Stabilization of the Dinitrogen Analogue,

Phosphorus Nitride

Jorge L. Martinez, Sean A. Lutz, Daniel M. Beagan, Xinfeng Gao, Maren Pink, Chun-Hsing Chen, Veronica Carta, Pierre Moënne-Loccoz, and Jeremy M. Smith
Table of Contents

Experimental Details .................................................................................. 3

General Considerations ............................................................................. 3

Synthesis of Complexes ........................................................................... 4

Supplementary Figures .............................................................................. 7

Computational Details ............................................................................ 24

X-ray Crystallography ............................................................................. 30

X-ray/dark and X-ray/LED light experiments .......................................... 30
Experimental Details

General Considerations

All manipulations involving air- or moisture sensitive compounds and their preparations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun Labmaster glovebox. Glassware was dried at 130 °C overnight before cooling under dynamic vacuum in an antechamber. Diethyl ether (Et₂O), pentane, tetrahydrofuran (THF), and toluene were purified by the Glass Contour solvent purification system. Before use, an aliquot of each solvent was tested with 1 drop of solution of sodium benzophenone ketyl in THF. Celite was dried under vacuum at 130 °C overnight. The complexes PhB(Pr₂Im)₃Fe≡N¹ and (triphos)RhCl² were prepared according to literature procedures, while (N₃N)Mo≡P³ was prepared similar to a literature procedure by reacting LiPHPh(THF)⁴ and (N₃N)MoCl⁵ in toluene for two days at 80 °C. All other reagents were purchased from commercial vendors and used as received. Benzene-d₆ (C₆D₆, Cambridge Isotope Laboratories) was degassed by three consecutive freeze-pump-thaw cycles and stored over molecular sieves for at least 12 h prior to use. THF-d₈ (Sigma-Aldrich) was stored over molecular sieves for at least 12 h prior to use. ¹H NMR data were recorded on a Varian Inova 500 spectrometer equipped with a FTS-Systems Air Jet TC-84 temperature controller. ¹⁵N NMR data were recorded on a Varian Inova 500 spectrometer referenced to NH₃ at δ = 0 (δ = −380 ppm vs. CH₃NO₂). Resonance Raman spectra were obtained using a McPherson 2061/207 spectrograph equipped with a liquid-nitrogen cooled CCD detector (LN-1100PB, Princeton Instruments). The 407 nm line of a Kr laser (Innova 300, Coherent) and 442 nm line of a HeCd laser (Liconix) were used in combination with long-pass filters (RazorEdge, Semrock) to attenuate the Rayleigh scattering. Data acquisition on powder and solution samples were collected at cryogenic and room temperatures using a 180° scattering geometry. Frequencies were calibrated relative to aspirin and
indene and are accurate to ± 1 cm\(^{-1}\). Elemental analysis was conducted by Midwest Microlabs, LLC (Indianapolis, IN). The isomer shifts are reported relative to the centroid of the spectrum of \(\alpha\)-Fe at 298 K. Samples were prepared by grinding crystallized material into a fine powder and then mounting in a cup, plugged with a fitted O-ring sealed cap. Data analysis was performed using the program WMOSS\(^6\) and quadrupole doublets were fitted to Lorentzian lineshapes.

**Synthesis of Complexes**

\textbf{PhB(Pr\textsubscript{2}I\textsubscript{m})\textsubscript{3}FeNPMo(N\textsubscript{3}N) (1).} Solid PhB(Pr\textsubscript{2}I\textsubscript{m})\textsubscript{3}Fe≡N (202 mg, 0.383 mmol) and (N\textsubscript{3}N)Mo≡P (186 mg, 382 mol) were charged into a scintillation vial. The solid mixture was dissolved in toluene and stirred overnight. The solution was filtered through Celite and concentrated as much as possible making a thin film to which a small amount of Et\textsubscript{2}O was added (1-2 mL) while constantly swirling the scintillation vial until the solution was homogenous. The vial was stored at \(-35\) °C overnight to yield an olive-green crystalline material that was washed with cold pentane (290 mg, 69 %). Alternatively, 1 can also be crystallized by layering hexamethyldisiloxane on a concentrated THF solution at \(-35\) °C. Crystals suitable for X-ray diffraction were grown from concentrated toluene-diethyl ether mixture over several days. \(^1\)H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C): \(\delta\) 76 (3H, Im-\(H\)), 51 (2H, \(m/o\)-B(C\textsubscript{6}H\textsubscript{5})), 25 (2H, \(m/o\)-B(C\textsubscript{6}H\textsubscript{5})), 21 (1H, \(p\)-B(C\textsubscript{6}H\textsubscript{5})), 14 (6H, NCH\textsubscript{2}), 12 (27H, NSi(CH\textsubscript{3})\textsubscript{3}), 2.78 (6H, NCH\textsubscript{2}), \(-0.16\) (18H, CH(CH\textsubscript{3})\textsubscript{2}), \(-5.53\) (3H, CH(CH\textsubscript{3})\textsubscript{2}), \(-34\) (18H, CH(CH\textsubscript{3})\textsubscript{2}). Resonance Raman (407 nm, DCM) \(v_{PN} = 1259, v_{P}^{15}N = 1233\). Despite multiple attempts, we could not obtain reliable elemental analysis data of this complex.

\textbf{[PhB(Pr\textsubscript{2}I\textsubscript{m})\textsubscript{3}Fe(CN\textsubscript{Bu})\textsubscript{3}][((N\textsubscript{3}N)MoPN] (2).} To a solution of 1 (273 mg, 0.249 mmol) in 5 mL of THF, 84 \(\mu\)L of CN\textsubscript{Bu} (0.747 mmol) were added. An immediate color change to orange was observed and the reaction was stirred for 30 min. The solution was filtered through Celite and
volatiles were removed under vacuum in the dark to yield an orange powder. Orange crystals suitable for X-ray diffraction were grown by layering pentane into a THF solution (203 mg, 61 %). $^1$H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 8.32 (d, $J_{HH} = 7.4$ Hz, 2H, $m/o$-B(C$_6$H$_5$)), 7.51 (t, $J_{HH} = 7.5$ Hz, 2H, $m/o$-B(C$_6$H$_5$)), 7.35 (m, 1H, $p$-B(C$_6$H$_5$)), 7.04 (s, 3H, Im-H), 5.47 (sept, $J_{HH} = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), 3.89 (t, $J_{HH} = 5.1$ Hz, 6H, NCH$_2$), 2.75 (sept, $J_{HH} = 6.7$ Hz, 1H, CH(CH$_3$)$_2$), 2.33 (t, $J_{HH} = 5.4$ Hz, 6H, NCH$_2$), 1.96 (s, 27H, NSi(CH$_3$)$_3$), 1.39 (d, $J_{HH} = 7.0$ Hz, 18H, CH(CH$_3$)$_2$), 1.06 (s, 27H, CNC(CH$_3$)$_3$), 0.70 (d, $J_{HH} = 6.7$ Hz, 18H, CH(CH$_3$)$_2$). $^{31}$P{$^1$H} NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 312 (s, 1P, PN). 2-$^{15}$N: $^{15}$N NMR (500 MHz, C$_6$D$_6$, 25 °C): δ 445 (d, $J_{PN} = 103.9$ Hz, 1N, PN). IR (KBr) ν$_{CN}$ = 2136, 2092 cm$^{-1}$.

(N$_3$N)Mo-PN-Rh(triphos) (3a). Solid 2 (67.0 mg, 0.050 mmol) is dissolved in 3 mL of THF and is slowly added dropwise to a suspension of (triphos)RhCl (67 mg, 0.100 mmol) in an equal volume of THF (3 mL) at room temperature. The reaction is stirred for 2 h and [PhB(Pr$_2$Im)$_3$Fe(CN$_3$Bu)$_3$][Cl] precipitates out as a white solid. Volatiles were removed under vacuum and the crude solid was extracted with minimal amount of diethyl ether and filtered through Celite. The ether solution is stored at −35 °C overnight, affording orange crystals in 40 % yield. Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane over several days to a concentrated THF solution at −35 °C. Anal. Calcd. for C$_{49}$H$_{72}$MoN$_3$P$_4$RhSi$_3$: C 51.71, H 6.38, N 6.15; Found C 43.81, H 6.57, N 5.75. Carbon was consistently low for this complex. $^1$H NMR (THF-d$_8$, 25 °C) δ 8.45 (4H, PC$_6$H$_5$), 8.34 (2H, P(C$_6$H$_5$)), 7.72 (4H, P(C$_6$H$_5$)), 7.41-7.20 (ov m, 15H, P(C$_6$H$_5$)$_2$), 3.51 (t, $J_{HH} = 4.87$ Hz, 6H, NCH$_2$), 2.51 (t, $J_{HH} = 4.88$ Hz, 6H, NCH$_2$), 2.32 (m, H, PCH$_2$), 1.44 (m, H, PCH$_2$), −0.01 (s, 27H, NSi(CH$_3$)$_3$). $^{31}$P{$^1$H} NMR (400 MHz, THF-d$_8$, 25 °C): δ 254 (m, 1P, PN), 111 (m, 1P, PPh), 42 (d d, $^1$J$_{PRh} = 154$ Hz, $^2$J$_{PP} = 36$ Hz, 2P, PPh$_2$).
The linkage isomer, \((N_3N)Mo-NP-Rh\text{(triphos)}\ (3b)\), was identified in all reaction mixtures by \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectroscopy in various ratios. Formation of 3b was favored in similar reaction conditions by fast addition of 2 (99.5 mg, 0.074 mmol) to one equivalent of (triphos)RhCl (50 mg, 0.074 mmol) in THF at −78 °C. 3b could not be isolated independently from 3a. \(^{31}\text{P}\{^{1}\text{H}\}\) NMR (THF-\text{d}_8, 25 °C): \(\delta\) 258 (m, 1P, PN), 109 (m, 1P, PPh), 39.5 (d d, \(J_{PRh} = 151\) Hz, \(J_{PP} = 31\) Hz, 2P, PPh). 31P{1H} NMR (THF-d8, 25 °C): \(\delta\) 258 (m, 1P, PN), 109 (m, 1P, PPh), 39.5 (d d, \(J_{PRh} = 151\) Hz, \(J_{PP} = 31\) Hz, 2P, PPh). 31P{1H} NMR (THF-d8, 25 °C): \(\delta\) 258 (m, 1P, PN), 109 (m, 1P, PPh), 39.5 (d d, \(J_{PRh} = 151\) Hz, \(J_{PP} = 31\) Hz, 2P, PPh).

\((N_3N)MoPNSiMe_3\) (4). Neat Me\text{3}SiCl (90.3 mg, 0.83 mmol) was added dropwise in a scintillation vial containing a THF solution (5 mL) of 2 (95.2 mg, 16.6 mmol). Within a few minutes \([LiPr_2Fe(CN^{tBu})_3]\)Cl precipitated out as a white solid. Volatiles were removed under vacuum after stirring for 1 h. The crude solid was extracted in pentane and filtered through Celite, affording a yellow powder in 93 % yield. Crystals suitable for X-ray diffraction were grown from a concentrated pentane solution. \(^1\text{H}\) NMR (C\text{6}D\text{6}) \(\delta\) 3.40 (t, \(J_{HH} = 5.28\) Hz, 6H, NCH\text{2}), 2.13 (t, \(J_{HH} = 5.46\) Hz, 6H, NCH\text{2}), 0.56 (s, 27H, NSi(CH\text{3})\text{3}), 0.44 (s, 9H, PNSi(CH\text{3})\text{3}). \(^{31}\text{P}\{^{1}\text{H}\}\) NMR (400 MHz, C\text{6}D\text{6}, 25 °C): \(\delta\) 199 (s, 1P, PN). \(^{31}\text{P}\{^{1}\text{H}\}\) NMR (400 MHz, C\text{6}D\text{6}, 25 °C): \(\delta\) 199 (d, \(J_{PN} = 72\) Hz, 1P, PN). \(^{15}\text{N}\) NMR (500 MHz, C\text{6}D\text{6}, 25 °C): \(\delta\) 194 (d, \(J_{PN} = 72\) Hz, 1N, PN). Anal. Calcd. for C\text{18}H\text{48}MoN\text{5}PSi\text{4}: C 37.67, H 8.43, N 12.20; Found: C 37.93, H 8.26, N 12.00.
Supplementary Figures

Figure S1. $^1$H NMR spectrum of PhB(iPr$_2$Im)$_3$Fe(=N-P-Mo(N$_3$N)) (1) in C$_6$D$_6$ (*).

Figure S2. $^1$H NMR spectrum of [PhB(iPr$_2$Im)$_3$Fe(CN$i'$/Bu)$_3$][(N$_3$N)MoPN] (2) in THF-d$_8$ (*).
Figure S3. $^{31}$P{${}^1$H} NMR spectrum of [PhB(Pr$_2$Im)$_3$Fe(CNBut)$_3$][(N$_3$N)MoPN] (2) in THF-d$_8$. 

Figure S4. $^{31}$P{${}^1$H} NMR spectrum of [PhB(Pr$_2$Im)$_3$Fe(CNBut)$_3$][(N$_3$N)MoP$_{^{15}}$N] (2-$^{15}$N) (50% enriched) in THF-d$_8$. (❶) Indicates isotopically enriched atoms.
**Figure S5.** $^{15}$N{$^1$H} NMR spectrum of [PhB($^{1}$Pr$_2$Im)$_3$Fe(CN$_{t}$Bu)$_3$][(N$_3$N)MoP$^{15}$N] (2-$^{15}$N (50 % enriched) in THF-d$_8$. (○) Indicates isotopically enriched atoms.

**Figure S6.** $^1$H NMR spectrum of (N$_3$N)Mo-P=NSiMe$_3$ (4) in C$_6$D$_6$ (*).
Figure S7. $^{31}\text{P}^\{^1\text{H}\}$ NMR spectrum of $\text{(N}_3\text{N)}\text{Mo-}\text{P}=\text{NSiMe}_3 \ (4)$ in $\text{C}_6\text{D}_6$.

Figure S8. $^{31}\text{P}^\{^1\text{H}\}$ NMR spectrum of $\text{(N}_3\text{N)}\text{Mo-}\text{P}^{=15}\text{NSiMe}_3 \ (4^{=15}\text{N})$ (50 % enriched) in $\text{C}_6\text{D}_6$. ( ) Indicates isotopically enriched atoms.
Figure S9. $^{15}$N NMR spectrum of (N$_3$N)Mo-P=^{15}NSiMe$_3$ (4-^{15}N) (50 % enriched) in C$_6$D$_6$. (○) Indicates isotopically enriched atoms.

Figure S10. $^1$H NMR spectrum of (N$_3$N)Mo-P=N-Rh(triphos) (3a) at THF-d$_8$ (*).
Figure S11. $^{31}$P-$^1$H spectrum (black) and simulation (red) of (N$_3$N)Mo-P=N-Rh(triphos) (3a) at room temperature in THF-d$_8$. Chemical shifts ($\delta$): a = 254 ppm; b = 111 ppm; c = 42 ppm.
Figure S12. $^{31}\text{P}-^{31}\text{P}$ Homonuclear Decoupling NMR spectrum (black) and simulation (red) of (N$_3$N)Mo-P=N-Rh(triphos) (3a) in THF-d$_8$ showing triphos resonance P(b) at 42 ppm. Decoupling of triphos P(c) resonance shows coupling to Rh ($^{1}J_{PRh} = 154$ Hz, experimental) with no coupling to P(a) from PN ligand.
Figure S13. $^{31}\text{P} - ^{31}\text{P}$ Homonuclear Decoupling NMR spectrum (black) and simulation (red) of (N$_3$N)Mo-P=N-Rh(triphos) (3a) in THF-d$_8$ showing triphos resonance P(c) at 111 ppm. Decoupling of triphos P(b) resonance shows coupling to Rh ($^1J_{\text{PRh}} = 135$ Hz, experimental) and coupling to P(a) ($^3J_{\text{PP}} = 25$ Hz, simulation) and N ($^2J_{\text{PN}} = 29$ Hz, simulation) from the PN ligand.
Figure S14. $^{31}$P-$^{31}$P Homonuclear Decoupling NMR spectrum (black) and simulation (red) of (N$_3$N)Mo-P=N-Rh(triphos) (3a) in THF-d$_8$ showing triphos resonance P(c) at 111 ppm. Decoupling of PN resonance P(a) shows coupling to Rh ($^1J_{PRh} = 135$ Hz, experimental) and coupling to P(b) from triphos ligand ($^2J_{PP} = 36$ Hz, experimental) and N ($^2J_{PN} = 29$ Hz, simulation) from PN ligand.
Figure S15. $^{31}$P-$^{31}$P Homonuclear Decoupling NMR spectrum (black) and simulation (red) of (N$_3$N)Mo-P=N-Rh(triphos) (3a) in THF-d$_8$ showing PN resonance P(a) at 254 ppm. Decoupling of triphos resonance P(c) shows coupling to Rh ($^2J_{PRh} = 14$ Hz, simulation) and coupling to $^{14}$N ($^1J_{PN} = 57$ Hz, simulation) with no coupling to triphos P(b) resonance.
Figure S16. $^{31}\text{P} \{^{1}\text{H}\}$ VT NMR spectrum of (N₃N)Mo-P=N-Rh(triphos) (3a) showing potential evidence for thermal decoupling of the PN resonance with decreasing temperatures.
Figure S17. $^{31}$P$^1$H NMR spectrum of (N$_3$N)Mo-N=P-Rh(triphos) (3b) in THF showing PN resonance P(a) at 258 ppm. (§) Indicates linkage isomer 3a.
Figure S18. $^{31}$P-¹H NMR spectrum of (N₃N)Mo-N=P-Rh(triphos) (3b) in THF showing PPh triphos resonance P(c) at 109 ppm. (§) Indicates linkage isomer 3a.
Figure S19. $^{31}$P$^1$H NMR spectrum of (N$_3$N)Mo-N=P-Rh(triphos) (3b) in THF showing PPh triphos resonance P(b) at 109 ppm. (§) Indicates linkage isomer 3a.
Figure S20. Solid state $^{57}$Fe Mössbauer spectrum of PhB($^i$Pr$_2$Im)$_3$FeNPMo(N$_3$N) (1) measured at 80 K and zero applied field. Parameters: $\delta$ 0.63 mm s$^{-1}$, $\Delta E_Q$ 1.61 mm s$^{-1}$, $\Gamma_L$ 0.38 $\Gamma_R$ 0.50.

Figure S21. Solid state $^{57}$Fe Mössbauer spectrum of [PhB($^i$Pr$_2$Im)$_3$Fe(CN$^t$Bu)$_3$][(N$_3$N)MoPN] (2) measured at 80 K and zero applied field. Parameters: $\delta$ −0.02 mm s$^{-1}$, $\Delta E_Q$ 0.25 mm s$^{-1}$, $\Gamma_L$ 0.31 $\Gamma_R$ 0.31.
**Figure S22.** Room-temperature resonance Raman spectra of 2 (powder in capillaries, 442-nm laser excitation, top traces) show a dominant vibration at 1003 cm\(^{-1}\) that downshifts –36 cm\(^{-1}\) with \(^{15}\)N-labeling, identifying this signal as a \(\nu\)(Mo-N) from a molybdenum nitride product generated under laser irradiation of 2; efforts to minimize this process using lower laser power, solution samples, and cryogenic temperatures were unsuccessful. Resonance Raman spectra of 4 show a strong band at 1082 cm\(^{-1}\) also presumed to correspond to a \(\nu\)(Mo-N) mode (middle back trace, same conditions as above). Reduced laser power and comparison of successive short data acquisition identify a weak signal at 1251 cm\(^{-1}\) consistent with a \(\nu\)(P-N) from 4 (bottom traces, 10% laser power).
Figure S23. Qualitative molecular orbital diagram for (N₃N)Mo-PN.
Computational Details

All optimizations were performed using density functional theory (DFT) as implemented in the ORCA 3.0.3 computational software package. Geometry optimizations were performed with the def2-SVP basis set and the B3LYP functional. Electronic energies (single point energy) were evaluated using def2-TZVP. Additionally, Grimme D3BJ dispersion corrections were included for all atoms. The Fe center was treated with the SDD effective core potential to increase computational efficiency. All complexes structures were verified to be minima on the potential energy surface with no imaginary modes present in the vibrational frequency calculations.

Figure S24. Kohn-Sham representation of the HOMO for \([N_3N]Mo-L^-\) (L = PN, P2, PO, NP, N2 and CO) as calculated by density functional theory (def2-tzvp/B3LYP/dkh2) shown at isodensity 0.05.
Quantum Theory of Atoms in molecules (QTAIM) analysis was performed using DFT in Gaussian 16\textsuperscript{11} with the B3LYP functional and the 6-31G\textsuperscript{*} basis set. Wiberg bond indices were calculated with NBO\textsuperscript{12} as implemented in Gaussian 16 with the B3LYP functional and the 6-31G\textsuperscript{*} basis set. Visualization of the Laplacian of the charge density at the bond critical bond was done using the Gaussian 16 “.wfn” file with the AIMAll\textsuperscript{13} program.

NBO analysis reveals a PN triple bond in \textit{[(N\textsubscript{3}N)Mo(PN)]\textsuperscript{−}} that is composed of one \textit{σ} bond from \textit{sp} hybrids on P and N and two \textit{π} bonds from \textit{p} orbitals on P and N. All of these bonds are polarized towards the N atom (Table S1). By contrast, NBO reveals a PN single bond in \textit{[(N\textsubscript{3}N)Mo(NP)]\textsuperscript{−}} in which the \textit{σ} bond is formed from an N \textit{sp} hybrid and a \textit{p} orbital on P.

NBO reveals single bonds for CO in \textit{[(N\textsubscript{3}N)Mo(CO)]\textsuperscript{−}} ((Wiberg bond index 1.699) and N\textsubscript{2} in \textit{[(N\textsubscript{3}N)Mo(N\textsubscript{2})]\textsuperscript{−}} (Wiberg bond index 0.563). The CO bond is polarized towards the O atom, whereas the N\textsubscript{2} bond shows little polarization.
### Table S1. Summary of NBO analysis.

| Complex | $c_A^2$ (%) | Hybridization | Assignment |
|---------|-------------|---------------|------------|
| [(N$_3$N)Mo(PN)]$^-$ | 32.25 | P 36.26% s, 63.23% p, 0.51% d | $\sigma$ |
| | 67.75 | N 36.33% s, 63.51% p, 0.16% d | |
| | 35.77 | P 0% s, 98.72% p, 1.28% d | $\pi$ |
| | 64.23 | N 0% s, 99.74% p, 0.26% d | |
| | 35.76 | P 0% s, 98.71% p, 1.29% d | $\pi$ |
| | 64.24 | N 0% s, 99.74% p, 0.26% d | |
| [(N$_3$N)Mo(NP)]$^-$ | 75.29 | N 44.30% s, 55.63% p, 0.51% d | $\sigma$ |
| | 24.74 | P 16.12% s, 82.46% p, 1.42% d | |
| [(N$_3$N)MoN$_2$]$^-$ | 53.51 | N$_{\alpha}$ 38.60% s, 61.33% p, 0.07% d | $\sigma$ |
| | 46.49 | N$_{\beta}$ 36.38% s, 63.50% p, 0.13% d | |
| [(N$_3$N)Mo(CO)]$^-$ | 31.60 | C 32.18% s, 67.65% p, 0.17% d | $\sigma$ |
| | 68.40 | O 45.24% s, 54.43% p, 0.33% d | |
Figure S25. Plot of the Laplacian of charge density ($\nabla^2 \rho$) for [(N$_3$N)MoPN]$^-$ (left), [(N$_3$N)MoPP]$^-$(middle), and [(N$_3$N)MoPO] (right) complexes. Plots of charge depletion are shown with blue curves and areas of charge concentration are shown with red curves. The bond and ring critical points are plotted with green and red spheres, respectively.
Table S2. Topological analysis at selected bond critical points. Electron density at the bond critical point (\(\rho\)), the Laplacian of the charge density (\(\nabla^2(\rho)\)), and ellipticity (\(\varepsilon\)) are shown.

| Complex          | \(\rho\) | \(\nabla^2(\rho)\) | \(\varepsilon\) |
|------------------|----------|---------------------|-----------------|
| [(N3N)MoPP]^-   | 0.147    | +0.0029             | 0.00012         |
| [(N3N)MoPN]^-   | 0.216    | +1.347              | 0.000032        |
| [(N3N)MoPO]^-   | 0.210    | +1.593              | 0.00006         |

Table S3. Topological analysis at selected bond critical points. Electron density at the bond critical point (\(\rho\)), the Laplacian of the charge density (\(\nabla^2(\rho)\)), and ellipticity (\(\varepsilon\)) are shown.

| Complex          | \(\rho\) | \(\nabla^2(\rho)\) | \(\varepsilon\) |
|------------------|----------|---------------------|-----------------|
| [(N3N)MoNN]^-   | 0.560    | -1.551              | 0.00017         |
| [(N3N)MoNP]^-   | 0.087    | +0.552              | 0.000022        |
| [(N3N)MoCO]^-   | 0.397    | +0.526              | 0.00014         |

A linear synchronous transit (LST) calculation was undertaken to provide insight into the barrier for linkage isomerization from [(N3N)MoPN]^- to [(N3N)MoNP]^- The Mo-P-N bond angle was incrementally adjusted, starting from the PN isomer (180 °) and ending with the NP isomer (0 °). While no transition state was located, the LST data provide an estimate of the barrier for isomerization. An approximate transition state was located at around 90 °, with the energy 40
kcal/mol higher in energy than the PN isomer. This suggests that linkage isomerization is not possible under thermal conditions.

**Figure S26.** LST of fixed Mo-P-N angles to assess the approximate barrier of ligand isomerization.
X-ray Crystallography

X-ray/dark and X-ray/LED light experiments

Data collection

The X-ray intensity data were measured ($\lambda = 0.71073 \text{ Å}$) with a D8 Venture diffractometer from Bruker. Two sequences (A and B) of data collection experiments were undertaken in order to determine whether PN linkage isomerization is promoted by X-ray or by white light irradiation. The measurements carried out in the dark were labelled as A-(1-4) while measurements performed under LED light were labelled as B-(1-7). The spectrum of the LED lamp is shown in Figure S26. Between the measurements, samples were exposed to X-rays for A-(1-4) and to LED light for B(1-4) according to the times shown in Table S3.

Figure S27. Output of LUXEON Altilon LED used for crystal irradiation.
Table S4. Summary of single crystal X-ray data collection for complex 2 with X-ray (A) and white light (B) irradiation.

| Label | Experiment | h:min - data collection time, also time period for site occupancy average | h:min - exposure time after data collection | h:min – exposure time before data collection + data collection time | Major site Mo-P-N in %P/N | Minor site Mo-P-N in %N/P |
|-------|------------|--------------------------------------------------------------------------|--------------------------------|---------------------------------------------------------------|------------------------|------------------------|
| 2     | pre-experiment | 1:20                                                                 | 1:07                          | 1:20                                                             | 82.83                  | 17.17                  |
| A-1   | X-ray/dark   | 1:15                                                                    | 3:05                          | 2:22                                                             | 83.67                  | 16.33                  |
| A-2   | X-ray/dark   | 1:15                                                                    | 3:05                          | 4:20                                                             | 81.19                  | 18.81                  |
| A-3   | X-ray/dark   | 1:15                                                                    | 3:05                          | 4:00                                                             | 81.94                  | 18.06                  |
| A-4   | X-ray/dark   | 1:15                                                                    | 2:19                          | 4:20                                                             | 81.69                  | 18.31                  |
| B-1   | X-ray and LED| 1:15                                                                    | 1:07                          | 1:15                                                             | 70.17                  | 29.83                  |
| B-2   | X-ray and LED| 1:15                                                                    | 3:09                          | 2:22                                                             | 51.59                  | 48.41                  |
| B-3   | X-ray and LED| 1:15                                                                    | 3:05                          | 4:24                                                             | 38.76                  | 61.24                  |
| B-4   | X-ray and LED| 1:15                                                                    | 3:05                          | 4:20                                                             | 33.37                  | 66.63                  |
| B-5   | X-ray and LED| 1:15                                                                    | 3:15                          | 4:20                                                             | 28.86                  | 71.14                  |
| B-6   | X-ray and LED| 1:06                                                                    | 3:05                          | 4:21                                                             | 25.98                  | 74.02                  |
| B-7   | X-ray and LED| 1:24                                                                    | 4:29                          | 23.71                                                             | 76.29                  |
**Figure S28.** Percentage occupancy of the Mo-P-N site as a function of LED light exposure for a single crystal of 2

The frames were integrated with the Bruker SAINT software package \(^\text{15}\) using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total number of reflections detailed in Tables S4-1 to S15-1. to a maximum θ angle of about 27°. (0.76 Å resolution). The number of independent reflections, average redundancy, completeness, \(R_{\text{int}}\), \(R_{\text{sig}}\), and observed reflections [greater than 2σ(\(F^2\))] are also listed. The final cell constants were calculated for each dataset individually from strong reflections (above 20 σ(I)) in an approximate angle range of 5° < 2θ < 50°. Data were corrected for absorption effects using the multi-scan method (SADABS).\(^\text{16}\) The ratio of minimum to maximum apparent transmission was calculated.
The structure was solved and refined using the Bruker SHELX software package,\textsuperscript{17} using the space group P -1, with $Z = 2$, the same overall structural model and the same atom labeling. Disorder was refined for the P1-N14 moiety and all solvent sites. One pentane solvent molecule is disordered over a special position and was refined with isotropic replacement parameters while all other solvent molecules (pentane and THF) are disordered at a general position. Restraints and constraints were used in the disorder refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters, which exception of the aforementioned pentane molecule. The final full-matrix least-squares refinement on $F^2$ with 946 variables converged at individual $R_1$, $wR_2$, and goodness-of-fit values, listed in Tables S4-1 to S15-1. The largest peak in the final difference electron density synthesis and the largest hole are listed as well. Selected atom coordinates, geometrical parameters and displacement parameters are listed in Tables S4-2, -3, -4 to S15-2, -3, -4.

\textbf{Figure S29}. Asymmetric unit for 2.
Figure S30. Close up view of the Mo complex, P-N/N-P disorder shown, hydrogen atoms omitted for clarity.
Table S5-1. Crystal data and structure refinement for 2.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                            | C74.94 H143.76 B Fe Mo N14 O0.56 P Si3     |
| Formula weight                                | 1527.87                                    |
| Crystal color, shape, size                   | orange block, 0.23 × 0.17 × 0.10 mm³       |
| Temperature                                   | 100(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system, space group                   | Triclinic, P-1                             |
| Unit cell dimensions                          | a = 15.5830(6) Å                           |
|                                              | b = 15.7178(7) Å                           |
|                                              | c = 20.1820(9) Å                           |
|                                              | α = 90.5300(10)°.                          |
|                                              | β = 102.1070(10)°.                         |
|                                              | γ = 114.5590(10)°.                         |
| Volume                                        | 4370.1(3) Å³                              |
| Z                                             | 2                                          |
| Density (calculated)                          | 1.161 Mg/m³                                |
| Absorption coefficient                        | 0.416 mm⁻¹                                 |
| F(000)                                        | 1652                                       |

Data collection

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Diffractometer                                | Venture D8, Bruker                         |
| Source                                        | IμS III, Incoatec                          |
| Theta range for data collection               | 1.038 to 27.509°.                          |
| Index ranges                                  | -20<=h<=20, -20<=k<=20, -26<=l<=26         |
| Reflections collected                         | 140952                                     |
| Independent reflections                       | 20069 [Rint = 0.1044]                     |
| Observed Reflections                          | 13747                                      |
| Completeness to theta = 25.242°               | 99.9 %                                     |
**Solution and Refinement**

| Parameter                                      | Description                                               |
|------------------------------------------------|-----------------------------------------------------------|
| Absorption correction                         | Semi-empirical from equivalents                           |
| Max. and min. transmission                     | 0.7456 and 0.6990                                          |
| Solution                                       | Intrinsic methods                                         |
| Refinement method                              | Full-matrix least-squares on $F^2$                        |
| Weighting scheme                               | $w = [\sigma^2F_o^2 + AP^2 + BP]^1$, with                 |
|                                                | $P = (F_o^2 + 2F_c^2)/3, A = 0.1013, B = 12.6911$        |
| Data / restraints / parameters                 | 20069 / 1102 / 946                                        |
| Goodness-of-fit on $F^2$                        | 1.072                                                     |
| Final R indices [$I>2\sigma(I)$]                | $R_1 = 0.0712, wR_2 = 0.1811$                            |
| R indices (all data)                           | $R_1 = 0.1089, wR_2 = 0.2153$                            |
| Largest diff. peak and hole                    | 1.794 and -1.463 e.$\text{Å}^{-3}$                       |
| Disorder ratio $\text{Mo-P1-N14/Mo-N14D-P1D}$  | 0.8283/0.1717                                              |

---

Goodness-of-fit = $[\Sigma w(F_o^2 - F_c^2)^2]/N_{\text{observed}} - N_{\text{params}}]^{1/2}$, all data.

$R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|, \quad wR_2 = \left[ \Sigma (wF_o^2 - F_c^2)^2 / \Sigma w(F_o^2) \right]^{1/2}$. 

---

S36
### Table S5-2. Selected Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for 2. Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

|     | x    | y    | z    | U(eq) |
|-----|------|------|------|-------|
| Mo1 | 2589(1) | 6473(1) | 298(1) | 18(1) |
| P1  | 3275(1) | 6762(1) | -573(1) | 19(1) |
| N14 | 3709(13) | 6934(12) | -1196(6) | 26(1) |
| N14D | 3070(20) | 6680(20) | -393(16) | 19(1) |
| P1D | 3660(20) | 6930(20) | -1040(10) | 26(1) |

### Table S5-3. Selected bond lengths [Å] and angles [°] for 2.

| Bond | Length [Å] | Angle [°] |
|------|------------|-----------|
| Mo1-N14D | 1.69(3) | Mo1-N13 | 2.025(4) |
| Mo1-N11 | 2.028(4) | Mo1-N12 | 2.034(4) |
| Mo1-P1 | 2.200(2) | Mo1-N10 | 2.244(3) |
| P1-N14 | 1.524(8) | N14D-P1D | 1.70(3) |
| N14-P1-Mo1 | 177.6(7) | Mo1-N14D-P1D | 175(2) |
Table S5-4. Selected anisotropic displacement parameters ($\AA^2 \times 10^3$) for 2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^* U^{11} + ... + 2h k a^* b^* U^{12} ]$

|       | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Mo1   | 20(1)    | 18(1)    | 17(1)    | 2(1)     | 5(1)     | 8(1)     |
| P1    | 23(1)    | 21(1)    | 16(1)    | 2(1)     | 8(1)     | 10(1)    |
| N14   | 34(3)    | 35(2)    | 14(5)    | 0(4)     | 10(4)    | 18(2)    |
| N14D  | 23(1)    | 21(1)    | 16(1)    | 2(1)     | 8(1)     | 10(1)    |
| P1D   | 34(3)    | 35(2)    | 14(5)    | 0(4)     | 10(4)    | 18(2)    |
**Table S6-1.** Crystal data and structure refinement for **A-1**.

| Property                              | Value                        |
|---------------------------------------|------------------------------|
| **Empirical formula**                 | C74.94 H143.76 B Fe Mo N14 O0.56 P Si3 |
| **Formula weight**                    | 1527.87                      |
| **Crystal color, shape, size**        | orange block, 0.23 × 0.17 × 0.10 mm³ |
| **Temperature**                       | 100(2) K                     |
| **Wavelength**                        | 0.71073 Å                    |
| **Crystal system, space group**       | Triclinic, P-1               |
| **Unit cell dimensions**              | a = 15.5835(6) Å, α = 90.5290(10)°. |
|                                       | b = 15.7173(7) Å, β = 102.1060(10)°. |
|                                       | c = 20.1840(9) Å, γ = 114.5640(10)°. |
| **Volume**                            | 4370.4(3) Å³                |
| **Z**                                 | 2                            |
| **Density (calculated)**              | 1.161 Mg/m³                  |
| **Absorption coefficient**            | 0.416 mm⁻¹                   |
| **F(000)**                            | 1652                         |

**Data collection**

| Property                              | Value                        |
|---------------------------------------|------------------------------|
| **Diffractometer**                    | Venture D8, Bruker          |
| **Source**                            | IμS III, Incoatec           |
| **Theta range for data collection**   | 1.038 to 27.521°.           |
| **Index ranges**                      | -20≤h≤20, -20≤k≤20, -26≤l≤26 |
| **Reflections collected**             | 140584                       |
| **Independent reflections**           | 20074 [Rint = 0.1058]       |
| **Observed Reflections**              | 13722                        |
| **Completeness to theta = 25.242°**   | 99.9 %                       |
**Solution and Refinement**

Absorption correction  
Semi-empirical from equivalents

Max. and min. transmission  
0.7454 and 0.7033

Solution  
Intrinsic methods

Refinement method  
Full-matrix least-squares on F^2

Weighting scheme  
\[ w = [\sigma^2F_o^2 + AP^2 + BP]^1, \text{ with} \]
\[ P = (F_o^2 + 2F_c^2)/3, \ A = 0.0997, \ B = 13.7720 \]

Data / restraints / parameters  
20074 / 1101 / 946

Goodness-of-fit on F^2  
1.069

Final R indices [I>2\sigma(I)]  
R1 = 0.0713, wR2 = 0.1808

R indices (all data)  
R1 = 0.1095, wR2 = 0.2160

Largest diff. peak and hole  
1.733 and -1.523 e.Å^-3

Disorder ratio Mo-P1-N14/Mo-N14D-P1D  
0.8367/0.1633

---

Goodness-of-fit = \[ \frac{\sum[w(F_o^2 - F_c^2)^2]}{N_{\text{observ}} - N_{\text{params}}} \]^{1/2}, all data.

\[ R1 = \frac{\sum[|F_o| - |F_c|]}{\sum |F_o|} \quad \text{wR2} = \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]} \]^{1/2}. 
**Table S6-2.** Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for A-1. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|        | x      | y      | z      | $U_{eq}$ |
|--------|--------|--------|--------|----------|
| Mo1    | 2589(1) | 6473(1) | 298(1) | 18(1)    |
| P1     | 3275(1) | 6763(1) | -573(1)| 20(1)    |
| N14    | 3731(12)| 6966(12)| -1183(7)| 26(1)   |
| N14D   | 3090(20)| 6660(20)| -397(18)| 20(1)   |
| P1D    | 3610(20)| 6870(20)| -1063(12)| 26(1)  |

**Table S6-3.** Selected bond lengths [Å] and angles [°] for A-1.

| Bond                | Length [Å] | Angle [°] |
|---------------------|------------|-----------|
| Mo1-N14D            | 1.71(4)    |           |
| Mo1-N11             | 2.029(4)   |           |
| Mo1-P1              | 2.2000(19) |           |
| P1-N14              | 1.519(8)   |           |
| N14-P1-Mo1          | 178.8(6)   |           |
| Mo1-N13             | 2.024(4)   |           |
| Mo1-N12             | 2.031(4)   |           |
| Mo1-N10             | 2.241(4)   |           |
| N14D-P1D            | 1.68(4)    |           |
| P1D-N14D-Mo1        | 178(3)     |           |
Table S6-4. Selected anisotropic displacement parameters (Å² × 10³) for A-1. The anisotropic displacement factor exponent takes the form: -2π²[ h² a*²U¹¹ + ... + 2 h k a* b* U¹² ].

|       | U¹¹  | U²²  | U³³  | U²³  | U¹³  | U¹²  |
|-------|------|------|------|------|------|------|
| Mo1   | 19(1)| 18(1)| 17(1)| 2(1) | 5(1) | 8(1) |
| P1    | 24(1)| 22(1)| 17(1)| 4(1) | 9(1) | 10(1)|
| N14   | 27(5)| 30(4)| 21(4)| 7(3) | 13(2)| 10(4)|
| N14D  | 24(1)| 22(1)| 17(1)| 4(1) | 9(1) | 10(1)|
| P1D   | 27(5)| 30(4)| 21(4)| 7(3) | 13(2)| 10(4)|
**Table S6-1.** Crystal data and structure refinement for A-2.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Empirical formula              | C75 H144.01 B Fe Mo N14 O0.50 P Si3        |
| Formula weight                  | 1527.87                                    |
| Crystal color, shape, size      | orange block, 0.23 × 0.17 × 0.10 mm³       |
| Temperature                     | 100(2) K                                   |
| Wavelength                      | 0.71073 Å                                  |
| Crystal system, space group     | Triclinic, P-1                             |
| Unit cell dimensions            | a = 15.5829(6) Å, α = 90.5270(10)°         |
|                                 | b = 15.7156(7) Å, β = 102.1060(10)°        |
|                                 | c = 20.1841(9) Å, γ = 114.5660(10)°        |
| Volume                          | 4369.7(3) Å³                               |
| Z                               | 2                                          |
| Density (calculated)            | 1.161 Mg/m³                                 |
| Absorption coefficient          | 0.416 mm⁻¹                                 |
| F(000)                          | 1652                                       |

**Data collection**

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Diffractometer                  | Venture D8, Bruker                         |
| Source                          | IμS III, Incoatec                          |
| Theta range for data collection | 1.038 to 27.513°.                          |
| Index ranges                    | -20≤h≤20, -20≤k≤20, -26≤l≤26               |
| Reflections collected           | 142275                                     |
| Independent reflections         | 20078 [Rint = 0.1209]                      |
| Observed Reflections            | 13400                                      |
| Completeness to theta = 25.242° | 99.9 %                                     |
Solution and Refinement

Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  0.7454 and 0.7033
Solution  Intrinsic methods
Refinement method  Full-matrix least-squares on F^2
Weighting scheme  
\[ w = \left[ \sigma^2 F_o^2 + AP^2 + BP \right]^{-1}, \text{ with} \]
\[ P = (F_o^2 + 2 F_c^2)/3, \ A = 0.1088, \ B = 0 \]
Data / restraints / parameters  20078 / 1107 / 946
Goodness-of-fit on F^2  1.026
Final R indices [I>2\sigma(I)]  R1 = 0.0628, wR2 = 0.1754
R indices (all data)  R1 = 0.0979, wR2 = 0.1990
Largest diff. peak and hole  1.552 and -1.255 e.Å^-3
Disorder ratio Mo-P1-N14/Mo-N14D-P1D  0.8119/0.1881

Goodness-of-fit = \[ \left[ \sum \left( w(F_o^2 - F_c^2)^2 \right) / N_{\text{obs}} - N_{\text{params}} \right]^{1/2}, \text{ all data.} \]

R1 = \[ \sum \left( |F_o| - |F_c| \right) / \sum |F_o|, \quad wR2 = \left[ \sum \left( w(F_o^2 - F_c^2)^2 \right) / \sum \left[ w(F_o^2)^2 \right] \right]^{1/2}. \]
Table S7-2. Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for A-2. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|      | x            | y            | z            | $U_{eq}$ |
|------|--------------|--------------|--------------|---------|
| Mo1  | 2589(1)      | 6473(1)      | 298(1)       | 19(1)   |
| P1   | 3277(1)      | 6765(1)      | -574(1)      | 21(1)   |
| N14  | 3767(11)     | 6975(11)     | -1174(7)     | 28(2)   |
| N14D | 3070(20)     | 6620(20)     | -476(17)     | 21(1)   |
| P1D  | 3585(17)     | 6867(17)     | -1088(10)    | 28(2)   |

Table S7-3. Selected bond lengths [Å] and angles [°] for A-2.

|          | Bond Lengths [Å] | Angles [°]          |
|----------|-----------------|---------------------|
| Mo1-N14D | 1.85(3)         | Mo1-N11             | 2.023(3)   |
| Mo1-N13  | 2.024(3)        | Mo1-N12             | 2.028(3)   |
| Mo1-P1   | 2.2018(16)      | Mo1-N10             | 2.244(3)   |
| P1-N14   | 1.533(7)        | N14D-P1D            | 1.58(3)    |
| N14-P1-Mo1 | 179.3(7)    | P1D-N14D-Mo1        | 173(2)     |
Table S7-4. Selected anisotropic displacement parameters (Å² × 10³) for A-2. The anisotropic displacement factor exponent takes the form: $-2\pi²\left[ h^2 a^*U_{11} + ... + 2hk a^* b^* U_{12} \right]$

|     | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-----|------|------|------|------|------|------|
| Mo1 | 22(1)| 19(1)| 17(1)| 1(1) | 5(1) | 8(1) |
| P1  | 23(1)| 21(1)| 20(1)| 3(1) | 8(1) | 9(1) |
| N14 | 23(6)| 32(4)| 29(3)| 5(2) | 15(2)| 7(4) |
| N14D| 23(1)| 21(1)| 20(1)| 3(1) | 8(1) | 9(1) |
| P1D | 23(6)| 32(4)| 29(3)| 5(2) | 15(2)| 7(4) |
Table S8-1. Crystal data and structure refinement for A-3.

| Property                                      | Value                          |
|-----------------------------------------------|--------------------------------|
| Empirical formula                            | C75 H144 B Fe Mo N14 O0.50 P Si3 |
| Formula weight                                | 1527.87                        |
| Crystal color, shape, size                    | orange block, 0.23 × 0.17 × 0.10 mm³ |
| Temperature                                   | 100(2) K                       |
| Wavelength                                    | 0.71073 Å                      |
| Crystal system, space group                   | Triclinic, P-1                 |
| Unit cell dimensions                          | a = 15.5851(6) Å, α = 90.5250(10)°, b = 15.7181(7) Å, β = 102.1100(10)°, c = 20.1884(9) Å, γ = 114.5680(10)° |
| Volume                                        | 4371.8(3) Å³                   |
| Z                                             | 2                              |
| Density (calculated)                          | 1.161 Mg/m³                    |
| Absorption coefficient                        | 0.415 mm⁻¹                     |
| F(000)                                        | 1652                           |

Data collection

| Property                                      | Value                          |
|-----------------------------------------------|--------------------------------|
| Diffractometer                                | Venture D8, Bruker             |
| Source                                        | IμS III, Incoatec              |
| Theta range for data collection               | 1.038 to 27.508°.              |
| Index ranges                                  | -20≤h≤20, -20≤k≤20, -26≤l≤26    |
| Reflections collected                         | 142408                         |
| Independent reflections                       | 20077 [Rint = 0.1190]          |
| Observed Reflections                          | 12937                          |
| Completeness to theta                         | 99.9 %                         |
## Solution and Refinement

| Description                                    | Details                                      |
|------------------------------------------------|----------------------------------------------|
| Absorption correction                         | Semi-empirical from equivalents              |
| Max. and min. transmission                     | 0.7454 and 0.7033                            |
| Solution                                       | Intrinsic methods                            |
| Refinement method                              | Full-matrix least-squares on F²              |
| Weighting scheme                               | $w = [\sigma^2 F_o^2 + A P^2 + B P]^{-1}$, with $P = (F_o^2 + 2 F_c^2)/3$, $A = 0.1341$, $B = 0$ |
| Data / restraints / parameters                  | 20077 / 1098 / 946                          |
| Goodness-of-fit on F²                           | 1.077                                        |
| Final R indices [I>2σ(I)]                      | $R1 = 0.0707$, $wR2 = 0.1961$                |
| R indices (all data)                            | $R1 = 0.1108$, $wR2 = 0.2312$                |
| Largest diff. peak and hole                     | 1.750 and -1.698 e.Å⁻³                       |
| Disorder ratio Mo-P1-N14/Mo-N14D-P1D            | 0.8194/0.1806                                |

Goodness-of-fit = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{\text{obs}} - N_{\text{params}})]^{1/2}$, all data.

$R1 = \frac{\sum(|F_o| - |F_c|)}{\sum |F_o|}$, $wR2 = \sqrt{\frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]}}^{1/2}$. 
Table S8-2. Selected atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for A-3. U_eq is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

|       | x       | y       | z       | U(eq)  |
|-------|---------|---------|---------|--------|
| Mo1   | 2590(1) | 6473(1) | 298(1)  | 19(1)  |
| P1    | 3276(1) | 6765(1) | -573(1) | 20(1)  |
| N14   | 3753(12)| 6970(13)| -1179(8)| 28(1)  |
| N14D  | 3080(20)| 6630(20)| -442(17)| 20(1)  |
| P1D   | 3600(20)| 6870(20)| -1080(11)| 28(1) |

Table S8-3. Selected bond lengths [Å] and angles [°] for A-3.

| Bond              | Length [Å] | Bond              | Length [Å] |
|-------------------|------------|-------------------|------------|
| Mo1-N14D          | 1.79(3)    | Mo1-N11           | 2.029(4)   |
| Mo1-N13           | 2.030(4)   | Mo1-N12           | 2.033(4)   |
| Mo1-P1            | 2.2010(17) | Mo1-N10           | 2.243(4)   |
| P1-N14            | 1.529(8)   | N14D-P1D          | 1.63(3)    |
| N14-P1-Mo1        | 179.9(7)   | P1D-N14D-Mo1      | 174(2)     |
Table S8-4. Selected anisotropic displacement parameters (Å² × 10³) for A-3. The anisotropic displacement factor exponent takes the form: \(-2\pi²[ h² a*²U_{11} + ... + 2 \text{h k a* b* } U_{12} \] )

|     | U³₁ | U³₂ | U³₃ | U³₄ | U³₅ | U³₆ |
|-----|-----|-----|-----|-----|-----|-----|
| Mo1 | 21(1) | 19(1) | 17(1) | 1(1) | 5(1) | 8(1) |
| P1  | 23(1) | 22(1) | 17(1) | 3(1) | 8(1) | 10(1) |
| N14 | 25(6) | 35(4) | 26(4) | 5(2) | 15(2) | 10(4) |
| N14D| 23(1) | 22(1) | 17(1) | 3(1) | 8(1) | 10(1) |
| P1D | 25(6) | 35(4) | 26(4) | 5(2) | 15(2) | 10(4) |
### Table S9-1. Crystal data and structure refinement for A-4.

| Property                                      | Value                                                                |
|-----------------------------------------------|----------------------------------------------------------------------|
| Empirical formula                            | C74.99 H143.98 B Fe Mo N14 O0.51 P Si3                                |
| Formula weight                                | 1527.87                                                              |
| Crystal color, shape, size                    | orange block, 0.23 × 0.17 × 0.10 mm³                                  |
| Temperature                                   | 100(2) K                                                             |
| Wavelength                                    | 0.71073 Å                                                            |
| Crystal system, space group                   | Triclinic, P-1                                                       |
| Unit cell dimensions                          | a = 15.5853(6) Å; b = 15.7180(7) Å; c = 20.1871(9) Å               |
|                                              | α = 90.5250(10)°; β = 102.1050(10)°; γ = 114.5690(10)°              |
| Volume                                        | 4371.6(3) Å³                                                        |
| Z                                             | 2                                                                   |
| Density (calculated)                          | 1.161 Mg/m³                                                          |
| Absorption coefficient                        | 0.415 mm⁻¹                                                           |
| F(000)                                        | 1652                                                                |

**Data collection**

| Property                                      | Value                                                                |
|-----------------------------------------------|----------------------------------------------------------------------|
| Diffractometer                                | Venture D8, Bruker                                                   |
| Source                                        | IμS III, Incoatec                                                    |
| Theta range for data collection               | 1.038 to 27.506°                                                    |
| Index ranges                                  | -20<≤h<≤20, -20<≤k<≤20, -26<≤l<≤26                                  |
| Reflections collected                         | 140945                                                              |
| Independent reflections                       | 20070 [R int = 0.1178]                                               |
| Observed Reflections                          | 12861                                                               |
| Completeness to theta                         | 25.242°; 99.9%                                                      |
Solution and Refinement

Absorption correction
Semi-empirical from equivalents

Max. and min. transmission
0.7454 and 0.7033

Solution
Intrinsic methods

Refinement method
Full-matrix least-squares on F^2

Weighting scheme
\[ w = \left| \sigma^2 F_o^2 + AP^2 + BP \right|^{-1}, \text{ with} \]
\[ P = (F_o^2 + 2F_c^2)/3, \quad A = 0.1341, \quad B = 0 \]

Data / restraints / parameters
20070 / 1102 / 946

Goodness-of-fit on F^2
1.078

Final R indices [I>2\sigma(I)]
R1 = 0.0712, wR2 = 0.1974

R indices (all data)
R1 = 0.1118, wR2 = 0.2322

Largest diff. peak and hole
1.736 and -1.684 e.Å^-3

Disorder ratio Mo-P1-N14/Mo-N14D-P1D
0.8169/0.1831

Goodness-of-fit = \[ \left( \sum \left( w(F_o^2 - F_c^2)^2 \right)/N_{\text{observ}} - N_{\text{params}} \right)^{1/2}, \text{ all data.} \]

R1 = \[ \sum |F_o| - |F_c| / \sum |F_o|, \quad wR2 = \left[ \sum \left( w(F_o^2 - F_c^2)^2 \right) / \sum \left( w(F_o^2)^2 \right) \right]^{1/2}. \]
**Table S9-2.** Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for A-4. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|       | x      | y      | z      | U(eq) |
|-------|--------|--------|--------|-------|
| Mo1   | 2590(1)| 6473(1)| 298(1) | 19(1) |
| P1    | 3275(1)| 6762(1)| -574(1)| 20(1) |
| N14   | 3745(14)| 6970(14)| -1181(8)| 28(1) |
| N14D  | 3080(20)| 6670(20)| -434(17)| 20(1) |
| P1D   | 3610(20)| 6880(20)| -1077(12)| 28(1) |

**Table S9-3.** Selected bond lengths [Å] and angles [°] for A-4.

|       | Mo1-N14D | Mo1-N11 | Mo1-N13 | Mo1-N12 | Mo1-P1  | Mo1-N10 | P1-N14 | N14D-P1D | N14-P1-Mo1 | P1D-N14D-Mo1 |
|-------|----------|---------|---------|---------|---------|---------|--------|----------|------------|-------------|
| Mo1-N14D | 1.77(3)  |         |         |         |         |         |        |          |            |             |
| Mo1-N13  | 2.029(4) |         |         |         |         |         |        |          |            |             |
| Mo1-P1   | 2.2017(18)|        |         |         |         |         |        |          |            |             |
| P1-N14   | 1.525(8) |         |         |         |         |         |        |          |            |             |
| N14-P1-Mo1 | 179.3(7)|        |         |         |         |         |        |          |            |             |
| P1D-N14D-Mo1 |        |         |         |         |         |         |        |          | 176(2)     |             |
Table S9-4. Selected anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for A-4. The anisotropic displacement factor exponent takes the form: $-2\pi^2 \{ h^2 a^* u_{11} + ... + 2 h k a^* b^* u_{12} \}$

|       | $u_{11}$ | $u_{22}$ | $u_{33}$ | $u_{12}$ | $u_{13}$ | $u_{23}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Mo1   | 21(1)    | 19(1)    | 16(1)    | 1(1)     | 5(1)     | 8(1)     |
| P1    | 23(1)    | 23(1)    | 17(1)    | 2(1)     | 9(1)     | 11(1)    |
| N14   | 29(5)    | 35(4)    | 24(4)    | 5(3)     | 16(2)    | 13(4)    |
| N14D  | 23(1)    | 23(1)    | 17(1)    | 2(1)     | 9(1)     | 11(1)    |
| P1D   | 29(5)    | 35(4)    | 24(4)    | 5(3)     | 16(2)    | 13(4)    |

Table S10-1. Crystal data and structure refinement for B-1.

- **Empirical formula**: C74.96 H143.82 B Fe Mo N14 O0.54 P Si3
- **Formula weight**: 1527.87
- **Crystal color, shape, size**: orange block, 0.23 × 0.17 × 0.10 mm$^3$
- **Temperature**: 100(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system, space group**: Triclinic, P-1
- **Unit cell dimensions**: $a = 15.5855(6)$ Å, $\alpha = 90.5370(10)^\circ$, $b = 15.7156(7)$ Å, $\beta = 102.1340(10)^\circ$. 
c = 20.2048(9) Å  \quad \gamma = 114.5480(10)°.

Volume  4374.9(3) Å³

Z  2

Density (calculated)  1.160 Mg/m³

Absorption coefficient  0.415 mm⁻¹

F(000)  1652

**Data collection**

Diffractometer  Venture D8, Bruker

Source  \( \mu \)S III, Incoatec

Theta range for data collection  1.037 to 27.516°.

Index ranges  -20 ≤ h ≤ 20, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26

Reflections collected  141234

Independent reflections  20094 [R(int) = 0.1083]

Observed Reflections  13719

Completeness to theta = 25.242°  99.9 %

**Solution and Refinement**

Absorption correction  Semi-empirical from equivalents

Max. and min. transmission  0.7454 and 0.7024

Solution  Intrinsic methods

Refinement method  Full-matrix least-squares on F²

Weighting scheme  \( w = [\sigma^2Fo^2 + AP^2 + BP]^{-1} \), with

\[ P = (Fo^2 + 2Fe^2)/3, \quad A = 0.1105, \quad B = 12.3843 \]

Data / restraints / parameters  20094 / 1101 / 946

Goodness-of-fit on F²  1.058
Final R indices [I>2σ(I)]

\[ R1 = 0.0730, \; wR2 = 0.1876 \]

R indices (all data)

\[ R1 = 0.1115, \; wR2 = 0.2238 \]

Largest diff. peak and hole

1.798 and -1.613 e.Å\(^{-3}\)

Disorder ratio Mo-P1-N14/Mo-N14D-P1D

0.7017/0.2983

Goodness-of-fit = \[ \frac{\sum(w(F_o^2 - F_c^2)^2)}{N_{\text{observ}} - N_{\text{params}}} \]\(^{1/2}\), all data.

\[ R1 = \frac{\sum|F_o| - |F_c|}{\sum|F_o|}, \; \; wR2 = \left[ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]} \right]^{1/2}. \]
Table S10-2. Selected atomic coordinates \((\times 10^4)\) and equivalent isotropic displacement parameters \((\text{Å}^2 \times 10^3)\) for B-1. \(U_{eq}\) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

|       | x     | y     | z     | \(U_{eq}\) |
|-------|-------|-------|-------|------------|
| Mo1   | 2589(1)| 6472(1)| 298(1)| 19(1)      |
| P1    | 3278(2)| 6763(2)| -573(1)| 21(1)      |
| N14   | 3745(16)| 6973(16)| -1173(9)| 27(1)      |
| N14D  | 3095(15)| 6681(14)| -418(11)| 21(1)      |
| P1D   | 3616(12)| 6873(11)| -1070(7)| 27(1)      |

Table S10-3. Selected bond lengths [Å] and angles [°] for B-1.

| Bond                  | Length [Å] | Angle [°] |
|-----------------------|------------|-----------|
| Mo1-N14D              | 1.76(2)    |           |
| Mo1-N11               | 2.028(4)   |           |
| Mo1-P1                | 2.205(2)   |           |
| P1-N14                | 1.512(10)  |           |
| N14-P1-Mo1            | 179.1(9)   |           |
| Mo1-N13               | 2.027(4)   |           |
| Mo1-N12               | 2.031(4)   |           |
| Mo1-N10               | 2.246(4)   |           |
| N14D-P1D              | 1.65(2)    |           |
| P1D-N14D-Mo1          | 177.4(15.6)|           |

Table S10-4. Selected anisotropic displacement parameters \((\text{Å}^2 \times 10^3)\) for B-1. The anisotropic displacement factor exponent takes the form: \(-2\pi^2[ h^2 a^* a U_{11} + ... + 2 h k a^* b^* U_{12} ]\)

|       | \(U_{11}\) | \(U_{22}\) | \(U_{33}\) | \(U_{23}\) | \(U_{13}\) | \(U_{12}\) |
|-------|------------|------------|------------|------------|------------|------------|

S57
|      | Mo1   |     |     |     |     |     |
|------|-------|-----|-----|-----|-----|-----|
| P1   | 24(1) | 24(1)| 19(1)| 3(1)| 9(1)| 11(1)|
| N14  | 26(4) | 29(3)| 27(3)| 7(2)| 12(2)| 11(3)|
| N14D | 24(1) | 24(1)| 19(1)| 3(1)| 9(1)| 11(1)|
| P1D  | 26(4) | 29(3)| 27(3)| 7(2)| 12(2)| 11(3)|
**Table S11-1. Crystal data and structure refinement for B-2.**

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                            | C75.03 H144.11 B Fe Mo N14 O0.47 P Si3     |
| Formula weight                                | 1527.87                                    |
| Crystal color, shape, size                    | orange block, 0.23 × 0.17 × 0.10 mm³       |
| Temperature                                   | 100(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system, space group                   | Triclinic, P-1                             |
| Unit cell dimensions                          | a = 15.5883(6) Å, α = 90.5450(10)°         |
|                                              | b = 15.7107(7) Å, β = 102.2230(10)°        |
|                                              | c = 20.2311(9) Å, γ = 114.5370(10)°        |
| Volume                                        | 4378.5(3) Å³                               |
| Z                                             | 2                                          |
| Density (calculated)                          | 1.159 Mg/m³                                 |
| Absorption coefficient                        | 0.415 mm⁻¹                                 |
| F(000)                                        | 1652                                       |

**Data collection**

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Diffractometer                                | Venture D8, Bruker                         |
| Source                                        | IμS III, Incoatec                          |
| Theta range for data collection               | 1.036 to 27.520°                           |
| Index ranges                                  | -20<=h<=20, -20<=k<=20, -26<=l<=26          |
| Reflections collected                         | 116586                                     |
| Independent reflections                       | 20119 [Rint = 0.1154]                      |
| Observed Reflections                          | 12649                                      |
| Completeness to theta                         | 25.242°                                   |
|                                              | 99.9 %                                     |
**Solution and Refinement**

| Description                                      | Details |
|--------------------------------------------------|---------|
| Absorption correction                            | Semi-empirical from equivalents |
| Max. and min. transmission                        | 0.7456 and 0.7065 |
| Solution                                         | Intrinsic methods |
| Refinement method                                 | Full-matrix least-squares on $F^2$ |
| Weighting scheme                                 | $w = [\sigma^2 F_o^2 + AP^2 + BP]^1$, with $P = (F_o^2 + 2 F_c^2)/3$, $A = 0.1287$, $B = 0$ |
| Data / restraints / parameters                    | 20119 / 1101 / 946 |
| Goodness-of-fit on $F^2$                          | 1.066 |
| Final R indices [$I > 2\sigma(I)$]                | $R1 = 0.0719$, $wR2 = 0.1964$ |
| R indices (all data)                              | $R1 = 0.1150$, $wR2 = 0.2309$ |
| Largest diff. peak and hole                       | 1.660 and -1.547 e.$\text{Å}^{-3}$ |
| Disorder ratio Mo-P1-N14/Mo-N14D-P1D              | 0.5159/0.4841 |

---

Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c)^2]/N_{\text{obs}}]/N_{\text{params}}]^{1/2}$, all data.

$R1 = \Sigma(|F_o| - |F_c|)/\Sigma |F_o|$, $wR2 = [\Sigma[w(F_o^2 - F_c)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. 
**Table S11-2.** Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for B-2. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|     | x        | y        | z        | $U_{eq}$ |
|-----|----------|----------|----------|----------|
| Mo1 | 2591(1)  | 6472(1)  | 299(1)   | 19(1)    |
| P1  | 3278(3)  | 6763(3)  | -575(2)  | 21(1)    |
| N14 | 3748(17) | 6977(17) | -1174(11)| 26(1)    |
| N14D| 3119(11) | 6676(11) | -422(7)  | 21(1)    |
| P1D | 3628(5)  | 6880(5)  | -1066(3)| 26(1)    |

**Table S11-3.** Selected bond lengths [Å] and angles [°] for B-2.

| Bond              | Bond Length [Å] | Bond Angle [°] |
|-------------------|-----------------|----------------|
| Mo1-N14D          | 1.791(13)       | Mo1-N11        | 2.021(4)     |
| Mo1-N13           | 2.025(4)        | Mo1-N12        | 2.027(4)     |
| Mo1-P1            | 2.211(3)        | Mo1-N10        | 2.257(4)     |
| P1-N14            | 1.516(15)       | N14D-P1D       | 1.631(13)    |
| N14-P1-Mo1        | 179.1(9)        | P1D-N14D-Mo1   | 178.5(12)    |
Table S11-4. Selected anisotropic displacement parameters (Å² × 10³) for B-2. The anisotropic displacement factor exponent takes the form: -2p²[ h² a*²U₁₁ + ... + 2 h k a* b* U₁₂ ]

|     | U¹¹ | U²² | U³³ | U²³ | U¹³ | U¹² |
|-----|-----|-----|-----|-----|-----|-----|
| Mo1 | 21(1)| 18(1)| 17(1)| 1(1)| 5(1)| 9(1) |
| P1  | 24(2)| 23(1)| 20(2)| 4(1)| 11(1)| 10(1)|
| N14 | 29(2)| 29(2)| 21(2)| 4(1)| 10(1)| 12(2)|
| N14D| 24(2)| 23(1)| 20(2)| 4(1)| 11(1)| 10(1)|
| P1D | 29(2)| 29(2)| 21(2)| 4(1)| 10(1)| 12(2)|
Table S12-1. Crystal data and structure refinement for B-3.

| Property                                      | Value                                                  |
|-----------------------------------------------|--------------------------------------------------------|
| Empirical formula                            | C74.98 H143.92 B Fe Mo N14 O0.52 P Si3                 |
| Formula weight                                | 1527.87                                                |
| Crystal color, shape, size                    | orange block, 0.23 × 0.17 × 0.10 mm³                   |
| Temperature                                   | 100(2) K                                               |
| Wavelength                                    | 0.71073 Å                                              |
| Crystal system, space group                   | Triclinic, P-1                                         |
| Unit cell dimensions                          |                                                       |
| a                                             | 15.5911(6) Å                                           |
| b                                             | 15.7056(7) Å                                           |
| c                                             | 20.2558(9) Å                                           |
| α                                             | 90.5570°                                               |
| β                                             | 102.2900°                                              |
| γ                                             | 114.5480°                                              |
| Volume                                        | 4381.3(3) Å³                                           |
| Z                                             | 2                                                      |
| Density (calculated)                          | 1.158 Mg/m³                                            |
| Absorption coefficient                        | 0.414 mm⁻¹                                             |
| F(000)                                        | 1652                                                   |

**Data collection**

| Property                                      | Value                                                  |
|-----------------------------------------------|--------------------------------------------------------|
| Diffractometer                                | Venture D8, Bruker                                     |
| Source                                        | IμS III, Incoatec                                      |
| Theta range for data collection               | 1.035 to 27.505°.                                     |
| Index ranges                                  | -20≤h≤20, -20≤k≤20, -26≤l≤26                          |
| Reflections collected                         | 140442                                                 |
| Independent reflections                       | 20128 [Rint = 0.1077]                                  |
| Observed Reflections                          | 13683                                                  |
| Completeness to theta = 25.242°               | 99.9 %                                                 |
Solution and Refinement

Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.7456 and 0.7032
Solution: Intrinsic methods
Refinement method: Full-matrix least-squares on F²
Weighting scheme: \[ w = [\sigma^2 F_o^2 + AP^2 + BP]^{-1}, \] with \[ P = \frac{(F_o^2 + 2 F_c^2)}{3}, \] \( A = 0.1126, B = 10.4779 \)
Data / restraints / parameters: 20128 / 1102 / 946
Goodness-of-fit on F²: 1.058
Final R indices [I>2\sigma(I)]: R₁ = 0.0721, wR₂ = 0.1860
R indices (all data): R₁ = 0.1116, wR₂ = 0.2224
Largest diff. peak and hole: 1.649 and -1.453 e.Å⁻³
Disorder ratio Mo-P1-N14/Mo-N14D-P1D: 0.3876/0.6124

Goodness-of-fit = \[ \frac{\sum [w(F_o^2 - F_c^2)^2]}{N_{\text{obs}} - N_{\text{params}}} \]¹⁄₂, all data.

\[ R₁ = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR₂ = \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]}^{1/2}. \]
Table S12-2. Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for B-3. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|      | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| Mo1  | 2593(1) | 6471(1) | 300(1) | 19(1) |
| P1   | 3277(4) | 6768(4) | 576(3) | 22(1) |
| N14  | 3730(20) | 6970(20) | 1179(13) | 27(1) |
| N14D | 3135(10) | 6681(9) | 422(6) | 22(1) |
| P1D  | 3632(4) | 6879(4) | 1065(2) | 27(1) |

Table S12-3. Selected bond lengths [Å] and angles [°] for B-3.

| Bond          | Length  | Bond          | Length  |
|---------------|---------|---------------|---------|
| Mo1-N14D      | 1.807(10) | Mo1-N13      | 2.022(4) |
| Mo1-N12       | 2.022(4)  | Mo1-N11      | 2.024(4) |
| Mo1-P1        | 2.215(4)  | Mo1-N10      | 2.260(4) |
| N14-P1-Mo1    | 179.3(12) | P1D-N14D-Mo1 | 179.4(11) |
Table S12-4. Selected anisotropic displacement parameters (Å$^2 \times 10^3$) for B-3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[a^2U_{11} + ... + 2hkab^*U_{12}]$

|      | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|------|----------|----------|----------|----------|----------|----------|
| Mo1  | 21(1)    | 18(1)    | 18(1)    | 1(1)     | 5(1)     | 9(1)     |
| P1   | 24(2)    | 24(2)    | 21(2)    | 4(1)     | 11(1)    | 11(2)    |
| N14  | 31(2)    | 30(1)    | 22(2)    | 5(1)     | 11(1)    | 13(1)    |
| N14D | 24(2)    | 24(2)    | 21(2)    | 4(1)     | 11(1)    | 11(2)    |
| P1D  | 31(2)    | 30(1)    | 22(2)    | 5(1)     | 11(1)    | 13(1)    |
**Table S13-1. Crystal data and structure refinement for B-4.**

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Empirical formula                     | C75.04 H144.17 B Fe Mo N14 O0.46 P Si3     |
| Formula weight                        | 1527.87                                    |
| Crystal color, shape, size            | orange block, 0.23 × 0.17 × 0.10 mm$^3$    |
| Temperature                           | 100(2) K                                   |
| Wavelength                            | 0.71073 Å                                  |
| Crystal system, space group           | Triclinic, P-1                             |
| Unit cell dimensions                  | $a = 15.5964(7)$ Å, $\alpha = 90.5550(10)^\circ$. |
|                                       | $b = 15.7050(7)$ Å, $\beta = 102.3390(10)^\circ$. |
|                                       | $c = 20.2728(10)$ Å, $\gamma = 114.5680(10)^\circ$. |
| Volume                                | 4384.6(4) Å$^3$                           |
| Z                                     | 2                                          |
| Density (calculated)                  | 1.157 Mg/m$^3$                             |
| Absorption coefficient                | 0.414 mm$^{-1}$                            |
| F(000)                                | 1652                                       |

**Data collection**

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Diffractometer                        | Venture D8, Bruker                         |
| Source                                | IμS III, Incoatec                         |
| Theta range for data collection       | 1.035 to 27.506°.                         |
| Index ranges                          | $-20 \leq h \leq 20, -20 \leq k \leq 20, -26 \leq l \leq 26$ |
| Reflections collected                 | 139338                                     |
| Independent reflections               | 20152 [R(int) = 0.1244]                    |
| Observed Reflections                  | 12671                                      |
| Completeness to theta = 25.242°       | 100.0 %                                    |
**Solution and Refinement**

Absorption correction  
Semi-empirical from equivalents

Max. and min. transmission  
0.7454 and 0.7024

Solution  
Intrinsic methods

Refinement method  
Full-matrix least-squares on $F^2$

Weighting scheme  
$w = [\sigma^2 F_0^2 + AP^2 + BP]^{-1}$, with  
$P = (F_0^2 + 2F_c^2)/3$, $A = 0.1368$, $B = 0$

Data / restraints / parameters  
20152 / 1097 / 946

Goodness-of-fit on $F^2$  
1.058

Final R indices [$I > 2\sigma(I)$]  
R1 = 0.0733, wR2 = 0.1988

R indices (all data)  
R1 = 0.1172, wR2 = 0.2361

Largest diff. peak and hole  
1.589 and -1.673 eÅ$^{-3}$

Disorder ratio Mo-P1-N14/Mo-N14D-P1D  
0.3337/0.6663

Goodness-of-fit = $[\sum w(F_0^2 - F_c^2)^2/(N_{\text{obs}} - N_{\text{params}})]^{1/2}$, all data.

$R1 = \sum (|F_0| - |F_c|)/\sum |F_0|$.  
$wR2 = [\sum w(F_0^2 - F_c^2)^2]/\sum [w(F_0^2)^2]^{1/2}$. 

S68
**Table S13-2.** Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for B-4. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|        | x    | y    | z    | $U_{eq}$ |
|--------|------|------|------|----------|
| Mo1    | 2594(1) | 6471(1) | 301(1) | 20(1)    |
| P1     | 3280(6)  | 6764(6)  | -569(3)  | 24(1)    |
| N14    | 3750(30) | 6980(30) | -1151(18) | 26(1)    |
| N14D   | 3130(10) | 6679(9)  | -420(6)  | 24(1)    |
| P1D    | 3631(4)  | 6874(3)  | -1066(2) | 26(1)    |

**Table S13-3.** Selected bond lengths [Å] and angles [°] for B-4.

| Bond                  | Length [Å] | Bond                  | Length [Å] |
|-----------------------|------------|-----------------------|------------|
| Mo1-N14D              | 1.801(9)   | Mo1-N11               | 2.019(4)   |
| Mo1-N12               | 2.020(4)   | Mo1-N13               | 2.023(4)   |
| Mo1-P1                | 2.209(5)   | Mo1-N10               | 2.268(4)   |
| P1-N14                | 1.48(3)    | N14D-P1D              | 1.634(10)  |
| N14-P1-Mo1            | 178.8(15)  | P1D-N14D-Mo1          | 179.1(11)  |
**Table S13-4.** Selected anisotropic displacement parameters ($\AA^2 \times 10^3$) for **B-4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^* U^{11} + \ldots + 2 \ h \ k \ a^* \ b^* \ U^{12} ]$

|      | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|------|----------|----------|----------|----------|----------|----------|
| Mo1  | 22(1)    | 20(1)    | 17(1)    | 1(1)     | 4(1)     | 9(1)     |
| P1   | 26(3)    | 28(2)    | 23(3)    | 4(2)     | 12(1)    | 12(2)    |
| N14  | 30(2)    | 29(2)    | 22(2)    | 3(1)     | 9(1)     | 13(1)    |
| N14D | 26(3)    | 28(2)    | 23(3)    | 4(2)     | 12(1)    | 12(2)    |
| P1D  | 30(2)    | 29(2)    | 22(2)    | 3(1)     | 9(1)     | 13(1)    |
Table S14-1. Crystal data and structure refinement for B-5.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C75.04 H144.15 B Fe Mo N14 O0.46 P Si3     |
| Formula weight                                | 1527.87                                    |
| Crystal color, shape, size                    | orange block, 0.23 × 0.17 × 0.10 mm³       |
| Temperature                                   | 100(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system, space group                   | Triclinic, P-1                             |
| Unit cell dimensions                          | a = 15.5984(7) Å, b = 15.7039(7) Å, c = 20.2878(10) Å |
|                                              | α = 90.5570(10)°, β = 102.3710(10)°, γ = 114.5830(10)° |
| Volume                                        | 4386.8(4) Å³                              |
| Z                                             | 2                                          |
| Density (calculated)                          | 1.157 Mg/m³                                |
| Absorption coefficient                        | 0.414 mm⁻¹                                 |
| F(000)                                        | 1652                                       |

**Data collection**

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Diffractometer                                | Venture D8, Bruker                         |
| Source                                        | IμS III, Incoatec                          |
| Theta range for data collection              | 1.034 to 27.517°                           |
| Index ranges                                  | -20 ≤ h ≤ 20, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26  |
| Reflections collected                         | 140576                                     |
| Independent reflections                       | 20167 [Rint = 0.1259]                     |
| Observed Reflections                          | 12547                                      |
| Completeness to theta                         | 25.242°                                   |
|                                               | 100.0 %                                    |

Solution and Refinement

Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  0.7454 and 0.7024
Solution  Intrinsic methods
Refinement method  Full-matrix least-squares on F^2
Weighting scheme  \( w = \left[ \sigma^2 F_o^2 + A P^2 + B P \right]^{-1} \), with
\( P = (F_o^2 + 2 F_c^2)/3 \), \( A = 0.1361 \), \( B = 0 \)
Data / restraints / parameters  20167 / 1096 / 946
Goodness-of-fit on F^2  1.061
Final R indices [I>2\( \sigma(I) \)]  R1 = 0.0739, wR2 = 0.1999
R indices (all data)  R1 = 0.1188, wR2 = 0.2369
Largest diff. peak and hole  1.610 and -1.768 e.Å^3
Disorder ratio Mo-P1-N14/Mo-N14D-P1D  0.2886/0.7114

Goodness-of-fit = \( \left[ \Sigma [w(F_o^2 - F_c^2)^2]/N_{\text{observ}} - N_{\text{params}} \right]^{1/2} \), all data.
R1 = \( \Sigma |F_o| - |F_c|) / \Sigma |F_o| \), \( wR2 = \left[ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)] \right]^{1/2} \).
Table S14-2. Selected atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for B-5. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

|        | x       | y       | z       | U(eq)  |
|--------|---------|---------|---------|--------|
| Mo1    | 2596(1) | 6471(1) | 301(1)  | 20(1)  |
| P1     | 3279(7) | 6767(7) | -569(4) | 25(1)  |
| N14    | 3740(30)| 6970(30)| -1150(20)| 27(1) |
| N14D   | 3134(10)| 6679(9) | -419(6) | 25(1)  |
| P1D    | 3634(4) | 6876(4) | -1064(2)| 27(1)  |

Table S14-3. Selected bond lengths [Å] and angles [°] for B-5.

|          |         |          |          |         |
|----------|---------|----------|---------|---------|
| Mo1-N14D | 1.804(9)| Mo1-N11  | 2.017(4)|
| Mo1-N13  | 2.020(4)| Mo1-N12  | 2.022(4)|
| Mo1-P1   | 2.209(6)| Mo1-N10  | 2.269(4)|
| P1-N14   | 1.48(3) | N14D-P1D | 1.631(9)|
| N14-P1-Mo1| 179.7(19)| P1D-N14D-Mo1 | 179.3(11)|
Table S14-4. Selected anisotropic displacement parameters (Å² × 10³) for B-5. The anisotropic displacement factor exponent takes the form: -2π²[ h² a*²U₁₁ + ... + 2 h k a* b* U₁₂ ]

|      | U₁₁  | U₂₂  | U₃₃  | U₂₃  | U₁₃  | U₁₂  |
|------|------|------|------|------|------|------|
| Mo1  | 22(1)| 20(1)| 17(1)| 0(1) | 4(1) | 9(1) |
| P1   | 26(3)| 27(2)| 26(3)| 4(2) | 12(2)| 12(2)|
| N14  | 31(2)| 29(2)| 22(2)| 3(1) | 10(1)| 13(1)|
| N14D | 26(3)| 27(2)| 26(3)| 4(2) | 12(2)| 12(2)|
| P1D  | 31(2)| 29(2)| 22(2)| 3(1) | 10(1)| 13(1)|
Table S15-1. Crystal data and structure refinement for B-6.

Empirical formula          C75.05 H144.18 B Fe Mo N14 O0.45 P Si3
Formula weight             1527.88
Crystal color, shape, size orange block, 0.23 × 0.17 × 0.10 mm³
Temperature               100(2) K
Wavelength                0.71073 Å
Crystal system, space group Triclinic, P-1
Unit cell dimensions
    a = 15.6007(7) Å   α = 90.5540(10)°.
    b = 15.7039(7) Å   β = 102.4070(10)°.
    c = 20.3019(10) Å  γ = 114.5960(10)°.
Volume                     4389.3(4) Å³
Z                          2
Density (calculated)       1.156 Mg/m³
Absorption coefficient     0.414 mm⁻¹
F(000)                     1652

Data collection

Diffractometer            Venture D8, Bruker
Source                     IμS III, Incoatec
Theta range for data collection 1.033 to 27.525°.
Index ranges              -20<=h<=20, -20<=k<=20, -26<=l<=26
Reflections collected      139627
Independent reflections   20184 [Rint = 0.1276]
Observed Reflections      12472
Completeness to theta = 25.242° 100.0 %
Solution and Refinement

Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  0.7454 and 0.7024
Solution  Intrinsic methods
Refinement method  Full-matrix least-squares on F^2
Weighting scheme  \( w = \left[ \sigma^2 F_o^2 + AP^2 + BP \right]^{-1}, \) with
\[ P = \frac{(F_o^2 + 2 F_c^2)}{3}, \ A = 0.1398, \ B = 0 \]
Data / restraints / parameters  20184 / 1090 / 946
Goodness-of-fit on F^2  1.040
Final R indices [I>2\(\sigma(I)\)]  R1 = 0.0744, wR2 = 0.1997
R indices (all data)  R1 = 0.1211, wR2 = 0.2388
Largest diff. peak and hole  1.702 and -1.869 e.Å\(^{-3}\)
Disorder ratio Mo-P1-N14/Mo-N14D-P1D  0.2598/0.7402

Goodness-of-fit = \( \frac{\sum [w(F_o^2 - F_c^2)^2]}{N_{\text{observ}}} - N_{\text{params}} \)^{1/2}, all data.

\[ R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}. \quad wR2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}. \]
**Table S15-2.** Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for B-6. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|   | x   | y   | z  | U(eq) |
|---|-----|-----|----|-------|
| Mo1 | 2597(1) | 6471(1) | 302(1) | 20(1) |
| P1  | 3276(8) | 6766(8) | -572(5) | 26(1) |
| N14 | 3760(30) | 6980(30) | -1140(20) | 27(1) |
| N14D | 3140(9) | 6681(9) | -416(6) | 26(1) |
| P1D | 3632(3) | 6875(3) | -1065(2) | 27(1) |

**Table S15-3.** Selected bond lengths [Å] and angles [°] for B-6.

| Bond | Length [Å] | Angle [°] |
|------|------------|-----------|
| Mo1-N14D | 1.805(9) | Mo1-N11 | 2.014(4) |
| Mo1-N12  | 2.018(4) | Mo1-N13 | 2.023(4) |
| Mo1-P1   | 2.213(7) | Mo1-N10 | 2.272(4) |
| P1-N14  | 1.48(3)   | N14D-P1D | 1.633(9) |
| N14-P1-Mo1 | 178(2) | P1D-N14D-Mo1 | 179.8(8) |
**Table S15-4.** Selected anisotropic displacement parameters (Å² × 10³) for B-6. The anisotropic displacement factor exponent takes the form: \(-2\pi^2[ h^2 a^* U^{11} + ... + 2 h k a^* b^* U^{12} \] )

|       | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|--------|--------|--------|--------|--------|--------|
| Mo1   | 23(1)  | 20(1)  | 18(1)  | 0(1)   | 4(1)   | 10(1)  |
| P1    | 27(3)  | 27(2)  | 24(3)  | 4(2)   | 10(2)  | 11(2)  |
| N14   | 31(2)  | 30(2)  | 23(1)  | 4(1)   | 11(1)  | 13(1)  |
| N14D  | 27(3)  | 27(2)  | 24(3)  | 4(2)   | 10(2)  | 11(2)  |
| P1D   | 31(2)  | 30(2)  | 23(1)  | 4(1)   | 11(1)  | 13(1)  |
Table S16-1. Crystal data and structure refinement for B-7.

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Empirical formula                     | C75.05 H144.21 B Fe Mo N14 O0.45 P Si3     |
| Formula weight                        | 1527.87                                    |
| Crystal color, shape, size            | orange block, 0.23 × 0.17 × 0.10 mm³       |
| Temperature                           | 100(2) K                                   |
| Wavelength                            | 0.71073 Å                                  |
| Crystal system, space group           | Triclinic, P-1                             |
| Unit cell dimensions                  | a = 15.6017(11) Å, α = 90.572(2)°          |
|                                      | b = 15.7015(12) Å, β = 102.466(2)°         |
|                                      | c = 20.3141(16) Å, γ = 114.617(2)°         |
| Volume                                | 4389.3(6) Å³                               |
| Z                                     | 2                                          |
| Density (calculated)                  | 1.156 Mg/m³                                |
| Absorption coefficient                | 0.414 mm⁻¹                                 |
| F(000)                                | 1652                                       |

Data collection

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Diffractometer                        | Venture D8, Bruker                         |
| Source                                | IμS III, Incoatec                         |
| Theta range for data collection       | 1.033 to 27.699°.                         |
| Index ranges                          | -20≤h≤20, -20≤k≤20, -26≤l≤26               |
| Reflections collected                 | 139898                                     |
| Independent reflections              | 20246 [Rint = 0.1364]                     |
| Observed Reflections                 | 12197                                      |
| Completeness to theta = 25.242°      | 100.0 %                                   |
Solution and Refinement

Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.7456 and 0.6913
Solution: Intrinsic methods
Refinement method: Full-matrix least-squares on $F^2$
Weighting scheme: $w = \left[ \sigma^2 F_o^2 + A P^2 + B P \right]^{-1}$, with
$P = \left( F_o^2 + 2 F_e^2 \right)/3$, $A = 0.1502$, $B = 0$
Data / restraints / parameters: 20246 / 1091 / 946
Goodness-of-fit on $F^2$: 1.023
Final R indices [I>2$\sigma$(I)]: $R_1 = 0.0772$, $wR_2 = 0.2077$
R indices (all data): $R_1 = 0.1278$, $wR_2 = 0.2502$
Largest diff. peak and hole: 1.600 and -1.948 e.$\text{Å}^{-3}$
Disorder ratio Mo-P1-N14/Mo-N14D-P1D: 0.2371/0.7629

Goodness-of-fit = $\left[ \Sigma [w(F_o^2 - F_e^2)^2]/(N_{\text{observ}} - N_{\text{param}}) \right]^{1/2}$, all data.

$R_1 = \Sigma |F_o| - |F_e| / \Sigma |F_o|$, $wR_2 = \left[ \Sigma [w(F_o^2 - F_e^2)^2] / \Sigma [w(F_o^2)^2] \right]^{1/2}$. 
**Table S16-2.** Selected atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for B-7. Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| Mo1 | 2598(1) | 6472(1) | 302(1) | 21(1) |
| P1  | 3282(10) | 6761(9) | -568(6) | 27(1) |
| N14 | 3730(40) | 6970(40) | -1150(30) | 28(1) |
| N14D| 3139(9) | 6690(9) | -414(6) | 27(1) |
| P1D | 3635(4) | 6876(4) | -1063(2) | 28(1) |

**Table S16-3.** Selected bond lengths [Å] and angles [°] for B-7.

| Bond                  | Length/Angle |
|-----------------------|--------------|
| Mo1-N14D              | 1.802(9)     |
| Mo1-N13               | 2.018(4)     |
| Mo1-P1                | 2.213(8)     |
| P1-N14                | 1.47(4)      |
| N14-P1-Mo1            | 179(2)       |
| Mo1-N11               | 2.012(4)     |
| Mo1-N12               | 2.019(4)     |
| Mo1-N10               | 2.276(4)     |
| N14D-P1D              | 1.637(9)     |
| P1D-N14D-Mo1          | 179.1(8)     |
Table S16-4. Selected anisotropic displacement parameters (Å² × 10³) for B-7. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [ h^2 a^*U_{11} + ... + 2hk a^* b^* U_{12} ]$

|        | U¹¹ | U¹² | U¹³ | U²³ | U¹² | U³³ |
|--------|-----|-----|-----|-----|-----|-----|
| Mo1    | 24(1)| 21(1)| 18(1)| 0(1)| 4(1)| 10(1)|
| P1     | 30(3)| 29(2)| 25(3)| 1(2)| 11(2)| 12(2)|
| N14    | 34(2)| 31(2)| 22(2)| 3(1)| 10(1)| 14(1)|
| N14D   | 30(3)| 29(2)| 25(3)| 1(2)| 11(2)| 12(2)|
| P1D    | 34(2)| 31(2)| 22(2)| 3(1)| 10(1)| 14(1)|
Complex 1. PhB(Pr2Im)3Fe-NP-Mo(N3N)

Data collection

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 182 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 120 seconds and a detector distance of 4.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50° steps in ω and φ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 5511 strong reflections from the actual data collection after integration (SAINT).15 The intensity data were corrected for absorption (SADABS).16

Structure solution and refinement

The space group P-1 was determined based on intensity statistics and systematic absences. The structure was solved using Superflip18 and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.19 The charge-flipping method provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms.

The structure exhibits significant disorder, which was refined successfully. The 2-part disorder was modeled that the occupancies of major and minor components summed to 1. All major components of the 2-part disorder on the main structure was refined with anisotropic displacement parameters, and the minor components as well as solvent disorder were modeled isotropically. The rest of the ordered, non-hydrogen atoms were refined with anisotropic displacement parameters.
The hydrogen atoms were placed in ideal positions and refined as riding atoms. The final full matrix least squares refinement converged to $R_1 = 0.0749$ and $wR_2 = 0.2009$ ($F^2$, all data).
### Table S17. Crystal data and structure refinement

| Property                                      | Value                                           |
|-----------------------------------------------|-------------------------------------------------|
| **Empirical formula**                         | C52 H99 B1 Fe1 Mo1 N11 O1.00 P1 Si3             |
| **Formula weight**                            | 1172.26                                         |
| **Crystal color, shape, size**                | yellow plate, 0.30 × 0.25 × 0.10 mm³            |
| **Temperature**                               | 173 K                                           |
| **Wavelength**                                | 0.71073 Å                                       |
| **Crystal system, space group**               | Triclinic, P-1                                  |
| **Unit cell dimensions**                      | a = 10.1184(6) Å, α = 71.492(2)°.               |
|                                               | b = 15.4620(8) Å, β = 78.041(2)°.               |
|                                               | c = 21.5377(10) Å, γ = 81.087(2)°.              |
| **Volume**                                    | 3111.5(3) Å³                                   |
| **Z**                                         | 2                                               |
| **Density (calculated)**                      | 1.251 Mg/m³                                     |
| **Absorption coefficient**                    | 0.562 mm⁻¹                                     |
| **F(000)**                                    | 1252                                            |

**Data collection**

| Property                                      | Value                                           |
|-----------------------------------------------|-------------------------------------------------|
| **Diffractometer**                           | Bruker Apex Kappa Duo, Bruker                  |
| **Theta range for data collection**           | 1.395 to 25.113°.                              |
| **Index ranges**                              | -12≤h≤12, -18≤k≤18, -25≤l≤25                    |
| **Reflections collected**                     | 35770                                           |
| **Independent reflections**                   | 10988 [R(int) = 0.083]                          |
| **Observed Reflections**                      | 6528                                            |
| **Completeness to theta = 25.113°**           | 99.0 %                                          |
### Solution and Refinement

| Description                                      | Details                                                |
|--------------------------------------------------|--------------------------------------------------------|
| Absorption correction                           | Semi-empirical from equivalents                       |
| Max. and min. transmission                       | 0.95 and 0.87                                          |
| Solution                                         | Direct methods                                         |
| Refinement method                                | Full-matrix least-squares on $F^2$                     |
| Weighting scheme                                 | $w = [\sigma^2 F_o^2 + AP^2 + BP]^1$, with            |
|                                                  | $P = (F_o^2 + 2 F_c^2)/3$, $A = 0.067$, $B = 20.600$ |
| Data / restraints / parameters                   | 10940 / 343 / 692                                      |
| Goodness-of-fit on $F^2$                         | 0.9710                                                 |
| Final R indices [I>2sigma(I)]                    | R1 = 0.0749, wR2 = 0.1655                              |
| R indices (all data)                             | R1 = 0.1333, wR2 = 0.2009                              |
| Largest diff. peak and hole                      | 2.46 and -2.16 eÅ⁻³                                    |
Complex 3. (N₃N)Mo-PN-Rh(triphos) and (N₃N)Mo-NP-Rh(triphos)

Data collection

The data collection was carried out using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) with a frame time of 20 seconds and a detector distance of 40 mm. A collection strategy was calculated and complete data to a resolution of 0.80 Å with a redundancy of 4 were collected. The total exposure time was 9.46 hours. The frames were integrated with the Bruker SAINT ¹⁵ software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 20837 reflections to a maximum θ angle of 25.38° (0.83 Å resolution). The final cell constants of \( a = 25.3056(15) \) Å, \( b = 19.7149(15) \) Å, \( c = 13.1491(8) \) Å, \( β = 106.942(4)° \), volume = 6275.3(7) Å³, are based upon the refinement of the XYZ-centroids of 6053 reflections above 20 σ(I) with 5.26° < 2θ < 50.44°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).¹⁶ The ratio of minimum to maximum apparent transmission was 0.845.

Structure solution and refinement

The space group C 1 2/m 1 was determined based on intensity statistics and systematic absences. The structure was solved using XT¹⁷,²⁰ and refined using full-matrix least-squares on \( F^2 \) within the OLEX2 suite.²¹ A intrinsic phasing solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to \( R1 = 0.0618 \) and \( w\text{R}2 = 0.1944 \) (\( F^2 \), all data). The goodness-of-fit was
1.090. On the basis of the final model, the calculated density was 1.205 g/cm3 and \( F(000) \), 2360 e-. Residual electron density due to the presence of disordered solvent molecules (toluene and pentane) close to a special position was present. Attempts to model it were unsuccessful and did not lead to anything chemically sensible. Therefore, it was necessary to use PLATON SQUEEZE.\(^{22}\)

**Structure description**

The structure was found as a bimetallic rhodium and molybdenum complex. The two metals are linked by a P-N bridge. Disorder around the P-N bridge showed that two different complexes are present. In one complex (modelled as part 1, 0.94 occupancy) the phosphorus atom is coordinated to the molybdenum, and the nitrogen to the rhodium. In the second complex (modelled as part 2, 0.06 occupancy) the P-N bridge flips, with the phosphorus coordinating to the rhodium, and the nitrogen to the molybdenum. This second species is present with a significantly smaller occupancy.

The complex is divided by a mirror plane perpendicular to the crystallographic direction \( b \). The asymmetric unit corresponds to half a molecule \( (Z'=0.5) \). Positional disorder on a phenyl ring located on the mirror plane was modelled by diving the phenyl group into two parts with 0.5 occupancy. Correlated disorder was also present on the ethyleneamine bridges.
Table S18. Crystal data and structure refinement

| Property                               | Value                                      |
|----------------------------------------|--------------------------------------------|
| Empirical formula                      | C49 H72 Mo N5 P4 Rh Si3                    |
| Formula weight                         | 1138.11                                    |
| Crystal color, shape, size             | orange plate, 0.45 × 0.23 × 0.08 mm³       |
| Temperature                            | 173.15 K                                   |
| Wavelength                             | 0.71073 Å                                  |
| Crystal system, space group            | Monoclinic, C 1 2/m 1                      |
| Unit cell dimensions                   | a = 25.3056(15) Å, α = 90°.                |
|                                        | b = 19.7149(15) Å, β = 106.942(4)°.        |
|                                        | c = 13.1491(8) Å, γ = 90°.                 |
| Volume                                 | 6275.3(7) Å³                               |
| Z                                      | 4                                          |
| Density (calculated)                   | 1.205 g/cm³                                |
| Absorption coefficient                 | 0.654 mm⁻¹                                 |
| F(000)                                 | 2360                                       |

Data collection

| Property                               | Value                                      |
|----------------------------------------|--------------------------------------------|
| Diffractometer                         | Bruker APEX-II CCD                         |
| Theta range for data collection        | 1.332 to 25.383°.                          |
| Index ranges                           | -30≤h≤30, -21≤k≤23, -15≤l≤15              |
| Reflections collected                  | 20837                                      |
| Independent reflections                | 5912 [Rint = 0.0471]                       |
| Observed Reflections                   | 4169                                       |
| Completeness to theta = 25.242°        | 99.8 %                                     |
Solution and Refinement

Absorption correction
None

Max. and min. transmission
0.7452 and 0.6231

Solution
Intrinsic methods

Refinement method
Full-matrix least-squares on F^2

Weighting scheme
w = [σ^2Fo^2 + AP^2 + BP]^{-1}, with
P = (Fo^2 + 2Fc^2)/3, A = 0.0844, B = 66.3368

Data / restraints / parameters
5912 / 51 / 343

Goodness-of-fit on F^2
1.090

Final R indices [I>2σ(I)]
R1 = 0.0618, wR2 = 0.1594

R indices (all data)
R1 = 0.0974, wR2 = 0.1944

Extinction coefficient
n/a

Largest diff. peak and hole
1.305 and -0.982 e.Å^{-3}

Disorder ratio Mo1-P1-N1/Mo1-N2-P2
0.9418/0.0582
Complex 4. (N₃N)Mo-P=N-SiMe₃

Data collection
A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 338 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50° steps in ω and ϕ scans. Data to a resolution of 0.77 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9992 strong reflections from the actual data collection after integration (SAINT).¹⁵ The intensity data were corrected for absorption (SADABS).¹⁶

Structure solution and refinement
The space group Pna2₁ was determined based on intensity statistics and systematic absences. The structure was solved using Superflip¹⁸ and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.¹⁹ The charge-flipping solution provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms. The final full matrix least squares refinement converged to R1 = 0.0288 and wR2 = 0.0657 (F², all data).
**Table S19. Crystal data and structure refinement**

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| **Empirical formula**                        | C18 H48 Mo1 N5 P1 Si4        |
| **Formula weight**                           | 573.87                       |
| **Crystal color, shape, size**               | orange block, 0.20 × 0.20 × 0.10 mm³ |
| **Temperature**                              | 173 K                        |
| **Wavelength**                               | 0.71073 Å                    |
| **Crystal system, space group**              | Orthorhombic, Pna2₁          |
| **Unit cell dimensions**                     |                              |
| a                                             | 19.4151(9) Å                 |
| b                                             | 12.4197(5) Å                 |
| c                                             | 12.5653(5) Å                 |
| **Volume**                                    | 3029.9(2) Å³                 |
| **Z**                                         | 4                            |
| **Density (calculated)**                     | 1.258 Mg/m³                  |
| **Absorption coefficient**                   | 0.658 mm⁻¹                   |
| **F(000)**                                    | 1216                         |

**Data collection**

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| **Diffractometer**                           | Bruker Apex Kappa Duo, Bruker|
| **Theta range for data collection**           | 1.947 to 33.142°.            |
| **Index ranges**                             | -27=<h=<22, -19=<k=<11, -18=<l=<12 |
| **Reflections collected**                     | 25784                        |
| **Independent reflections**                   | 8222 [R(int) = 0.040]        |
| **Observed Reflections**                     | 7265                         |
| **Completeness to theta = 25.188°**           | 98.1 %                       |
**Solution and Refinement**

| Description                        | Details                                      |
|------------------------------------|----------------------------------------------|
| Absorption correction              | Semi-empirical from equivalents              |
| Max. and min. transmission          | 0.94 and 0.88                                |
| Solution                           | Direct methods                               |
| Refinement method                  | Full-matrix least-squares on $F^2$           |
| Weighting scheme                   | $w = [\sigma^2 F_o^2 + AP^2 + BP^2]^1$, with |
|                                   | $P = (F_o^2 + 2 F_c^2)/3$, $A = 0.030$, $B = 0.500$ |
| Data / restraints / parameters      | 8197 / 19 / 290                              |
| Goodness-of-fit on $F^2$            | 0.9885                                       |
| Final R indices [$I>2\sigma(I)$]   | $R_1 = 0.0288$, $wR_2 = 0.0626$              |
| R indices (all data)                | $R_1 = 0.0349$, $wR_2 = 0.0657$              |
| Largest diff. peak and hole         | 0.45 and -0.47 e.Å$^{-3}$                    |
References
1. Martinez, J. L.; Lin, H. J.; Lee, W. T.; Pink, M.; Chen, C. H.; Gao, X.; Dickie, D. A.; Smith, J. M., Cyanide Ligand Assembly by Carbon Atom Transfer to an Iron Nitride. J. Am. Chem. Soc. 2017, 139 (40), 14037-14040.
2. Westcott, S. A.; Stringer, G.; Anderson, S.; Taylor, N. J.; Marder, T. B., Synthesis, Structure, and Reactivity of RhCl(PhP\{CH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}\}). Inorg. Chem. 1994, 33, 4589-4594.
3. Zanetti, N. C.; R.R., S.; Davis, W. M., Monomeric Molybdenum and Tungsten Complexes That Contain a Metal-Phosphorous Triple Bond. Angew. Chem. Int. Ed. Engl. 1995, 34, 2044-2046.
4. Hou, Z.; Breen, T. L.; Stephan, D. W., Formation and Reactivity of the Early Metal Phosphides and Phosphinidenes Cp\textsuperscript{*}Zr=PR, Cp\textsuperscript{*}Zr(PR)\textsubscript{2}, and Cp\textsuperscript{*}Zr(PR)\textsubscript{3}. Organometallics 1993, 12, 3158-3167.
5. Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Shih, K.-Y.; O’Donoghue, M. B.; Davis, W. M.; Reif, W. M., Synthesis and Decomposition of Alkyl Complexes of Molybdenum(IV) That Contain a [(Me\textsubscript{3}SiNCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N] Ligand. Direct Detection of α-Elimination Processes That Are More than Six Orders of Magnitude Faster than β-Elimination Processes. J. Am. Chem. Soc. 1997, 119, 11876-11893.
6. Prisecaru, I., WMOSS4 Mössbauer Spectral Analysis Software, www.wmoss.org. 2009-2016.
7. Neese, F., The ORCA Program System. WIREs Comput. Mol. Sci. 2012, 2, 73-78.
8. Pantazis, D. A.; Chen, X.-Y.; Landis, C. R.; Neese, F., All-Electron Scalar Relativistic Basis Sets for Third-Row Transition Metal Atoms. J. Chem. Theory Comp. 2008, 4, 908-919.
9. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A Consistent and Accurate ab initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. J. Chem. Phys. 2010, 132, 154104.
10. Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the Damping Function in Dispersion Corrected Density Functional Theory J. Comput. Chem. 2011, 32, 1456-1465.
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foreman, J. B.; Fox, D. J. Gaussian, Inc.: Wallingford, CT, 2016.
12. Glendening, E. D.; J, E. R.; Carpenter, J. E.; Weinhold, F. N.B.O. , 6; Theoretical Chemistry Institute: 2013.
13. Keith, T. A. AIMA11, 17.11.14; TK Gristmill Software: 2017.
14. Bader, R. F. W., A Quantum Theory of Molecular Structure and Its Applications. Chem. Rev. 1991, 91, 893-928.
15. SAINT, 8.38A; Bruker Analytical X-Ray Systems: Madison, WI, 2016.
16. Blessing, R., An Empirical Correction for Absorption Anisotropy. *Acta Cryst.* **1995, A51**, 33-38.
17. Sheldrick, G. M., A Short History of SHELX. *Acta Cryst.* **2008, A64**, 112-122.
18. L., P.; G., C., Superflip - a Computer Program for the Solution of Crystal Structures by Charge Flipping in Arbitrary Dimensions. *J. Appl. Cryst.* **2007, 40**, 786-790.
19. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J., CRYSFALS Version 12: Software for Guided Crystal Structure Analysis. *J. Appl. Cryst.* **2003, 36**, 1487.
20. Sheldrick, G. M., SHELXT - Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015, A71**, 3-8.
21. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009, 42**, 339-341.
22. Spek, A. L., PLATON SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. *Acta Cryst.* **2015, C71**, 9-18.