Supporting Information

Molybdenum-Mediated N$_2$-Splitting and Functionalization in the Presence of a Coordinated Alkyne

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Synthesis of complex 1.

Mo(ths)(1.44 mmol, 1.00 g), 1.0 eq 2,2’-bis(diisopropylphosphanyl)tolane (1.44 mmol, 592 mg) and 4.0 eq Sn powder (5.77 mmol, 685 mg) were suspended in toluene (50 mL) and stirred at room temperature for 2 d. The reaction mixture was filtered over a pad of Celite® and the filter pad was rinsed with additional toluene (70 mL). The filtrate was evaporated in vacuo to afford the product 1 as a dark blue solid (767 mg, 70%). Single crystals for x-ray diffraction were grown from thf/pentane at -40°C. 1H NMR (thf-d8, 600 MHz, 22°C): δ [ppm] = 8.29 (d, 3JCH = 7.6 Hz, 2H), 7.88 (d, 3JCH = 7.4 Hz, 2H), 7.70 (dd, 3JCH = 7.4 Hz, 3.19 Hz, 2H), 7.45 (dd, 3JCH = 7.4 Hz, 3.19 Hz, 2H), 3.44-3.39 (m, 4H, 6OCH), 1.44-1.41 (m, 12H, 8 CH3), 0.90 (br s, 12H, 8 CH3). 13C[1H] NMR (thf-d8, 151 MHz, 22°C): δ [ppm] = 221.1 (Cp, dd, 3JCP = 12.3 Hz, 3JCP = 12.3 Hz, 2C, C-Mo), 151.4 (Cp, dd, JCP = 19.3 Hz, JCp = 17.9 Hz, 2C), 145.4 (Cp, dd, JCP = 16.6 Hz, JCp = 16.6 Hz, 2C), 132.2 (CH, 2C), 130.9 (CH, 2C), 128.6 (CH, dd, JCP = 1.9 Hz, JCp = 1.9 Hz, 2C), 124.2 (CH, dd, JCP = 5.1 Hz, JCp = 5.1 Hz, 2C), 26.5 (CH, dd, JCP = 7.6 Hz, JCp = 7.6 Hz, 4C), 19.5 (CH, broad, 4C), 18.9 (CH, dd, JCP = 2.6 Hz, JCp = 2.6 Hz, 4C). 31P[1H] NMR (thf-d8, 243 MHz, 22°C): δ [ppm] = 60.4 (s, 2P). MS (LIFDI, thf): Calcd. for [C9H10P2Mo2]⁺: 761.9430. Found: 762.1 [M⁺]. The expected isotopic pattern agrees well with the measurement. Anal. Calcd. for C9H10P2Mo2 (760.29 g/mol): C 41.07, H 4.77. Found: C 41.60, H 4.97.

Synthesis of complex 2 and 13N.

Complex 1 (1.02 mmol, 779 mg) and 1.2 eq Na/Pb (1.23 mmol, 283 mg) were suspended in thf (25 mL) and stirred under N2 atmosphere at room temperature for 1 d. The reaction was evaporated to dryness, the residue taken up in toluene (100 mL) and filtered through a pad of Celite®. The filtrate was evaporated in vacuo and the crude product recrystallized from toluene to afford the title compound as a beige solid (628 mg, 95%). Single crystals for x-ray diffraction were grown from toluene at 40°C, 1H NMR (thf-d8, 600 MHz, 22°C): δ [ppm] = 8.29 (d, 3JCH = 7.6 Hz, 2H), 7.93-7.91 (m, 2H), 7.68 (dd, 3JCH = 7.4 Hz, 3JCH = 7.4 Hz, 2H), 3.34-3.27 (m, 2H, 8CH3), 3.09-3.02 (m, 2H, 8CH3), 1.80-1.76 (m, 6H, 8CH3), 1.40-1.38 (m, 6H, 8CH3), 1.12-1.08 (m, 6H, 8CH3), 0.17-0.13 (m, 6H, 8CH3). 13C[1H] NMR (thf-d8, 151 MHz, 22°C): δ [ppm] = 147.8 (Cp, dd, JCP = 21.1 Hz, JCp = 18.0 Hz, 2C), 143.6 (Cp, dd, JCP = 13.3 Hz, JCp = 12.9 Hz, 2C), 132.9 (CH, 2C), 132.1 (Cp, dd, JCP = 7.1 Hz, JCp = 7.1 Hz, 2C), 131.9 (CH, 2C), 273 (CH, dd, JCP = 5.1 Hz, JCp = 5.1 Hz, 2C), 128.6 (CH, dd, JCP = 2.6 Hz, JCp = 2.6 Hz, 2C), 24.9 (CH, dd, JCP = 9.3 Hz, JCp = 9.3 Hz, 2C), 23.7 (CH, dd, JCP = 8.7 Hz, JCp = 8.7 Hz, 2C), 20.0 (CH3, dd, JCP = 2.9 Hz, JCp = 2.9 Hz, 2C), 18.3 (CH3, dd, JCP = 2.9 Hz, JCp = 2.9 Hz, 2C), 18.3 (CH3, dd, JCP = 3.3 Hz, JCp = 3.3 Hz, 2C), 16.4 (CH3, dd, JCP = 3.1 Hz, JCp = 3.1 Hz, 2C). 31P[1H] NMR (thf-d8, 243 MHz, 22°C): δ [ppm] = 68.0

Experimental Procedures

General Remarks.

All experiments were conducted under an atmosphere of dry and oxygen-free argon by using standard Schlenk techniques or in a glovebox (MBraun). Argon 5.0 was used and further dried by passing over columns of phosphorus pentoxide. Glassware was heated to 130°C overnight and evacuated while still hot. Dichloromethane, diethyl ether, hexane, pentane, thf and toluene were purified using an MBraun Solvent Purification System. Benzene and acetonitrile were dried over Na/benzophenone and calcium hydride, respectively. Deuterated solvents were dried over sodium (C2D6, thf-d8) or over calcium hydride (CD2Cl2, CD2CN) and distilled prior to use. Benzoyl chloride, methyl iodide, ethyl iodide, Me6SiCl and BuNC were purified by simple distillation under vacuum and stored over activated molecular sieves. 2,2’-Bis(diisopropylphosphanyl)tolane,[1] Mo(ths)[2] and [Mo2(CO)(NMe)(EICCEI)] [3] were prepared according to literature. All other chemicals were purchased from commercial suppliers and used as received.

One and two dimensional 1H, 13C, 31P and 15N NMR spectra were recorded on a Bruker Avance II 400 MHz or on a Bruker Avance III 600 spectrometer. Residual (undeuterated) solvent served as reference for 1H and 13C NMR spectra. Chemical shifts δ are given in parts per million (ppm), coupling constants J in Hertz (Hz). Signal multiplicities are stated using common abbreviations (e.g. s – singlet, d – doublet, dd – doublet of doublets). IR (ATR, solid state) measurements were recorded on a Bruker Alpha Spectrometer or on an Agilent Cary 630 FT IR spectrometer equipped with a diamond ATR unit. Mass spectra were recorded at the Department of Organic Chemistry at our University on Bruker ApexQe FT-ICR Instrument by ESI technique or on a JEOL AccuTOF GxQ Instrument by LIFDI technique. Elemental analyses were carried out at the Department of Inorganic Chemistry at Heidelberg University on an Elementar vario MICRO Cube.
The $^{15}$N-labeled complex 2-$^{15}$N was prepared on an NMR scale. A pressure-NMR tube was charged with complex 1 (19.7 μmol, 15.0 mg), 1.1 eq Na/Pb (21.7 μmol, 5.00 mg) and thf-ds (0.4 mL). The tube was then pressurized with ($^{15}$N)₂ (approx. 1 bar). The NMR tube was kept at room temperature for 2 d and monitored with $^{15}$N NMR spectroscopy. Upon complete conversion the head space of the NMR tube was evacuated to remove excess ($^{15}$N)₂. Complex 2-$^{15}$N was characterized by NMR spectroscopy: $^1$H and $^{13}$C NMR spectra agreed well with complex 2. $^{31}$P($^1$H) NMR (thf-ds, 243 MHz, 22°C): δ [ppm] = 68.0 (d, J$_{^1}$P-H = 1.4 Hz, 2P), $^{15}$N($^1$H) NMR (thf-ds, 61 MHz, 22°C): δ [ppm] = 825.4 (s, 1N).

**Synthesis of complex 3.**

Complex 2 (896 μmol, 580 mg) and 1.1 eq AgOTf (986 μmol, 253 mg) were dissolved in benzene (30 mL) and stirred at room temperature for 2 d. The reaction mixture was filtered through a pad of Celite® and the filter pad was rinsed with additional benzene (50 mL). The filtrate was evaporated in vacuo to afford the product 3 as a brown solid (542 mg, 90%). $^1$H NMR (thf-ds, 600 MHz, 22°C): δ [ppm] = 8.32 (d, J$_{^3}$CH = 7.7 Hz, 2H), 7.94-7.92 (m, 2H), 7.76 (dd, J$_{^3}$CH = 7.4 Hz, J$_{^1}$CH = 7.4 Hz, 2H), 7.59 (dd, J$_{^3}$CH = 7.4 Hz, J$_{^1}$CH = 7.4 Hz, 2H), 3.15-3.08 (m, 2H, $^3$PCH), 2.96-2.92 (m, 2H, $^3$PCH), 1.70-1.66 (m, 6H, $^3$PCH), 1.38-1.35 (m, 6H, $^3$PCH), 1.09-1.05 (m, 6H, $^3$PCH), 0.33-0.29 (m, 6H, $^3$PCH). $^{15}$C($^1$H) NMR (thf-ds, 151 MHz, 22°C): δ [ppm] = 144.1 (Ca, dd, J$_{^3}$P-C = 21.5 Hz, J$_{^1}$P-C = 21.5 Hz, 2C), 142.9 (Ca, dd, J$_{^3}$P-C = 12.6 Hz, J$_{^1}$P-C = 12.6 Hz, 2C), 133.9 (CH, 2C), 132.7 (CH, 2C), 132.5 (CH, dd, J$_{^3}$P-C = 5.1 Hz, J$_{^1}$P-C = 5.1 Hz, 2C), 132.2 (Ca, broad, 2C, C-Mo), 129.6 (CH, 2C), 23.7 (CH, dd, J$_{^3}$P-C = 9.1 Hz, J$_{^1}$P-C = 9.1 Hz, 2C), 23.3 (CH, dd, J$_{^3}$P-C = 7.8 Hz, J$_{^1}$P-C = 7.8 Hz, 2C), 19.2 (CH, dd, J$_{^3}$P-C = 3.2 Hz, J$_{^1}$P-C = 3.2 Hz, 2C), 18.8 (CH, dd, J$_{^3}$P-C = 3.9 Hz, J$_{^1}$P-C = 3.9 Hz, 2C), 18.3 (CHb, broad, 2C), 16.5 (CHa, dd, J$_{^3}$P-C = 3.1 Hz, J$_{^1}$P-C = 3.1 Hz, 2C). $^{31}$P($^1$H) NMR (thf-ds, 243 MHz, 22°C): δ [ppm] = 77.7 (s, 2P). MS (LIFDI, thf): Calcd. for [C$_2$H$_5$F$_3$M$_{0}$N$_2$P$_5$]$: 671.0892. Found: 671.1 [M]$^+$. The expected isotopic pattern agrees well with the measurement. Anal. Calcd. for C$_2$H$_5$F$_3$M$_{0}$N$_2$P$_5$: 669.55 g/mol): C 48.43, H 5.42, N 2.09. Found: C 48.55, H 5.64, N 1.70.

**Synthesis of complex [PCCP]Mo$_2$(CO).**

[Mo$_2$(CO)],[NCMe]((EtCCl)$_2$: (857 μmol, 500 mg) and 1.0 eq 2,2′ bis(diisopropylphosphophenyli)tolane (857 μmol, 352 mg) were dissolved in CH$_2$Cl$_2$ (10 mL) and stirred at room temperature for 20 h. The solvent was removed under reduced pressure and the residue washed with toluene (5 mL). The residual solid was extracted with CH$_2$Cl$_2$ and the CH$_2$Cl$_2$ phase evaporated in vacuo to afford the product as a brown solid (656 mg, 97%). The title compound may as well be synthesized by pressurizing a solution of 1 with CO. Single crystals were obtained from thf/pentane at -40°C. $^1$H NMR (CD$_2$Cl$_2$, 600 MHz, 22°C): δ [ppm] = 8.03 (d, J$_{^3}$CH = 7.3 Hz, 2H), 7.88-7.86 (m, 2H), 7.71-7.66 (m, 4H), 3.49-3.45 (m, 2H, $^3$CH), 3.25-3.19 (m, 2H, $^3$CH), 1.46-1.38 (m, 18H, $^3$CH), 0.82-0.78 (m, 6H, $^3$CH). $^{15}$C($^1$H) NMR (CD$_2$Cl$_2$, 151 MHz, 22°C): δ [ppm] = 229.0 (Ca, 1C, CO), 214.0 (Ca, 2C, C-Mo), 151.1 (Ca, 2C), 143.4(Ca, 2C), 131.8 (CH, 2C), 131.7 (CH, 2C), 130.7 (CH, 2C), 127.0 (CH, 2C), 28.9 (CH, 2C), 25.9 (CH, 2C), 19.4 (CH, 2C), 18.6 (CH, 2C), 18.3 (CH, 2C), 18.0 (CH, 2C). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, 243 MHz, 22°C): δ [ppm] = 53.4 (s, 2P). MS (LIFDI, CH$_2$Cl$_2$): Calcd. for [C$_2$H$_5$F$_3$Mo$_2$P$_5$]: 761.9430. Found: 761.9 [M-CO]$^+$. The expected isotopic pattern agrees well with the measurement. Anal. Calcd. for C$_2$H$_5$F$_3$Mo$_2$P$_5$ (788.30 g/mol): C 41.14, H 4.60. Found: C 41.28, H 4.57. IR (ATR, selected bands only): ν (in cm$^{-1}$) = 1957 (CO stretching vibration).

**Synthesis of complex 4.**

[PCCP]Mo$_2$(CO) (127 μmol, 100 mg) and 2.3 eq KC$_8$ (292 μmol, 39.4 mg) were suspended in thf (3 mL) and the resulting reaction mixture was stirred at room temperature for 30 h. The mixture was filtered through a pad of Celite® and the filter pad was rinsed with thf (10 mL). The filtrate was evaporated to dryness. The crude solid was dissolved in toluene (10 mL) and filtered through a PTFE syringe filter. The resulting clear solution was evaporated in vacuo to afford the title compound as a dark solid (64.4 mg, 95%). Alternatively, cobaltocene may be used as reducing agent. Single crystals for x-ray diffraction were isolated from toluene/pentane at -40°C. Evans Magnetic Moment (thf-ds, 600 MHz, 22°C): μ$_{eff}$ = 1.59μ$_B$. Anal. Calcd. for C$_2$H$_5$MoP$_2$ (661.40 g/mol): C 49.03, H 5.49. Found: C 48.68, H 5.15. IR (ATR, selected bands only): ν (in cm$^{-1}$) = 1839 (CO stretching vibration).
SUPPORTING INFORMATION

Synthesis of complex [7][OTf].

Complex 3 (74.7 µmol, 50.0 mg) was dissolved in thf (2 mL) and excess tert-butyl isocyanide (373 µmol, 42.2 µL) was added and the reaction mixture was stirred at room temperature for 1 h. Once the product started to precipitate from solution, the mixture was stored at -40°C for 1 d to complete precipitation. The supernatant was decanted and the crystalline product was washed twice with thf (2x each). The beige crystals were dried *in vacuo* to afford the title compound (31.2 mg, 56%). Single crystals for x-ray diffraction were grown from CH₂Cl₂/pentane at -40°C. ¹H NMR (CD₂Cl₂, 600 MHz, 22°C): δ [ppm] = 8.31 (d, J sub-H= 7.7 Hz, 2H), 7.91-7.89 (m, 2H), 7.83 (dd, J sub-H= 7.4 Hz, J sub-H= 4.7 Hz), 7.44 (s, 2P), 6.74 (dd, J sub-H= 7.4 Hz, J sub-H= 7.4 Hz), 7.64 (dd, J sub-H= 7.4 Hz, J sub-H= 7.4 Hz), 3.23-3.16 (m, 2H, 2PrCH) 2.58-2.51 (m, 2H, 2PrCH) 1.74 (s, 9H, 2Ch), 1.74-1.71 (m, 6H, 2PrCH) 1.39-1.36 (m, 6H, 2PrCH) 1.14-1.10 (m, 6H, 2PrCH) 0.24-0.20 (m, 6H, 2PrCH). ¹³C{¹H} NMR (CD₂Cl₂, 151 MHz, 22°C): δ [ppm] = 150.1 (C₆, broad, 2C, C-Mo), 144.9 (Cₐ, dd, J sub-Cₐ= 24.1 Hz, J sub-Cₐ= 18.9 Hz, 2C), 140.8 (Cₐ, dd, J sub-Cₐ= 15.5 Hz, J sub-Cₐ= 14.1 Hz 2H), 133.4 (CH, 2C), 133.0 (CH, dd, J sub-Cₐ= 6.7 Hz, J sub-Cₐ= 6.7 Hz, 2C), 133.0 (CH, dd, J sub-Cₐ= 6.7 Hz, J sub-Cₐ= 6.7 Hz, 2C). The expected isotopic pattern agrees well with the measurement. Crystals from CH₂Cl₂/pentane were used for elemental analysis. Anal. Calcld. for [C₆H₄Mo(N=Pr)₂]Cl: C 51.60, H 6.03, N 3.72. Found: C 50.80, H 6.07, N 3.80.

Synthesis of complex 8.

Complex 3 (149 µmol, 100 mg) was dissolved in benzene (4 mL) and 2.0 eq HCl (1 M in Et₂O, 299 µL) was added and the reaction mixture was stirred for 2 h. The beige precipitate was filtered off and dried in vacuo. The thus isolated intermediate, i.e., the chlorido derivative and 2.0 eq AgOTf (299 µmol, 76.8 mg) were dissolved in CH₂Cl₂ (4 mL) and stirred at room temperature for 6 h. The reaction mixture was filtered through a PTFE syringe filter, concentrated on product precipitation, the supernatant was decanted off. The residual solid was washed with a small amount of CH₂Cl₂ and dried in vacuo to afford the title compound as a yellow powder (62.4 mg, 51%). Single crystals for x-ray diffraction were obtained from CH₂Cl₂/pentane at -40°C. ¹H NMR (CD₂Cl₂, 600 MHz, 22°C): δ [ppm] = 8.19 (d, J sub-H= 7.7 Hz, 2H), 7.93-7.92 (m, 2H), 7.79 (dd, J sub-H= 7.5 Hz, J sub-H= 7.5 Hz, 2H), 7.62 (dd, J sub-H= 7.5 Hz, J sub-H= 7.5 Hz, 2H), 6.75 (broad s, 1H, N-H), 3.16-3.05 (m, 4H, 2PrCH), 1.53-1.49 (m, 6H, 2PrCH), 1.47-1.43 (m, 6H, 2PrCH), 1.39-1.35 (m, 6H, 2PrCH), 1.07-1.03 (m, 6H, 2PrCH). ¹³C{¹H} NMR (CD₂Cl₂, 151 MHz, 22°C): δ [ppm] = 143.4 (C₆, 2C), 140.0 (Cₐ, 2C), 139.3 (Cₐ, 2C, C-Mo), 133.0 (CH, 2C), 132.8 (CH, 2C), 132.6 (CH, 2C), 130.5 (CH, 2C), 119.5 (Cₐ, J sub-Cₐ= 318.0 Hz, 2H), 27.5 (CH, 2C, 2PrCH), 26.0 (CH, 2C, 2PrCH), 19.9 (CH₃, 2C, 2PrCH), 19.3 (CH₃, 2C, 2PrCH), 19.2 (CH₃, 2C, 2PrCH), 18.9 (CH₃, 2C, 2PrCH). ³¹P{¹H} NMR (CD₂Cl₂, 243 MHz, 22°C): δ [ppm] = 69.1 (s, 2P). MS (LIFDI, thiF): Calcd. for [C₆H₄Mo(N=Pr)₂]Cl: 605.2170. Found: 605.2 [M⁺].

Synthesis of complex 9.

Complex 3 (149 µmol, 100 mg) was dissolved in benzene (3 mL) and 3.0 eq MoOTf (448 µmol, 50.7 µL) was added dropwise. The resulting reaction mixture was stirred at room temperature for 20 h. The solution was evaporated to dryness and the residue was washed with small amounts of pentane and Et₂O. The solid was extracted with benzene and the extracted solution evaporated under reduced pressure. Recrystallization from thf/pentane afforded 9-thf as a light beige solid (83.1 mg, 66%). Single crystals for x-ray diffraction were grown from CH₂Cl₂/pentane at -40°C. ¹H NMR (CD₃CN, 600 MHz, 22°C): δ [ppm] = 8.34 (d, J sub-H= 7.7 Hz, 2H), 8.02-8.00 (m, 2H), 7.89 (dd, J sub-H= 7.5 Hz, J sub-H= 7.5 Hz), 7.74 (dd, J sub-H= 7.5 Hz, J sub-H= 7.5 Hz), 7.62 (dd, J sub-H= 7.4 Hz, J sub-H= 4.7 Hz), 3.28 (t, J sub-Pr= 3.6 Hz, 3H, N-H), 3.14-3.08 (m, 2H, 2PrCH), 3.05-2.99 (m, 2H, 2PrCH), 1.39-1.35 (m, 6H, 2PrCH), 1.34-1.30 (m, 6H, 2PrCH), 1.29-1.26 (m, 6H, 2PrCH), 1.26-1.22 (m, 6H, 2PrCH). ¹³C{¹H} NMR (CD₃CN, 151 MHz, 22°C): δ [ppm] = 142.9 (C₆, dd, J sub-C₆= 23.1 Hz, J sub-C₆= 20.9 Hz, 2C), 132.9 (Cₐ, dd, J sub-Cₐ= 12.6 Hz, J sub-Cₐ= 12.6 Hz, 2C), 134.2 (CH, 2C), 134.1 (CH, 2C), 134.0 (Cₐ, dd, J sub-Cₐ= 3.4 Hz, J sub-Cₐ= 3.4 Hz, 2C), 133.6 (CH, dd, J sub-Cₐ= 5.8 Hz, J sub-Cₐ= 5.8 Hz, 2C), 131.6 (CH, dd, J sub-Cₐ= 3.1 Hz, J sub-Cₐ= 3.1 Hz, 2C), 59.0 (CH₃, 1C, N-CH₃), 28.0 (CH, dd, J sub-Cₐ= 9.8 Hz, J sub-Cₐ= 9.8 Hz, 2C, 2PrCH), 26.3 (CH, dd, J sub-Cₐ= 10.0 Hz, J sub-Cₐ= 10.0 Hz, 2C, 2PrCH), 19.9 (CH₃, 2C, 2PrCH), 19.5 (CH₃, 2C, 2PrCH), 19.4 (CH₃, 2C, 2PrCH), 19.3 (CH₃, 2C, 2PrCH). ³¹P{¹H} NMR (CD₃CN, 243 MHz, 22°C): δ [ppm] = 69.7 (s, 2P). MS (LIFDI, thiF): Calcd. for [C₆H₄Mo(N=Pr)₂]Cl: 686.1272. Found: 686.1 [M⁺]. The expected isotopic pattern agrees well with the measurement. Crystals from CH₂Cl₂/pentane were used for elemental analysis. Anal. Calcld. for C₂₃H₂₇F₆MoNOP(S)₂: 833.65 g/mol): C 41.78, H 4.72, N 1.68. Found: C 41.98, H 5.07, N 1.57.
**SUPPORTING INFORMATION**

**Synthesis of complex [10][OTf].**

Complex 3 (279 µmol, 187 mg) was dissolved in benzene (8 mL) and excess benzoyl chloride (1.40 mmol, 162 µL) was added. The reaction mixture was stirred at room temperature for 16 h. The solution was concentrated, the precipitate was filtered off and washed with small amounts of benzene. Recrystallization from Et<sub>2</sub>O/CH<sub>3</sub>CN afforded the product as a red solid (129 mg, 57%). Single crystals for X-ray diffraction were isolated from CH<sub>2</sub>Cl<sub>2</sub>/pentane at -40°C. ¹H NMR (CD<sub>3</sub>CN, 600 MHz, 22°C): δ/ppm = 8.45 (d, J<sub>1H,H</sub> = 7.7 Hz, 2H), 7.98-7.95 (m, 2H), 7.91 (dd, J<sub>1H,H</sub> = 7.5 Hz, J<sub>1H,P</sub> = 7.7 Hz, 2H), 7.72 (dd, J<sub>1H,P</sub> = 7.5 Hz, J<sub>1H,H</sub> = 7.5 Hz, 2H), 7.45 (t, J<sub>1H,H</sub> = 7.4 Hz, 1H, benzoyl), 7.24 (d, J<sub>1H,H</sub> = 7.5 Hz, 2H, benzoyl), 7.15 (dd, J<sub>1H,H</sub> = 7.7 Hz, J<sub>1H,P</sub> = 7.7 Hz, 2H, benzoyl), 3.15-3.09 (m, 2H, Pr<sup>1</sup>CH<sub>2</sub>), 2.94-2.88 (m, 2H, Pr<sup>2</sup>CH), 1.49-1.45 (m, 6H, Pr<sup>3</sup>CH<sub>3</sub>), 1.35-1.29 (m, 12H, Pr<sup>3</sup>CH<sub>2</sub>), 0.87-0.83 (m, 6H, Pr<sup>3</sup>CH), 0.67-0.59 (m, 12H, Pr<sup>3</sup>CH<sub>2</sub>), 0.67 (m, 3H, Pr<sup>4</sup>CH). ¹³C<sup>1</sup>[H, ¹³P] NMR (CD<sub>3</sub>CN, 151 MHz, 22°C): δ/ppm = 173.1 (C<sub>q</sub>, 1C, C=C-O), 143.8 (C<sub>q</sub>, 2C), 141.0 (C<sub>q</sub>, 2C, C-Mo), 139.3 (C<sub>q</sub>, 2C), 135.7 (CH, 2C, benzoyl), 134.5 (CH, 2C, benzoyl), 134.0 (CH, 2C), 133.8 (CH, 2C), 132.4 (C<sub>q</sub>, 1C, benzoyl), 131.8 (CH, 2C), 130.6 (CH, 2C, benzoyl), 129.9 (CH, 2C, benzoyl), 121.2 (C<sub>q</sub>, q, J<sub>1C,P</sub> = 321.1 Hz, 1C), 29.2 (CH, 2C, Pr<sup>1</sup>CH), 27.9 (CH, 2C, Pr<sup>2</sup>CH), 20.0 (CH, 2C, Pr<sup>3</sup>CH<sub>2</sub>), 19.8 (CH, 2C, Pr<sup>3</sup>CH), 19.3 (CH, 2C, Pr<sup>3</sup>CH, Pr<sup>4</sup>CH). ¹³P<sup>[1]</sup>H NMR (CD<sub>3</sub>CN, 243 MHz, 22°C): δ/ppm = 67.8 (s, 2P). MS (LIFDI, thf): Calcd. for [C<sub>2</sub>H<sub>12</sub>Cl<sub>2</sub>MoNOP<sub>2</sub>P<sub>2</sub>S]: 662.1400. Found: 662.2 [M]⁺. The expected isotopic pattern agrees well with the measurement. Anal. Calcd. for C<sub>2</sub>H<sub>12</sub>Cl<sub>2</sub>MoNOP<sub>2</sub>P<sub>2</sub>S: C 50.61, H 5.16, N 2.53. Found: C 50.68, H 5.24, N 2.62.

**Synthesis of complex [11][OTf].**

Complex [10][OTf] (61.7 µmol, 50 mg) was dissolved in CH<sub>3</sub>CN (2 mL) and 1.0 eq trans-2,3-butyleneoxide (61.7 µmol, 5.54 µL) was added. The reaction mixture was stirred at 60°C for 3 d. A dark purple solid precipitated upon cooling to -40°C overnight. The solid was decanted and recrystallized from CH<sub>3</sub>CN/Et<sub>2</sub>O at -40°C to afford the product as a dark purple solid with metallic lustre (26.7 mg, 51%). Single crystals for X-ray diffraction were obtained from the mother liquor (i.e. from CH<sub>3</sub>CN) at room temperature and identified as the corresponding N-H deprotonated monocation. ¹H NMR (CD<sub>3</sub>CN, 600 MHz, 22°C): δ/ppm = 9.85 (s, 2H, NH), 8.40 (d, J<sub>1H,H</sub> = 7.7 Hz, 4H), 8.08 (d, J<sub>1H,H</sub> = 7.5 Hz, 7.5 Hz, 4H, Pr<sup>1</sup>CH), 7.96-7.94 (m, 4H), 7.91 (dd, J<sub>1H,H</sub> = 7.6 Hz, J<sub>1H,P</sub> = 7.7 Hz, 4H), 7.76-7.72 (m, 6H, Pr<sup>2</sup>CH), 7.63 (dd, J<sub>1H,H</sub> = 7.8 Hz, J<sub>1H,P</sub> = 7.7 Hz, 4H, Pr<sup>3</sup>CH), 5.65 (s, 2H, alkene), 3.07-3.01 (m, 4H, Pr<sup>3</sup>CH), 2.43-2.39 (m, 4H, Pr<sup>4</sup>CH), 1.34-1.30 (m, 12H, Pr<sup>3</sup>CH), 1.22-1.18 (m, 12H, Pr<sup>3</sup>CH), 0.99-0.96 (m, 12H, Pr<sup>3</sup>CH), 0.71-0.67 (m, 12H, Pr<sup>3</sup>CH). ¹³C<sup>1</sup>[H, ¹³P] NMR (CD<sub>3</sub>CN, 151 MHz, 22°C): δ/ppm = 186.8 (C<sub>q</sub>, 2C, C=C-O), 154.1 (C<sub>q</sub>, 2C, C-Mo), 143.7 (C<sub>q</sub>, dd, J<sub>1C,P</sub> = 21 Hz, J<sub>1P,H</sub> = 14 Hz, 4C), 141.0 (C<sub>q</sub>, 2C, N=C=N⁻H, identified by HMBC NMR). 140.9 (C<sub>q</sub>, dd, J<sub>1C,P</sub> = 14 Hz, J<sub>1P,H</sub> = 13 Hz, 4C), 135.5 (CH, 2C, Pr<sup>1</sup>CH), 134.2 (CH, 4C), 133.1 (CH, dd, J<sub>1C,P</sub> = 5 Hz, J<sub>1P,H</sub> = 5 Hz, 4C), 132.1 (CH, 4C), 130.7 (C<sub>q</sub>, 2C, Pr<sup>2</sup>CH), 130.2 (CH, 4C, Pr<sup>2</sup>CH), 129.4 (CH, 4C, Pr<sup>3</sup>CH), 122.1 (C<sub>q</sub>, q, J<sub>1C,P</sub> = 321.1 Hz, 2C, OTf), 108.4 (CH, 2C, alkene), 27.8 (CH, dd, J<sub>1P,H</sub> = 7 Hz, J<sub>1P,H</sub> = 8 Hz, 4C, Pr<sup>3</sup>CH), 26.5 (CH, dd, J<sub>1P,H</sub> = 10 Hz, J<sub>1P,H</sub> = 10 Hz, 4C, Pr<sup>3</sup>CH), 20.1 (CH, 4C, Pr<sup>4</sup>CH), 19.8 (CH, 2C, Pr<sup>3</sup>CH, Pr<sup>4</sup>CH). ¹³P<sup>[1]</sup>H NMR (CD<sub>3</sub>CN, 243 MHz, 22°C): δ/ppm = 59.4 (s, 4P). MS (LIFDI, CH3CN): Calcd. for [C<sub>17</sub>H<sub>33</sub>ClMo2N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>S]: 1401.3755. Found: 1401.4 [M-Cl-OH]⁺. The expected isotopic pattern agrees well with the measurement. Anal. Calcd. for C<sub>17</sub>H<sub>33</sub>ClMo2N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>S: C 51.08, H 5.29, N 3.26. Found: C 51.51, H 5.36, N 3.49.
Preliminary Experiments (See Article)

Synthesis of complex [PCCP]MoNeI(OTf)₂.
In an NMR tube, complex 3 (17.9 μmol, 12.0 mg) was dissolved in benzene and excess ethyl iodide (125 μmol, 10.0 μL) was added. The reaction mixture was kept at 65°C for 2 d before 1.0 eq AgOTf (17.9 μmol, 4.60 mg) was added at room temperature. After 3 h the reaction mixture was filtered through a PTFE syringe filter and the resulting clear solution was dried in vacuo. The beige solid was dissolved in C₆D₆ for NMR characterization. ¹H NMR (C₆D₆, 600 MHz, 22°C): δ [ppm] = 7.89 (d, 3JCH = 7.6 Hz, 2H), 7.41-7.39 (m, 2H), 7.24 (dd, 3JCH = 7.3 Hz, 3JCH = 7.3 Hz, 2H), 7.05 (dd, 3JCH = 7.4 Hz, 3JCH = 7.4 Hz, 2H), 3.51-3.46 (m, 2H, 6CH₂), 3.19-3.13 (m, 4H, 4PCH), 1.70-1.66 (m, 6H, 6PCH), 1.39-1.35 (m, 6H, 6PCH), 1.09-1.04 (m, 12H, 8PCH), 0.22 (t, 3JCH = 7.0 Hz, 3H, 31CH₃). 31P(¹H) NMR (C₆D₆, 243 MHz, 22°C): δ [ppm] = 65.2 (s, 2P).

Synthesis of complex [PCCP]MoNSiMe₃(Cl)][OTf].
Complex 3 (149 μmol, 100 mg) was dissolved in benzene (4 mL) and excess trimethylsilyl chloride (747 μmol, 94.8 μL) was added and the reaction mixture was stirred for 20 h. The bright blue precipitate was filtered off and washed with benzene to afford the product (51.0 mg) for characterization. The product is not stable in solution, which interfered with the collection of ³¹C NMR spectroscopic data. ¹H NMR (thf-d₈, 600 MHz, 22°C): δ [ppm] = 8.65 (d, 3JCH = 6.6 Hz, 2H), 8.22 (broad s, 2H), 7.97 (dd, 3JCH = 7.2 Hz, 3JCH = 7.2 Hz, 2H), 7.81 (dd, 3JCH = 7.1 Hz, 3JCH = 7.1 Hz, 2H), 3.60-3.54 (m, 2H, 6PCH), 2.92-2.87 (m, 2H, 4PCH), 1.79-1.75 (m, 6H, 6PCH), 1.37-1.31 (m, 12H, 8PCH), 0.16-0.12 (m, 6H, 8PCH), -0.38 (broad s, 9H, 3¹MSCH₃), 31P(¹H) NMR (thf-d₈, 243 MHz, 22°C): δ [ppm] = 78.5 (broad s, 2P). Anal. Calcd. for C₃₀H₄₅ClF₃MoNO₃P₂₃Si (778.19 g/mol) thf: C 48.03, H 6.28, N 1.65. Found: C 47.72, H 6.06, N 1.63.

Synthesis of complex [PCCP]MoNSiMe₃(OTf). Complex 3 (44.7 μmol, 30 mg) was dissolved in benzene (4 mL) and excess trimethylsilyl chloride (224 μmol, 28.4 μL) was added and the reaction mixture was stirred at room temperature for 17 h. The reaction mixture was evaporated to dryness and the residue was re-dissolved in benzene/thf (10 mL/1 mL) and 1.0 eq AgOTf (44.7 μmol, 11.5 mg) was added. The mixture was stirred at room temperature for 5 h, which led to the precipitation of AgCl. The latter silver salt was removed by filtration through a PTFE syringe filter. The filtrate was concentrated and stored at -40°C. By decanting the supernatant, the beige precipitate was isolated and dried in vacuo to afford the product in sufficient amounts to allow for a characterization by NMR spectroscopy. ¹H NMR (thf-d₈, 600 MHz, 22°C): δ [ppm] = 8.31 (d, 3JCH = 7.7 Hz, 2H), 7.94-7.92 (m, 2H), 7.74 (dd, 3JCH = 7.5 Hz, 3JCH = 7.5 Hz, 2H), 7.58 (dd, 3JCH = 7.4 Hz, 3JCH = 7.4 Hz, 2H), 3.15-3.09 (m, 2H, 4PCH), 3.00-2.95 (m, 2H, 6PCH), 1.72-1.68 (m, 6H, 8PCH), 1.38-1.35 (m, 6H, 8PCH), 1.16-1.12 (m, 6H, 8PCH), 0.40 (broad s, 9H, 3¹MSCH₃), 0.39-0.35 (m, 6H, 8PCH), 3¹P(¹H) NMR (thf-d₈, 243 MHz, 22°C): δ [ppm] = 77.2 (broad s, 2P).

Synthesis of complex [(PCCP)Mo(β-benzoyl-NCPh)][OTf].
Complex 10(OTf) (24.7 μmol, 20.0 mg) and 1.0 eq AgOTf (24.7 μmol, 6.34 mg) were suspended in thf (1 mL) and excess benzonitrile (50.0 μmol, 5.16 μL) was added and the reaction mixture was stirred at room temperature for 2.5 h. The reaction mixture was filtered through a PTFE syringe filter and evaporated to dryness. The residue was washed once with Et₂O/pentane and twice with Et₂O. After drying in vacuo the product was obtained as a dark red solid in sufficient amounts to allow for a characterization by NMR spectroscopy. ¹H NMR (thf-d₈, 600 MHz, 22°C): δ [ppm] = 8.45 (d, 3JCH = 7.3 Hz, 2H, 4PCCPCH), 8.04-8.03 (m, 2H, 4PCCPCH), 7.96 (d, 3JCH = 7.5 Hz, 2H, benzyloxyCH), 7.84 (dd, 3JCH = 7.4 Hz, 3JCH = 7.3 Hz, 2H, 4PCCPCH), 7.71 (d, 3JCH = 7.3 Hz, 2H, benzylCH), 7.66-7.62 (m, 3H, 4PCCPCH, 4PCCPCH, 4PCCPCH), 7.56-7.50 (m, 3H, 4PCCPCH, benzyloxyCH), 7.34 (dd, 3JCH = 7.6 Hz, 3JCH = 7.6 Hz, 2H, benzylCH), 3.34-3.28 (m, 2H, 4PCH), 3.15-3.09 (m, 2H, 4PCH), 1.58-1.54 (m, 6H, 8PCH), 1.49-1.46 (m, 6H, 8PCH), 1.19-1.16 (m, 6H, 8PCH), 1.04-1.00 (m, 6H, 8PCH). 3¹P(¹H) NMR (thf-d₈, 243 MHz, 22°C): δ [ppm] = 69.2 (2P).
Figure S1. $^1$H NMR spectrum of 1 (thf-d$_8$, 600 MHz, 22°C).

Figure S2. $^{13}$C($^1$H) NMR spectrum of 1 (thf-d$_8$, 151 MHz, 22°C).
Figure S3. $^{31}$P [$^1$H] NMR spectrum of 1 (thf-d$_8$, 243 MHz, 22°C).

Figure S4. $^1$H NMR spectrum of 2 (thf-d$_8$, 600 MHz, 22°C).
Figure S5. $^{13}$C($^1$H) NMR spectrum of 2 (thf-d$_8$, 151 MHz, 22°C).

Figure S6. $^{31}$P($^1$H) NMR spectrum of 2 (thf-d$_8$, 243 MHz, 22°C).
Figure S7. $^{31}$P$[{^1}H]$ NMR spectrum of 2-$^{15}$N (thf-d$_8$, 243 MHz, 22°C).

Figure S8. $^{15}$N$[{^1}H]$ NMR spectrum of 2-$^{15}$N (thf-d$_8$, 61 MHz, 22°C).
Figure S9. $^1$H NMR spectrum of 3 (thf-d$_8$, 600 MHz, 22°C).

Figure S10. $^{13}$C($^1$H) NMR spectrum of 3 (thf-d$_8$, 151 MHz, 22°C).
Figure S11. $^{31}$P($^1$H) NMR spectrum of 3 (thf-d$_8$, 243 MHz, 22°C).

Figure S12. $^1$H NMR spectrum of [PCCP]MoI$_2$(CO) (CD$_2$Cl$_2$, 600 MHz, 22°C).
Figure S13. $^{13}$C($^1$H, $^{31}$P) NMR spectrum of [PCCP]MoI$_2$(CO) (CD$_2$Cl$_2$, 151 MHz, 22°C).

Figure S14. $^{31}$P($^1$H) NMR spectrum of [PCCP]MoI$_2$(CO) (CD$_2$Cl$_2$, 243 MHz, 22°C).
Figure S15. $^1$H NMR spectrum of [7][OTf] (CD$_2$Cl$_2$, 600 MHz, 22°C).

Figure S16. $^{13}$C($^1$H) NMR spectrum of [7][OTf] (CD$_2$Cl$_2$, 151 MHz, 22°C).
Figure S17. $^{31}$P/$^1$H NMR spectrum of [7]/OTf (CD$_2$Cl$_2$, 243 MHz, 22°C).

Figure S18. $^1$H NMR spectrum of 8 (CD$_2$Cl$_2$, 600 MHz, 22°C).
**Figure S19.** $^{13}$C($^{1}$H, $^{31}$P) NMR spectrum of 8 (CD$_2$Cl$_2$, 151 MHz, 22°C).

**Figure S20.** $^{31}$P($^{1}$H) NMR spectrum of 8 (CD$_2$Cl$_2$, 243 MHz, 22°C).
Figure S21. $^{15}$N-$^1$H HMBC NMR spectrum of 8 (CD$_2$Cl$_2$, 61 MHz, 600 MHz, 22°C).

Figure S22. $^1$H NMR spectrum of 9·thf (CD$_3$CN, 600 MHz, 22°C). The signals of residual thf from crystallization are not integrated (approx. 1eq).
Figure S23. $^{13}$C{$^{1}$H} NMR spectrum of 9·thf (CD$_2$Cl$_2$, 151 MHz, 22°C).

Figure S24. $^{31}$P{$^{1}$H} NMR spectrum of 9·thf (CD$_3$CN, 243 MHz, 22°C).
Figure S25. $^1$H NMR spectrum of [10][OTf] (CD$_3$CN, 600 MHz, 22°C).

Figure S26. $^{13}$C($^1$H) NMR spectrum of [10][OTf] (CD$_3$CN, 151 MHz, 22°C).
Figure S27. $^{31}P(\textsl{H})$ NMR spectrum of [10][OTf] (CD$_3$CN, 243 MHz, 22°C).

Figure S28. $^1$H NMR spectrum of [11][OTf]$_2$ (CD$_3$CN, 800 MHz, 22°C).
Figure S29. $^{13}$C{[$^1$H]} NMR spectrum of [11][OTf]$_2$ (CD$_3$CN, 151 MHz, 22°C).

Figure S30. $^{31}$P{[$^1$H]} NMR spectrum of [11][OTf]$_2$ (CD$_3$CN, 243 MHz, 22°C).
NMR spectroscopic monitoring of the conversion 1→2. The conversion of 1→2 was monitored by $^{31}$P{1H} NMR spectroscopy at 22°C (see Figure S31). Prior to the measurement, the sample was kept at −78°C in the dark. Given that the sample was not removed from the magnet during the measurement, a photochemical N$_2$-splitting was excluded. In a separate experiment, a pre-cooled sample was injected into the pre-cooled NMR spectrometer (−40°C). When the temperature was slowly raised to 0°C, an essentially blank $^1$H NMR spectrum was recorded (see Figure S32), i.e. no diamagnetic intermediates of the reaction were detectable. This is in line with the proposed $S = 1$ ground state of $^6$E. Upon raising the temperature to 22°C, the formation of 2 was observed.

Figure S31. Conversion of 1 to 2 determined by $^{31}$P{1H} NMR spectroscopy (thf-d$_8$, 243 MHz, 22°C).

Figure S32. $^1$H NMR (thf-d$_8$, 400 MHz, 0°C) of the reaction mixture (1 + Na/Pb) after slowly raising the temperature from −40°C to 0°C. Only the signals of residual undeuterated thf and the signal of a minor silicon grease impurity were detected.
## Computational Data

The geometries of the monomeric compounds 1 (S = 0), 2 (S = 0) and 5 (S = 1/2) were optimized using the ORCA program suite (version 4.2.1). All atoms were described with the spin unrestricted (UKS) PBE0 functional in conjunction with the valence triple-ζ basis set Def2-TZVP including polarization functions. The RJCOSX approximation was employed using the auxiliary def2/J basis set. Dispersion interactions (GD3) and solvation effects (CPCM for thf) were taken into account during the geometry optimizations. The structures were identified as minima by numerical frequency calculations.

For 1, an alternative electronic structure with one unpaired electron on the ligand was considered using a broken symmetry BS(1,1) ansatz. This ansatz, however, converged to a solution with one unpaired electron on the ligand and three unpaired electrons on the metal, i.e. an overall triplet due to antiferromagnetic coupling. Compared to the singlet, this solution is higher in energy and interpreted as an excited state. Given that a singlet ground state is observed experimentally, this solution was excluded. For 2, a similar BS(1,1) converged to the closed shell singlet.

To confirm the spin ground states configurations of 1, 2 and 5, CASSCF calculations were carried out on the optimized geometries. Energies were corrected by second-order perturbation theory (NEVPT2). The active space was chosen as stated in captions of Figures S33 - S35. The root 0 configurations and the optimized coordinates for 1, 2 and 5 are provided below.

### CASSCF states for 1 (MULT= 1)

| Root 0 | E | E0 (E0+dE) | Total Correction: dE |
|--------|---|------------|-----------------------|
| 0.89892 | -2348.4364988322 | | |
| 0.00838 | 71.0022000000 | 0.00323 | 427; 202220000 |
| 0.00743 | 167; 2121110100 | 0.00271 | 29; 221110010 |
| 0.00671 | 835; 121211000 | 0.00264 | 1809; 02220020 |
| 0.00670 | 11; 222002000 | | |
| 0.00602 | 214; 211210010 | | |
| 0.00580 | 28; 221110010 | | |
| 0.00568 | 795; 122101100 | | |
| 0.00420 | 213; 211210010 | | |
| 0.00348 | 1057; 112200010 | | |
| 0.00340 | 176; 212100110 | | |
| 0.00330 | 796; 122101010 | | |

### CASSCF states for 2 (MULT= 1)

| Root 0 | E | E0 (E0+dE) | Total Correction: dE |
|--------|---|------------|-----------------------|
| 0.83483 | -2106.3260708320 | | |
| 0.01291 | 35; 22221110000 | 0.00345 | 2076; 22112000020 |
| 0.01252 | 7; 22220020000 | 0.00304 | 1639; 2212101010 |
| 0.01290 | 15125; 22222002000 | 0.00274 | 2073; 22112200200 |
| 0.00909 | 32432; 11222001010 | | |
| 0.00889 | 111; 22220200000 | | |
| 0.00814 | 351; 22211201010 | | |
| 0.00542 | 26385; 121222001010 | | |
| 0.00408 | 3876; 222200000020 | | |
| 0.00402 | 49732; 02222002000 | | |
| 0.00390 | 785; 2222200002000 | | |
| 0.00390 | 1649; 222120000 | | |

### CASSCF states for 5 (MULT= 2)

| Root 0 | E | E0 (E0+dE) | Total Correction: dE |
|--------|---|------------|-----------------------|
| 0.84833 | -2160.7662078478 | | |
| 0.01419 | 384; 2222021200000 | 0.00314 | 1563; 22121110010 |
| 0.01387 | 147; 2222111110000 | 0.00354 | 1639; 22121201010 |
| 0.00993 | 47; 2222201020000 | 0.00274 | 2073; 22112200200 |
| 0.00839 | 11522; 22220200000 | | |
| 0.00778 | 2457; 2222022000020 | | |
| 0.00779 | 2457; 22222101010 | | |
| 0.00609 | 26639; 21122101010 | | |
| 0.00337 | 76359; 121221011100 | | |
| 0.00326 | 9; 22221110000 | | |
Optimized coordinates of 1 (S = 0, UKS PBE0/def2-TZVP-GD3-PCM(thf) RUCOSX level of theory)

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | -3.723266000 | 2.336735000 | -4.508284000 |
| H    | 0.377125000  | 1.704733000 | -3.430950000 |
| H    | -4.464403000 | 1.250398000 | -2.424947000 |
| H    | -2.033678000 | -1.750521000 | -2.642316000 |
| H    | -4.576872000 | -1.105379000 | -2.476448000 |
| H    | 5.076124000  | 1.630476000 | -2.225691000 |
| H    | 2.620858000  | 1.389455000 | -2.445006000 |
| H    | -4.826141000 | -2.753627000 | -1.906828000 |
| H    | -2.469767000 | -3.348175000 | -2.023457000 |
| H    | -1.223494000 | -2.401212000 | -1.210454000 |
| H    | -5.430614000 | -1.404451000 | -0.952357000 |
| H    | 2.746805000  | -2.467277000 | -0.596700000 |
| H    | 6.220587000  | 0.866593000 | -0.177184000 |
| H    | -3.956323000 | 2.656459000  | -0.226276000 |
| H    | -5.039693000 | 0.424517000  | -0.159725000 |
| H    | 2.172070000  | -4.047655000 | -0.048549000 |
| H    | 1.029736000  | -2.720451000 | -0.255734000 |
| H    | -3.354991000 | -2.339071000 | 0.048969000  |
| H    | -5.094274000 | 2.521490000  | 1.120108000  |
| H    | 4.454293000  | -2.481842000 | 1.416083000  |
| H    | -3.352732000 | 2.420266000  | 1.417150000  |
| H    | 3.796545000  | -0.078714000 | 1.765351000  |
| H    | 4.944958000  | -0.171681000 | 1.658551000  |
| H    | -4.664613000 | -1.141259000 | 1.739126000  |
| H    | -5.469646000 | 0.335209000  | 2.287631000  |
| H    | 1.539610000  | -3.097330000 | 2.138522000  |
| H    | -3.739953000 | 0.101220000  | 2.587484000  |
| H    | 3.838883000  | -2.859919000 | 3.047180000  |
| H    | 3.410770000  | 1.496165000  | 2.980775000  |
| H    | 3.490302000  | -0.930395000 | 3.525794000  |
| H    | 1.801245000  | 1.604259000  | 3.690105000  |
| H    | 1.466844000  | -2.123372000 | 4.364624000  |
| H    | 0.602733000  | -0.587365000 | 4.466888000  |
| H    | 3.195061000  | 1.188754000  | 4.707678000  |
| H    | 2.000016000  | -0.887761000 | 5.512608000  |
| I    | -1.301525000 | -2.542103000 | 2.077155000  |
| I    | -0.803693000 | 1.825252000  | 2.553627000  |
| Mo   | -0.410104000 | -0.232461000 | 0.848850000  |
| P    | -2.707673000 | -0.075188000 | -0.198869000 |
| P    | 1.874821000  | -0.783606000 | 1.778556000  |

H atoms omitted
Optimized coordinates of 2 (S = 0, UKS PBE0/def2-TZVP-GD3-PCM(thf) RIJCOSX level of theory)

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Mo   | -0.000226000 | -0.148482000 | 0.507820000 |
| I    | -0.000020000 | -2.833607000 | -0.407089000 |
| P    | 2.516488800 | -0.208682000 | 0.177422000 |
| P    | -2.516742000 | -0.208574000 | 0.176641000 |
| N    | -0.000730000 | -0.112566000 | 2.153982000 |
| C    | 3.025535000 | 1.534408000 | 0.029945000 |
| C    | 1.938425000 | 2.403233000 | -0.138327000 |
| C    | 2.160758000 | 3.767346000 | -0.336532000 |
| H    | 1.319465000 | 4.436685000 | -0.472316000 |
| C    | 3.456347000 | 4.255193000 | -0.339739000 |
| H    | 3.632111000 | 5.314688000 | -0.486035000 |
| C    | 4.533276000 | 3.395819000 | -0.142973000 |
| H    | 5.543104000 | 3.788864000 | -0.132220000 |
| C    | 4.320791000 | 2.035660000 | 0.038855000 |
| H    | 5.167962000 | 1.378726000 | 0.194201000 |
| C    | -3.025940000 | 1.534470000 | 0.029140000 |
| C    | -1.938647000 | 2.403410000 | -0.138181000 |
| C    | -2.160914000 | 3.767769000 | -0.334791000 |
| H    | -1.319510000 | 4.437237000 | -0.469194000 |
| C    | -3.456808000 | 4.255705000 | -0.337591000 |
| H    | -3.632073000 | 5.315437000 | -0.482303000 |
| C    | -4.533482000 | 3.396116000 | -0.141980000 |
| H    | -5.543327000 | 3.789125000 | -0.130928000 |
| C    | -4.321025000 | 2.035966000 | 0.038562000 |
| H    | -5.168329000 | 1.378762000 | 0.193359000 |
| C    | 0.640402000 | 1.796547000 | -0.046557000 |
| C    | -0.640630000 | 1.796646000 | -0.046575000 |

H atoms omitted
Optimized coordinates of 5 (S = 1/2, UKS PBE0/def2-TZVP-GD3-PCM(thf) RIJCOSX level of theory)

H atoms omitted
Figure S33. Natural frontier orbitals of 2 derived from a NEVPT2-CASSCF(9,8) calculation (molecular geometry optimized on the PBE0/def2-TZVP-GD3-PCM(thf) level of theory). Active space: π|| (2e\textsuperscript{−}), π\perp (2e\textsuperscript{−}), 5 d-orbitals (4e\textsuperscript{−}), π||\textsuperscript{*} and π\perp\textsuperscript{*} with overall 8e\textsuperscript{−}. 
Figure S34. Natural frontier orbitals of 3 derived from a NEVPT2-CASSCF(12,12) calculation (molecular geometry optimized on the PBE0/def2-TZVP-GD3-PCM(thf) level of theory). Active space: $n_{\parallel}$ (2e$^-$), $n_{\perp}$ (2e$^-$), $n_{\sigma}$ (2e$^-$), $n_{\pi}$ (2e$^-$), $n_{\delta}$ (2e$^-$), 5 d-orbitals (2e$^-$), $n_{\parallel}^*$ and $n_{\perp}^*$ with overall 12e$^-$. 

$\pi_{\parallel} - d_{\nu'\nu'}$

$\pi_{\parallel} - d_{\nu'\nu'}$

$d_{\nu'\nu'} - p_{\nu'\nu'}$

$\pi_{\parallel}^* - d_{\nu'\nu'}$

$\pi_{\parallel}^* - d_{\nu'\nu'}$

$\pi_{\parallel}^* - d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

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$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$

$\delta_{\parallel} - \pi_{\parallel}^* + d_{\nu'\nu'}$
Figure S35. Natural frontier orbitals of 5 derived from a NEVPT2-CASSCF(13,13) calculation (molecular geometry optimized on the UKS-PBE0/def2-TZVP-GD3-PCM(thf) level of theory). Active space: $\pi_{||} - d_{x^2-y^2}$, $\pi_{\perp} - d_{z^2}$, $\pi_{||}^* - d_{xy} \mid ^{NN} \pi_{yz}^*$, $d_{xz} - ^{NN} \pi_{xz}^*$, $\pi_{\perp}^* - d_{yz}$, $d_{yz} - ^{NN} \pi_{yz}^*$, $d_{xz} + ^{NN} \pi_{xz}^*$, $\pi_{\parallel}^* + d_{xy}$, $\pi_{\perp}^* + d_{yz} + ^{NN} \pi_{y}$, $\pi_{\perp} + d_{xz} + ^{NN} \pi_{xz}$, $d_{yz} + ^{NN} \pi_{yz}$, $\pi_{||} \mid ^{NN} \pi_{xz}$, $\pi_{||} + d_{x^2-y^2}$, $\pi_{\parallel}^*$, $\pi_{\perp}^*$, $\pi_{\parallel}^*$, $\pi_{\perp}^*$ and $\pi_{\parallel}^*$ with overall 13e⁻.
Comparison to related complexes. To evaluate the role of the [PCCP] ligand scaffold in 1 and 2, a computational comparison to related [PNP]-, [PPP]- and [PCP]-coordinated complexes seemed appropriate. Given that an \(S = 0\) ground state was found for 1 and 2, all related species, i.e. 1-py, 2-py, 1-P₃, 2-P₃, 1-NHC and 2-NHC,\(^{[14]}\) were treated using a spin restricted approach (\(S = 0\); note that some of the complexes shown in Figure S36 have not been observed experimentally, for 1-py\(^{[14]}\) an \(S = 1\) ground state was found experimentally). To allow for an accurate comparison (vide infra), only complexes bearing neutral ligands have been selected for our analysis. The structures of all these species (see Figure S36) were optimized with Gaussian 16 (G16RevB.01)\(^{[15]}\) using the PBE1PBE functional.\(^{[6]}\) All atoms were described with the valence triple-ζ basis set Def2-TZVP including polarization functions.\(^{[7]}\) The optimized structures are shown in Figure S37. Optimized coordinates for 1-py, 2-py, 1-P₃, 2-P₃, 1-NHC and 2-NHC are provided below.

As mentioned in the article, a certain degree of non-innocence is noticed upon comparing the alkyne unit in and 2 (as judged on basis of the \(^{13}\)C NMR chemical shifts of the alkyne carbons and on basis of metrical parameters). This non-innocence is also reflected in the IR spectra of 1 and 2, which were modeled computationally to verify the assignment of the bands (see Figure S38). A lower \(\nu(C\equiv C)\) is found for the alkyne in 1 as compared to 2, which is in line with a stronger C≡C bond in 2. Hence, electron donation from the alkyne to the molybdenum is less pronounced in 2, implying that the alkyne in 2 is best interpreted as a 2e°-donor. In 1, the alkyne is best interpreted as a 4e°-donor (see article). Overall, the electronic structure of the alkyne is altered significantly during the conversion of 1 to 2 (ligand non-innocence).

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**Figure S36.** Structures of 1 and 2 together with related complexes bearing a [PNP] (1-py and 2-py), [PPP] (1-P₃ and 2-P₃) or [PCP] (1-NHC and 2-NHC) ligand scaffold.

**Figure S37.** DFT-optimized structures of 1, 2, 1-py, 2-py, 1-P₃, 2-P₃, 1-NHC and 2-NHC.
Given that the non-innocence of the alkyne units in 1 and 2 is reflected in our DFT analysis (see IR spectroscopic analysis provided above), different DFT-calculated charges (on the donor atoms and on the central molybdenum atom) in all complexes 1, 2, 1-py, 2-py, 1-P₃, 2-P₃, 1-NHC and 2-NHC were compared to estimate the influence of the individual ligand scaffolds. The Hirshfeld, Voronoi, AIM (Bader’s atoms in molecules theory), NPA (natural population analysis) and CM5 (charge model 5) charge partitioning schemes have been probed for this analysis (see Table S1). All charges were calculated using the MultiWFN 3.7 program suite in conjunction with NBO 7.0 for NPA charges. As pointed out previously, AIM charges are well-suited to roughly estimate the oxidation states of the atoms in question. To estimate the electronic differences at the molybdenum cores during N₂-cleavage, the AIM charge differences at the Mo centers were inspected (see Table S2). The smallest difference is found between 1 and 2 (AIM charge difference = 0.285, see Table S2). For the pyridine- and NHC-based ligands, higher AIM charge differences are noticed at the respective Mo cores (0.342 1-py vs. 2-py and 0.356 for 1-NHC vs. 2-NHC), i.e. the charges are not leveled out as well as in 1 vs. 2. In comparison to the [PCCP] pincer ligand used herein, this is indicative of a less pronounced non-innocence of the pyridine and NHC-based ligand, respectively. For the molybdenum cores in 1-P₃ and 2-P₃, the highest AIM charge difference was found (0.392). Overall, these observations are in line with the expectations: Electron delocalization and redistribution (between the ligand and the metal) is most likely in 1 vs. 2 (as implied by CASSCF calculations, vide supra) and least likely for 1-P₃ vs. 2-P₃, given that the overlap between the metal-centered d-orbitals and the σ⁺ₚₓc orbitals is far from ideal in the latter complexes.

Table S1. Charges on the donor atoms and the central molybdenum atom in complexes 1, 2, 1-py, 2-py, 1-P₃, 2-P₃, 1-NHC and 2-NHC.

| compound | atom(s)     | Hirshfeld | Voronoi | AIM [b] | NPA [b] | CM5   |
|----------|-------------|-----------|---------|---------|---------|-------|
| 1        | Mo          | 0.370     | 0.422   | 1.197   | -0.107  | 0.752 |
|          | C≡C [a]     | -0.210    | -0.301  | -0.649  | -0.183  | -0.361|
| 2        | Mo          | 0.408     | 0.534   | 1.482   | 0.230   | 1.106 |
|          | C≡C [a]     | -0.206    | -0.282  | -0.581  | -0.213  | -0.311|
| 1-py     | Mo          | 0.268     | 0.252   | 0.936   | -0.251  | 0.640 |
|          | py-N        | -0.083    | -0.116  | -1.208  | -0.398  | -0.359|
| 2-py     | Mo          | 0.292     | 0.365   | 1.278   | 0.108   | 1.006 |
|          | py-N        | -0.083    | -0.101  | -1.211  | -0.437  | -0.356|
| 1-P₃     | Mo          | 0.238     | 0.228   | 0.822   | -0.539  | 0.638 |
|          | central P   | 0.145     | 0.112   | 1.526   | 1.178   | -0.111|
| 2-P₃     | Mo          | 0.273     | 0.365   | 1.214   | -0.103  | 0.981 |
|          | central P   | 0.181     | 0.124   | 1.584   | 1.074   | -0.074|
| 1-NHC    | Mo          | 0.275     | 0.307   | 0.975   | -0.265  | 0.626 |
|          | NHC-C       | -0.052    | -0.120  | 0.612   | 0.332   | 0.022 |
| 2-NHC    | Mo          | 0.306     | 0.418   | 1.331   | 0.047   | 0.990 |
|          | NHC-C       | -0.034    | -0.090  | 0.719   | 0.287   | 0.055 |

[a] Sum of charges on both alkyne carbons; [b] determined via basin analysis (incl. refinement of the basin boundaries) using MultiWFN 3.7; [c] determined using NBO 7.0.
Table S2. Charge differences on the central molybdenum atom in complexes 1-2, 1-py, 2-py, 1-Pt, 2-Pt, 1-NHC and 2-NHC.

| compounds | Hirshfeld | Voronoi | AIM | NPA | CM5 |
|-----------|-----------|---------|-----|-----|-----|
| 1          | 0.038     | 0.112   | 0.285 | 0.337 | 0.354 |
| 1-py       | 0.024     | 0.113   | 0.342 | 0.359 | 0.366 |
| 1-Pt       | 0.035     | 0.137   | 0.392 | 0.436 | 0.343 |
| 1-NHC      | 0.031     | 0.111   | 0.356 | 0.552 | 0.364 |

Optimized coordinates of 1-py (S = 0, RKS PBE1PBE/def2-TZVP)

![Diagram of 1-py](image)

H atoms omitted

| H atoms omitted | Mo | 1.194143000 | 0.983555000 | 2.893500000 |
|-----------------|----|-------------|-------------|-------------|
|                 | P  | -2.117157000 | 0.056448000 | -0.578263000 |
|                 | P  | -2.162644000 | 0.211098000 | -0.579120000 |
|                 | N  | -0.998141000 | 1.731810000 | -0.517480000 |
|                 | C  | -3.506971000 | -0.927227000 | 0.350883000 |
|                 | C  | -3.635821000 | -2.326726000 | -0.246354000 |
|                 | H  | -4.073990000 | -2.321084000 | -1.251919000 |
|                 | H  | -2.998990000 | -2.855959000 | -0.267885000 |
|                 | H  | -4.335914000 | -2.920726000 | 0.387536000 |
|                 | C  | -4.867986000 | -0.228636000 | 0.387679000 |
|                 | H  | -5.327256000 | -0.120760000 | -0.592405000 |
|                 | H  | -5.543354000 | -0.835706000 | 0.999429000 |
|                 | H  | -4.813308000 | 0.755515000 | 0.856700000 |
|                 | C  | -3.035680000 | -1.087486000 | 1.795999000 |
|                 | H  | -2.081929000 | -1.616805000 | 1.862820000 |
|                 | H  | -2.932422000 | -0.135285000 | 2.317666000 |
|                 | H  | -3.776563000 | -1.685591000 | 2.337420000 |
|                 | C  | -2.586360000 | 0.048066000 | -2.434242000 |
|                 | H  | -1.898875000 | -1.164415000 | -3.058366000 |
|                 | H  | -2.293306000 | -2.107216000 | -2.677172000 |
|                 | H  | -2.047131000 | -1.148773000 | -4.143771000 |
|                 | H  | -0.826909000 | -1.155483000 | -2.856615000 |
|                 | C  | -4.070284000 | 0.040979000 | -2.793890000 |
|                 | H  | -4.582477000 | -0.874909000 | -2.503944000 |
|                 | H  | -4.602493000 | 0.890971000 | -2.361246000 |
|                 | H  | -4.156933000 | 0.129168000 | -3.882641000 |
|                 | C  | -2.003212000 | 1.328081000 | -3.036712000 |

Optimized coordinates of 1-py (S = 0, RKS PBE1PBE/def2-TZVP)

![Diagram of 1-py](image)

H atoms omitted

| H atoms omitted | Mo | 1.194143000 | 0.983555000 | 2.893500000 |
|-----------------|----|-------------|-------------|-------------|
|                 | P  | -2.117157000 | 0.056448000 | -0.578263000 |
|                 | P  | -2.162644000 | 0.211098000 | -0.579120000 |
|                 | N  | -0.998141000 | 1.731810000 | -0.517480000 |
|                 | C  | -3.506971000 | -0.927227000 | 0.350883000 |
|                 | C  | -3.635821000 | -2.326726000 | -0.246354000 |
|                 | H  | -4.073990000 | -2.321084000 | -1.251919000 |
|                 | H  | -2.998990000 | -2.855959000 | -0.267885000 |
|                 | H  | -4.335914000 | -2.920726000 | 0.387536000 |
|                 | C  | -4.867986000 | -0.228636000 | 0.387679000 |
|                 | H  | -5.327256000 | -0.120760000 | -0.592405000 |
|                 | H  | -5.543354000 | -0.835706000 | 0.999429000 |
|                 | H  | -4.813308000 | 0.755515000 | 0.856700000 |
|                 | C  | -3.035680000 | -1.087486000 | 1.795999000 |
|                 | H  | -2.081929000 | -1.616805000 | 1.862820000 |
|                 | H  | -2.932422000 | -0.135285000 | 2.317666000 |
|                 | H  | -3.776563000 | -1.685591000 | 2.337420000 |
|                 | C  | -2.586360000 | 0.048066000 | -2.434242000 |
|                 | H  | -1.898875000 | -1.164415000 | -3.058366000 |
|                 | H  | -2.293306000 | -2.107216000 | -2.677172000 |
|                 | H  | -2.047131000 | -1.148773000 | -4.143771000 |
|                 | H  | -0.826909000 | -1.155483000 | -2.856615000 |
|                 | C  | -4.070284000 | 0.040979000 | -2.793890000 |
|                 | H  | -4.582477000 | -0.874909000 | -2.503944000 |
|                 | H  | -4.602493000 | 0.890971000 | -2.361246000 |
|                 | H  | -4.156933000 | 0.129168000 | -3.882641000 |
|                 | C  | -2.003212000 | 1.328081000 | -3.036712000 |
Optimized coordinates of 2-py (S = 0, RKS PBE1PBE/def2-TZVP)

H atoms omitted
Optimized coordinates of 1-Ps (S = 0, RKS PBE1PBE/def2-TZVP)

H atoms omitted
### Optimized coordinates of 1-NHC (S = 0, RKS PBE1PBE/def2-TZVP)

| Atom | x          | y          | z          |
|------|------------|------------|------------|
| C    | -3.38932000| -2.34122800| 1.42538700 |
| C    | -1.94356900| -3.65216100| -0.09740700|
| H    | -4.40307300| 3.13146400 | 0.36550700 |
| H    | -0.04071900| 5.38321000 | -0.60655400|
| H    | 1.80711300 | 3.47365000 | -0.07318700|
| H    | 1.19967200 | 2.91816100 | -1.63719400|
| H    | -3.81254500| 0.77816400 | -0.20952900|
| H    | -3.14924100| 0.14470900 | 1.31278800 |
| H    | 4.95562900 | 0.09295000 | -1.03543000|
| H    | 3.75911400 | -1.12994100| -1.49677800|
| H    | 4.69836600 | -0.28851700| -2.73345500|
| H    | 4.30799000 | 2.07689600 | -3.26675000|
| H    | 3.07585200 | 3.04227000 | -2.47583600|
| H    | 4.53530400 | 2.57191000 | -1.59601000|
| H    | 2.78677600 | 0.37887100 | -3.96941800|
| H    | 1.68414400 | -0.43575900| -2.84885600|
| H    | 1.43921600 | 1.27153600 | -3.27157900|
| H    | 5.12965700 | 1.62374800 | 0.23954500 |
| H    | 4.19244900 | 3.10485000 | 0.50883500 |
| H    | 4.93118100 | 2.26343600 | 1.86474100 |
| H    | 2.69873800 | -0.65545600| 2.05265700 |
| H    | 4.08238400 | -0.69724900| 0.97180600 |
| H    | 4.21910700 | 0.04310300 | 2.57352500 |
| H    | 2.94461600 | 2.02891000 | 3.16045000 |
| H    | 2.19494300 | 3.08020700 | 1.97432700 |
| H    | 1.40197300 | 1.56733000 | 2.45065500 |
| H    | -1.50072700| 0.82669600 | -3.85856700|
| H    | -1.96649000| 1.60715100 | -2.34725500|
| H    | -0.46085200| 0.67636300 | -2.42946900|
| H    | -4.29943200| -1.25266900| -2.82527100|
| H    | -4.20422600| 0.41639400 | -2.25043600|
| H    | -3.68834300| 0.01207500 | -3.87618900|
| H    | -0.58774700| -1.89554400| -2.88319900|
| H    | -2.17124100| -2.65857800| -3.05282900|
| H    | -1.63320300| -1.48326100| -4.25294300|
| H    | -3.88939000| -3.03260600| -1.89612600|
| H    | -4.62582700| -3.64822600| -0.42569100|
| H    | -4.86073200| -1.96076500| -0.86603400|
| H    | -2.60611200| -2.02818200| 2.11566500 |
| H    | -4.23694600| -1.65826400| 1.51813400 |
| H    | -3.73584900| -3.32862700| 1.74616700 |
| H    | -2.49808800| -4.56469100| 0.14605600 |
| H    | -1.50214300| -3.77692200| -1.08683900|
| H    | -1.12104100| -3.55568300| 0.61150500 |
| H    | -2.16308000| 6.66186000 | -0.59079500|
| H    | -4.30306100| 5.56255500 | -0.11286100|
| I    | -0.35960500| -0.63602200| 2.95866000 |
| I    | 1.56856200 | -2.74737800 | -0.71909000|

**Supporting Information**

- H atoms omitted
Initial geometries. The initial geometries of the $^6$N$_2$-brided dimers $^6$6 and $^1$6 (closed-shell) were modeled with Gaussian 16 (G16Rev.B.01) using the PBE1PBE functional. All atoms were described with the valence triple-$\zeta$ basis set Def2-TZVP including polarization functions. Dispersion interactions (GD3BJ) were taken into account during the geometry optimizations without applying symmetry restrictions. Solvation effects were considered during optimization using the polarizable continuum model (PCM for thf) as implemented in Gaussian. The initial geometries for the minimum energy crossing point (MECP) and for TS were obtained from PES scans along the N‒N bond and the I‒Mo–‡Mo–I dihedral angle (see Figure S39).

Functional dependence. Starting from the aforementioned initial coordinates for $^6$6, $^1$6 MECP and TS, the structures were optimized using several functionals (B3LYP, PBE0, PBE, M06L and TPSSh, basis set: Def2-TZVP on all atoms). ORCA (version 4.2.1) was employed and the RI-J (PBE, M06L) or RI-J-COSX (B3LYP, PBE0, TPSSh) approximations with the related auxiliary basis set def2/tzvp were used to save computational costs. Solvation effects (PCPM for thf) and dispersion corrections (GD3zero for M06L, GD3BJ for all other functionals) were taken into account during geometry optimizations. For PBE and M06L, geometrical counterpoise corrections (gCP) were applied to correct for basis set superposition errors. B3LYP/Def2-TZVP-GD3-CPCM(thf) was excluded as an incorrect spin ground state was obtained with this functional (see Table S3). PBE/Def2-TZVP-GD3-CPCM(thf)-gCP was found to give the best results for the description of the thermodynamic data. A similar observation was reported recently for $^6$N$_2$ splitting in a W($\mu$-N$_2$)W species. The electronic energies of $^6$6, $^1$6 (closed-shell) and TS for the different functional are summarized in Table S3.

Table S3. Comparison of electronic energies (EE) for $^6$6, $^1$6 and TS on different levels of theory.

| Method                     | EE($^6$6) [a.u.] | EE($^1$6) [a.u.] | EE(TS) [a.u.] | $\Delta$EE($^6$6=TS) [kcal/mol] |
|----------------------------|------------------|------------------|---------------|----------------------------------|
| B3LYP/Def2-TZVP-GD3-CPCM(thf) | -4231.51509312   | -4231.51513152   | -4231.48049834 | 21.71                  |
| PBE0/Def2-TZVP-GD3-CPCM(thf) | -4229.94475706   | -4229.93970889   | -4229.89409269 | 31.79                  |
| TPSSh/Def2-TZVP-GD3-CPCM(thf) | -4233.16624053   | -4233.15803520   | -4233.11538469 | 31.91                  |
| PBE/Def2-TZVP-GD3-CPCM(thf)-gCP | -4229.52301976   | -4229.51823580   | -4229.47972256 | 27.17                  |
| M06L/Def2-TZVP-GD3-CPCM(thf)-gCP | -4232.86137617   | -4232.85733189   | -4232.79706116  | 40.38                  |

[b] With B3LYP, an incorrect spin ground state of 6 was obtained; [b] corresponding to $\Delta G$ = 26.02 kcal/mol (numerical frequency analysis).

Spin states of 6. Employing the PBE0 and the PBE functional, the different spin states of 6 were inspected in more detail. Along these lines, the quintet, septet, nonet and undecet were considered in addition to broken symmetry solutions for the singlet state. Single point calculation on the triplet coordinates of 6 revealed that the former spin states are all higher in energy. Our attempts to optimize the geometries of $^6$6, $^1$6, 6 and 16 led to dissociation of the molecule to two [PCCP]MoI fragments and $^6$N$_2$ in each case.

For the singlet configuration of 6, attempts to attain an open-shell solution were made using the broken symmetry approach (BS(1,1) with $S = 0$). On the PBE level of theory, the open-shell solution converged to the closed-shell configuration. On the PBE0 level of theory, a BS(1,1) solution with a stable wavefunction was found (via the spin flip procedure implemented in Gaussian and via the Na/NB formalism implemented in ORCA), but this solutions collapsed to the closed-shell solution on the PBE level of theory. A closer inspection of the BS(1,1) solution on the PBE0 level of theory revealed that this solution is slightly higher in energy ($\Delta$EE = 2.5 kcal/mol and $\Delta G$ =
1.2 kcal/mol compared to the closed-shell singlet). The corresponding MECP ($^3\text{6} \rightarrow ^1\text{6}$ (open-shell)) was found at $\Delta G = 1.4$ kcal/mol above the MECP ($^3\text{6} \rightarrow ^1\text{6}$ (closed-shell)), but no broken symmetry solution was found for $^1\text{TS}$. A comparison of the optimized geometries of $^1\text{6}$ (closed-shell vs. open-shell), $^1\text{MECP}$ (closed-shell vs. open-shell) and $^3\text{6}$ revealed that slightly compressed $\text{N}=\text{N}$ bonds were computed for the open-shell species (PBE0/Def2-TZVP-GD3-CPCM(thf) level of theory: $d_{\text{N}=\text{N}}(^3\text{6}) = 1.188 \text{ Å}; d_{\text{N}=\text{N}}(^1\text{6} \text{ closed-shell}) = 1.178 \text{ Å}; d_{\text{N}=\text{N}}(\text{MECP} (^3\text{6} \rightarrow ^1\text{6} \text{ closed-shell})) = 1.166 \text{ Å}; \text{MECP} (^3\text{6} \rightarrow ^1\text{6} \text{ open-shell})) = 1.164 \text{ Å). The broken symmetry solutions were therefore considered less likely, which is in line with their higher energies and the observation that the BS(1,1) solutions collapse to the closed-shell solutions on the PBE level of theory.}

**Alternativ intermediates.** In the article, only $^3\text{6}$ is presented as an intermediate in the $\text{N}_2$-cleavage reaction, although it is mentioned in a footnote that other possibilities were considered, but excluded. The excluded alternative intermediates $^3\text{6}+\text{N}_2$ and $^3\text{6}+(\text{N}_2)_2$ are shown in Scheme S1 and Figure S40. A comparison of the ground state energies of $^3\text{6}+\text{N}_2$ and $^3\text{6}$ suggests that both species may coexist. The transition state for the $\text{N}_2$-cleavage in $^3\text{6}+\text{N}_2$, however, is not accessible under the reaction conditions. The formation of $^3\text{6}+(\text{N}_2)_2$ was excluded given that the reaction between $\text{N}_2$ and $^3\text{6}+\text{N}_2$ to afford $^3\text{6}+(\text{N}_2)_2$ is endergonic (see Scheme S1).

**Scheme S1.** Alternative intermediates $^3\text{6}+\text{N}_2$ and $^3\text{6}+(\text{N}_2)_2$. Note that $^3\text{6}+\text{N}_2$ may be generated en route to $^3\text{6}$ or even coexist with $^3\text{6}$, but the transition state for $\text{N}_2$-splitting is too high in energy for $^3\text{6}+\text{N}_2$.

**Figure S40.** Optimized structures $^3\text{6}+\text{N}_2$ ($S = 1$) (left), $^1\text{TS}$ ($^3\text{6}+\text{N}_2$) ($S = 0$) (middle) and $^3\text{6}+(\text{N}_2)_2$ ($S = 1$) (right) on the PBE0/Def2-TZVP-GD3-CPCM(thf) level of theory.

**Reaction Profile.** In the final reaction profile shown in the article, Gibbs free energy values on the PBE/Def2-TZVP-GD3-CPCM(thf)-gCP level of theory are reported. These values were obtained by numerical frequency analysis at the stationary points, which were identified as minima or saddle points, respectively. Test calculation revealed that the inclusion of scalar relativistic effects (ZORA)\[^{[29]}\] only led to insignificantly small changes with respect to the geometries and energies of the compounds in question. Therefore, relativistic effects were neglected. The optimized coordinates are provided below.
Optimized coordinates of $^6$ (S = 1, UKS PBE/def2-TZVP-GD3-CPM(THF)-gCP (RI-J level of theory))

**H atoms omitted**
Optimized coordinates of $^6$ (S = 0, RKS PBE/def2-TZVP-GD3-CPMC(thf)-gCP (RI-J) level of theory)

H  -3.61749000  0.554327000  3.776477000
C  -3.796446000  2.610770000  4.418626000
C  -2.868559000  2.622248000  5.007946000
H  -4.625880000  2.402081000  5.114552000
H  -3.960010000  3.618051000  4.005988000
C  -5.126676000  1.502518000  2.577371000
H  -5.322900000  2.449755000  2.050942000
H  -5.154678000  0.686010000  1.839952000
C  -0.854683000  1.998292000  3.075165000
H  -1.126919000  2.756790000  3.828640000
C  0.246682000  2.567805000  2.177838000
H  0.501577000  1.872934000  1.367626000
C  1.159299000  2.730192000  2.772652000
H  -0.041658000  3.527800000  1.726836000
C  -0.404012000  0.717634000  3.785648000
H  -1.179952000  0.316787000  4.455101000
H  0.498598000  0.913936000  4.384597000
H  -0.156878000  0.062976000  3.051427000
C  -4.752425000  2.678339000  1.048957000
H  -4.608379000  3.198923000  0.085728000

Mo  2.450200000  0.180129000  0.178668000
I  3.572893000  1.779779000  2.247634000
P  3.028354000  1.825833000  1.612950000
P  2.503823000  2.301973000  1.217401000
N  0.595764000  0.060632000  0.494776000
### Optimized coordinates of $^{15}$MECP (Surfcross, $S = 1\rightarrow 0$, UKS PBE/def2-TZVP-GD3-CPCM(θl)-gCP (RI-J) level of theory)

|   | Optimized Coordinates |
|---|-----------------------|
| H | -6.387138000 -2.979448000 -2.945864000 |
| H | -4.748539000 -3.384930000 -3.493162000 |
| C | -2.130214000 2.634228000 2.729647000 |
| H | -2.683737000 2.855516000 3.658399000 |
| C | -0.737960000 -2.120866000 -3.097639000 |
| H | -0.785085000 -1.260640000 -3.779479000 |
| H | -0.168099000 -2.918561000 3.600198000 |
| H | -0.168277000 -1.817707000 -2.208336000 |
| C | -2.051844000 -3.907948000 -1.881303000 |
| H | -1.543867000 -3.711154000 -0.925417000 |
| H | -1.476476000 -4.674110000 -2.425651000 |
| H | -3.043378000 -4.325023000 -1.652662000 |
| C | -3.939640000 0.515783000 3.630497000 |
| C | -3.929322000 -0.574941000 3.802570000 |
| C | -3.999037000 1.243922000 4.975197000 |
| C | -3.160631000 0.986350000 5.637720000 |
| C | -4.929876000 0.965882000 5.496415000 |
| H | -4.008854000 2.336276000 4.838824000 |
| C | -5.162274000 0.848798000 2.770489000 |
| H | -5.168666000 1.908943000 2.472780000 |
| H | -6.082897000 0.649251000 3.342390000 |
| H | -5.194603000 0.236135000 1.857768000 |
| C | -1.004030000 0.526491000 3.916592000 |
| C | -1.184241000 1.264064000 4.717621000 |
| C | 0.353595000 0.817140000 3.276266000 |
| H | 0.591958000 0.083989000 2.494490000 |
| H | 1.145002000 0.762556000 4.039396000 |
| C | 0.390934000 1.815816000 2.815300000 |
| C | -1.061111000 -0.880967000 4.517882000 |
| H | -1.976520000 -1.045888000 5.106252000 |
| H | -0.197694000 -1.033980000 5.184653000 |
| H | -1.027343000 1.076174000 3.730131000 |
| C | -4.853385000 -1.999631000 1.785326000 |
| H | -4.763090000 -2.812388000 -0.104288000 |
| Mo | 2.4626878000 0.028420000 -0.332066000 |
| I | 3.094825000 -1.156497000 -2.639881000 |
| P | 0.092152000 -2.054713000 0.994178000 |
| P | 2.365104000 2.058796000 -1.886066000 |
| N | 0.593697000 -0.308988000 0.038767000 |
| C | -3.285698000 0.062970000 -3.055170000 |
| C | -3.352609000 1.308460000 -2.385111000 |
| C | -3.608824000 2.480464000 -3.119705000 |
| H | -3.683319000 3.439985000 -2.603826000 |
| C | -3.738301000 2.409935000 -4.508635000 |
| H | -3.915564000 3.321692000 5.083205000 |
| C | -3.627544000 1.311088000 -1.854784000 |
| H | -3.713643000 1.181100000 5.070928000 |
| C | -3.414863000 1.319399000 -6.258556000 |
| H | -3.343216000 0.001331000 -4.443228000 |
| C | -2.367643000 2.610714000 2.406974000 |
| C | -2.771149000 2.936088000 1.087378000 |
| C | -2.929910000 4.287767000 0.722850000 |
| H | -3.246813000 4.543172000 -0.290424000 |
| C | -2.654444000 5.290518000 1.653149000 |
| H | -2.762030000 6.339607000 1.366198000 |
| C | -2.223609000 4.964263000 2.945668000 |
| C | -1.994503000 5.756683000 3.661959000 |
| C | -2.087689000 3.620670000 3.325915000 |
| H | -1.755189000 3.380425000 4.337988000 |
| C | -3.086146000 1.246557000 -0.969370000 |
| C | -2.932521000 1.806135000 0.218035000 |
| C | -5.813899000 0.950000000 -1.217002000 |
| C | -5.497017000 0.308038000 -0.222708000 |
| H | -6.819727000 -1.366910000 -1.111366000 |
| H | -5.891625000 -0.073120000 -1.878227000 |
| H | -5.375738000 -2.570368000 -3.104280000 |
| H | -5.451609000 -1.790855000 -3.878211000 |

**H atoms omitted**
Optimized coordinates of *TS* (S = 0, RKS PBE/Def2-TZVP-GD3-PCM(THF)-gCP (RI-J level of theory))

- Mo: -2.413099715, -0.218606756, -0.016503608
- I: -3.492713819, -2.723512085, -0.850472889
- P: -3.469952792, 0.782726540, -2.10396372
- P: -1.732865058, -1.346987917, 2.152798417
- N: -0.792732571, 0.027585734, -0.748112863

H: 2.491067000, 5.184161000, -2.155764000
C: 3.254285000, 0.608633000, 1.460455000
C: 3.169244000, 1.680033000, 0.687015000
C: 5.786756000, -1.623790000, 0.367712000
H: 5.459144000, -0.811780000, -0.306588000
H: 6.735258000, -2.023268000, -0.025534000
H: 5.987289000, -1.183535000, 1.356813000
C: 5.265240000, -3.918041000, 1.293664000
H: 5.470557000, -3.611180000, 2.330850000
H: 6.212474000, -4.282292000, 0.862820000
H: 4.566091000, -4.766193000, 1.315072000
C: 2.000213000, -3.537405000, 1.229158000
C: 2.561952000, -4.223740000, 1.883204000
H: 0.707302000, -3.128292000, 1.939248000
H: 0.910646000, -2.637749000, 2.901530000
H: 0.093019000, -4.021529000, 2.135721000
H: 0.106736000, -2.442836000, 1.325640000
C: 1.720361000, -4.230980000, -0.105990000
H: 1.214710000, -3.548710000, -0.804880000
H: 1.063335000, -5.099441000, 0.063497000
H: 2.639064000, -4.588605000, -0.593301000
C: 3.644054000, 2.069578000, -3.242457000

H atoms omitted

Molecular structure of *TS*
**SUPPORTING INFORMATION**

### X-Ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Tables S4 - S6. Full shells of intensity data were collected at low temperature on an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu-Kα radiation, microfocus X-ray tubes, multilayer mirror optics).

Detector frames (typically α-, occasionally ϕ-scans, scan width 0.5 or 1°) were integrated by profile fitting.\[^{30}\] Data were corrected for air and detector absorption, Lorentz and polarization effects\[^{30b}\] and scaled essentially by application of appropriate spherical harmonic functions.\[^{30b,31,32}\] Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling procedure), and augmented by a spherical correction\[^{30b,31,32}\] or numerically (Gaussian grid).\[^{32,33}\] An illumination correction was performed as part of the numerical absorption correction.\[^{32}\]

The structures were solved by the heavy atom method (compounds 1·0.5 n-pentane\[^{34}\] and 8·CH\(_2\)Cl\(_2\)\[^{35}\]), by intrinsic phasing (compounds 2·2 toluene and [11-H][OTf]·3 MeCN)\[^{36}\] by ab initio dual space methods involving difference Fourier syntheses (VLD procedure, compound [7][OTf])\[^{35}\] or by the charge flip procedure (all other structures).\[^{37}\] Refinement was carried out by full-matrix least squares methods based on \(F^2\) against all unique reflections.\[^{38}\] All non-hydrogen atoms were given anisotropic displacement parameters.

Hydrogen atoms were generally input at calculated positions and refined with a riding model.\[^{39}\] The positions of the hydrogen atoms on nitrogen were taken from difference Fourier syntheses and refined ([11-H][OTf]·3 MeCN: riding on N; 8: without constraints) Split atom models were used to refine disordered groups and/or solvent molecules. When found necessary, suitable geometry and adp restraints were applied.\[^{39,40}\]

Due to severe disorder and fractional occupancy, electron density attributed to solvent of crystallization was removed from the structures of 1·0.5 n-pentane (n-pentane), [10][OTf]·CH\(_2\)Cl\(_2·0.5\) n-pentane (n-pentane) and [11-H][OTf]·3 MeCN (acetonitrile) with the BYPASS procedure,\[^{41}\] as implemented in PLATON (squeeze/hybrid).\[^{42}\] Partial structure factors from the solvent masks were included in the refinement as separate contributions to \(F_{\text{calc}}\).

CCDC 2103549 - 2103557 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre’s and FIZ Karlsruhe’s joint Access Service via https://www.ccdc.cam.ac.uk/structures/.

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**Figure S41.** ORTEP plot of the molecular structure of 1 (displacement ellipsoids drawn at 50% probability; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mo-C13 2.0056(13), Mo-C14 2.0054(13), Mo-P1 2.5291(4), Mo-P2 2.5267(4), Mo-I1 2.74365(14), Mo-I2 2.69959(14), C13-C14 1.5209(18), P2-Mo-P1 167.377(12), C14-C13-C2 152.90(13), C13-C14-C8 152.54(13).
Figure S42. ORTEP plot of the molecular structure of 2 (displacement ellipsoids drawn at 50% probability; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mo-C13 2.1497(15), Mo-C14 2.1447(15), Mo-N1 1.6605(13), Mo-P1 2.5453(4), Mo-P2 2.5315(4), Mo-I 2.83487(15), C13-C14 1.276(2), C14-C13-C2 155.12(15), C13-C14-C8 154.78(15), N1-Mo-C13 103.69(6), N1-Mo-C14 103.57(6).

Figure S43. ORTEP plot of the molecular structure of [PCCP]MoI$_2$(CO) (displacement ellipsoids drawn at 50% probability; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mo-C7 2.0286(18), Mo-C14 2.0259(18), Mo-P1 2.5664(5), Mo-P2 2.5786(5), Mo-I1 2.90656(18), Mo-I2 2.7873(2), C27-Mo-C7 1.312(3), P1-Mo-P2 174.049(16), C14-C7-C2 150.57(18), C7-C14-C9 150.08(18), C27-Mo-C7 82.18(7), C27-Mo-C14 82.97(7).

Figure S44. ORTEP plot of the molecular structure of 4 (displacement ellipsoids drawn at 50% probability; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mo-C13 2.077(2), Mo-C14 2.077(2), Mo-P1 2.5117(6), Mo-P2 2.5044(6), Mo-I 2.8243(2), C27-Mo-C13 1.887(3), C13-C14 1.300(3), P2-Mo-P1 171.34(2), C14-C13-C2 153.3(2), C13-C14-C8 153.4(2), C27-Mo-C13 98.32(12), C27-Mo-C14 99.89(12).
SUPPORTING INFORMATION

Figure S45. ORTEP plot of the molecular structure of [7]+ (displacement ellipsoids drawn at 50% probability; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mo-C13 2.178(2), Mo-C14 2.176(2), Mo-P1 2.5249(6), Mo-P2 2.5310(6), Mo-N1 1.657(2), Mo-C27 2.192(2), C13-C14 1.269(3), N2-C27 1.147(3), P1-Mo-P2 164.63(2), C14-C13-C2 156.2(2), C13-C14-C8 156.0(2), N1-Mo-C13 104.89(9), N1-Mo-C14 104.70(9).

Figure S46. Packing diagram of [7][OTf] (hydrogen atoms omitted for clarity, view along the b axis).

Figure S47. ORTEP plot of the molecular structure of 8 (displacement ellipsoids drawn at 50% probability; hydrogen atoms except H1 omitted). Selected bond lengths (Å) and angles (°): Mo-C13 2.1345(11), Mo-C14 2.1290(11), Mo-P1 2.5857(3), Mo-P2 2.6051(3), Mo-N1 1.7079(10), Mo-O1 2.2097(8), Mo-O4 2.2016(9), C13-C14 1.2742(16), N1-H1 0.86(2), P1-Mo-P2 177.155(10), C14-C13-C2 155.48(11), C13-C14-C8 154.86(11), N1-Mo-C13 103.73(5), N1-Mo-C14 100.91(5).
Figure S48. ORTEP plot of the molecular structure of 9 (displacement ellipsoids drawn at 50% probability; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mo-C(13) 2.130(2), Mo-C14 2.131(2), Mo-P1 2.5885(7), Mo-P2 2.5971(7), Mo-N1 1.716(2), Mo-O11 2.2117(17), Mo-O21 2.2257(16), C13-C14 1.273(3), N1-C27 1.439(3), P1-Mo-P2 174.86(2), C14-C13-C2 154.4(2), C13-C14-C8 154.0(2), N1-Mo-C13 102.48(9), N1-Mo-C14 102.13(9), C27-N1-Mo 173.28(19).

Figure S49. ORTEP plot of the molecular structure of [10]+ (displacement ellipsoids drawn at 50% probability; hydrogen atoms omitted) Selected bond lengths (Å) and angles (°): Mo-C13 2.0921(19), Mo-C14 2.089(2), Mo-P1 2.5448(5), Mo-P2 2.5462(5), Mo-N1 1.7193(17), Mo-C11 2.4047(5), C13-C14 1.286(3), N1-C27 1.416(3), P1-Mo-P2 158.188(19), C14-C13-C2 155.7(2), C13-C14-C8 155.4(2), N1-Mo-C13 104.10(8), N1-Mo-C14 104.94(8), C27-N1-Mo 161.15(15).

Figure S50. Packing diagram of [10][OTf] (hydrogen atoms and co-crystallized solvents omitted for clarity, view along the a axis).
Figure S51. ORTEP plot of the molecular structure of the singly deprotonated monocation of [11]− (denoted as [11-H]+), displacement ellipsoids drawn at 50% probability. Ph groups on the phosphorus atoms and hydrogen atoms (except those within the bridging ligand) omitted. Selected bond lengths (Å) and angles (°): Mo1-C7 2.129(4), Mo1-C8 2.132(3), Mo1-P1 2.5831(10), Mo1-P2 2.5957(10), Mo1-N2 1.775(3), Mo1-O1 2.150(2), Mo1-Cl1 2.4604(10), Mo2-C34 2.110(4), Mo2-C35 2.112(4), Mo2-P3 2.5670(10), Mo2-P4 2.5837(11), Mo2-N4 1.787(3), Mo2-O2 2.4226(10), C7-C8 1.274(5), C34-C35 1.272(6), C1-C54 1.296(4), C1-C54 1.316(5), N1-C68 1.373(4), N2-C68 1.380(4), O2-C61 1.258(4), N3-C61 1.341(5), N3-C71 1.427(5), N4-C71 1.342(5), C68-C69 1.386(5), C68-C70 1.386(5), P1-Mo1-P2 174.59(4), P1-Mo1-P2 174.59(4), P3-Mo2-P4 175.14(3), C8-C7-C6 153.9(4), C7-C8-C9 154.2(4), C34-C35-C36 156.8(4), N2-Mo1-C7 104.55(13), N2-Mo1-C7 103.37(14), N2-Mo1-O1 81.44(11), N4-Mo2-C34 103.33(14), N4-Mo2-C35 106.74(14), N4-Mo2-O2 80.31(12), C7-Mo1-C11 92.41(10), C8-Mo1-C11 93.10(10), C34-Mo2-C34 96.70(11), C35-Mo2-C32 92.02(11), C69-C68-N2 117.8(3), C68-C69-C70 125.5(3), C71-C70-C69 121.8(3), N4-C71-C70 122.3(4).

Figure S52. Packing diagram of [11-H][OTf] (hydrogen atoms and co-crystallized solvents omitted for clarity, one additional [11-H][OTf] moiety in the background is not visible due to Z-clipping, view along the a axis).
### Table S4. Crystal data and details of the structure determinations of 1·0.5 n-pentane, 2·2 toluene and [PCCP]MoI₂(CO).

| Compound | 1·0.5 n-pentane | 2·2 toluene | [PCCP]MoI₂(CO) |
|----------|----------------|-------------|----------------|
| Empirical Formula | C_{28.5}H_{42}I_{2}MoP_{2} | C_{40}H_{52}IMoNP_{2} | C_{27.5}H_{36}I_{2}MoOP_{2} |
| Formula Weight | 796.30 | 831.60 | 788.24 |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | P 2₁/c | P 2₁/c | P 2₁/n |
| a /Å | 15.80830(10) | 15.97861(4) | 8.22550(7) |
| b /Å | 11.68350(10) | 13.89008(3) | 18.18540(17) |
| c /Å | 17.51940(10) | 17.73159(3) | 19.26804(19) |
| V /Å³ | 3098.71(4) | 3859.407(14) | 2870.82(5) |
| Z | 4 | 4 | 4 |
| F₀₀₀ | 1564 | 1696 | 1536 |
| d, /Mg m⁻³ | 1.707 | 1.431 | 1.824 |
| μ /mm⁻¹ | 2.534 | 10.039 | 2.737 |
| max, min transmission factors | 1.000, 0.823ᵃ | 0.751, 0.195ᵇ | 1.000, 0.557ᵃ |
| X-ray radiation, λ /Å | Mo Kα, 0.71073 | Cu Kα, 1.54184 | Mo Kα, 0.71073 |
| data collect. temperature /K | 120(1) | 120(1) | 120(1) |
| θ range /° | 2.1 - 34.2 | 2.8 - 71.2 | 2.122 - 32.420 |
| index ranges h, k, l | ±24, ±18, -27 ... 26 | -18 ... 19, ±17, ±21 | ±12, -27 ... 26, -29 ... 28 |
| reflections measured | 186979 | 601611 | 76619 |
| unique [Rint] | 12598 [0.0457] | 7459 [0.038] | 9972 [0.047] |
| observed [I > 2σ(I)] | 11313 | 7392 | 8684 |
| parameters refined [restraints] | 288 [0] | 416 [0] | 306 [0] |
| GooF on F² | 1.051 | 1.093 | 1.035 |
| R indices [Fo > 2σ(Fo)] R(F), wR(F²) | 0.0223, 0.0450 | 0.0167, 0.0435 | 0.0256, 0.0461 |
| R indices (all data) R(F), wR(F²) | 0.0277, 0.0464 | 0.0169, 0.0436 | 0.0336, 0.0485 |
| difference density: max, min /e Å⁻³ | 0.866, -0.804 | 0.842, -0.233 | 0.653, -0.754 |
| deposition number CCDC | 2103549 | 2103550 | 2103551 |

ᵃ semi-empirical absorption correction.ᵇ numerical absorption correction.
### Table S5. Crystal data and details of the structure determinations of 4·2 toluene, [7][OTf] and 8·CH2Cl2.

| Compound | 4·2 toluene | [7][OTf] | 8·CH2Cl2 |
|----------|-------------|----------|----------|
| Empirical Formula | C41H52MoOP2 | C32H43F3MoN2O3P2S | C32H39Cl6F6MoNO6P2S2 |
| Formula Weight | 845.60 | 752.64 | 904.51 |
| Crystal system | monoclinic | monoclinic | triclinic |
| Space group | P 21/c | P 21/c | P -1 |
| a /Å | 15.76564(8) | 12.33952(8) | 11.07575(8) |
| b /Å | 14.18816(8) | 11.74931(6) | 11.70399(16) |
| c /Å | 17.94289(10) | 25.30612(16) | 16.6054(2) |
| α ° | 108.9807(11) | | |
| β ° | 101.1303(5) | 100.0244(6) | 96.3405(2) |
| γ ° | | | 108.4629(9) |
| V /Å³ | 3938.32(4) | 3612.89(4) | 1875.29(4) |
| Z | 4 | 4 | 2 |
| F000 | 1724 | 1560 | 920 |
| d₀ /Mg m⁻³ | 1.426 | 1.384 | 1.602 |
| μ /mm⁻¹ | 1.228 | 4.759 | 0.760 |
| max, min transmission factors | 1.000, 0.728 a | 0.979, 0.707 b | 1.000, 0.919 a |
| X-ray radiation, λ /Å | Mo Kα, 0.71073 | Cu Kα, 1.54184 | Mo Kα, 0.71073 |
| data collect. temperature /K | 120(1) | 120(1) | 120(1) |
| θ range /° | 2.1 - 34.2 | 3.5 - 71.2 | 2.2 - 34.2 |
| index ranges h, k, l | ±24, ±22, ±28 | ±15, ±14, ±30 | ±17, ±18, ±26 |
| reflections measured | 154026 | 139150 | 156656 |
| unique [F00] | 15874 [0.038] | 6951 [0.052] | 15119 [0.043] |
| observed [I > 2σ(I)] | 13571 | 6273 | 13605 |
| parameters refined [restraints] | 425 [0] | 408 [0] | 454 [0] |
| GooF on F² | 1.104 | 1.058 | 1.031 |
| R indices [F0 > 4σ(F0)] R(F), wR(F)² | 0.0450, 0.1229 | 0.0304, 0.0763 | 0.0281, 0.0631 |
| R indices (all data) R(F), wR(F)² | 0.0552, 0.1287 | 0.0355, 0.0792 | 0.0334, 0.0653 |
| difference density: max, min /e Å⁻³ | 1.817, -2.086 | 0.942, -0.541 | 1.292, -1.242 |
| deposition number CCDC | 2103552 | 2103553 | 2103554 |

a semi-empirical absorption correction. b numerical absorption correction.
Table S6. Crystal data and details of the structure determinations of 9·2 CH₂Cl₂, [10][OTf]·CH₂Cl₂·0.5 n-pentane and [11-H][OTf]·3 CH₃CN.

| Compound | 9·2 CH₂Cl₂ | [10]OTf·CH₂Cl₂·0.5 n-pentane | [11-H][OTf]·3 CH₃CN |
|----------|------------|-------------------------------|---------------------|
| **Empirical Formula** | C₃₁H₄₃Cl₅F₃MoNO₆P₂S₂ | C₃₇₇H₄₉Cl₅F₃MoNO₆P₂S | C₇₇H₇₄Cl₅Mo₂N₃O₅P₃S |
| **Formula Weight** | 1003.46 | 931.06 | 1673.31 |
| **Crystal system** | monoclinic | triclinic | monoclinic |
| **Space group** | P 2₁/c | P -1 | P 2₁/c |
| a/Å | 9.38067(19) | 11.1845(5) | 16.9514(10) |
| b/Å | 26.1753(5) | 13.1469(5) | 21.32690(10) |
| c/Å | 17.4784(4) | 15.4337(4) | 23.6861(2) |
| α/° | | | |
| β/° | 67.826(3) | | |
| γ/° | 101.8453(19) | 84.624(3) | 108.8460(10) |
| V/Å³ | 4200.29(15) | 2069.51(13) | 8103.95(10) |
| Z | 4 | 2 | 4 |
| F₀₀₀ | 2040 | 958 | 3200 |
| d₀ /Mg m⁻³ | 1.587 | 1.494 | 1.371 |
| μ/mm⁻¹ | 0.810 | 0.691 | 4.557 |
| max, min transmission factors | 1.000, 0.875 a | 1.000, 0.856 a | 1.000, 0.645 b |
| X-ray radiation, λ/Å | Mo Kα, 0.71073 | Mo Kα, 0.71073 | Cu Kα, 1.54184 |
| data collect. temperature /K | 120(1) | 120(1) | 120(1) |
| θ range /° | 2.2 - 34.2 | 2.3 - 34.2 | 2.8 - 67.1 |
| index ranges h, k, l | ±14, -39 ... 40, -26 ... 27 | ±17 ... 16, ±20, ±24 | ±20, ±25, ±28 |
| reflections measured | 126252 | 62039 | 219433 |
| unique [Rint] | 16865 [0.123] | 16243 [0.065] | 14472 [0.040] |
| observed [I > 2σ(I)] | 10836 | 12101 | 12755 |
| parameters refined [restraints] | 535 [248] | 459 [0] | 972 [167] |
| GooF on F² | 1.036 | 1.031 | 1.018 |
| R indices [Fo > 4σ(Fo)] R(F), wR(F)² | 0.0542, 0.0976 | 0.0474, 0.0917 | 0.0468, 0.1218 |
| R indices (all data) R(F), wR(F)² | 0.1034, 0.1158 | 0.0738, 0.1024 | 0.0530, 0.1270 |
| difference density: max, min /e Å⁻³ | 0.922, -0.974 | 1.284, -1.163 | 1.266, -0.881 |
| deposition number CCDC | 2103555 | 2103556 | 2103557 |

a semi-empirical absorption correction. b numerical absorption correction.
Author Contributions

H. Wagner conducted all the experiments, H. Wadepohl solved and refined the X-ray data, J. Ballmann conducted the computational analysis and wrote the original draft. All authors contributed their share to the Supporting Information.