.1988	0.0010
0.0053	-0.0011	-0.5268	-0.0138	-0.0081
-0.0013	-0.3331	-0.0157	0.0023	0.0644
-0.0148	0.0676	-0.0019	-0.4993	0.0078
0.3273	-0.0329	0.1942	0.0094	0.0191
0.0092	-0.0240	0.0479	0.0206	-0.0126
0.0188				

39. (1.90737) BD (1) N 13 -Mo 35

85.48% 0.9246* N 13 s(37.37%) p 1.68(62.62%) d 0.00(0.01%)

0.0002	0.6109	0.0233	-0.0002	-0.1694
-0.0115	0.5753	0.0350	0.5144	0.0239
0.0006	0.0022	-0.0069	-0.0007	0.0004

14.52% 0.3810*Mo 35 s(16.27%) p 2.64(42.87%) d 2.49(40.44%) f 0.03(0.43%)

0.0001	0.4032	0.0069	0.0030	-0.0020
-0.0008	-0.0002	0.0000	0.2204	-0.0004
0.0091	-0.0014	-0.5008	-0.0154	-0.0037
-0.0010	-0.3588	-0.0141	-0.0020	-0.2880
-0.0015	-0.2016	0.0196	0.4227	-0.0313
-0.2166	-0.0038	0.2318	0.0087	0.0174
0.0124	-0.0283	0.0456	0.0223	-0.0139
0.0150				

44. (1.90753) BD (1) N 14 -Mo 35

85.48% 0.9246* N 14 s(37.34%) p 1.68(62.65%) d 0.00(0.01%)

-0.0002	-0.6106	-0.0233	0.0002	0.6418
0.0353	-0.0267	-0.0074	0.4604	0.0251
-0.0008	0.0030	0.0016	0.0063	0.0014

14.52% 0.3811*Mo 35 s(16.30%) p 2.63(42.81%) d 2.48(40.47%) f 0.03(0.42%)

-0.0001	-0.4036	-0.0069	-0.0030	0.0020
0.0008	0.0002	-0.0011	-0.5534	-0.0137
-0.0090	0.0001	0.1134	-0.0013	0.0039
-0.0013	-0.3293	-0.0153	0.0023	-0.0438
-0.0041	-0.5016	0.0080	-0.0149	-0.0008
-0.3327	0.0359	0.1970	0.0092	0.0195
-0.0242	0.0054	-0.0518	0.0047	-0.0227
0.0027				

49. (1.90739) BD (1) N 15 -Mo 35

85.48% 0.9245* N 15 s(37.32%) p 1.68(62.67%) d 0.00(0.01%)

0.0002	0.6105	0.0233	-0.0002	0.5974
0.0365	-0.0853	-0.0062	0.5105	0.0237
0.0010	-0.0071	0.0012	0.0005	0.0005

14.52% 0.3811*Mo 35 s(16.28%) p 2.63(42.81%) d 2.49(40.49%) f 0.03(0.42%)

0.0001	0.4034	0.0069	0.0030	-0.0021
-0.0009	-0.0002	-0.0013	-0.5313	-0.0152
-0.0052	-0.0002	0.1402	-0.0030	0.0083
-0.0010	-0.3544	-0.0138	-0.0020	-0.2135
-0.0002	0.4476	-0.0339	-0.1372	0.0147
0.2982	0.0038	0.2231	0.0089	0.0180
-0.0289	0.0079	-0.0502	0.0073	-0.0200

0.0059

128. (1.35055) LP (1)Mo 35 s(0.00%) p 1.00(0.84%) d99.99(99.15%) f 0.01(0.01%)

0.0000	0.0009	0.0000	0.0000	-0.0001
0.0000	0.0000	0.0000	-0.0682	0.0078
-0.0031	0.0000	0.0599	-0.0066	0.0026
0.0000	-0.0008	-0.0001	0.0000	0.1321
0.0053	-0.4522	-0.0178	0.3825	0.0149
0.7885	0.0309	0.0070	0.0002	0.0001
-0.0048	0.0042	-0.0024	-0.0004	-0.0037

130. (1.08781) LP (3)Mo 35 s(0.00%) p 1.00(25.99%) d 2.84(73.93%) f 0.00(0.07%)

0.0000	**0.0015**	**0.0001**	**-0.0001**	**0.0000**
0.0000	**0.0000**	**0.0000**	**-0.1962**	**0.0021**
-0.0022	**0.0000**	**-0.2263**	**0.0022**	**-0.0024**
0.0000	**-0.4125**	**0.0040**	**-0.0044**	**0.3954**
-0.0051	**0.1547**	**-0.0020**	**0.1873**	**-0.0024**
-0.0622	**0.0008**	**-0.7211**	**0.0083**	**0.0153**
-0.0046	**-0.0058**	**-0.0020**	**0.0126**	**-0.0144**

685. (0.28017) BD*(2) N 36 - N 37

49.54% 0.7038* N 36 s(0.00%) p 1.00(99.75%) d 0.00(0.25%)

0.0000	0.0000	0.0001	0.0000	-0.3873
-0.0079	-0.4482	-0.0092	-0.8038	-0.0165
0.0238	0.0097	0.0114	-0.0036	-0.0417

50.46% -0.7103* N 37 s(0.00%) p 1.00(99.69%) d 0.00(0.31%)

0.0000	0.0002	0.0000	0.0000	-0.3870
0.0055	-0.4479	0.0064	-0.8040	0.0115
-0.0261	-0.0106	-0.0125	0.0040	0.0457

686. (0.23931) BD*(3) N 36 - N 37

47.72% 0.6908* N 36 s(0.00%) p 1.00(99.76%) d 0.00(0.24%)

0.0000	-0.0002	-0.0001	0.0000	0.7581
0.0194	-0.6498	-0.0167	-0.0030	-0.0001
-0.0060	0.0220	-0.0187	-0.0387	-0.0001

52.28% -0.723* N 37 s(0.00%) p 1.00(99.68%) d 0.00(0.32%)

0.0000	-0.0005	0.0001	0.0000	0.7571
-0.0113	-0.6507	0.0098	-0.0020	0.0000
0.0069	-0.0254	0.0217	0.0448	0.0001

Selected NBOs of 4 that span the input AO space

(Occupancy) Bond orbital/ Coefficients/ Hybrids

2. (1.88211) BD (1)Mo 1 - P 4

26.16%	0.5114*Mo	1	s(18.05%) p 2.77(49.91%) d 1.77(31.95%) f 0.00(0.09%)			
		-0.0005	0.4249	-0.0009	0.0004	-0.0007
		0.0003	0.0000	0.0001	0.0816	-0.0064
		-0.0004	-0.0002	-0.0007	0.0151	0.0033
		0.0002	-0.7015	-0.0098	-0.0030	-0.0094
		0.0030	-0.1208	0.0028	0.0001	0.0111
		0.0089	0.0014	0.5511	-0.0299	-0.0289
		0.0071	-0.0012	0.0001	0.0003	0.0014
		-0.0011				
73.84%	0.8593* P	4	s(43.18%) p 1.32(56.80%) d 0.00(0.02%)			
		0.0000	-0.0005	0.6567	0.0208	0.0010
		0.0000	-0.0202	0.0038	-0.0001	0.0417
		-0.0004	0.0003	0.7509	-0.0454	0.0001
		0.0000	-0.0001	-0.0007	0.0143	

3. (1.89838) BD (1)Mo 1 - P 7

25.55%	0.5055*Mo	1	s(15.76%) p 3.41(53.68%) d 1.93(30.42%) f 0.01(0.13%)			
		-0.0004	0.3959	-0.0286	-0.0037	0.0047
		0.0029	-0.0027	-0.0002	-0.2236	0.0041
		-0.0024	0.0003	0.6971	-0.0046	0.0028
		0.0000	-0.0288	-0.0011	0.0002	-0.2689
		0.0068	0.0152	0.0011	-0.0288	0.0035
		-0.3726	0.0136	-0.3029	0.0095	0.0022
		0.0063	-0.0208	0.0022	0.0013	0.0218
		-0.0191				
74.45%	0.8628* P	7	s(44.14%) p 1.27(55.84%) d 0.00(0.02%)			
		0.0000	-0.0004	0.6640	0.0228	0.0005
		0.0000	0.1872	-0.0127	-0.0002	-0.7199
		0.0472	0.0000	0.0526	-0.0027	-0.0050
		-0.0004	-0.0019	-0.0109	-0.0057	

4. (1.88631) BD (1)Mo 1 - P 10

25.68%	0.5068*Mo	1	s(17.29%) p 2.92(50.40%) d 1.86(32.23%) f 0.00(0.09%)			
		-0.0010	0.4157	-0.0061	-0.0003	-0.0017
		0.0008	-0.0003	0.0001	-0.6522	-0.0113
		-0.0042	0.0002	-0.2698	0.0048	0.0021
		0.0001	-0.0751	-0.0029	0.0000	0.3139
		-0.0108	0.1117	-0.0072	0.0366	-0.0022
		0.3494	-0.0229	-0.2948	0.0183	0.0046
		0.0150	0.0053	-0.0037	-0.0044	-0.0045
		-0.0230				
74.32%	0.8621* P	10	s(43.03%) p 1.32(56.95%) d 0.00(0.02%)			
		0.0000	-0.0006	0.6556	0.0229	0.0009
		0.0002	0.6422	-0.0422	0.0001	0.3906
		-0.0207	0.0000	0.0476	-0.0035	0.0126
		0.0013	-0.0005	0.0053	-0.0034	

5. (1.87892) BD (1)Mo 1 - P 17

26.41%	0.5139*Mo	1	s(17.77%) p 2.81(49.91%) d 1.81(32.23%) f 0.01(0.09%)			
		-0.0006	0.4216	-0.0044	-0.0002	-0.0012
		0.0002	0.0004	0.0001	-0.0947	-0.0035
		-0.0020	-0.0002	-0.0120	0.0143	0.0030
		-0.0002	0.6998	0.0086	0.0030	-0.0195
		0.0048	-0.1255	0.0082	-0.0202	-0.0088
		-0.0102	-0.0008	0.5517	-0.0331	0.0284
		-0.0088	-0.0020	0.0008	0.0003	0.0010
		-0.0009				
73.59%	0.8578* P	17	s(43.14%) p 1.32(56.84%) d 0.00(0.02%)			
		0.0000	-0.0005	0.6565	0.0203	0.0010
		0.0001	0.1171	-0.0072	0.0000	0.0476
		0.0002	-0.0003	-0.7419	0.0440	0.0006
		-0.0040	-0.0001	0.0001	0.0137	

6. (1.88345) BD (1)Mo 1 - P 21

26.61%	0.5159*Mo	1	s(17.74%) p 2.80(49.68%) d 1.83(32.49%) f 0.00(0.09%)			
		-0.0003	0.4212	-0.0033	-0.0002	0.0003
		-0.0001	-0.0001	-0.0001	0.6754	0.0053
		0.0032	-0.0001	0.1765	0.0170	0.0042
		-0.0002	0.0958	0.0023	-0.0007	0.2672
		-0.0214	0.1211	-0.0073	0.0319	-0.0031
		0.4000	-0.0126	-0.2772	0.0176	-0.0065
		-0.0148	-0.0051	0.0074	0.0045	0.0161
		0.0158				

73.39% 0.8567* P 21 s(42.83%) p 1.33(57.14%) d 0.00(0.02%)

0.0000 -0.0005 0.6541 0.0219 0.0010
-0.0002 -0.7326 0.0452 -0.0001 -0.1000
0.0092 -0.0001 -0.1499 0.0075 0.0038
0.0059 -0.0012 0.0123 -0.0064

117. (1.62917) LP (2)Mo 1 s(0.00%) p 1.00(0.06%) d99.99(99.94%) f 0.05(0.00%)

0.0001 0.0008 -0.0001 0.0012 0.0003
-0.0003 0.0001 0.0004 0.0088 -0.0037
-0.0003 0.0004 0.0088 -0.0015 0.0008
0.0019 0.0136 -0.0151 -0.0014 0.0947
-0.0017 -0.2959 -0.0106 0.9428 0.0261
-0.1043 -0.0055 -0.0467 0.0028 0.0044
0.0004 -0.0002 0.0027 0.0014 0.0002
0.0014

118. (1.62225) LP (3)Mo 1 s(0.00%) p 1.00(0.28%) d99.99(99.72%) f 0.02(0.01%)

-0.0004 0.0000 -0.0007 0.0018 0.0011
0.0002 0.0002 0.0029 0.0463 -0.0218
-0.0018 0.0005 0.0088 -0.0064 -0.0012
-0.0001 0.0019 0.0021 0.0004 0.7874
0.0226 0.0718 0.0003 -0.1213 -0.0052
-0.5959 -0.0169 0.0348 0.0090 0.0001
0.0041 0.0006 -0.0008 0.0001 0.0031

550. (0.22946) BD*(2) N 2 - N 3

49.31% 0.7022* N 2 s(0.01%) p99.99(99.71%) d20.25(0.27%)

0.0000 0.0114 -0.0026 0.0001 -0.0350
-0.0024 -0.0397 0.0002 -0.9968 -0.0268
0.0013 -0.0155 0.0500 -0.0022 -0.0013

50.69% - 0.7119* N 3 s(0.01%) p99.99(99.67%) d22.18(0.32%)

0.0000 0.0118 -0.0023 -0.0001 -0.0443
0.0003 -0.0103 -0.0008 -0.9972 0.0095
-0.0020 0.0171 -0.0538 0.0016 0.0008

551. (0.23306) BD*(3) N 2 - N 3

49.45% 0.7032* N 2 s(0.01%) p 1.00(99.72%) d 0.00(0.27%)

0.0000 -0.0088 0.0034 0.0000 -0.9537
-0.0258 -0.2914 -0.0091 0.0450 0.0002
0.0432 0.0003 -0.0024 -0.0296 0.0001

50.55% -0.711* N 3 s(0.01%) p 1.00(99.68%) d 0.00(0.32%)

0.0000 -0.0081 0.0016 0.0001 -0.9482
0.0075 -0.3091 0.0027 0.0452 -0.0007
-0.0457 -0.0001 0.0026 0.0325 0.0001

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis for 2

Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
128. LP (1)Mo 35	/686. BD*(3) N 36 - N 37	62.09	0.22	0.117
130. LP (3)Mo 35	/685. BD*(2) N 36 - N 37	269.77	0.05	0.130

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis for 4

Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
117. LP (2)Mo 1	/550. BD*(2) N 2 - N 3	56.28	0.26	0.112
118. LP (3)Mo 1	/550. BD*(2) N 2 - N 3	0.56	0.26	0.011
118. LP (3)Mo 1	/551. BD*(3) N 2 - N 3	54.19	0.26	0.110

References

1. H. I. Karunadasa, C. J. Chang and J. R. Long, *Nature*, 2010, **464**, 1329.
2. M. S. Dresselhaus and G. Dresselhaus, *Advances in Physics*, 1981, **30**, 139-326.
3. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
4. T. J. Del Castillo, N. B. Thompson and J. C. Peters, *J. Am. Chem. Soc.*, 2016, **138**, 5341-5350.
5. M. W. Weatherburn, *Anal. Chem.*, 1967, **39**, 971-974.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
7. G. Sheldrick, *Acta Crystallographica Section A*, 2015, **71**, 3-8.
8. G. Sheldrick, *Acta Crystallographica Section C*, 2015, **71**, 3-8.
9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
10. J.-D. Chai and M. Head-Gordon, *PCCP*, 2008, **10**, 6615-6620.
11. (a) B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibsom and T. L. Windus, *J. Chem. Inf. Model.*, 2019, **XXX**, XXX; (b) D. Feller, *J. Comput. Chem.*, 1996, **17**, 1571-1586; (c) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, *J. Chem. Inf. Model.*, 2007, **47**, 1045-1052; (d) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.