

Supporting Information for

Tripodal P₃^XFe–N₂ Complexes (X = B, Al, Ga): Effect of the Apical Atom on Bonding, Electronic Structure, and Catalytic N₂-to-NH₃ Conversion

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Experimental Methods

General Considerations

All manipulations were carried out using standard Schlenk or glovebox techniques under an N₂ atmosphere. Solvents were deoxygenated and dried by thoroughly sparging with N₂ gas followed by passage through an activated alumina column in the solvent purification system by SG Water, USA LLC. Non-halogenated solvents were tested with sodium benzophenone ketyl in tetrahydrofuran (THF) in order to confirm effective oxygen and moisture removal. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3 Å molecular sieves prior to use.

P₃^{Al} (**1b**)¹ and P₃^{Ga} (**1c**)² were synthesized from a modified literature procedure. [Na(12-c-4)₂][P₃^BFe–N₂],³ [H(OEt)₂][BAr^F₄] (HBAr^F₄, BAr^F₄[–] = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate),⁴ KC₈,⁵ [H₂NPh₂][OTf],^{6,7} and Cp*₂Co⁸ were prepared according to literature methods. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Diethyl ether (Et₂O) used for NH₃ generation experiments was stirred over Na/K (≥ 1 hour) and filtered before use.

NMR Spectroscopy

NMR measurements were obtained on Varian 300, 400, or 500 MHz spectrometers. ¹H NMR chemical shifts are reported in ppm relative to tetramethylsilane, using residual protio solvent as an internal standard. ³¹P NMR chemical shifts were externally referenced to 85% H₃PO₄ in H₂O. Solution phase magnetic measurements were performed by the method of Evans.⁹

EPR Spectroscopy

X-band EPR spectra were obtained on a Bruker EMX spectrometer.

IR Spectroscopy

IR measurements were obtained as solutions or thin films formed by evaporation of solutions using a Bruker Alpha Platinum ATR spectrometer with OPUS software in a glovebox under an N₂ atmosphere.

UV-Visible Spectroscopy

Optical spectroscopy measurements were collected with a Cary 50 UV-visible spectrophotometer using a 1 cm path length quartz cuvette. All samples had a blank sample background subtraction applied.

Electrochemistry

Electrochemical measurements were carried out in a glovebox under an N₂ atmosphere in a one compartment cell using a CH Instruments 600B electrochemical analyzer. A glassy carbon electrode was used as the working electrode and platinum wire was used as the auxiliary electrode. A silver pseudoreference electrode was used with the ferrocene couple (Fc^[1+/0]) as an internal reference. THF solutions of electrolyte (0.1 M [ⁿBu₄][PF₆]) and analyte (ca. 1 mM) were also prepared under an N₂ atmosphere.

Elemental Analysis

Elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, IN) or by the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a PerkinElmer 2400 Series II CHN Elemental Analyzer.

X-ray Crystallography

XRD studies were carried out at the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a Bruker three-circle SMART diffractometer with a SMART 1K CCD detector or Bruker Kappa Apex II diffractometer. Data was collected at 100 K using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Using OLEX2,¹⁰ structures were solved with the XT¹¹ structure solution program using Direct Methods and refined with the XL¹² refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 (1.5 for methyl groups) times the U_{eq} of the atoms to which they are bonded.

Computational Methods

All calculations were carried out using version 3.0.3 of the ORCA package.¹³ The calculations

were performed on the full P_3^XFe scaffolds using DFT-D₃ (Grimmes D₃ dispersion correction¹⁴) with a TPSS functional,¹⁵ a def2-TZVPP¹⁶ basis set on Fe, P, N, B, Al, Ga atoms, and a def2-SVP¹⁶ basis set on C, H atoms. Frequency calculations were performed on the geometry optimized structures to ensure a true minimum.

Synthetic Details and Characterization Data

Tris(2-(diisopropylphosphino)phenyl)alane (P_3^{Al}) (1b**).** This compound was synthesized according to a modified literature procedure as follows.¹ 3.4335 g (3.00 equiv, 12.6 mmol) of (2-bromophenyl)diisopropylphosphine was dissolved in Et₂O (30 mL) and cooled to -78 °C. 7.9 mL of *n*-BuLi (1.6 M in hexanes, 3.00 equiv, 12.6 mmol) was then added dropwise via a syringe. The reaction was allowed to stir for 30 minutes at -78 °C, followed by 30 minutes at room temperature.

Following removal of the Et₂O *in vacuo*, the remaining yellow-orange residue was dissolved in toluene (15 mL) and cooled to -78 °C in a glovebox coldwell. The solution was then transferred to a cooled (-78 °C) suspension of AlCl₃ (1.00 equiv, 4.19 mmol, 0.5587 g) in toluene. The vial was subsequently transferred from the coldwell to the freezer (-32 °C) and stored overnight.

After stirring the reaction mixture for 1 hour at room temperature, it was filtered through celite to remove the LiCl byproduct. Concentrating the yellow toluene solution under vacuum and triturating with pentane (3 x 20 mL) yielded **1b** as an off-white powder (2.4133 g, 95%). The ligand was stored in the freezer (-32 °C) and used without further purification.

¹H NMR (400 MHz, C₆D₆, 25 °C): δ(ppm) 8.41 (d, $J = 7.0$ Hz, 3H, Ar-*H*), 7.40 (t, $J = 7.5$ Hz, 3H, Ar-*H*), 7.26 (d, $J = 7.6$ Hz, 3H, Ar-*H*), 7.20 (t, $J = 7.3$ Hz, 3H, Ar-*H*), 2.01 (m, 6H, CH(CH₃)₂), 1.05 (m, 18H, CH(CH₃)₂), 0.88 (m, 18H, CH(CH₃)₂).

³¹P{¹H} NMR (121 MHz, C₆D₆, 25 °C): δ(ppm) 15.2 (s).

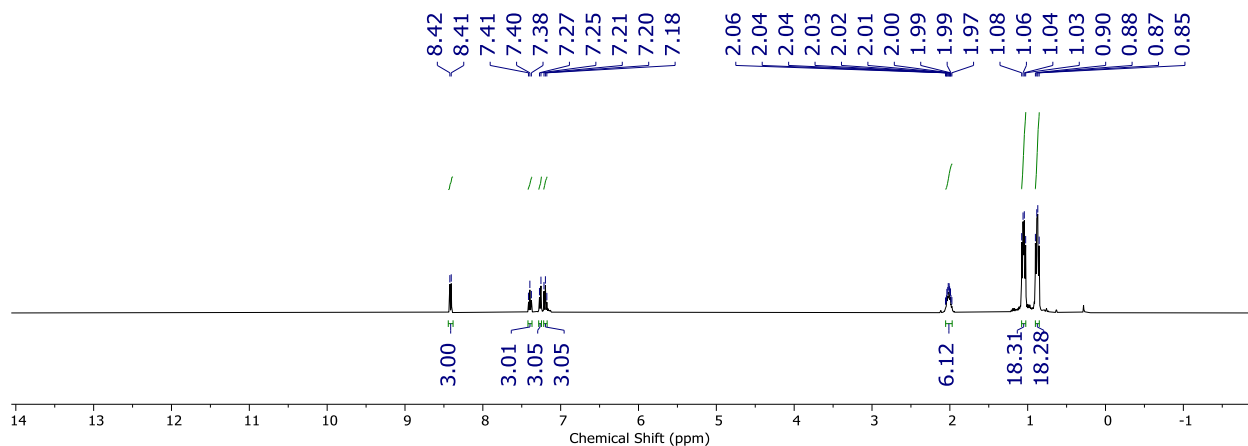


Figure S1. ^1H NMR spectrum (400 MHz, C_6D_6 , 25 °C) of P_3^{Al} (**1b**).

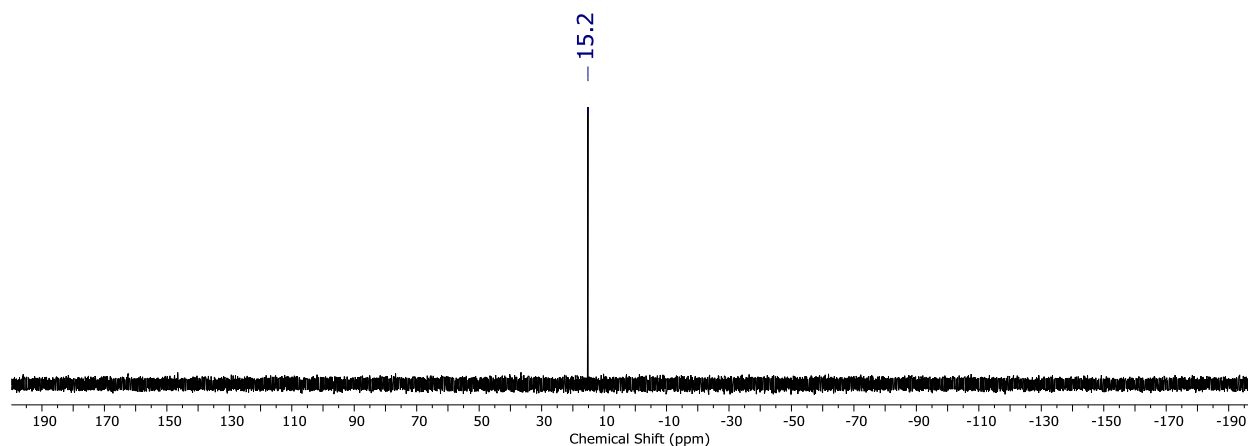


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, C_6D_6 , 25 °C) of P_3^{Al} (**1b**).

Tris(2-(diisopropylphosphino)phenyl)gallane (P_3^{Ga}) (1c**).** This compound was synthesized according to a modified literature procedure as follows.² 5.0953 g (3.00 equiv, 18.7 mmol) of (2-bromophenyl)diisopropylphosphine was dissolved in Et_2O (40 mL) and cooled to -78 °C. 11.7 mL of *n*-BuLi (1.6 M in hexanes, 3.00 equiv, 18.7 mmol) was then added dropwise via a syringe. The reaction was allowed to stir for 30 minutes at -78 °C, followed by 30 minutes at room temperature.

Following removal of the Et_2O *in vacuo*, the remaining yellow-orange residue was dissolved in toluene (15 mL) and cooled to -78 °C in a glovebox coldwell. While stirring, a cooled (-78 °C) toluene solution of GaCl_3 (1.00 equiv, 6.22 mmol, 1.0950 g) was added dropwise via pipette. After a few moments, the mixture became cloudy with the formation of LiCl . The vial was transferred

from the coldwell to the freezer ($-32\text{ }^{\circ}\text{C}$) and stored overnight.

After stirring the reaction mixture for 10 minutes at room temperature, it was filtered through celite to remove the salt byproduct. Concentrating the yellow toluene solution under vacuum and triturating with pentane (3 x 20 mL) yielded **1c** as a white powder (3.8665 g, 96%). The ligand was stored in the freezer ($-32\text{ }^{\circ}\text{C}$) and used without further purification.

^1H NMR (400 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ (ppm) 8.42 (d, $J = 9.7\text{ Hz}$, 3H, Ar- H), 7.40 (t, $J = 9.5\text{ Hz}$, 3H, Ar- H), 7.26 (d, $J = 10.0\text{ Hz}$, 3H, Ar- H), 7.18 (t, $J = 9.8\text{ Hz}$, 3H, Ar- H), 1.99 (m, 6H, $\text{CH}(\text{CH}_3)_2$), 1.05 (m, 18H, $\text{CH}(\text{CH}_3)_2$), 0.88 (m, 18H, $\text{CH}(\text{CH}_3)_2$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$): δ (ppm) 16.9 (s).

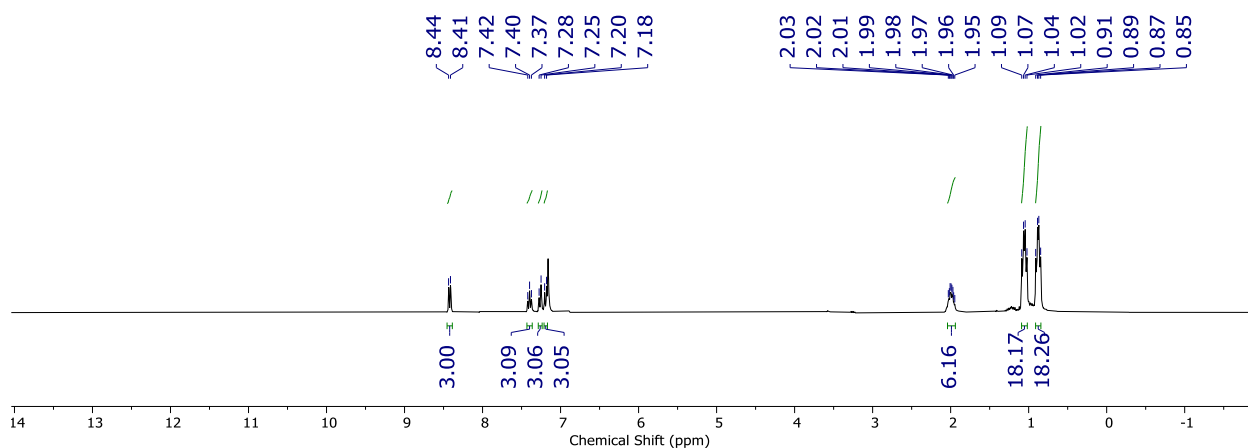


Figure S3. ^1H NMR spectrum (400 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$) of P_3^{Ga} (**1c**).

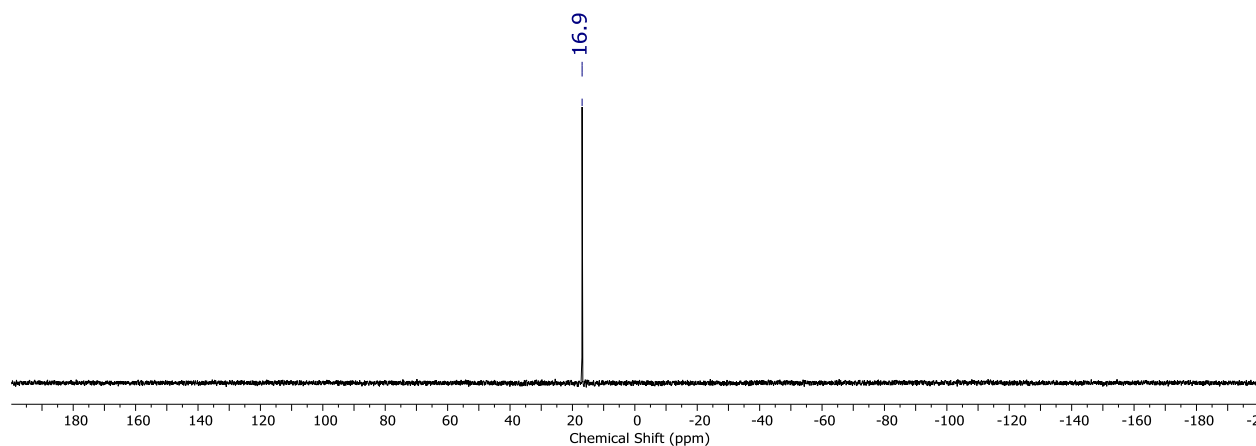


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$) of P_3^{Ga} (**1c**).

P₃AlFe-Br (2b). 0.1313 g (1.00 equiv, 0.609 mmol) of FeBr₂ was stirred vigorously in benzene for 2 hours to give a fine suspension. **1b** (1.00 equiv, 0.609 mmol, 0.3695 g) was then added as a benzene solution to the suspension and stirred at room temperature for an additional 2 hours. Finally, Na(Hg) (Na: 1.06 equiv, 0.648 mmol, 0.0149 g) was added to the reaction mixture and stirred vigorously for 15 hours.

After allowing the precipitate to settle, the green supernatant was decanted from Hg and filtered through celite. Lyophilization of the solution gave a green residue that was washed with HMDSO (3 x 15 mL) on a coarse frit packed with celite. The remaining bright green solid was filtered through the celite using toluene and then concentrated under vacuum. Layering the concentrated toluene solution with pentane and storing at -32 °C overnight afforded **2b** as green needles (0.2319 g, 51%). Subsequent recrystallization of the mother liquor afforded another 0.0718 g of product (total yield = 67%). Crystals suitable for XRD were obtained by slow concentration of a THF solution of **2b** in a closed vessel containing HMDSO.

¹H NMR (400 MHz, C₆D₆, 25 °C): δ(ppm) 8.30, 7.42, 5.65, 0.35, -0.71, -5.06.

μ_{eff} (Evans Method, C₆D₆, 25 °C): 4.3 μ_B.

UV-visible (THF, 25 °C, nm {M⁻¹ cm⁻¹}): 641 {71}, 784 {200}, 1056 {220}.

Anal. Calcd. for C₃₆H₅₄AlBrFeP₃ • C₆H₆: C, 61.48; H, 7.37. Found: C, 61.20; H, 7.41.

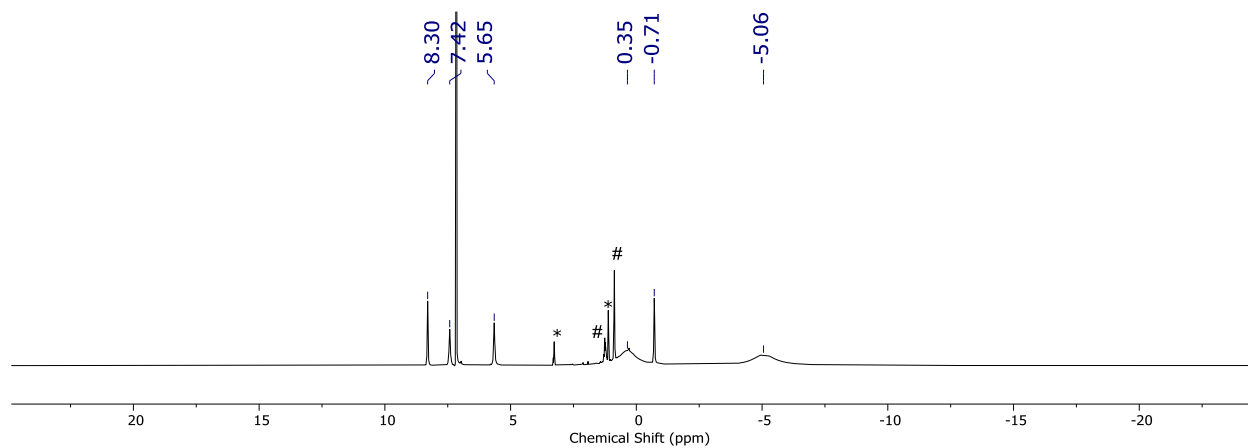


Figure S5. ^1H NMR spectrum (400 MHz, C_6D_6 , 25 °C) of $\text{P}_3\text{AlFe-Br}$ (**2b**) (* Et_2O , #pentane).

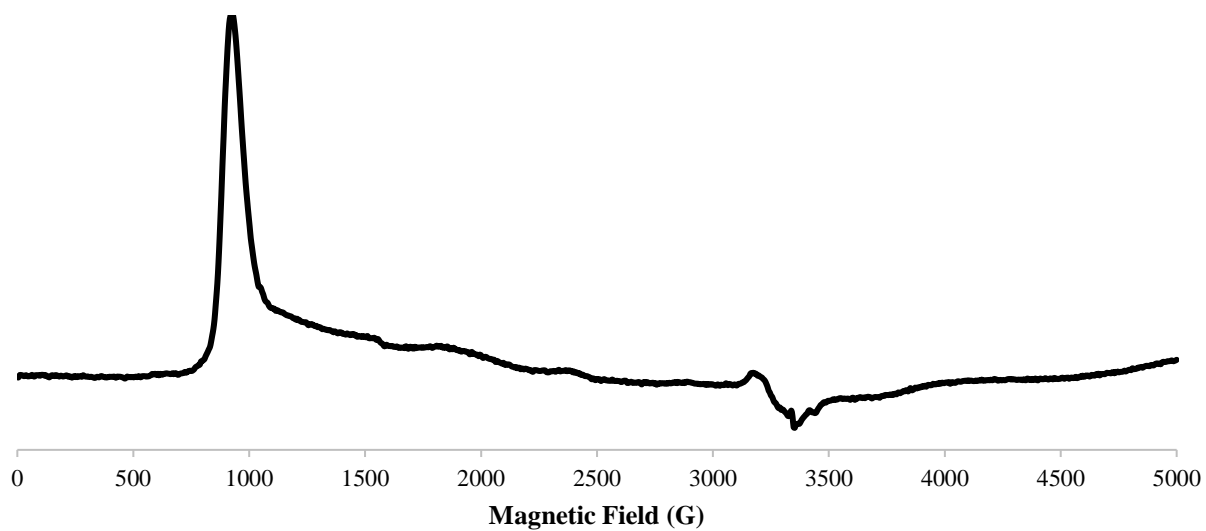


Figure S6. X-band EPR spectrum of $\text{P}_3\text{AlFe-Br}$ (**2b**) in toluene at 10 K.

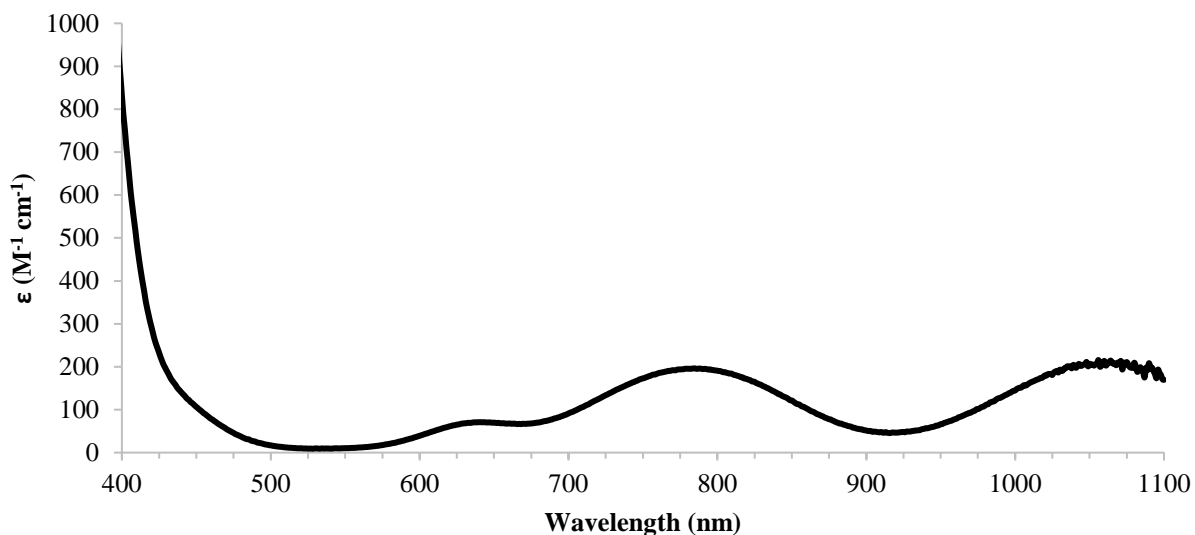


Figure S7. UV-visible spectrum of $P_3^{Al}Fe-Br$ (**2b**) in THF.

$P_3^{Ga}Fe-Br$ (2c**).** 0.1339 g (1.00 equiv, 0.621 mmol) of $FeBr_2$ was stirred vigorously in benzene for 2 hours to give a fine suspension. **1c** (1.00 equiv, 0.621 mmol, 0.4031 g) was then added as a benzene solution to the suspension and stirred at room temperature for an additional 2 hours. Finally, $Na(Hg)$ (Na: 1.07 equiv, 0.666 mmol, 0.0153 g) was added to the reaction mixture and stirred vigorously for 18 hours.

After allowing the precipitate to settle, the dark olive-green supernatant was decanted from Hg and filtered through celite. Lyophilization of the solution then gave a green residue that was washed with HMDSO (3 x 15 mL) on a coarse frit packed with celite. The remaining bright green solid was filtered through the celite using toluene and then concentrated under vacuum. Layering the concentrated toluene solution with pentane and storing at $-32\text{ }^\circ\text{C}$ overnight afforded **2c** as green needles (0.2778 g, 57%). Subsequent recrystallization of the mother liquor afforded another 0.0319 g of product (total yield = 64%). Crystals suitable for XRD were obtained by slow concentration of a THF solution of **2c** in a closed vessel containing HMDSO.

1H NMR (400 MHz, C_6D_6 , $25\text{ }^\circ\text{C}$): δ (ppm) 8.50, 7.94, 0.26, -3.12 , -4.68 , -5.30 .

μ_{eff} (Evans Method, C_6D_6 , 25 °C): 4.2 μB .

UV-visible (THF, 25 °C, nm $\{\text{M}^{-1} \text{cm}^{-1}\}$): 643 {73}, 802 {190}, 1064 {210}.

Anal. Calcd. For $\text{C}_{36}\text{H}_{54}\text{GaBrFeP}_3 \cdot \text{C}_6\text{H}_6$: C, 58.43; H, 7.01. Found: C, 58.05; H, 7.24.

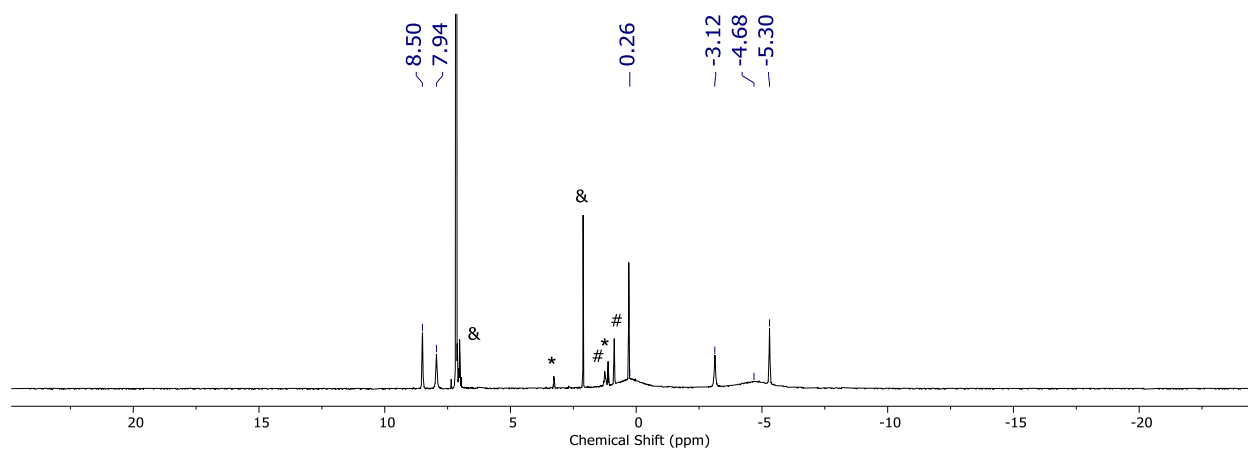


Figure S8. ^1H NMR spectrum (400 MHz, C_6D_6 , 25 °C) of $\text{P}_3^{\text{Ga}}\text{Fe}-\text{Br}$ (**2c**) (* Et_2O , #pentane, &toluene).

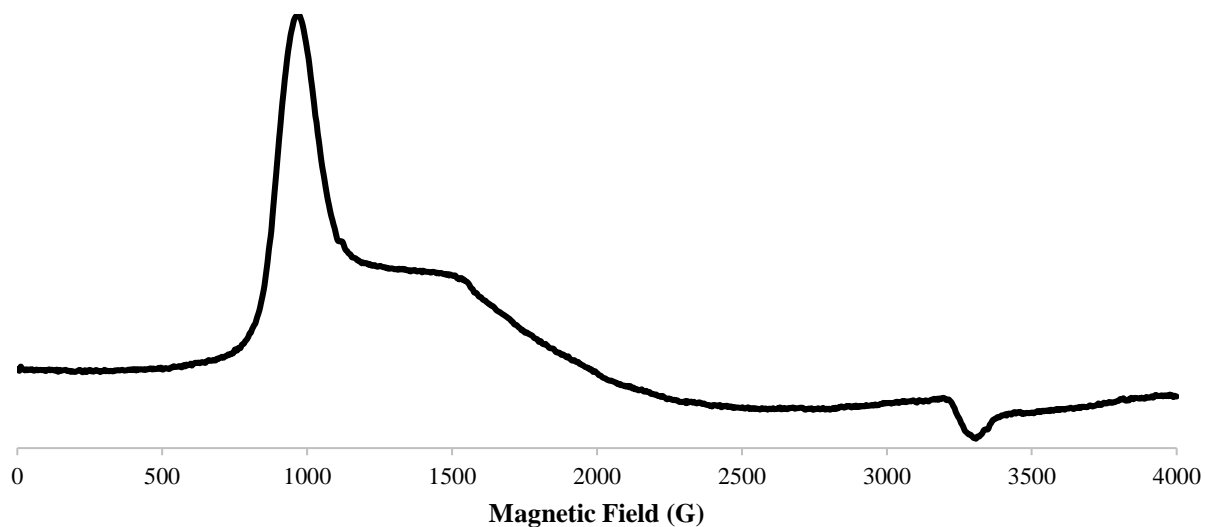


Figure S9. X-band EPR spectrum of $\text{P}_3^{\text{Ga}}\text{Fe}-\text{Br}$ (**2c**) in toluene at 10 K.

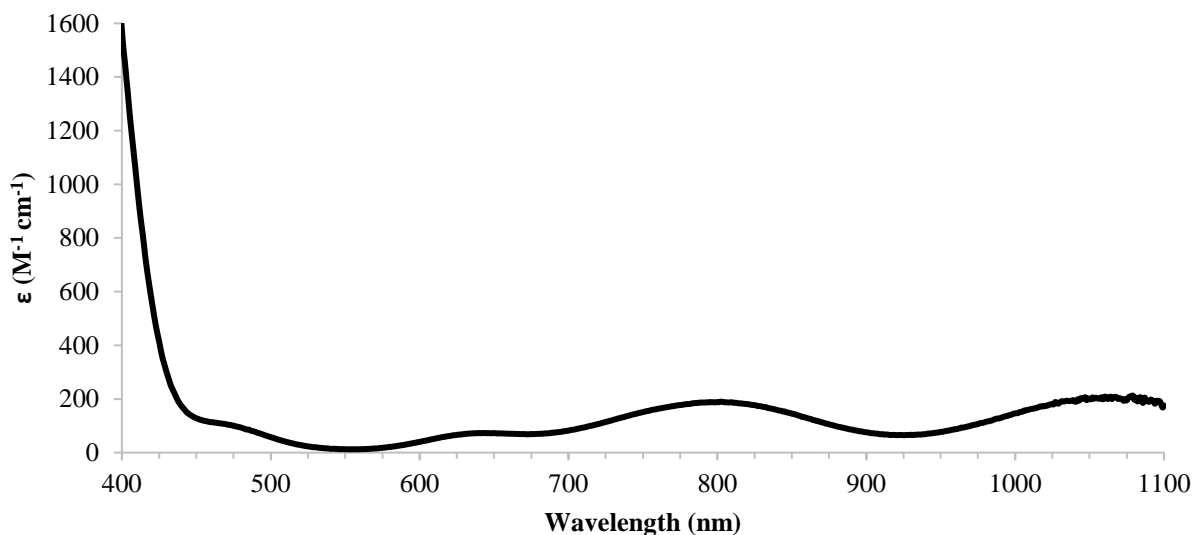


Figure S10. UV-visible spectrum of $P_3^{Ga}Fe-Br$ (**2c**) in THF.

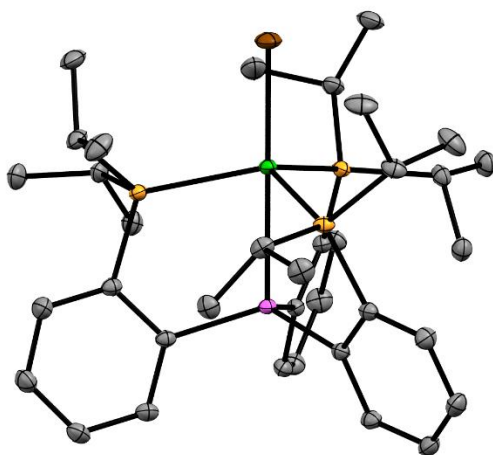


Figure S11. XRD structure of $P_3^{Ga}Fe-Br$ (**2c**) with thermal ellipsoids set at 50% probability. Hydrogen atoms and a co-crystallized HMDSO solvent molecule are omitted for clarity. Color code: Fe = green, P = orange, Ga = pink, Br = brown, C = gray.

$P_3^{Al}Fe-N_2$ (3b**).** 0.0534 g (1.00 equiv, 0.0719 mmol) of **2b** was dissolved in benzene (10 mL) to give a green solution. Excess Na(Hg) (Na: 7.62 equiv, 0.548 mmol, 0.0126 g) was then added and the reaction was stirred vigorously for 20 hours. Decanting the supernatant from Hg and filtering through celite yielded a dark yellow solution. Lyophilization of the solution afforded a brown solid

that was washed with pentane (2 x 4 mL) to give **3b** (0.0375 g, 76%). Crystals suitable for XRD were obtained by slow concentration of an Et₂O solution of **3b** in a closed vessel containing toluene.

¹H NMR (300 MHz, C₆D₆, 25 °C): δ(ppm) 8.88, 8.63, 8.44, 3.48, -1.11, -4.59.

μ_{eff} (Evans Method, C₆D₆, 25 °C): 3.1 μ_B.

IR (thin film from C₆D₆): ν(NN) = 2003 cm⁻¹.

IR (THF): ν(NN) = 2006 cm⁻¹.

UV-visible (THF, 25 °C, nm {M⁻¹ cm⁻¹}): 942 {530}.

E.A.: No combustion analysis data was obtained due to the lability of the dinitrogen ligand under vacuum.

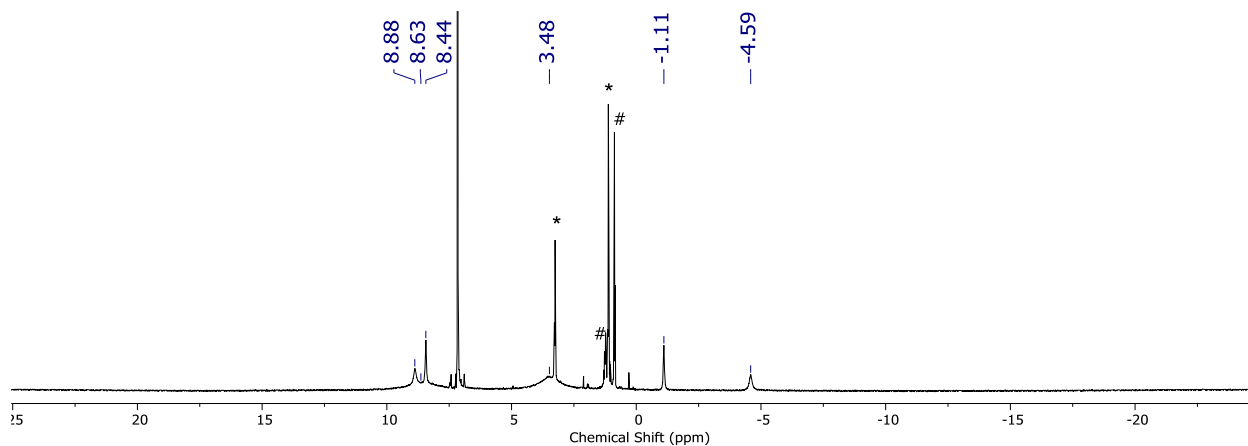


Figure S12. ¹H NMR spectrum (300 MHz, C₆D₆, 25 °C) of P₃AlFe-N₂ (**3b**) (*Et₂O, #pentane).

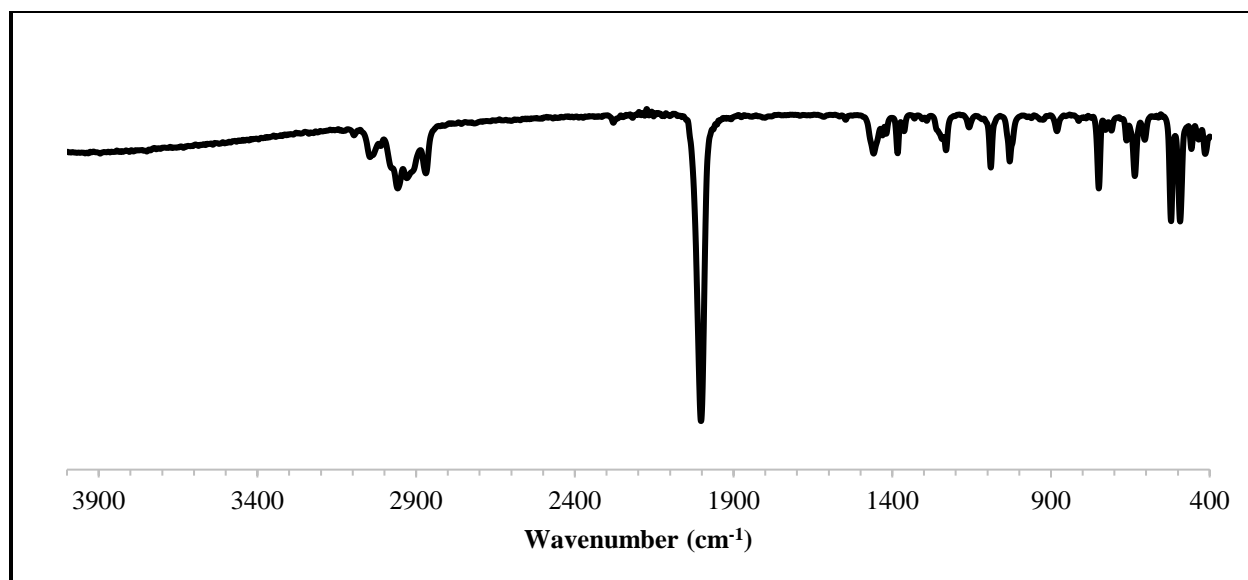


Figure S13. IR spectrum of $P_3^{Al}Fe-N_2$ (**3b**) deposited as a thin film from C_6D_6 .

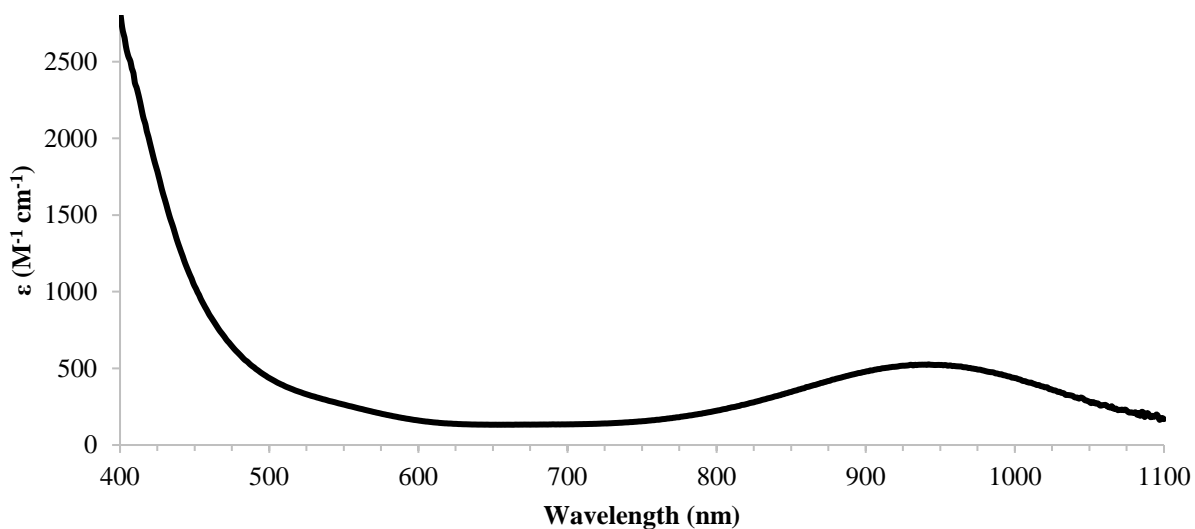


Figure S14. UV-visible spectrum of $P_3^{Al}Fe-N_2$ (**3b**) in THF.

$P_3^{Ga}Fe-N_2$ (3c**).** 0.0471 g (1.00 equiv, 0.0600 mmol) of **2c** was dissolved in benzene (10 mL) to give a green solution. Excess Na(Hg) (Na: 7.47 equiv, 0.448 mmol, 0.0103 g) was then added and the reaction was stirred vigorously for 20 hours. Decanting the supernatant from Hg and filtering through celite yielded a yellow solution. Lyophilization of the solution, followed by washing of the remaining residue with pentane (2 x 4 mL), afforded **3c** as a yellow solid (0.0364 g, 83%).

Crystals suitable for XRD were obtained by slow concentration of an Et₂O solution of **3c** in a closed vessel containing toluene.

¹H NMR (400 MHz, C₆D₆, 25 °C): δ(ppm) 11.15, 10.64, 9.08, 3.89, -4.76, -13.35.

μ_{eff} (Evans Method, C₆D₆, 25 °C): 2.8 μ_B.

IR (thin film from C₆D₆): ν(NN) = 1997 cm⁻¹.

IR (THF): ν(NN) = 1996 cm⁻¹.

UV-visible (THF, 25 °C, nm {M⁻¹ cm⁻¹}): 924 {440}.

E.A.: No combustion analysis data was obtained due to the lability of the dinitrogen ligand under vacuum.

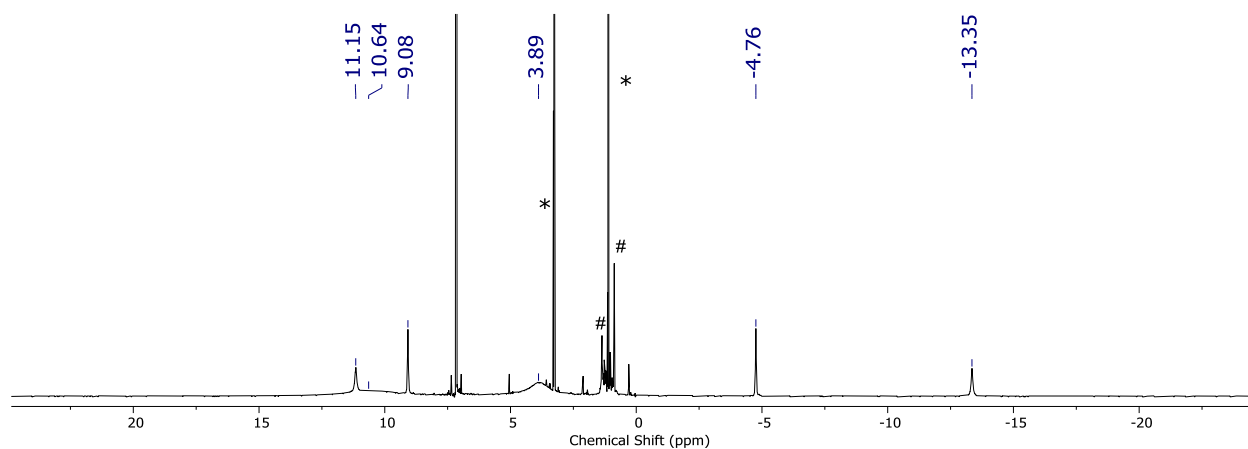


Figure S15. ¹H NMR spectrum (400 MHz, C₆D₆, 25 °C) of P₃^{Ga}Fe–N₂ (**3c**) (*Et₂O, #pentane).

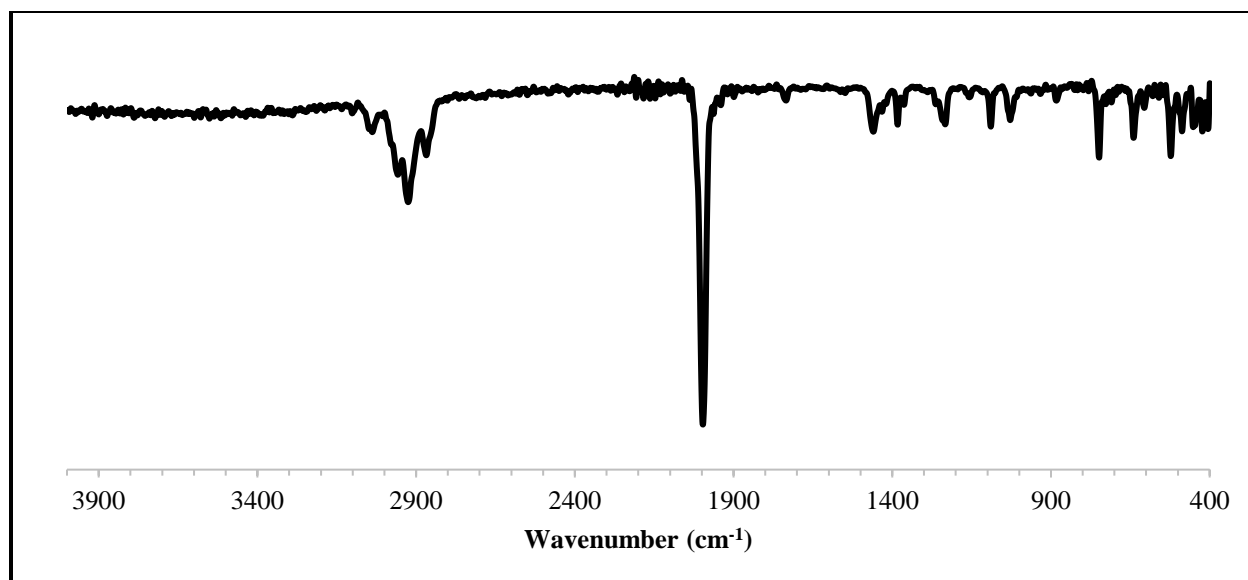


Figure S16. IR spectrum of $P_3^{Ga}Fe-N_2$ (**3c**) deposited as a thin film from C_6D_6 .

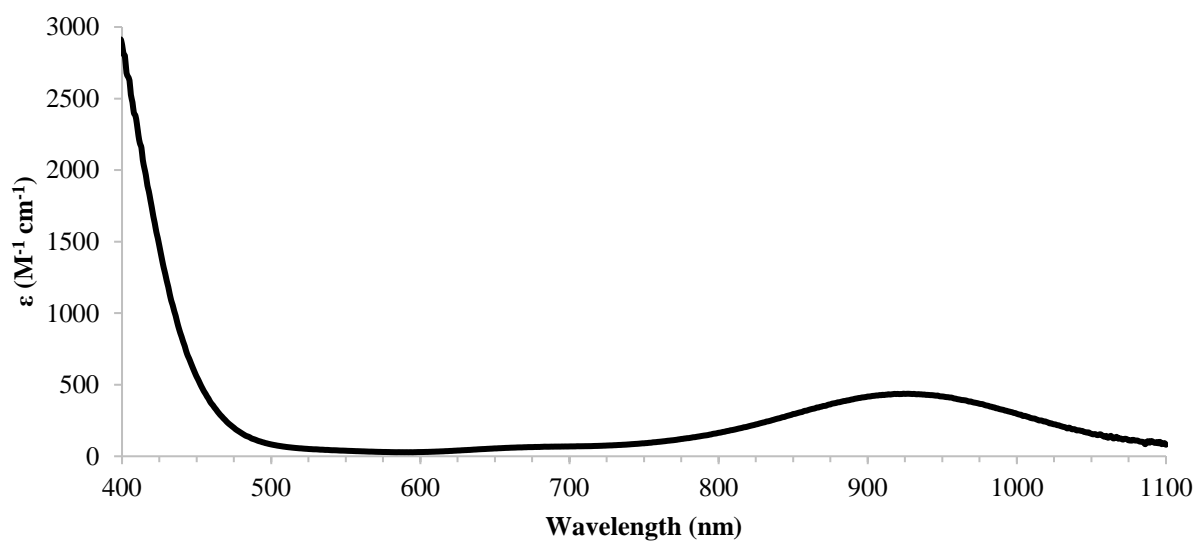


Figure S17. UV-visible spectrum of $P_3^{Ga}Fe-N_2$ (**3c**) in THF.

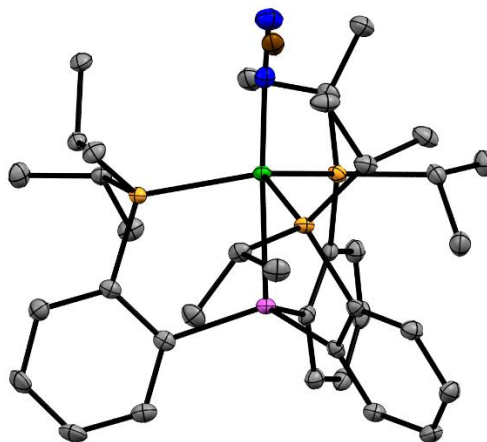


Figure S18. XRD structure of $P_3^{Ga}Fe-N_2$ (**3c**) with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. In addition to **3c**, the crystal for which data was collected contained **2c** as a minor component (shown above). Color code: Fe = green, P = orange, Ga = pink, N = blue, Br = brown, C = gray.

[Na(THF)₃][P₃^{Al}Fe-N₂] (4b). 0.0496 g (1.00 equiv, 0.0668 mmol) of **2b** was dissolved in THF (5 mL) to give a green solution. Excess Na(Hg) (Na: 7.68 equiv, 0.513 mmol, 0.0118 g) was then added and the reaction was stirred for 4 hours. After a few minutes, a color change from green to dark red was observed. Decanting the supernatant from Hg, followed by filtering through celite, yielded a red solution. Concentrating *in vacuo*, layering with pentane, and storing at $-32\text{ }^\circ\text{C}$ overnight yielded **4b** as a red solid (0.0515 g, 83%). Crystals suitable for XRD were grown by allowing pentane to slowly diffuse into a concentrated solution of **4b** in THF at $-32\text{ }^\circ\text{C}$.

^1H NMR (400 MHz, THF-*d*₈, 25 $^\circ\text{C}$): δ (ppm) 8.08, 7.77, 6.10, 4.41, 1.43, -2.34 .

μ_{eff} (Evans Method, THF-*d*₈, 25 $^\circ\text{C}$): 2.1 μB .

IR (thin film from THF): $\nu(\text{NN}) = 1883\text{ cm}^{-1}$.

IR (THF): $\nu(\text{NN}) = 1879, 1922\text{ cm}^{-1}$.

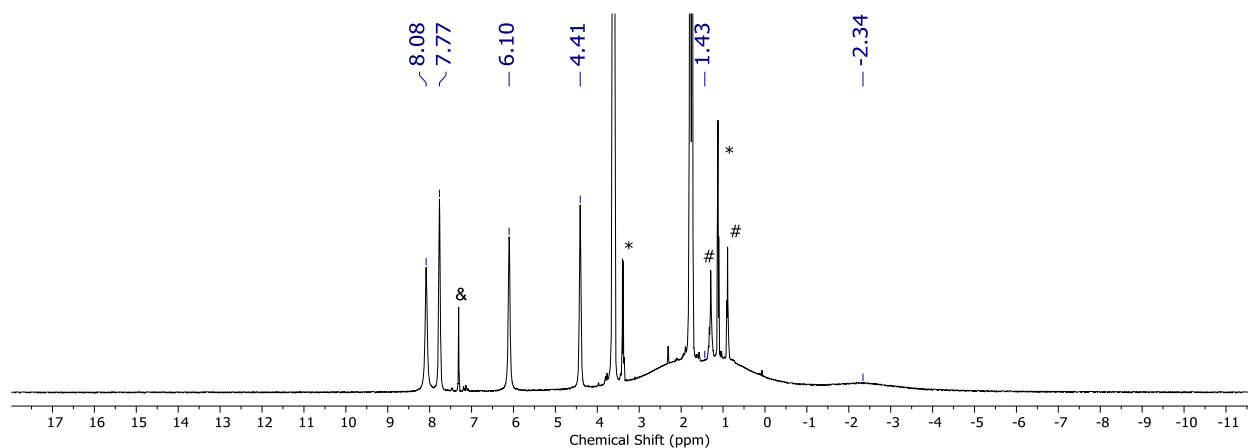


Figure S19. ¹H NMR spectrum (400 MHz, THF-*d*₈, 25 °C) of [Na(THF)₃][P₃^{Al}Fe-N₂] (**4b**) (*Et₂O, #pentane, &benzene).

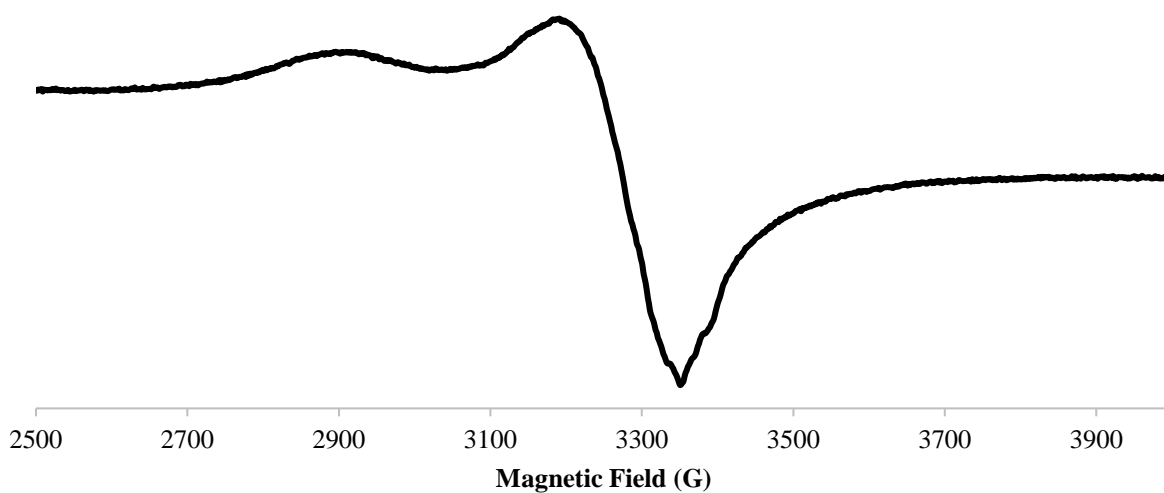


Figure S20. X-band EPR spectrum of [Na(THF)₃][P₃^{Al}Fe-N₂] (**4b**) in 2-MeTHF at 77 K.

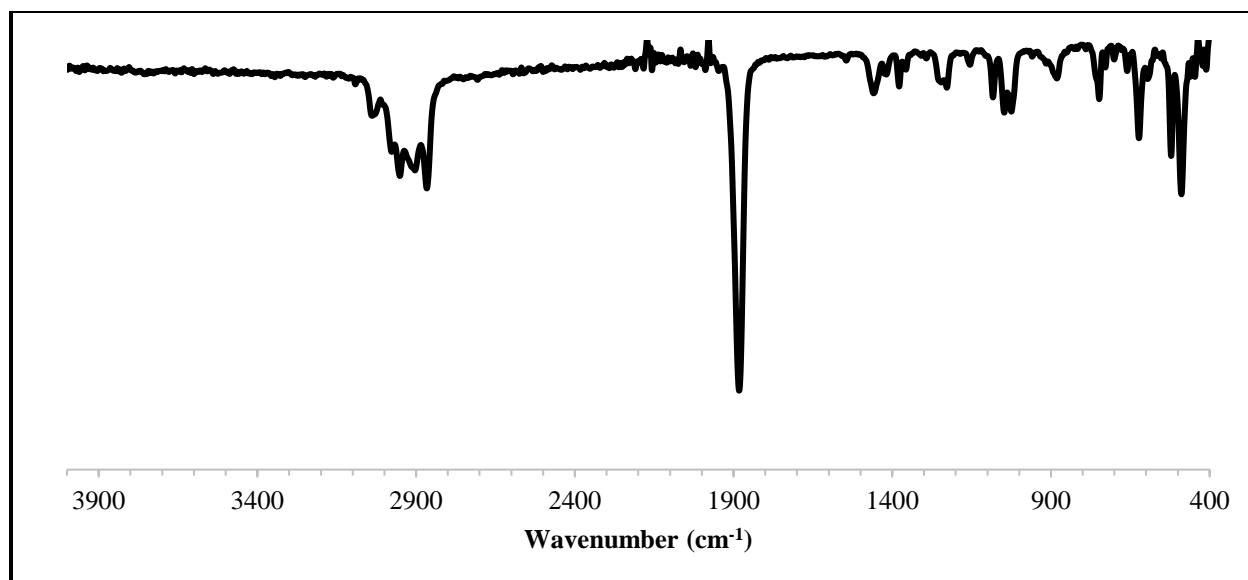


Figure S21. IR spectrum of $[\text{Na}(\text{THF})_3][\text{P}_3^{\text{Al}}\text{Fe}-\text{N}_2]$ (**4b**) deposited as a thin film from THF.

$[\text{Na}(\text{THF})_3][\text{P}_3^{\text{Ga}}\text{Fe}-\text{N}_2]$ (**4c**). 0.0766 g (1.00 equiv, 0.0976 mmol) of **2c** was dissolved in THF (5 mL) to give a green solution. Excess Na(Hg) (Na: 7.18 equiv, 0.700 mmol, 0.0161 g) was then added and the reaction was stirred for 4 hours. After a few minutes, a color change from green to dark red was observed. Decanting the supernatant from Hg, followed by filtering through celite, yielded a red solution. Concentrating *in vacuo*, layering with pentane, and storing at $-32\text{ }^\circ\text{C}$ overnight yielded **4c** as a red solid (0.0824 g, 87%). Crystals suitable for XRD were grown by allowing pentane to slowly diffuse into a concentrated solution of **4c** in THF at $-32\text{ }^\circ\text{C}$.

^1H NMR (400 MHz, $\text{THF}-d_8$, $25\text{ }^\circ\text{C}$): $\delta(\text{ppm})$ 7.92, 6.84, 6.63, 3.46, 1.45, -5.23 .

μ_{eff} (Evans Method, $\text{THF}-d_8$, $25\text{ }^\circ\text{C}$): $2.4\ \mu\text{B}$.

IR (thin film from THF): $\nu(\text{NN}) = 1879\text{ cm}^{-1}$.

IR (THF): $\nu(\text{NN}) = 1878, 1920\text{ cm}^{-1}$.

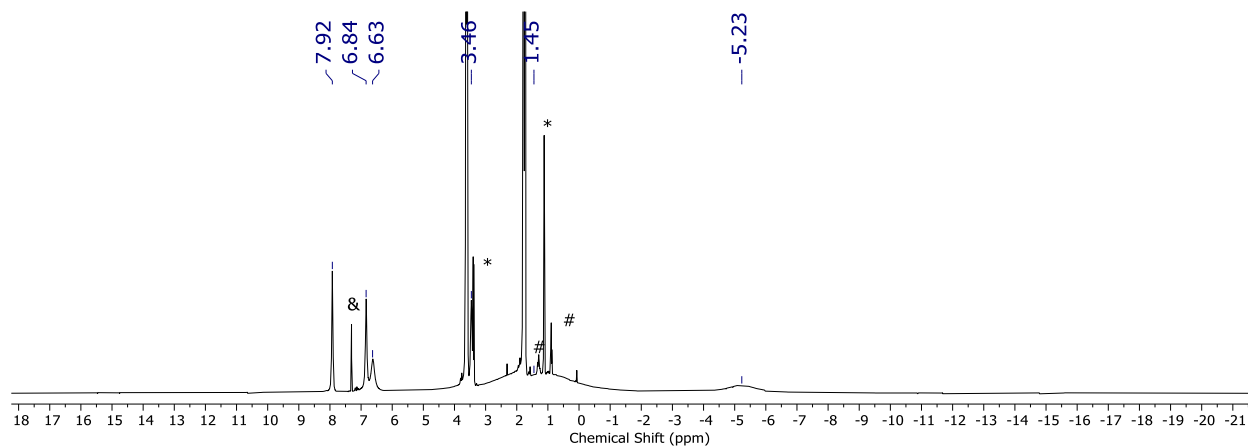


Figure S22. ^1H NMR spectrum (400 MHz, $\text{THF-}d_8$, 25 °C) of $[\text{Na}(\text{THF})_3][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**4c**) (* Et_2O , #pentane, &benzene).

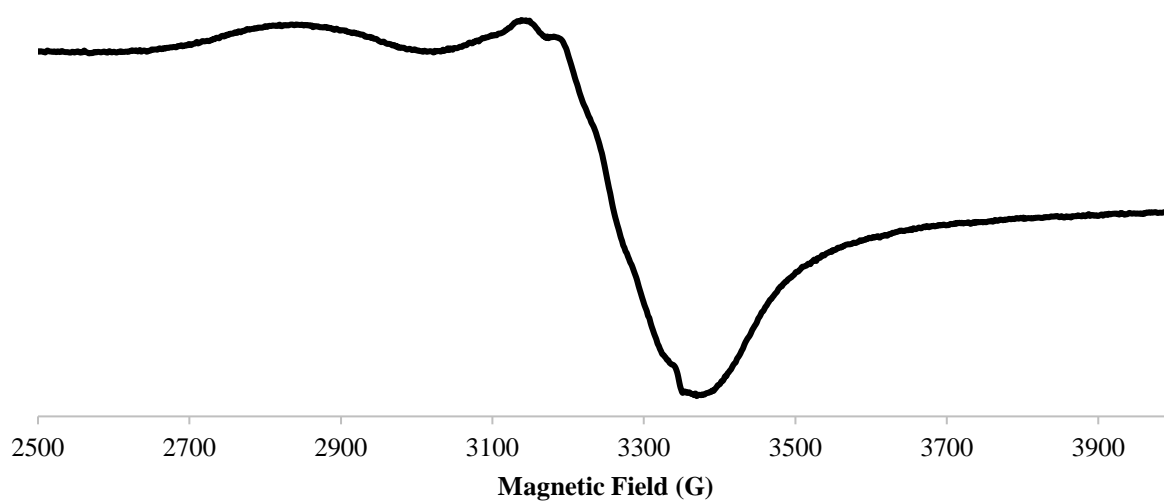


Figure S23. X-band EPR spectrum of $[\text{Na}(\text{THF})_3][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**4c**) in 2-MeTHF at 77 K.

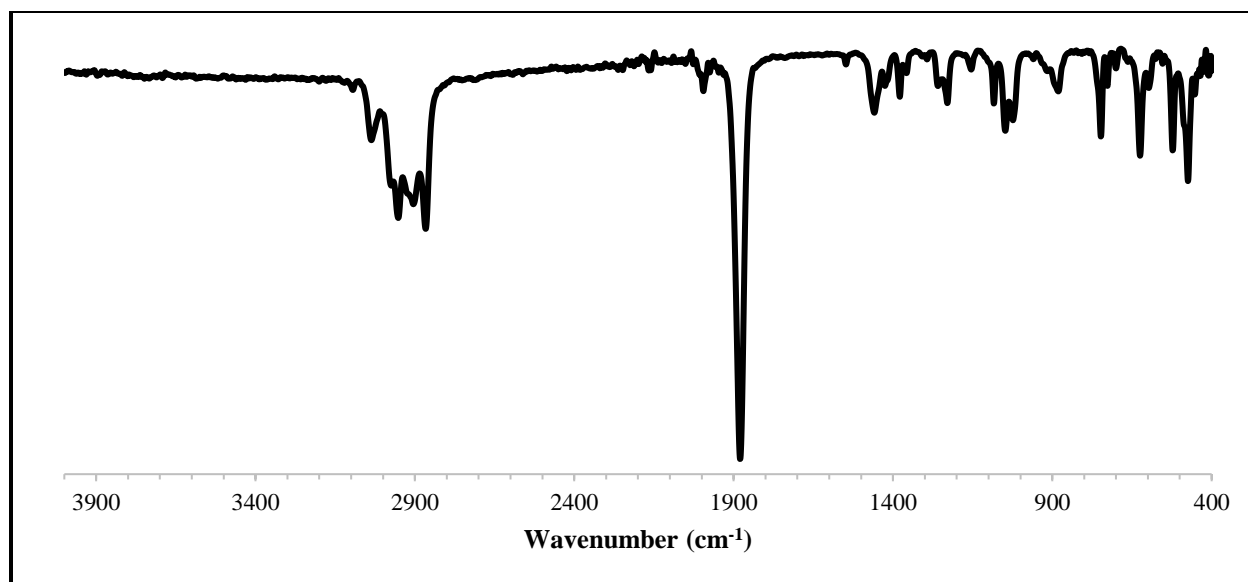


Figure S24. IR spectrum of $[\text{Na}(\text{THF})_3][\text{P}_3^{\text{Ga}}\text{Fe}-\text{N}_2]$ (**4c**) deposited as a thin film from THF.

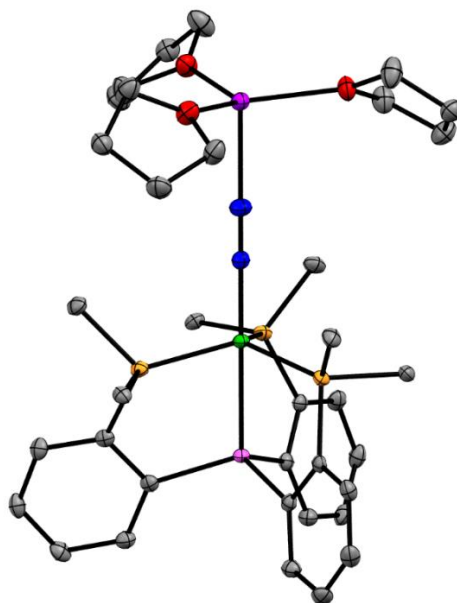


Figure S25. XRD structure of $[\text{Na}(\text{THF})_3][\text{P}_3^{\text{Ga}}\text{Fe}-\text{N}_2]$ (**4c**) with thermal ellipsoids set at 50% probability. For clarity, the isopropyl groups have been truncated and hydrogen atoms have been omitted. Color code: Fe = green, P = orange, Ga = pink, N = blue, Na = purple, O = red, C = gray.

$[\text{Na}(\text{12-c-4})_2][\text{P}_3^{\text{Al}}\text{Fe}-\text{N}_2]$ (**5b**). 0.0406 g (1.00 equiv, 0.0437 mmol) of **4b** was dissolved in THF

(4 mL). 12-crown-4 (3.19 equiv, 0.139 mmol, 0.0245 g) was then added as a THF solution (2 mL) and the reaction was stirred at room temperature for 2 hours. Removing the THF *in vacuo*, washing the remaining residue with Et₂O (3 x 6 mL), and drying under vacuum afforded **5b** as a dark red solid (0.0423 g, 91%).

IR (thin film from THF): $\nu(\text{NN}) = 1914 \text{ cm}^{-1}$.

IR (THF): $\nu(\text{NN}) = 1922 \text{ cm}^{-1}$.

Anal. Calcd. for C₅₂H₈₆AlFeN₂NaO₈P₃: C, 58.59; H, 8.13; N, 2.63. Found: C, 58.23; H, 7.90; N, 2.37.

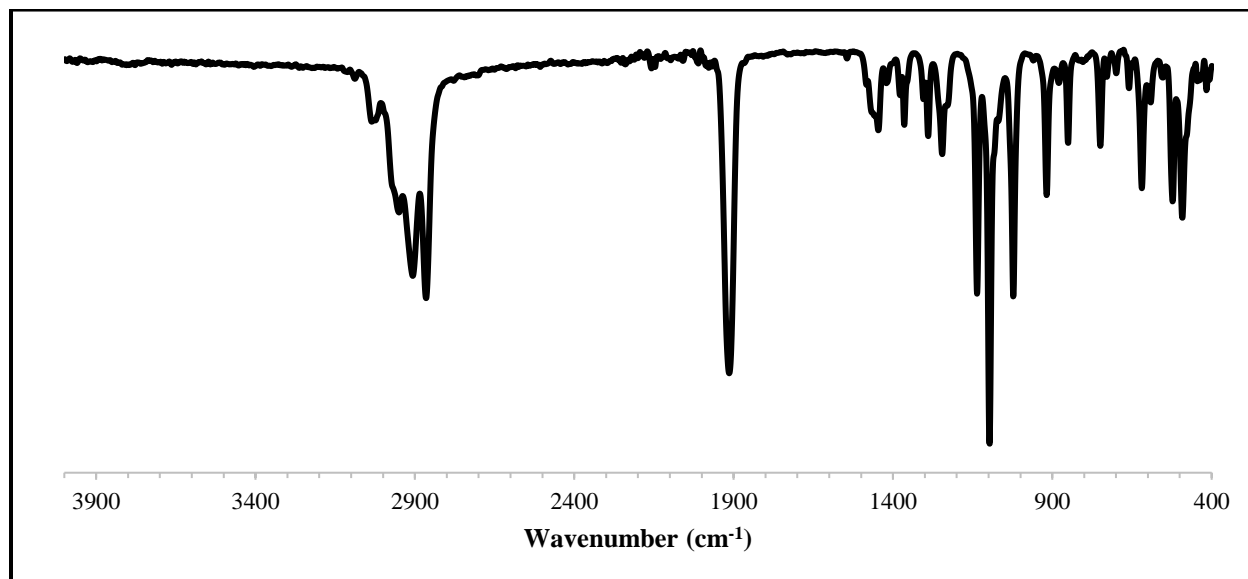


Figure S26. IR spectrum of [Na(12-c-4)₂][P₃^{Al}Fe-N₂] (**5b**) deposited as a thin film from THF.

[Na(12-c-4)₂][P₃^{Ga}Fe-N₂] (**5c**). 0.0501 g (1.00 equiv, 0.0515 mmol) of **4c** was dissolved in THF (4 mL). 12-crown-4 (3.58 equiv, 0.184 mmol, 0.0325 g) was then added as a THF solution (2 mL) and the reaction was stirred at room temperature for 2 hours. Removing the THF *in vacuo*, washing the remaining residue with Et₂O (3 x 6 mL), and drying under vacuum afforded **5c** as a dark red solid (0.0548 g, 96%).

IR (thin film from THF): $\nu(\text{NN}) = 1912 \text{ cm}^{-1}$.

IR (THF): $\nu(\text{NN}) = 1920 \text{ cm}^{-1}$.

Anal. Calcd. for $\text{C}_{52}\text{H}_{86}\text{FeGaN}_2\text{NaO}_8\text{P}_3$: C, 56.33; H, 7.82; N, 2.53. Found: C, 56.38; H, 7.60; N, 2.36.

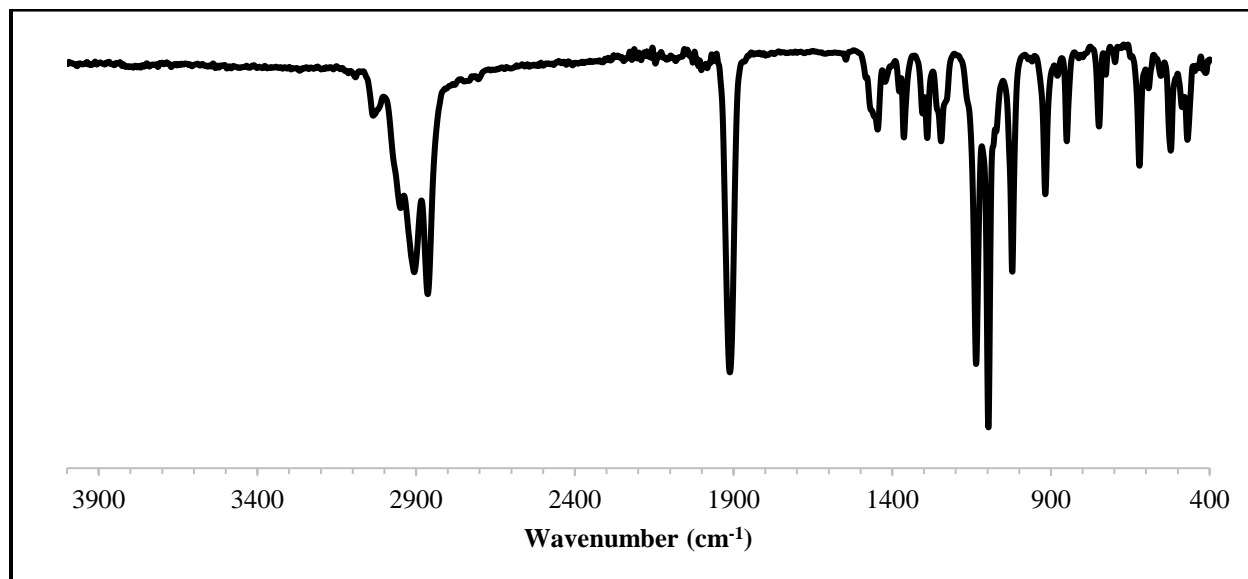


Figure S27. IR spectrum of $[\text{Na}(12\text{-c-}4)_2][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**5c**) deposited as a thin film from THF.

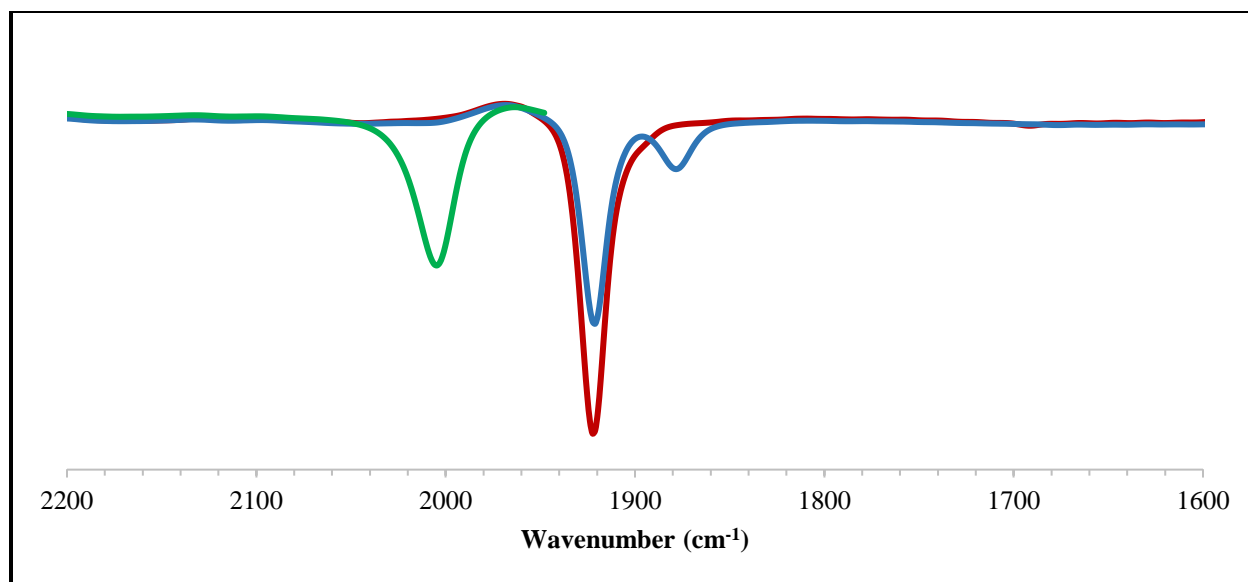


Figure S28. THF solution IR spectra of $P_3^{Al}Fe-N_2$ (**3b**, green), $[Na(THF)_3][P_3^{Al}Fe-N_2]$ (**4b**, blue), and $[Na(12-c-4)_2][P_3^{Al}Fe-N_2]$ (**5b**, red) in the region 1600–2200 cm^{-1} .

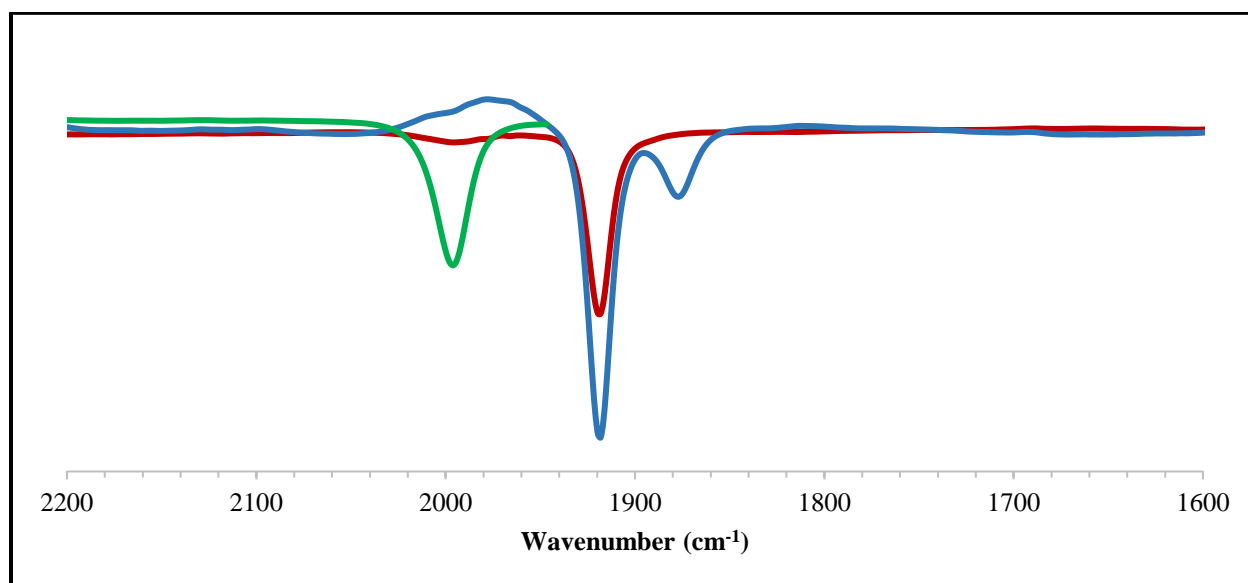


Figure S29. THF solution IR spectra of $P_3^{Ga}Fe-N_2$ (**3c**, green), $[Na(THF)_3][P_3^{Ga}Fe-N_2]$ (**4c**, blue), and $[Na(12-c-4)_2][P_3^{Ga}Fe-N_2]$ (**5c**, red) in the region 1600–2200 cm^{-1} .

Ammonia Production and Quantification Studies

Standard NH₃ Generation Reaction Procedure

All solvents were stirred with Na/K for ≥ 1 hour and filtered prior to use. In a nitrogen-filled

glovebox, the precatalyst (ca. 2.0 μmol) was weighed into a vial. The precatalyst was then transferred quantitatively into a Schlenk tube as a suspension in Et_2O . The Et_2O was then evaporated to provide a solid layer of precatalyst at the bottom of the Schlenk tube. The acid and reductant were then added as solids and the tube was equipped with a stir bar. The tube was then cooled to 77 K in the coldwell. To the cold tube was added 2.0 mL of Et_2O . The temperature of the system was allowed to equilibrate for 5 minutes and then the tube was sealed with a Teflon screw-valve. This tube was passed out of the box into a liquid nitrogen bath and transported to a fume hood. The tube was then transferred to a dry ice/acetone bath ($-78\text{ }^\circ\text{C}$) where it thawed and was allowed to stir at $-78\text{ }^\circ\text{C}$. For runs utilizing HBAr^{F}_4 , reactions were stirred at $-78\text{ }^\circ\text{C}$ for 1 hour, followed by stirring at room temperature for 45 minutes. For all other runs, reactions were allowed to stir and gradually warm to room temperature overnight. To ensure reproducibility, all experiments were conducted in 200 mL Schlenk tubes (51 mm OD) using 25 mm stir bars, and stirring was conducted at ~ 900 rpm.

Ammonia and Hydrazine Quantification

The catalytic reaction mixture was cooled to 77 K and allowed to freeze. The reaction vessel was then opened to atmosphere and to the frozen solution was added an excess (with respect to acid) solution of a NaO^tBu solution in MeOH (0.25 mM) dropwise over 1–2 minutes. This solution was allowed to freeze, then the headspace of the tube was evacuated and the tube was sealed. The tube was then allowed to warm to room temperature and stirred at room temperature for at least 10 minutes. An additional Schlenk tube was charged with HCl (3 mL of a 2.0 M solution in Et_2O , 6 mmol) to serve as a collection flask. The volatiles of the reaction mixture were vacuum transferred at room temperature into this collection flask. After completion of the vacuum transfer, the collection flask was sealed and warmed to room temperature. Solvent was removed *in vacuo*, and the remaining residue dissolved in 1 mL of DI H_2O . A 20 μL aliquot of this solution was then analyzed for the presence of NH_3 (present as $[\text{NH}_4][\text{Cl}]$) by the indophenol method.¹⁷ Quantification was performed with UV-visible spectroscopy by analyzing the absorbance at 635 nm. A further aliquot of this solution was analyzed for the presence of N_2H_4 (present as $[\text{N}_2\text{H}_5][\text{Cl}]$) by a standard colorimetric method.¹⁸ Quantification was performed with UV-visible spectroscopy by analyzing the absorbance at 458 nm.

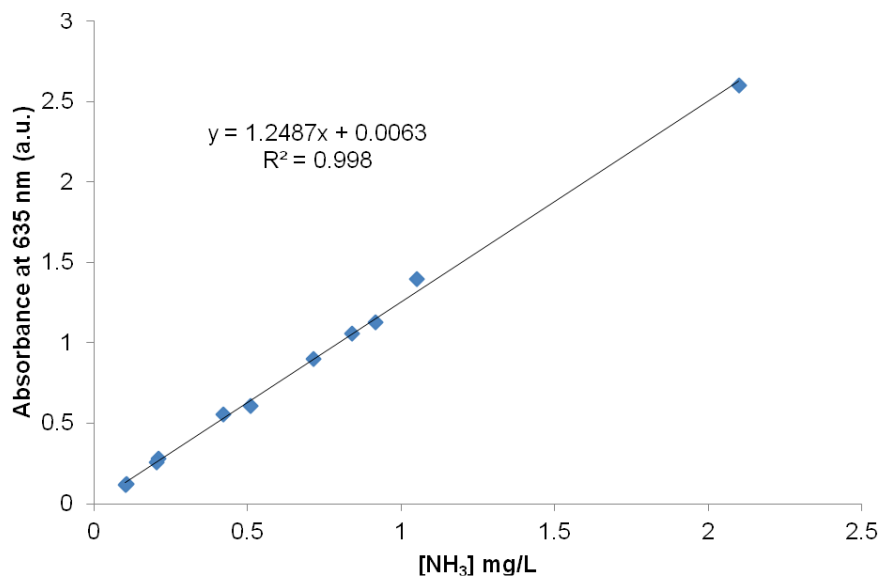


Figure S30. Calibration curve used for NH_3 quantification.

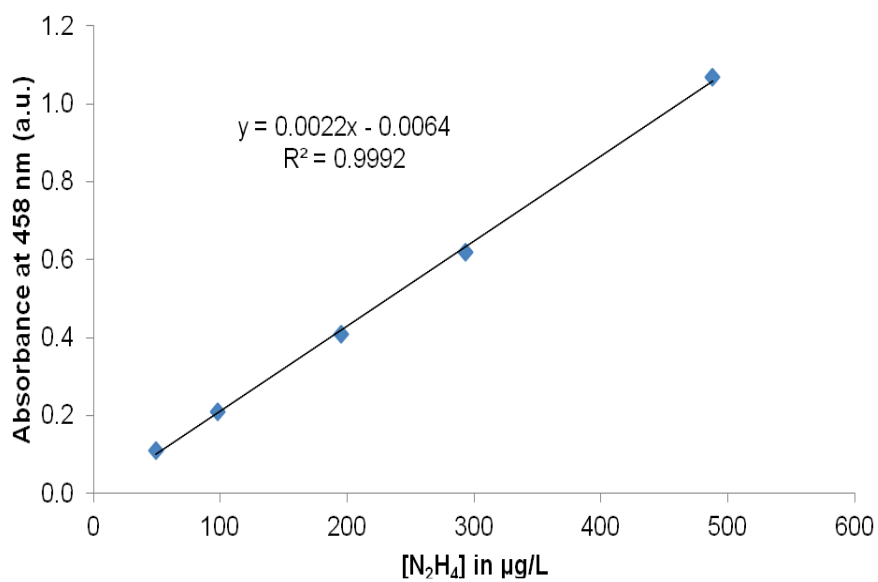


Figure S31. Calibration curve used for N_2H_4 quantification.

Table S1. UV-visible quantification results for standard NH₃ generation experiments with [Na(12-c-4)₂][P₃^{Al}Fe–N₂] (**5b**).

Entry	Total volume of Et ₂ O (mL)	Fe (μmol)	Acid (equiv)	Reductant (equiv)	NH ₄ Cl (μmol)	NH ₃ /Fe (equiv)	Yield NH ₃ /H ⁺ (%)
A	2.0	2.0	46 ^a	50 ^b	5.0	2.5	16
B	2.0	2.0	46 ^a	50 ^b	5.0	2.5	17
C	2.0	2.0	46 ^a	50 ^b	5.1	2.6	17
Avg.						2.5 ± 0.1	17 ± 1
D	2.0	2.0	46 ^c	50 ^d	6.3	3.2	21
E	2.0	2.1	46 ^c	50 ^d	8.5	4.1	27
F	2.0	2.0	46 ^c	50 ^d	10	5.1	33
Avg.						4.1 ± 0.9	27 ± 6

^aHBAr^F₄. ^bKC₈. ^c[H₂NPh₂][OTf]. ^dCp*₂Co.

*N₂H₄ was not detected in the catalytic runs.

Table S2. UV-visible quantification results for standard NH₃ generation experiments with [Na(12-c-4)₂][P₃^{Ga}Fe–N₂] (**5c**).

Entry	Total volume of Et ₂ O (mL)	Fe (μmol)	Acid (equiv)	Reductant (equiv)	NH ₄ Cl (μmol)	NH ₃ /Fe (equiv)	Yield NH ₃ /H ⁺ (%)
A	2.0	2.0	46 ^a	50 ^b	5.0	2.5	16
B	2.0	2.0	46 ^a	50 ^b	5.2	2.6	17
C	2.0	1.9	46 ^a	50 ^b	5.5	2.9	19
Avg.						2.7 ± 0.2	17 ± 1
D	2.0	2.0	46 ^c	50 ^d	6.8	3.4	22
E	2.0	2.0	46 ^c	50 ^d	6.9	3.5	23
F	2.0	2.0	46 ^c	50 ^d	7.7	3.9	25
Avg.						3.6 ± 0.3	24 ± 2

^aHBAr^F₄. ^bKC₈. ^c[H₂NPh₂][OTf]. ^dCp*₂Co.

*N₂H₄ was not detected in the catalytic runs.

Cyclic Voltammetry

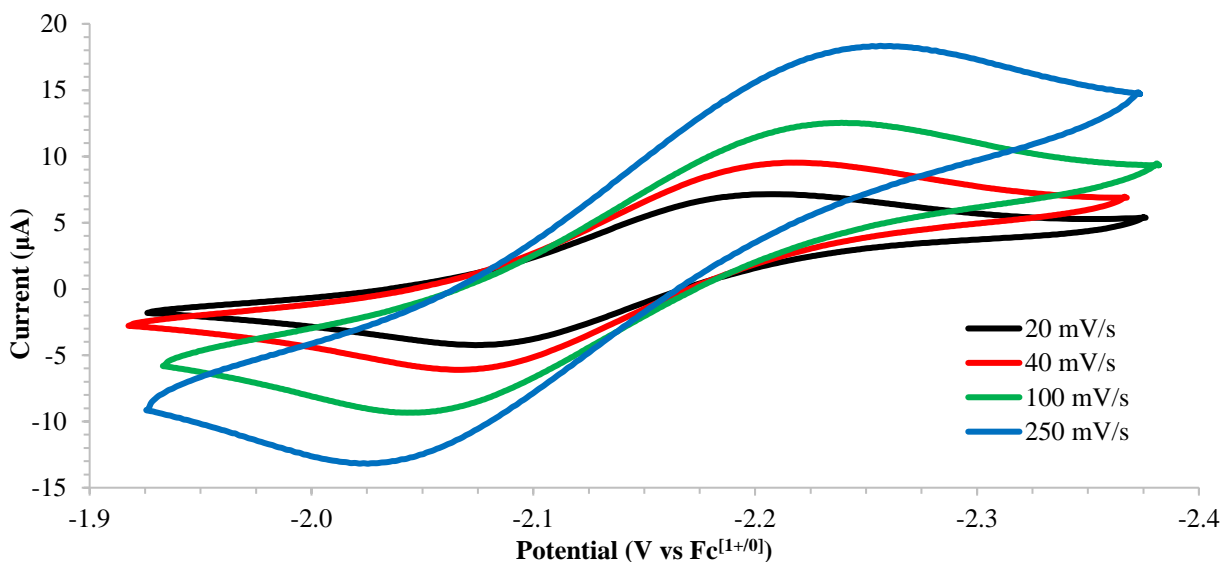


Figure S32. Cyclic voltammograms of $P_3^BFe-N_2$ (**3a**) in 0.1 M THF solution of $[^nBu_4][PF_6]$ at different scan rates.

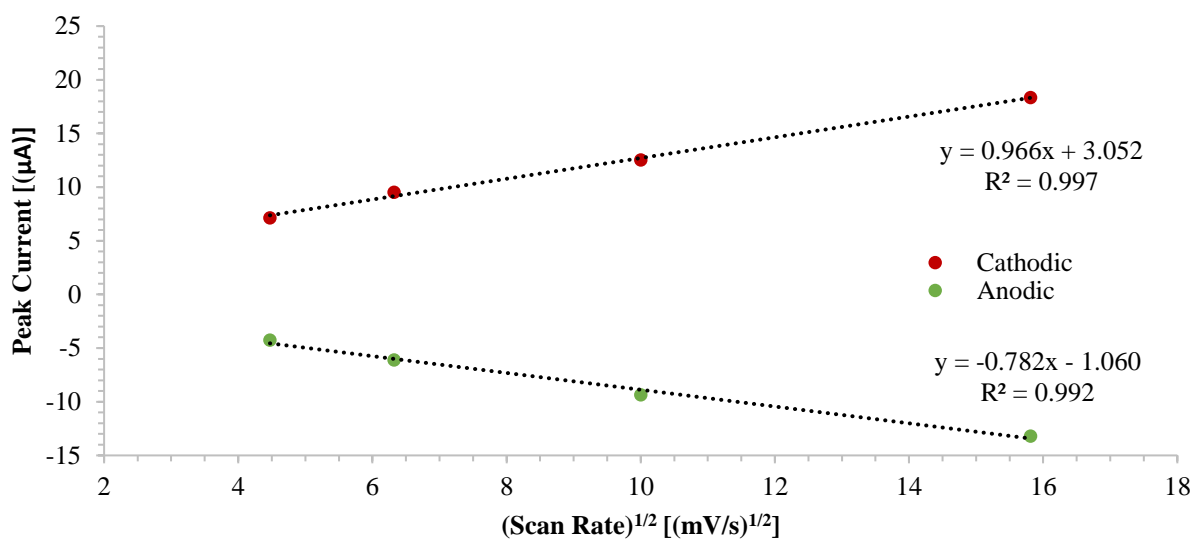


Figure S33. Plot of the cathodic/anodic peak current versus the square root of scan rate for $P_3^BFe-N_2$ (**3a**) in 0.1 M THF solution of $[^nBu_4][PF_6]$ at different scan rates.

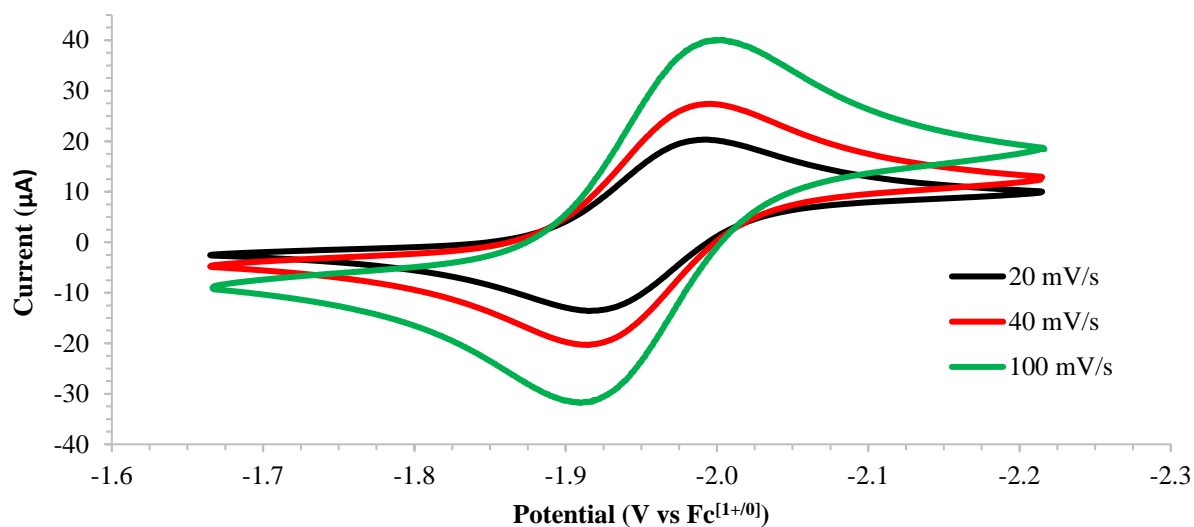


Figure S34. Cyclic voltammograms of $P_3^{Al}Fe-N_2$ (**3b**) in 0.1 M THF solution of $[tBu_4][PF_6]$ at different scan rates.

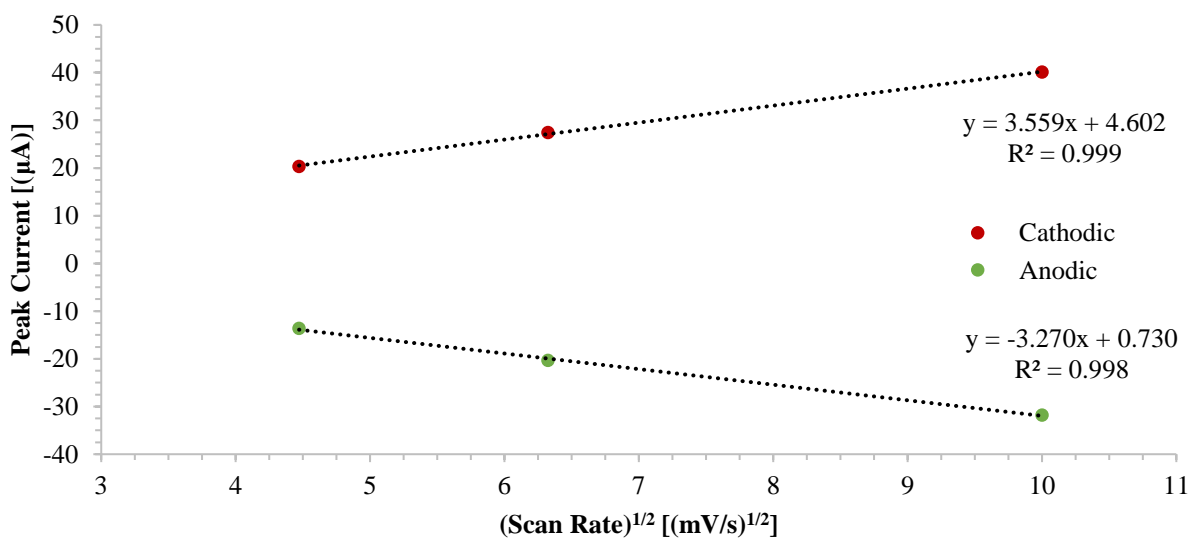


Figure S35. Plot of the cathodic/anodic peak current versus the square root of scan rate for $P_3^{Al}Fe-N_2$ (**3b**) in 0.1 M THF solution of $[tBu_4][PF_6]$ at different scan rates.

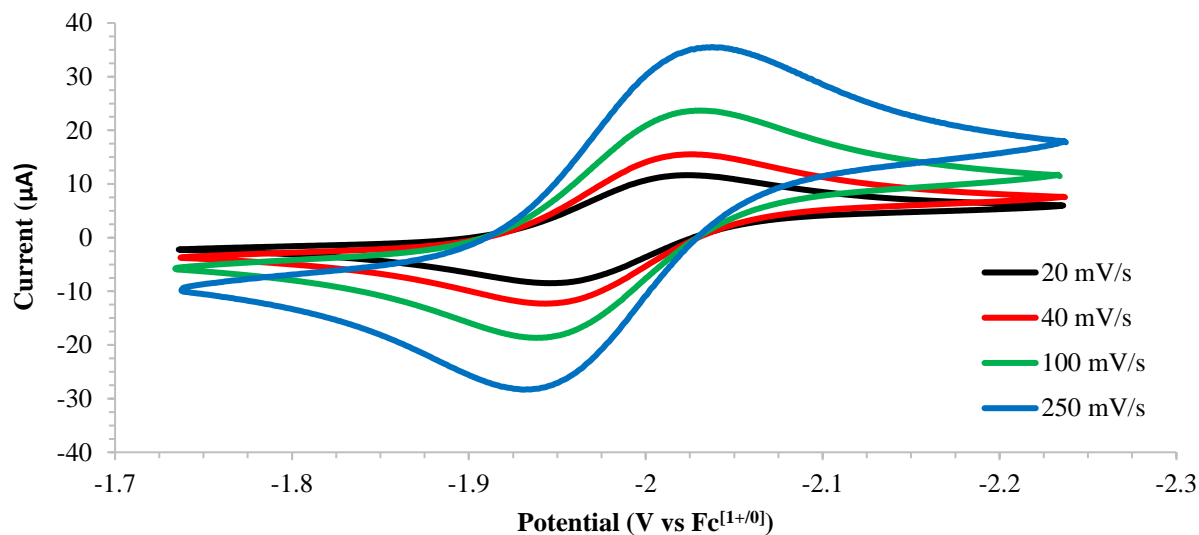


Figure S36. Cyclic voltammograms of $P_3^{Ga}Fe-N_2$ (**3c**) in 0.1 M THF solution of $[nBu_4][PF_6]$ at different scan rates.

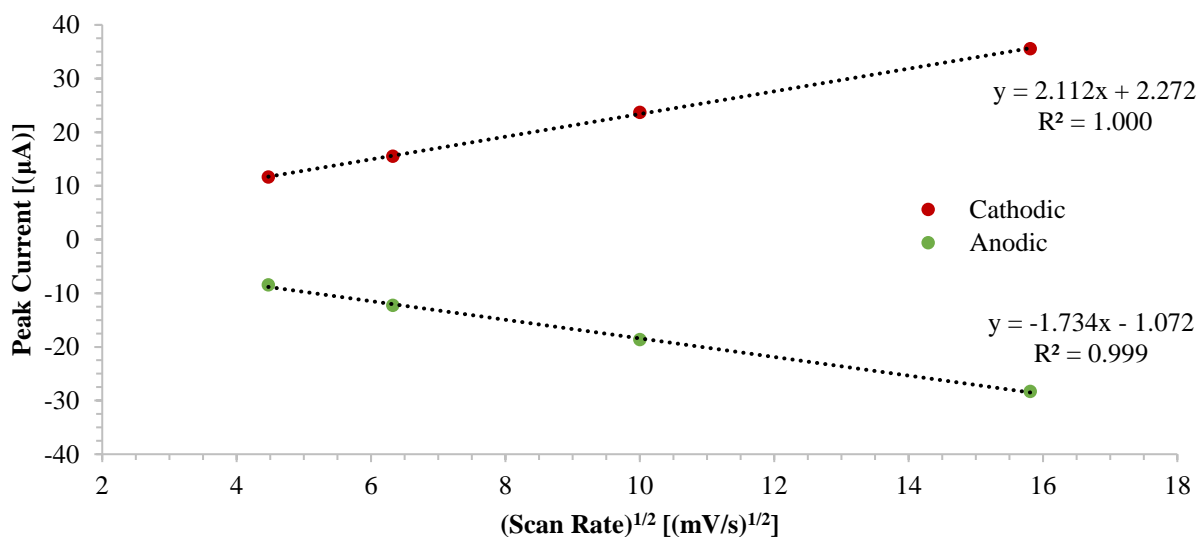


Figure S37. Plot of the cathodic/anodic peak current versus the square root of scan rate for $P_3^{Ga}Fe-N_2$ (**3c**) in 0.1 M THF solution of $[nBu_4][PF_6]$ at different scan rates.

Miscellaneous Experiments

Treatment of $[Na(12-c-4)_2][P_3^XFe-N_2]$ (5a-c**) with 10 equiv of $HBAr^F_4$ and 12 equiv of KC_8**

In the glovebox, $[Na(12-c-4)_2][P_3^XFe-N_2]$ (**5**, 9.3×10^{-3} mmol) was weighed out into a 20 mL

scintillation vial, equipped with a stir bar, and suspended in 1.5 mL of Et₂O. In a separate 4 mL vial, HBAr^F₄ (10 equiv, 0.093 mmol) was dissolved in 0.5 mL of Et₂O. Finally, in another 4 mL vial, KC₈ (12 equiv, 0.11 mmol) was suspended in 1 mL of Et₂O. All three vials were cooled to -78 °C for 30 minutes in the glovebox coldwell equipped with an external dry ice/acetone bath.

After the temperature had equilibrated, the HBAr^F₄ solution was added dropwise inside the -78 °C glovebox coldwell to the stirring vial containing **5**. Residual HBAr^F₄ was transferred using 0.5 mL of pre-chilled Et₂O. The reaction was stirred at -78 °C for 5 minutes before similarly delivering the KC₈ suspension. Residual KC₈ was transferred using 0.5 mL of pre-chilled Et₂O. The reaction vial was then capped and stirred for 1 hour at -78 °C followed by 20 minutes at room temperature. The reaction mixture was then filtered through glass filter paper into a 20 mL vial, concentrated to ½ the original volume, transferred to an NMR tube, and analyzed by ³¹P{¹H} NMR and IR spectroscopies. For **5a**, [M(solv)_x][P₃^BFe-N₂] (solv = solvent) and (P₃^B)(μ-H)Fe(L)(H) (L = H₂, N₂) were the Fe-containing products present. For **5b** and **5c**, analysis of the Et₂O filtrate revealed the presence of both [M(solv)_x][P₃^XFe-N₂] and free phosphine resulting from ligand decomposition.

In addition to the Et₂O filtrate, the residue remaining in the original reaction vessel and the pipet filter was extracted with a minimal amount of THF. The resulting dark red solution was also analyzed by ³¹P{¹H} NMR (silent; no signals) and IR spectroscopies. For **5a-c**, [M(solv)_x][P₃^XFe-N₂] was the only Fe-containing species observed. This was further confirmed by addition of 12-crown-4 to the THF solution, causing a shift in the ν(NN) to higher wavenumbers and matching that reported for [Na(12-c-4)₂][P₃^XFe-N₂].

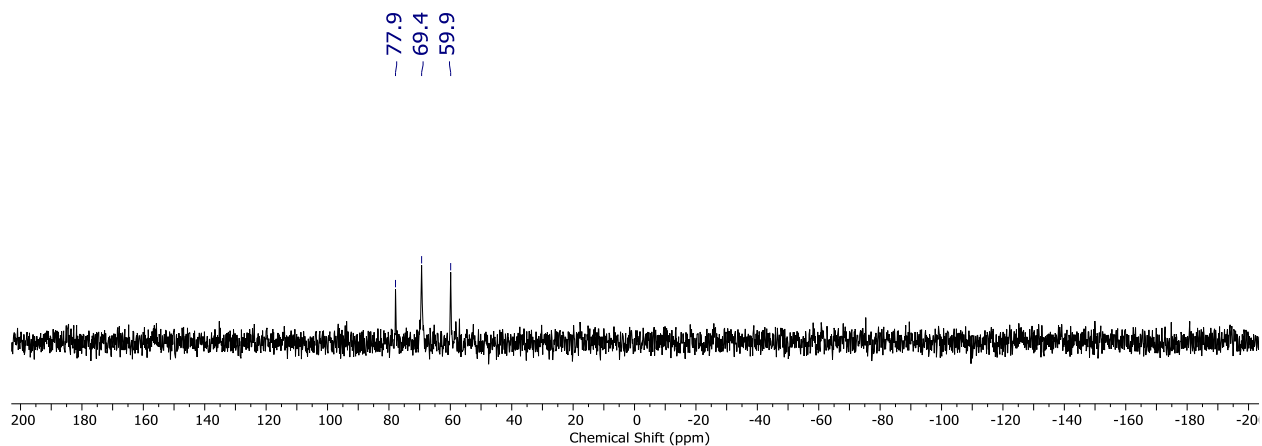


Figure S38. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, Et_2O , 25 °C) for the addition of 10 equiv HBAr^{F_4} and 12 equiv KC_8 to $[\text{Na}(12\text{-c-}4)_2][\text{P}_3^{\text{B}}\text{Fe-N}_2]$ (**5a**).

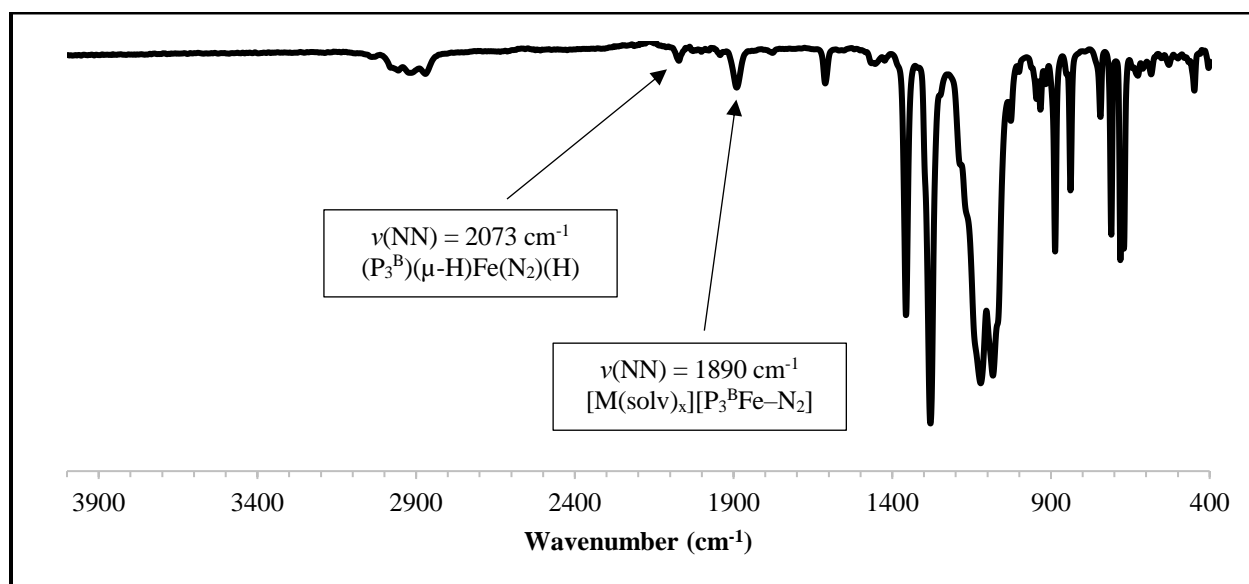


Figure S39. IR spectrum for the addition of 10 equiv HBAr^{F_4} and 12 equiv KC_8 to $[\text{Na}(12\text{-c-}4)_2][\text{P}_3^{\text{B}}\text{Fe-N}_2]$ (**5a**) from the Et_2O filtrate; deposited as a thin film from Et_2O .

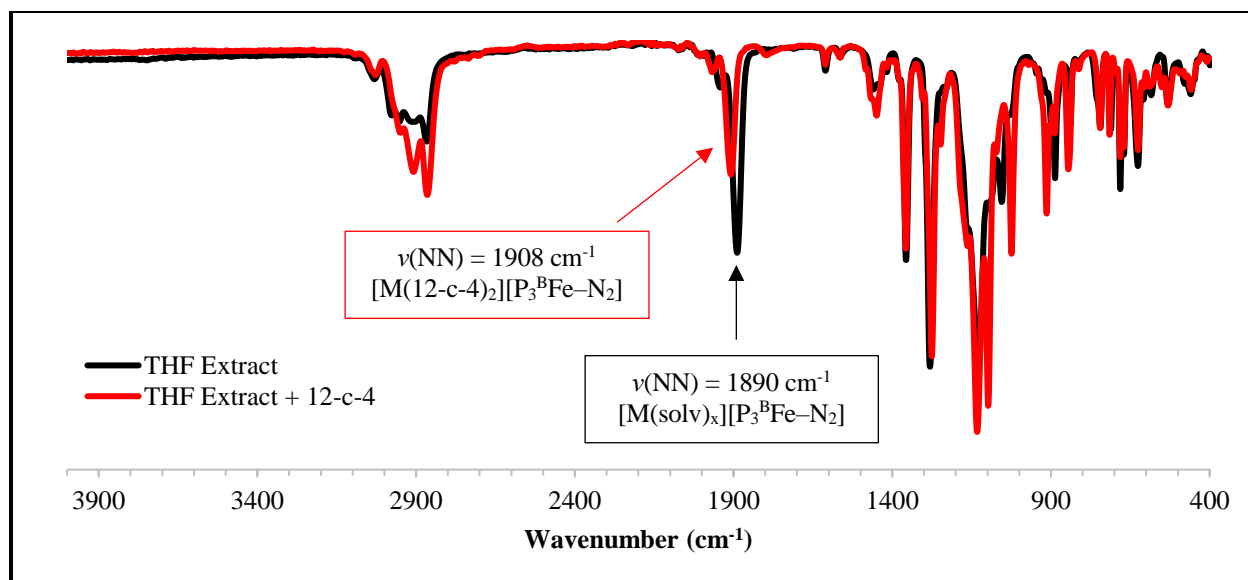


Figure S40. IR spectra for the addition of 10 equiv HBAr^F₄ and 12 equiv KC₈ to [Na(12-c-4)₂][P₃^BFe-N₂] (**5a**) from the THF extract before (black) and after (red) addition of 12-crown-4; deposited as a thin film from THF.

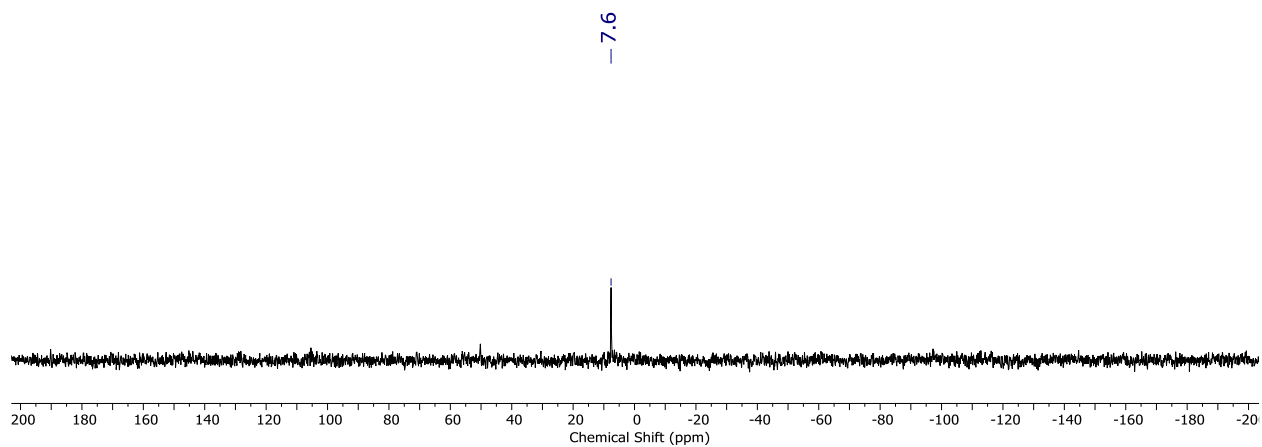


Figure S41. ³¹P{¹H} NMR spectrum (162 MHz, Et₂O, 25 °C) for the addition of 10 equiv HBAr^F₄ and 12 equiv KC₈ to [Na(12-c-4)₂][P₃^{Al}Fe-N₂] (**5b**).

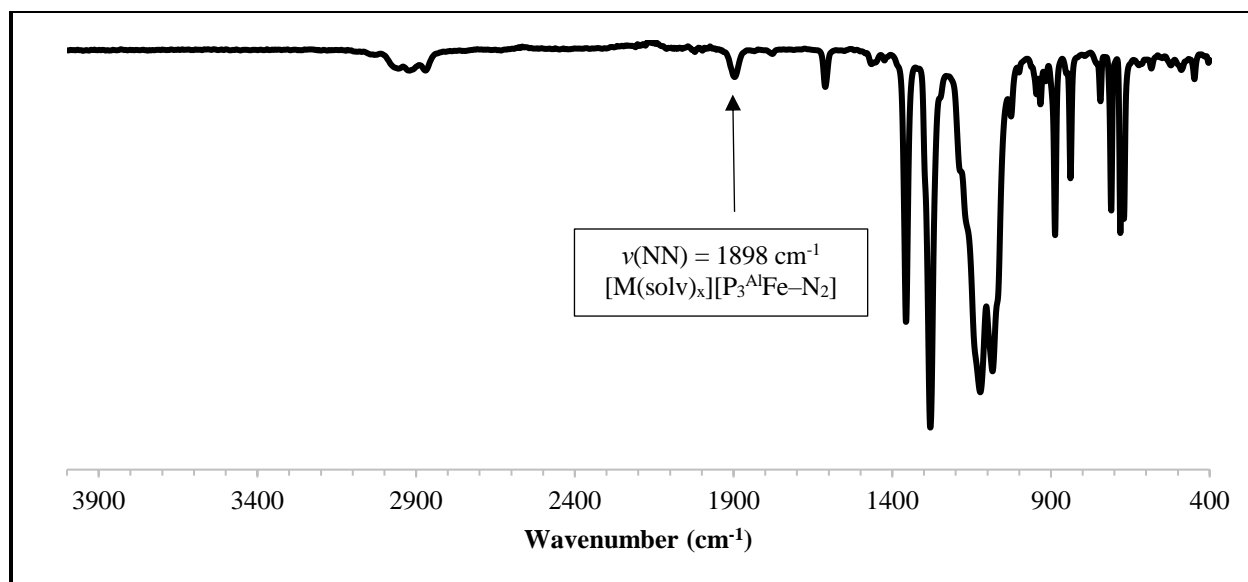


Figure S42. IR spectrum for the addition of 10 equiv HBAr^F₄ and 12 equiv KC₈ to [Na(12-c-4)₂][P₃^{Al}Fe-N₂] (**5b**) from the Et₂O filtrate; deposited as a thin film from Et₂O.

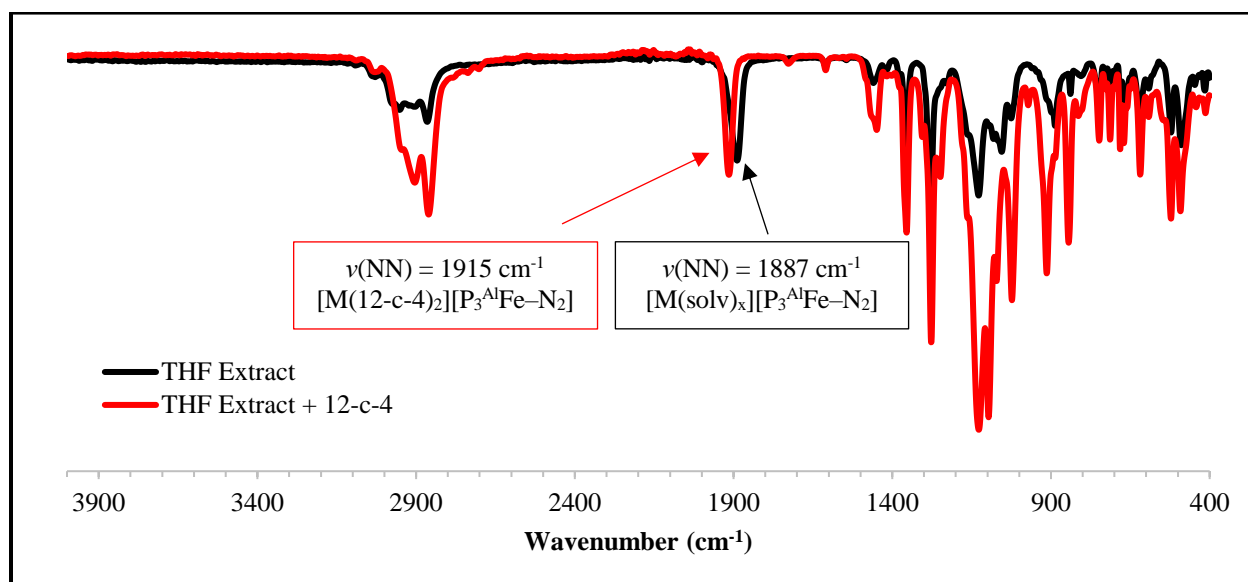


Figure S43. IR spectra for the addition of 10 equiv HBAr^F₄ and 12 equiv KC₈ to [Na(12-c-4)₂][P₃^{Al}Fe-N₂] (**5b**) from the THF extract before (black) and after (red) addition of 12-crown-4; deposited as a thin film from THF.

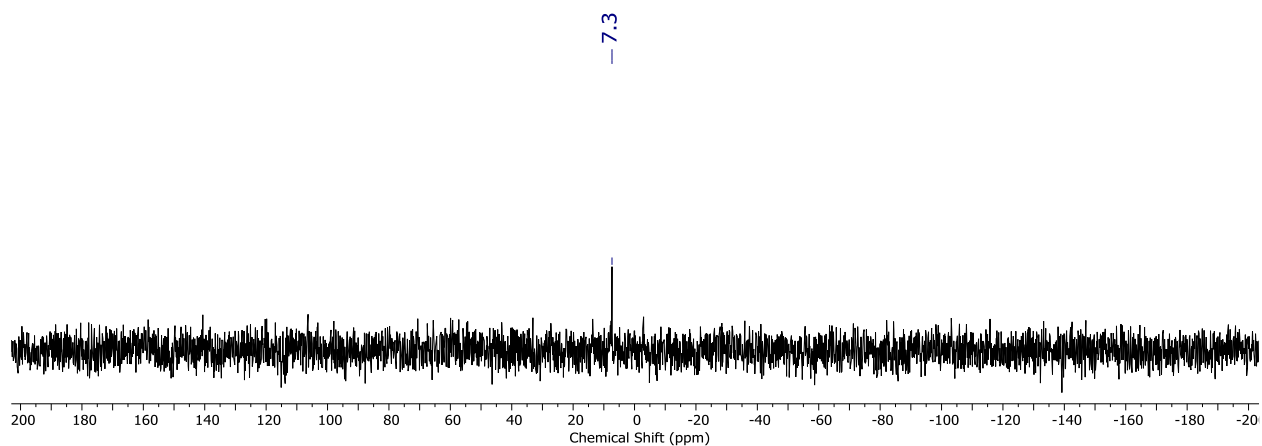


Figure S44. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, Et_2O , 25 °C) for the addition of 10 equiv HBAr^{F_4} and 12 equiv KC_8 to $[\text{Na}(12\text{-c-}4)_2][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**5c**).

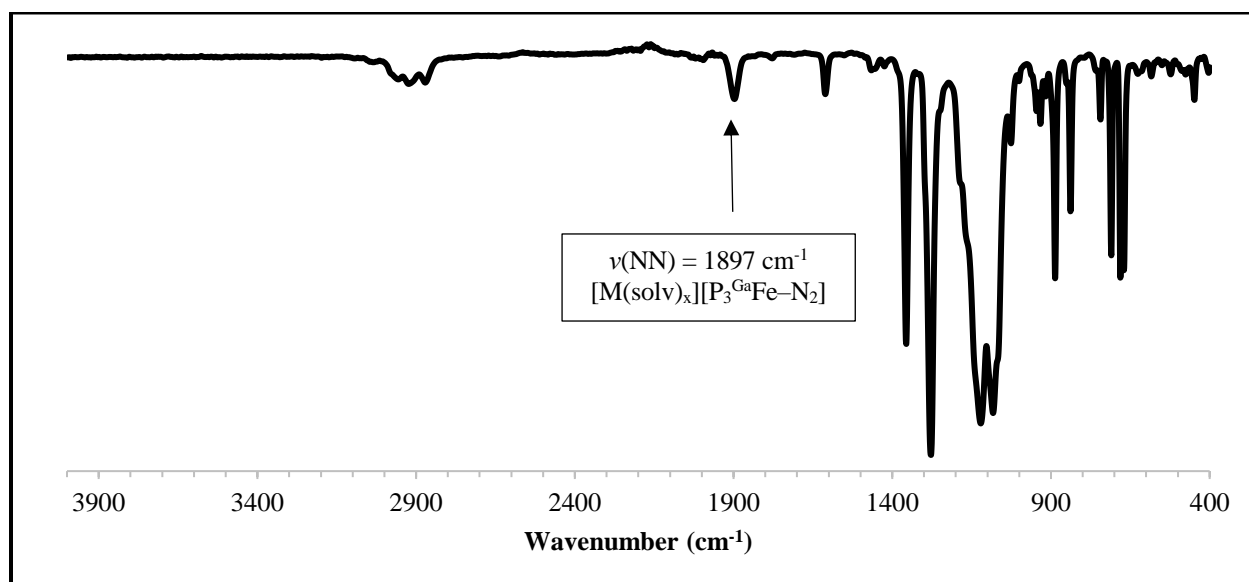


Figure S45. IR spectrum for the addition of 10 equiv HBAr^{F_4} and 12 equiv KC_8 to $[\text{Na}(12\text{-c-}4)_2][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**5c**) from the Et_2O filtrate; deposited as a thin film from Et_2O .

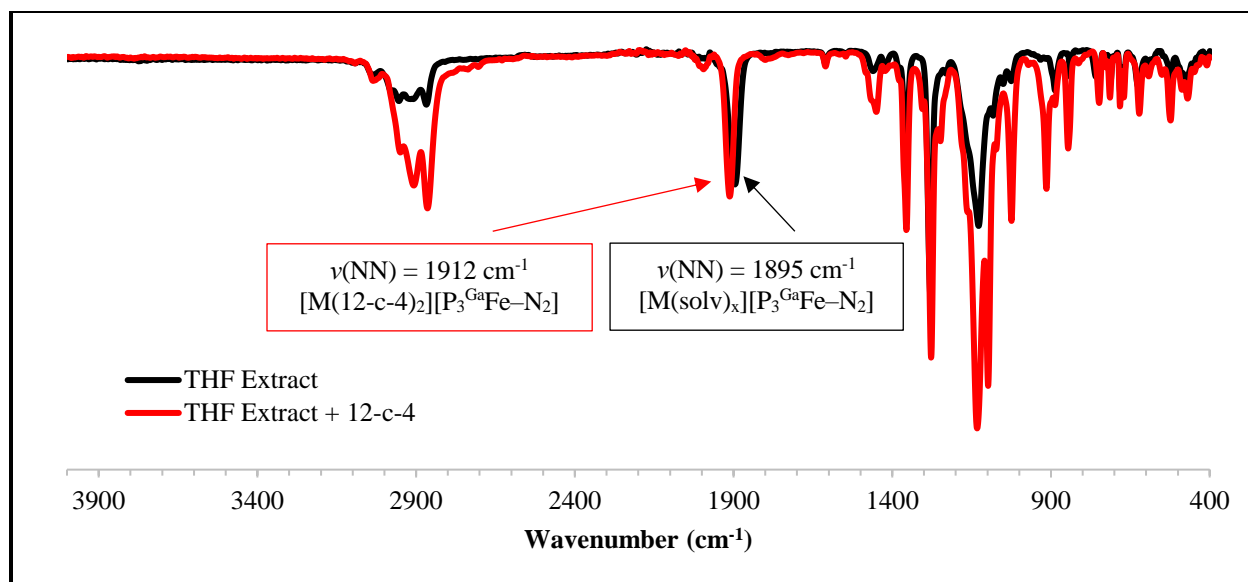


Figure S46. IR spectra for the addition of 10 equiv HBAr^F₄ and 12 equiv KC₈ to [Na(12-c-4)₂][P₃^{Ga}Fe-N₂] (**5c**) from the THF extract before (black) and after (red) addition of 12-crown-4; deposited as a thin film from THF.

Treatment of [Na(12-c-4)₂][P₃^XFe-N₂] (**5a-c**) with 10 equiv [H₂NPh₂][OTf] and 12 equiv Cp*₂Co

In the glovebox, [Na(12-c-4)₂][P₃^XFe-N₂] (**5**, 9.3 x 10⁻³ mmol) was weighed out into a 20 mL scintillation vial, equipped with a stir bar, and suspended in 1.5 mL of Et₂O. In a separate 4 mL vial, [H₂NPh₂][OTf] (10 equiv, 0.093 mmol) was suspended in 0.5 mL of Et₂O. Finally, in another 4 mL vial, Cp*₂Co (12 equiv, 0.11 mmol) was suspended in 1 mL of Et₂O. All three vials were cooled to -78 °C for 30 minutes in the glovebox coldwell equipped with an external dry ice/acetone bath.

After the temperature had equilibrated, the suspension of Cp*₂Co was added dropwise inside the -78 °C glovebox coldwell to the stirring vial containing **5**. Residual Cp*₂Co was transferred using 0.5 mL of pre-chilled Et₂O. The reaction was stirred at -78 °C for 5 minutes before similarly delivering the [H₂NPh₂][OTf] suspension. Residual [H₂NPh₂][OTf] was transferred using 0.5 mL of pre-chilled Et₂O. The reaction vial was then capped and stirred for 3 hours at -78 °C followed by 30 minutes at room temperature. The reaction mixture was then filtered through glass filter paper into a 20 mL vial, concentrated to ½ the original volume, transferred to an NMR tube, and analyzed by ³¹P{¹H}

NMR and IR spectroscopies. For **5a**, $P_3^B Fe-N_2$ and $(P_3^B)(\mu-H)Fe(N_2)(H)$ were the Fe-containing products present. For **5b** and **5c**, analysis of the Et_2O filtrate revealed a mixture of compounds that included $P_3^X Fe-N_2$ and uncoordinated phosphine resulting from $P_3^X Fe$ decomposition.

Further extraction of the reaction residue with THF did not reveal the presence of any $P_3^X Fe$ compounds upon analysis.

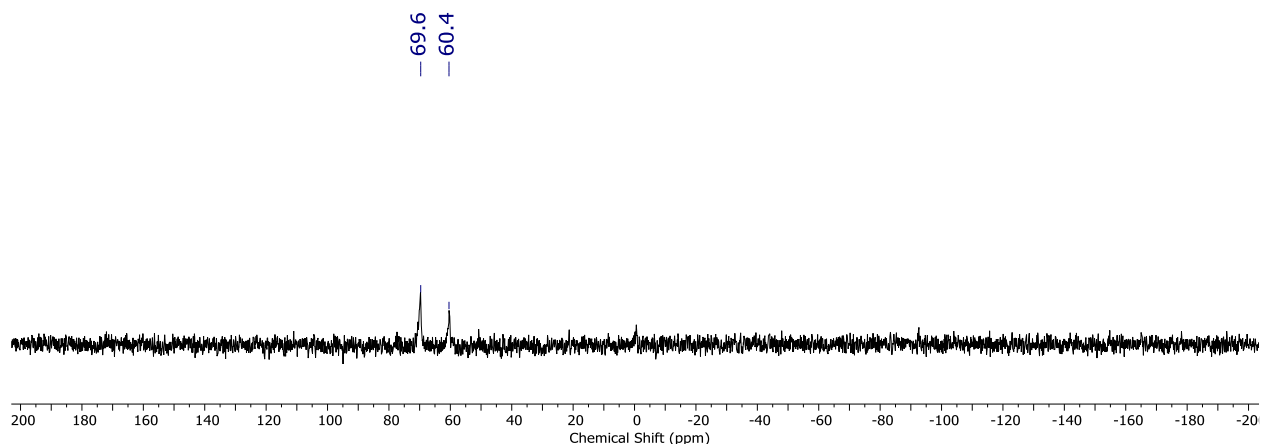


Figure S47. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, Et_2O , 25 °C) for the addition of 10 equiv $[H_2NPh_2][OTf]$ and 12 equiv Cp^*_2Co to $[Na(12-c-4)_2][P_3^B Fe-N_2]$ (**5a**).

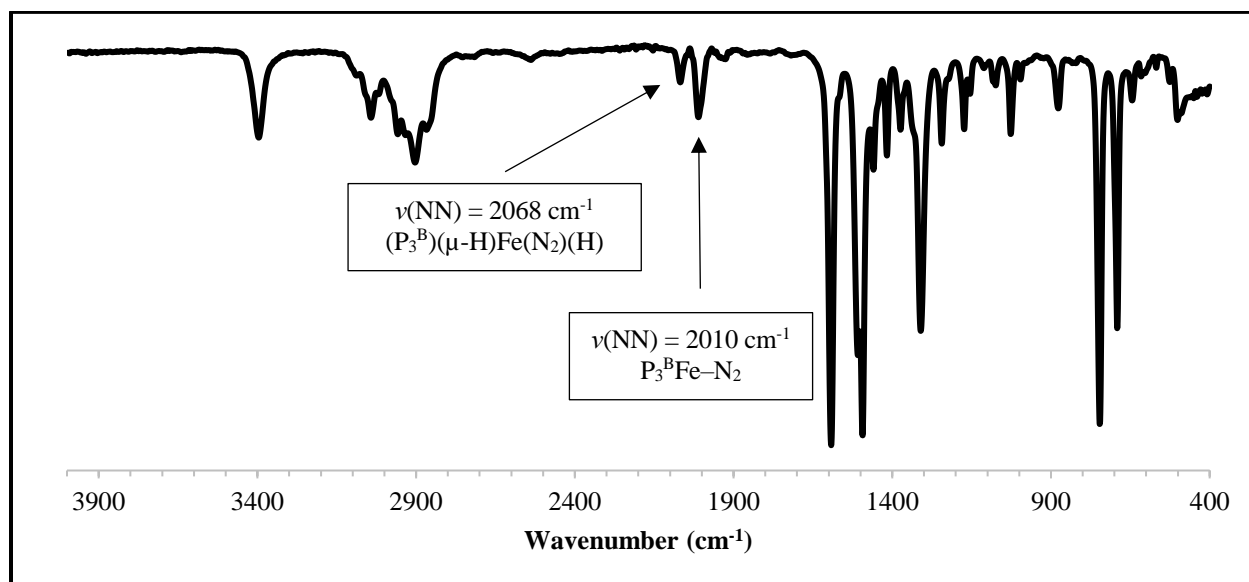


Figure S48. IR spectrum for the addition of 10 equiv $[H_2NPh_2][OTf]$ and 12 equiv Cp^*_2Co to $[Na(12-c-4)_2][P_3^B Fe-N_2]$ (**5a**) from the Et_2O filtrate; deposited as a thin film from Et_2O .

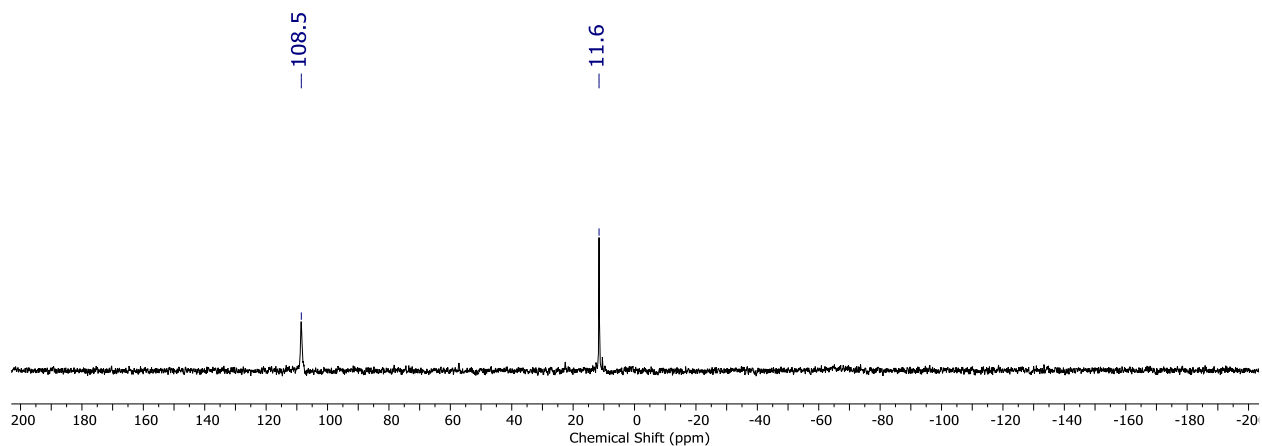


Figure S49. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, Et_2O , 25 °C) for the addition of 10 equiv $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 12 equiv Cp^*_2Co to $[\text{Na}(12\text{-c-4})_2][\text{P}_3^{\text{Al}}\text{Fe-N}_2]$ (**5b**).

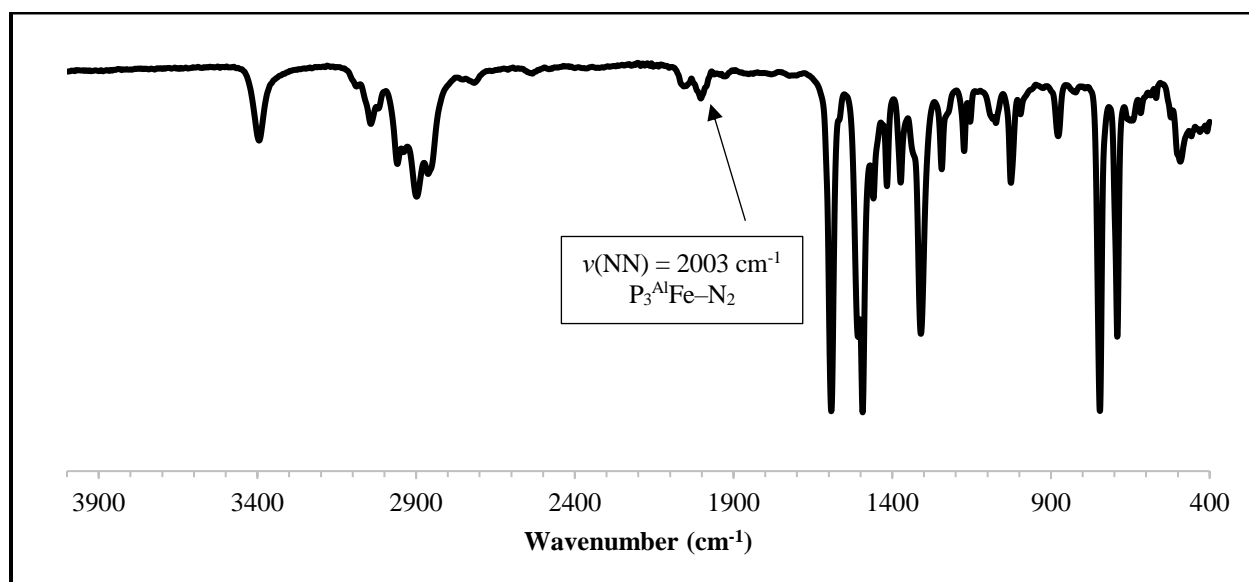


Figure S50. IR spectrum for the addition of 10 equiv $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 12 equiv Cp^*_2Co to $[\text{Na}(12\text{-c-4})_2][\text{P}_3^{\text{Al}}\text{Fe-N}_2]$ (**5b**) from the Et_2O filtrate; deposited as a thin film from Et_2O .

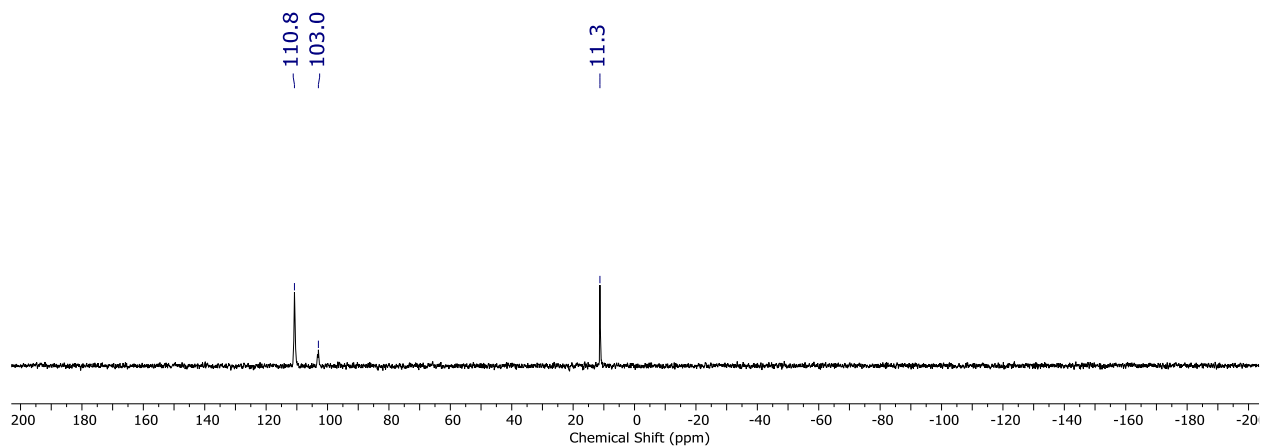


Figure S51. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, Et_2O , 25 °C) for the addition of 10 equiv $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 12 equiv Cp^*_2Co to $[\text{Na}(12\text{-c-4})_2][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**5c**).

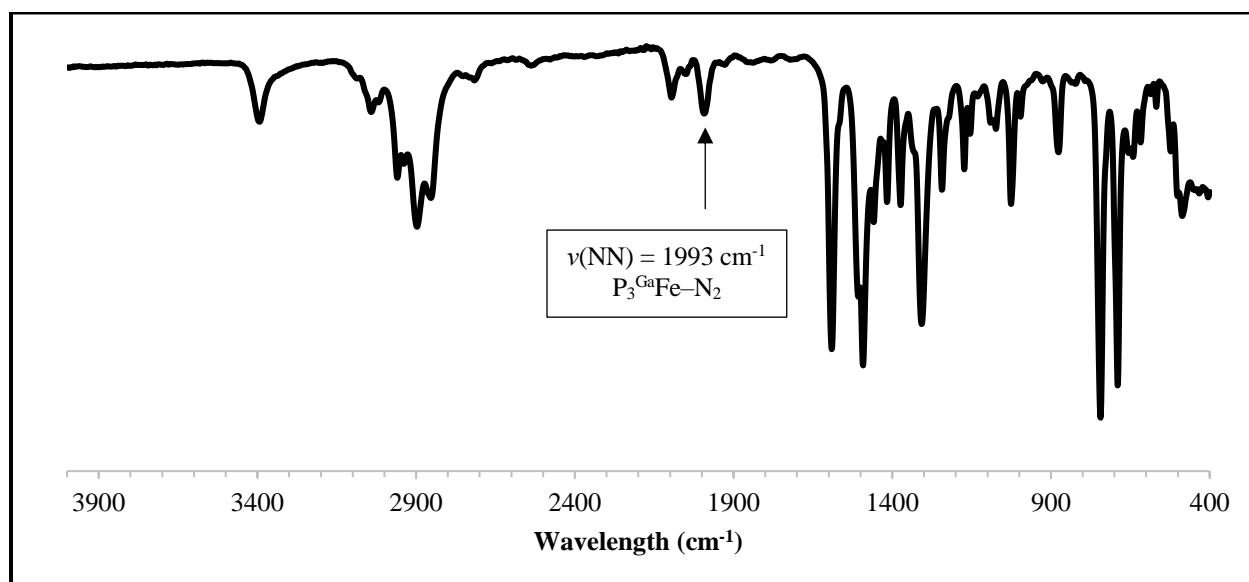


Figure S52. IR spectrum for the addition of 10 equiv $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 12 equiv Cp^*_2Co to $[\text{Na}(12\text{-c-4})_2][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**5c**) from the Et_2O filtrate; deposited as a thin film from Et_2O .

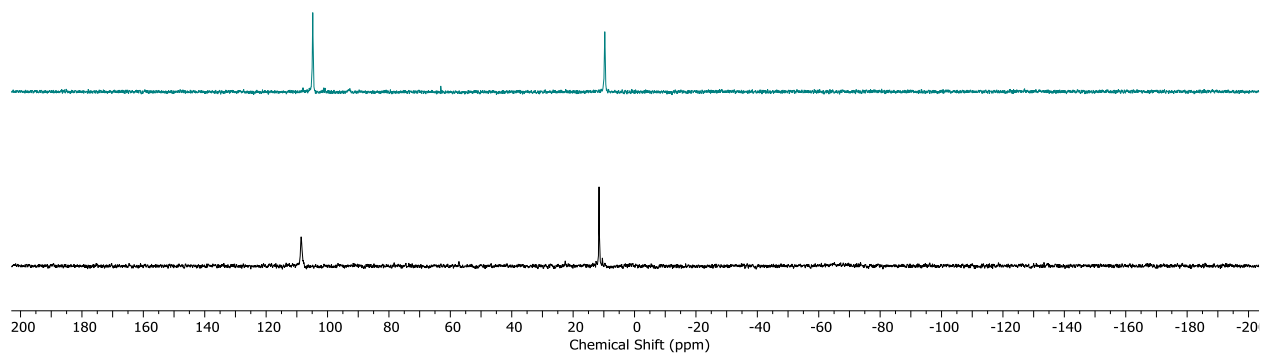


Figure S53. Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz, 25 °C) for the addition of 10 equiv $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 12 equiv Cp^*_2Co to $[\text{Na}(12\text{-c-}4)_2][\text{P}_3^{\text{Al}}\text{Fe-N}_2]$ (**5b**) (bottom, Et_2O) and the reaction of $\text{P}_3^{\text{Al}}\text{Fe-N}_2$ (**3b**) with 1 atm of H_2 at room temperature, followed by freeze-pump thawing and storing under an atmosphere of N_2 for 3 days (top, C_6D_6).

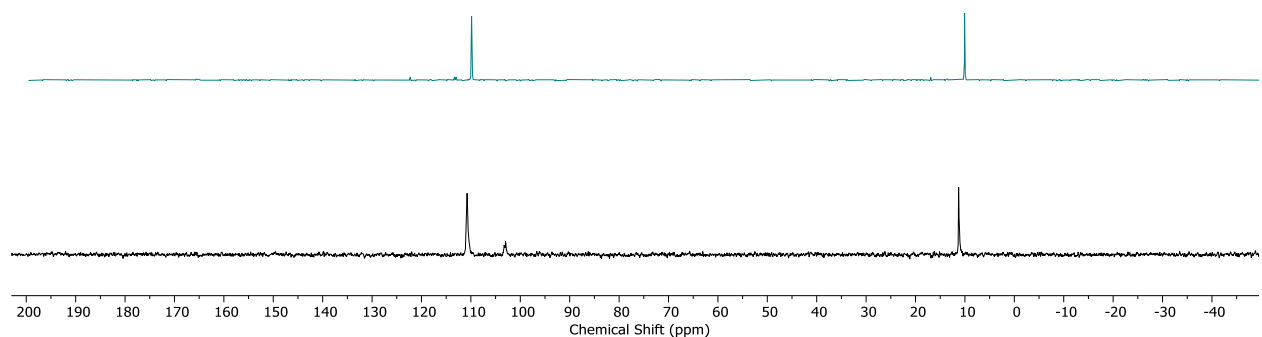


Figure S54. Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz, 25 °C) for the addition of 10 equiv $[\text{H}_2\text{NPh}_2][\text{OTf}]$ and 12 equiv Cp^*_2Co to $[\text{Na}(12\text{-c-}4)_2][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**5c**) (bottom, Et_2O) and the reaction of $\text{P}_3^{\text{Ga}}\text{Fe-N}_2$ (**3c**) with 1 atm of H_2 at room temperature, followed by freeze-pump thawing and storing under an atmosphere of N_2 for 3 days (top, C_6D_6).

X-Ray Data Tables

Table S3. Structural comparison of P₃^XFe complexes.

Metric X	P ₃ ^X Fe–Br			P ₃ ^X Fe–N ₂			[Na(THF) ₃][P ₃ ^X Fe–N ₂]		
	B	Al	Ga	B*	Al	Ga	B [‡]	Al	Ga
Fe–X ^a	2.458	2.662	2.666	2.417	2.539	2.544	2.311, 2.306	2.485	2.489
Fe–P ^a	2.383 2.403 2.435	2.460	2.469	2.306 2.312 2.404	2.378 2.384 2.422	2.390 2.397 2.434	2.232, 2.225 2.240, 2.263 2.307, 2.291	2.275	2.282
Fe–Br ^a	2.414	2.409	2.416	-----	-----	-----	-----	-----	-----
Fe–N ^a	-----	-----	-----	1.844	1.888	1.846	1.776, 1.773	1.769	1.759
N–N ^a	-----	-----	-----	1.129	1.062	1.118	1.149, 1.148	1.134	1.141
P–Fe–P ^b	106.8 113.8 122.1	114.9	115.3	109.9 111.4 124.5	113.6 114.6 119.7	113.7 114.7 120.4	107.3, 113.4 110.3, 114.1 134.6, 124.7	116.5	116.8
ΣP–Fe–P ^b	342.7	344.8	345.8	345.8	347.8	348.7	352.3, 352.3	349.6	350.4
C–X–C ^b	112.0 114.8 115.0	113.6	114.0	107.6 111.2 114.0	107.8 113.5 115.0	108.3 114.1 115.4	106.9, 107.6 109.7, 110.6 113.2, 112.1	111.6	111.9
ΣC–X–C ^b	341.8	340.8	341.9	332.8	336.2	337.8	329.8, 330.3	334.8	335.8
X–Fe–Br ^b	173.7	180.0	180.0	-----	-----	-----	-----	-----	-----
X–Fe–N ^b	-----	-----	-----	174.2	176.6	177.0	173.9, 178.8	180.0	180.0
Fe–N–N ^b	-----	-----	-----	177.0	177.6	177.4	175.9, 179.8	180.0	180.0
<i>r</i>	1.14	1.05	1.05	1.12	1.00	1.00	1.07, 1.07	0.98	0.98

^aUnits of Å. ^bUnits of °. *From DFT geometry optimized structure. [‡]Two independent molecules present in the asymmetric unit.

Table S4. Crystal data and structure refinement for **2b**, **3b**, and **4b**.

Compound	2b	3b	4b
Empirical formula	C ₃₉ H ₆₃ AlBrFeO _{0.5} P ₃ Si	C ₃₆ H ₅₄ AlFeN ₂ P ₃	C ₄₈ H ₇₈ AlFeN ₂ NaO ₃ P ₃
Formula weight	823.63	690.55	929.85
Temperature [K]	100	100	100
Crystal system	Trigonal	Orthorhombic	Trigonal
Space group	P $\bar{3}$	Pbca	R3
a [Å]	15.4455(5)	16.0945(17)	18.0659(5)
b [Å]	15.4455(5)	17.2155(18)	18.0659(5)
c [Å]	10.2238(4)	25.795(3)	12.9769(5)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	120	90	120
Volume [Å ³]	2112.26(16)	7147.1(13)	3667.9(2)
Z	2	8	3
ρ_{calc} [g/cm ³]	1.295	1.284	1.263
μ [mm ⁻¹]	1.493	0.608	0.475
F (000)	868.0	2944.0	1497.0
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
Reflections collected	37355	133330	23224
Unique reflections	6489	16490	4266
Data/restraints/parameters	6489/0/146	16490/0/400	4266/1/182
R(int)	0.0457	0.0809	0.0476
R ₁ (I > 2 σ (I))	0.0361	0.0453	0.0262
wR ₂ (all data)	0.0789	0.0898	0.0583
GOOF	1.019	1.028	1.036

Table S5. Crystal data and structure refinement for **2c**, **3c**, and **4c**.

Compound	2c	3c	4c
Empirical formula	C ₃₉ H ₆₃ BrFeGaO _{0.46} P ₃ Si _{0.94}	C ₄₈ H ₇₂ Br _{0.09} Fe _{1.33} Ga _{1.33} N _{2.5} P ₄	C ₄₈ H ₇₈ FeGaN ₂ NaO ₃ P ₃
Formula weight	864.04	982.13	972.59
Temperature [K]	100	100	100
Crystal system	Trigonal	Orthorhombic	Trigonal
Space group	P $\bar{3}$	Pbca	R3
a [Å]	15.4998(10)	16.0652(9)	18.0650(6)
b [Å]	15.4998(10)	17.1911(9)	18.0650(6)
c [Å]	10.2411(8)	25.8976(16)	12.9480(5)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	120	90	120
Volume [Å ³]	2130.7(3)	7152.4(7)	3659.4(3)
Z	2	6	3
ρ_{calc} [g/cm ³]	1.347	1.368	1.324
μ [mm ⁻¹]	2.076	1.392	0.998
F (000)	902.0	3099.0	1551.0
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
Reflections collected	44998	70848	14861
Unique reflections	7570	7690	4777
Data/restraints/parameters	7570/0/160	7690/12/410	4777/1/184
R(int)	0.0399	0.0569	0.0278
R ₁ (I > 2 σ (I))	0.0226	0.0279	0.0244
wR ₂ (all data)	0.0472	0.0579	0.0488
GOOF	0.931	1.038	0.992

DFT Calculations

Table S6. Optimized coordinates [Å] for P₃^BFe–N₂ (**3a**) (Charge = 0, *S* = 1).

Fe	2.70616	3.79764	2.47086
P	4.27362	4.83320	3.97078
P	0.52514	4.50167	2.16771
P	3.67546	3.33833	0.42933
N	2.49594	2.20005	3.36777
C	4.68707	4.77245	-0.05521
C	4.25825	5.97881	0.55535
C	3.74100	6.57077	4.00421
C	2.69847	2.93605	-1.14467
H	1.97296	2.16455	-0.82721
C	1.64746	7.45552	-0.30846
H	2.60656	7.83181	-0.68076
C	1.63672	6.45850	0.69493
C	2.61797	8.32077	2.78714
H	2.10358	8.68703	1.89234
C	4.08049	4.24207	5.74709
H	4.61598	4.98008	6.37090
C	3.10421	6.99038	2.80533
C	-0.82530	6.53022	0.62000
H	-1.79596	6.18394	0.98941
C	0.05393	1.75929	1.42624
H	-0.16455	1.43960	2.45886
H	1.13989	1.65610	1.26759
H	-0.45808	1.06038	0.74061
C	6.17438	4.90086	3.89130
H	6.47084	3.83724	3.84135
C	4.85990	1.88458	0.51339
H	5.44243	1.87095	-0.42598
C	3.37999	8.73711	5.05998
H	3.47150	9.39843	5.92891
C	3.87846	7.42927	5.11377
H	4.34934	7.07398	6.03674
C	1.92546	4.16638	-1.64400
H	2.61929	4.96929	-1.94558
H	1.26154	4.58788	-0.87770
H	1.31212	3.89298	-2.52209
C	6.69657	5.61735	2.64052
H	6.35709	6.66539	2.61965
H	6.36260	5.14297	1.70963
H	7.80192	5.61458	2.64985
C	0.37447	5.97048	1.10300
C	5.80477	4.73563	-0.91362

H	6.14331	3.79010	-1.35064
C	-1.95471	3.28091	1.20735
H	-2.38434	2.56253	0.48516
H	-2.33645	4.27773	0.93775
H	-2.34800	3.01631	2.20402
C	6.51515	5.91232	-1.18657
H	7.39616	5.88474	-1.83753
C	-0.59694	4.89840	3.60770
H	-1.58270	5.13226	3.16206
B	2.95849	6.00245	1.51256
C	-0.41936	3.19602	1.15378
H	-0.10653	3.46171	0.12830
C	0.45944	7.98110	-0.83211
H	0.49895	8.75262	-1.61074
C	6.09654	7.12274	-0.60947
H	6.65273	8.04463	-0.81575
C	2.75102	9.18049	3.88663
H	2.34969	10.19914	3.83299
C	-0.76093	3.70758	4.56481
H	0.21039	3.38420	4.97065
H	-1.21891	2.83615	4.06853
H	-1.40626	3.98768	5.41723
C	2.61347	4.24834	6.18798
H	2.01143	3.56265	5.57184
H	2.17318	5.25554	6.10861
H	2.52943	3.92122	7.24052
C	4.98729	7.15032	0.24653
H	4.69698	8.09659	0.71875
C	3.55187	2.37396	-2.29701
H	2.89838	2.16870	-3.16474
H	4.06909	1.43389	-2.04615
H	4.30663	3.11056	-2.62128
C	5.83298	2.06947	1.68548
H	5.28104	2.12926	2.64136
H	6.42524	2.99194	1.57340
H	6.53364	1.21650	1.74809
N	2.31263	1.23848	3.93008
C	6.83271	5.54057	5.13106
H	7.93015	5.52685	4.99619
H	6.61443	5.01625	6.07508
H	6.52946	6.59637	5.23773
C	-0.07690	6.16610	4.30860
H	-0.70078	6.40079	5.18989
H	-0.09037	7.03342	3.62833
H	0.96470	6.03944	4.64593
C	4.08499	0.56102	0.64272

H	4.79195	-0.28633	0.71116
H	3.42044	0.37192	-0.21677
H	3.46688	0.55536	1.55534
C	-0.78380	7.54001	-0.34912
H	-1.71379	7.96997	-0.73642
C	4.73878	2.86646	5.96237
H	4.58321	2.53770	7.00646
H	5.82583	2.88837	5.77933
H	4.30236	2.09865	5.30455

Table S7. Optimized coordinates [Å] for $\text{P}_3^{\text{B}}\text{Fe}-\text{N}_2^-$ (Charge = -1, $S = 1/2$).

Fe	-0.05319	-0.07911	-0.95871
P	2.16865	-0.57042	-0.69356
P	-1.96310	-1.10661	-0.54662
P	-0.43042	2.05641	-0.50154
N	-0.11336	-0.11189	-2.74703
C	0.39487	2.43226	1.09530
C	0.59932	1.26177	1.87566
C	2.18470	-1.65435	0.78428
C	-2.14552	2.86748	-0.19897
H	-2.75635	2.52382	-1.05454
C	-1.66170	-0.30022	3.38891
H	-0.92234	0.21293	4.01576
C	-1.37458	-0.51235	2.01889
C	0.97990	-2.24682	2.78882
H	0.14564	-2.09729	3.48398
C	2.85759	-1.69363	-2.05206
H	3.79874	-2.12557	-1.66570
C	1.09601	-1.39249	1.66411
C	-3.58527	-1.58221	1.82366
H	-4.34062	-2.09287	1.21733
C	-3.26616	0.27114	-2.68381
H	-3.00877	-0.46543	-3.46334
H	-2.41422	0.96314	-2.59972
H	-4.15425	0.83639	-3.02952
C	3.73372	0.51299	-0.45670
H	3.72250	1.17569	-1.34022
C	0.27583	3.33068	-1.70645
H	0.20830	4.33034	-1.23784
C	2.94257	-3.53462	2.14494
H	3.63623	-4.36783	2.31333
C	3.09491	-2.70305	1.02456
H	3.90878	-2.90360	0.31760
C	-2.78409	2.33828	1.09430

H	-2.19647	2.64398	1.97739
H	-2.84354	1.24241	1.11480
H	-3.80839	2.74305	1.20631
C	3.65801	1.38037	0.80405
H	3.59347	0.75221	1.70803
H	2.78498	2.04414	0.80604
H	4.56864	2.00592	0.88467
C	-2.38874	-1.11948	1.23974
C	0.83875	3.69452	1.53561
H	0.70218	4.58186	0.90614
C	-4.77640	-1.33885	-1.46521
H	-5.64914	-0.76441	-1.83446
H	-5.07296	-1.79950	-0.50997
H	-4.59247	-2.14991	-2.19124
C	1.50398	3.82053	2.76554
H	1.87486	4.79896	3.09467
C	-2.07766	-2.94645	-0.94114
H	-3.08453	-3.27785	-0.62217
B	0.06237	-0.17233	1.32380
C	-3.55868	-0.40575	-1.33511
H	-3.82124	0.38718	-0.61078
C	-2.86948	-0.71452	3.96745
H	-3.06254	-0.52543	5.03162
C	1.70649	2.67987	3.55902
H	2.23480	2.76838	4.51705
C	1.87812	-3.29805	3.02865
H	1.74152	-3.94562	3.90503
C	-1.91261	-3.21584	-2.44392
H	-0.96381	-2.79681	-2.81507
H	-2.72141	-2.76037	-3.03960
H	-1.90986	-4.30400	-2.64940
C	1.90503	-2.85805	-2.34248
H	0.92503	-2.48653	-2.67776
H	1.74425	-3.47603	-1.44376
H	2.31878	-3.50705	-3.13920
C	1.25651	1.42612	3.11715
H	1.45831	0.53807	3.73001
C	-2.17951	4.40655	-0.16481
H	-3.21612	4.74923	0.02489
H	-1.84815	4.87884	-1.10421
H	-1.55470	4.79659	0.65799
C	1.75219	3.03278	-1.99033
H	1.85932	2.01570	-2.40616
H	2.35514	3.09142	-1.06944
H	2.16530	3.75432	-2.72194
N	-0.15887	-0.17196	-3.88795

C	5.07344	-0.24838	-0.44047
H	5.89980	0.47842	-0.31554
H	5.27692	-0.81544	-1.36376
H	5.12118	-0.94632	0.41428
C	-1.02917	-3.68878	-0.09669
H	-1.00189	-4.76386	-0.35957
H	-1.24255	-3.59504	0.98088
H	-0.02438	-3.26394	-0.25849
C	-0.53649	3.32935	-3.01500
H	-0.13159	4.08176	-3.71988
H	-1.60234	3.56591	-2.85182
H	-0.48162	2.34401	-3.50570
C	-3.83057	-1.38029	3.18892
H	-4.77046	-1.72453	3.63782
C	3.17903	-0.88921	-3.32471
H	3.54660	-1.56668	-4.11986
H	3.95907	-0.12813	-3.14933
H	2.28312	-0.37743	-3.70952

Table S8. Optimized coordinates [Å] for $P_3^{Al}Fe-N_2$ (**3b**) (Charge = 0, $S = 1$).

Fe	2.72247	3.78850	2.43793
P	4.11750	4.93616	4.03355
P	0.54835	4.55294	2.04060
P	3.85029	3.31554	0.46463
N	2.48348	2.20010	3.35261
C	4.95798	4.60654	-0.22825
C	4.53768	5.93436	0.05261
C	3.64616	6.69671	4.19683
C	2.82270	2.89767	-1.07199
H	2.04701	2.20284	-0.70264
C	1.12587	7.89664	-0.21975
H	1.99049	8.41573	-0.65448
C	1.33134	6.75048	0.58095
C	2.93817	8.66513	2.99059
H	2.62785	9.16304	2.06282
C	3.98422	4.23084	5.77703
H	4.50523	4.95704	6.42591
C	3.28037	7.29450	2.96262
C	-1.10722	6.63211	0.90280
H	-1.98962	6.17417	1.36143
C	0.13205	1.80710	1.26670
H	-0.17336	1.47414	2.27201
H	1.22711	1.70336	1.20201
H	-0.31799	1.11564	0.53184

C	6.01403	5.04573	3.91863
H	6.33878	3.99099	3.86909
C	4.94303	1.80019	0.64371
H	5.53350	1.71635	-0.28641
C	3.29573	8.78412	5.39263
H	3.28627	9.35384	6.32894
C	3.65973	7.43073	5.40128
H	3.93906	6.95849	6.34937
C	2.14005	4.16331	-1.61883
H	2.88132	4.83664	-2.08199
H	1.62861	4.74317	-0.83440
H	1.39474	3.88856	-2.38681
C	6.48651	5.75897	2.64780
H	6.08221	6.78362	2.58964
H	6.18191	5.22816	1.73851
H	7.58949	5.82605	2.64909
C	0.18722	6.10193	1.10465
C	6.09641	4.34487	-1.01902
H	6.42796	3.31904	-1.21375
C	-1.85828	3.32972	0.93357
H	-2.24652	2.57727	0.22253
H	-2.21732	4.31323	0.59687
H	-2.30685	3.11147	1.91833
C	6.83248	5.41267	-1.55124
H	7.72938	5.21338	-2.14848
C	-0.55099	4.78836	3.53731
H	-1.55116	5.03512	3.13437
Al	3.03658	6.08305	1.36937
C	-0.32301	3.24591	0.96904
H	0.04936	3.51733	-0.03470
C	-0.15854	8.40246	-0.46318
H	-0.29545	9.29536	-1.08492
C	6.41794	6.73366	-1.31614
H	6.99368	7.56701	-1.73551
C	2.93880	9.40364	4.18376
H	2.64505	10.45990	4.17922
C	-0.68196	3.52529	4.39940
H	0.30164	3.15275	4.72311
H	-1.18559	2.70723	3.85823
H	-1.27493	3.74238	5.30642
C	2.53302	4.14359	6.26298
H	1.94159	3.45888	5.63686
H	2.04015	5.12873	6.25153
H	2.50487	3.76102	7.29975
C	5.28327	6.98290	-0.52839
H	4.99429	8.02518	-0.33658

C	3.61176	2.21125	-2.20106
H	2.93565	2.02462	-3.05538
H	4.04496	1.24179	-1.90643
H	4.42712	2.86212	-2.56159
C	5.90826	2.00668	1.82014
H	5.34293	2.13937	2.76120
H	6.54067	2.89799	1.67167
H	6.57158	1.13076	1.94187
N	2.25224	1.24732	3.91030
C	6.66289	5.71184	5.14793
H	7.75784	5.74547	4.99984
H	6.47745	5.17577	6.09292
H	6.31069	6.75124	5.26316
C	-0.03492	6.00834	4.32143
H	-0.63424	6.15984	5.23686
H	-0.08661	6.92681	3.71351
H	1.01840	5.87677	4.61514
C	4.11733	0.51398	0.81571
H	4.79255	-0.35844	0.88941
H	3.43170	0.33392	-0.02904
H	3.51519	0.54650	1.73663
C	-1.27599	7.77925	0.11755
H	-2.28031	8.18779	-0.04149
C	4.71361	2.87995	5.90313
H	4.56905	2.47128	6.92041
H	5.79846	2.97475	5.73422
H	4.32546	2.13620	5.18980

Table S9. Optimized coordinates [\AA] for $\text{P}_3^{\text{Al}}\text{Fe}-\text{N}_2^-$ (Charge = -1, $S = 1/2$).

Fe	-0.02207	0.02174	-1.07949
P	-2.05990	-0.83060	-0.71872
Al	-0.03626	-0.20269	1.38407
N	-0.01424	0.29080	-2.84380
N	-0.01612	0.43587	-3.97899
C	-3.62210	-3.29849	-0.79420
H	-4.10105	-3.07574	0.17562
H	-3.58651	-4.40048	-0.90128
H	-4.27439	-2.91046	-1.59442
C	-1.94175	-0.47429	2.00184
C	-2.46888	-0.36806	3.30702
H	-1.78240	-0.26032	4.15893
C	-3.85177	-0.35175	3.55191
H	-4.23340	-0.23903	4.57543
C	-3.42713	-0.36813	-1.94728

H	-4.38020	-0.77940	-1.56374
C	-2.19108	-2.73366	-0.83813
H	-1.74630	-2.96104	-1.82397
C	-3.55848	1.15667	-2.03703
H	-3.81391	1.60004	-1.06047
H	-4.34954	1.43918	-2.75882
H	-2.60547	1.59715	-2.37765
C	-2.87247	-0.60679	0.93415
C	-4.75115	-0.45457	2.47920
H	-5.83336	-0.42460	2.66043
C	-1.34254	-3.41354	0.24230
H	-0.29752	-3.07940	0.21123
H	-1.35871	-4.51228	0.10830
H	-1.72647	-3.18397	1.25135
C	-3.16508	-0.97104	-3.33900
H	-2.19880	-0.63188	-3.74285
H	-3.95577	-0.64887	-4.04434
H	-3.16094	-2.07486	-3.32815
C	-4.26288	-0.59427	1.17094
H	-4.97786	-0.67793	0.34364
P	1.92298	-1.07750	-0.69824
C	4.82982	-1.30697	-0.47933
H	4.78231	-1.99557	0.38226
H	5.78352	-0.74845	-0.40322
H	4.87742	-1.91091	-1.40082
C	1.14568	-1.77210	1.85541
C	1.14810	-2.55992	3.02715
H	0.55675	-2.23641	3.89538
C	1.84765	-3.77535	3.10540
H	1.80699	-4.38187	4.02013
C	2.30938	-2.23223	-2.15000
H	3.09028	-2.93930	-1.81397
C	3.65573	-0.31363	-0.45496
H	3.75529	0.37015	-1.31522
C	1.05986	-3.04428	-2.51885
H	0.71714	-3.65762	-1.66888
H	1.26992	-3.72200	-3.36863
H	0.23528	-2.37078	-2.81107
C	1.92569	-2.23369	0.75916
C	2.57976	-4.23072	1.99727
H	3.10775	-5.19129	2.03911
C	3.71944	0.51143	0.83647
H	2.95797	1.30197	0.86234
H	4.71453	0.98620	0.93396
H	3.55558	-0.12765	1.72129
C	2.85035	-1.45435	-3.36225

H	2.14253	-0.67581	-3.68668
H	3.00679	-2.14374	-4.21443
H	3.81851	-0.96916	-3.14930
C	2.63069	-3.45361	0.82932
H	3.20908	-3.82060	-0.02676
P	0.12637	2.18848	-0.44325
C	-1.11999	4.80662	0.04768
H	-0.54778	4.96179	0.97934
H	-2.07825	5.35143	0.15382
H	-0.56327	5.28090	-0.77758
C	0.74170	1.49491	2.14510
C	1.27323	1.69463	3.43770
H	1.13732	0.91615	4.20242
C	2.01480	2.84083	3.76849
H	2.44064	2.95628	4.77384
C	1.07967	3.31663	-1.63232
H	1.26480	4.26400	-1.09189
C	-1.40464	3.31012	-0.17626
H	-1.97049	3.19530	-1.11685
C	2.43920	2.69535	-1.97792
H	3.05243	2.55465	-1.07233
H	3.00099	3.34625	-2.67626
H	2.30033	1.70959	-2.45456
C	0.94929	2.52519	1.18718
C	2.23337	3.83136	2.79805
H	2.82869	4.72085	3.04024
C	-2.27077	2.79023	0.97667
H	-2.54577	1.73683	0.84047
H	-3.20327	3.38064	1.05408
H	-1.73591	2.86639	1.93994
C	0.27980	3.65010	-2.90488
H	0.04946	2.74560	-3.48692
H	0.87328	4.32515	-3.55275
H	-0.67185	4.16058	-2.68037
C	1.68949	3.68108	1.51287
H	1.86827	4.46477	0.76739

Table S10. Optimized coordinates [Å] for $P_3^{Ga}Fe-N_2$ (**3c**) (Charge = 0, $S = 1$).

Fe	2.72596	3.80343	2.43712
P	4.11595	4.93887	4.05084
P	0.53314	4.53458	2.02381
P	3.85460	3.32180	0.45868
N	2.48677	2.21779	3.34083
C	4.96413	4.61211	-0.23492

C	4.55844	5.94057	0.04638
C	3.66007	6.70481	4.21189
C	2.81854	2.91229	-1.07351
H	2.05275	2.20558	-0.70581
C	1.12031	7.91359	-0.19036
H	1.98896	8.45273	-0.59013
C	1.31615	6.75976	0.59756
C	2.97575	8.68487	3.00559
H	2.67477	9.18498	2.07635
C	3.97709	4.24170	5.79568
H	4.49896	4.96696	6.44517
C	3.30357	7.31355	2.98451
C	-1.12049	6.58968	0.84393
H	-2.00772	6.11027	1.26963
C	0.13324	1.78518	1.27437
H	-0.15437	1.45655	2.28640
H	1.22870	1.69603	1.19613
H	-0.31733	1.08216	0.55085
C	6.01127	5.03497	3.92946
H	6.32803	3.97762	3.88201
C	4.94470	1.80455	0.62871
H	5.53785	1.72213	-0.29981
C	3.33103	8.79670	5.40857
H	3.32752	9.36525	6.34553
C	3.68003	7.43915	5.41614
H	3.95414	6.96352	6.36399
C	2.11835	4.17561	-1.60242
H	2.85210	4.87505	-2.03793
H	1.58192	4.72490	-0.81420
H	1.39228	3.90237	-2.38926
C	6.48237	5.74049	2.65393
H	6.08781	6.76882	2.59630
H	6.16488	5.21117	1.74834
H	7.58605	5.79594	2.64685
C	0.17610	6.08001	1.08052
C	6.09930	4.34863	-1.02961
H	6.42438	3.32180	-1.22948
C	-1.88165	3.27766	0.95953
H	-2.26930	2.51012	0.26452
H	-2.26125	4.25060	0.61550
H	-2.31216	3.06618	1.95365
C	6.84012	5.41422	-1.56011
H	7.73373	5.21160	-2.16101
C	-0.55842	4.78953	3.52222
H	-1.56020	5.03757	3.12391
Ga	3.05151	6.10628	1.37155

C	-0.34468	3.21583	0.97264
H	0.00889	3.48311	-0.03912
C	-0.16603	8.39803	-0.46682
H	-0.30043	9.29704	-1.08017
C	6.43467	6.73648	-1.31833
H	7.01410	7.56849	-1.73528
C	2.98249	9.42151	4.20030
H	2.70063	10.48105	4.19564
C	-0.68491	3.53505	4.39760
H	0.30120	3.16460	4.71641
H	-1.19385	2.71225	3.86885
H	-1.26964	3.76222	5.30748
C	2.52285	4.16137	6.27446
H	1.93410	3.47415	5.64830
H	2.03221	5.14760	6.25407
H	2.48746	3.78489	7.31323
C	5.30351	6.99048	-0.52641
H	5.01910	8.03200	-0.32696
C	3.60693	2.24500	-2.21446
H	2.92479	2.05083	-3.06225
H	4.05987	1.28176	-1.92899
H	4.40730	2.91136	-2.57998
C	5.90712	2.00494	1.80888
H	5.33927	2.13763	2.74844
H	6.54327	2.89427	1.66460
H	6.56689	1.12635	1.93062
N	2.27084	1.26355	3.90329
C	6.66935	5.70048	5.15406
H	7.76431	5.72281	5.00355
H	6.48034	5.17072	6.10191
H	6.32732	6.74376	5.26504
C	-0.02942	6.01368	4.29149
H	-0.62059	6.17684	5.21020
H	-0.08022	6.92713	3.67593
H	1.02546	5.87774	4.57841
C	4.11522	0.51985	0.79445
H	4.78808	-0.35383	0.87434
H	3.43676	0.34072	-0.05623
H	3.50536	0.55424	1.71043
C	-1.28784	7.74418	0.06881
H	-2.29489	8.13445	-0.11619
C	4.69913	2.88743	5.92786
H	4.55094	2.48359	6.94653
H	5.78472	2.97559	5.75996
H	4.30746	2.14317	5.21694

Table S11. Optimized coordinates [\AA] for $\text{P}_3^{\text{Ga}}\text{Fe}-\text{N}_2^-$ (Charge = -1 , $S = 1/2$).

Ga	0.04761	-0.20997	1.33001
Fe	0.01185	0.04111	-1.13410
P	-1.94450	-1.06259	-0.76543
C	-4.84853	-1.28552	-0.51312
H	-4.91097	-1.87369	-1.44383
H	-4.79162	-1.98850	0.33617
H	-5.79885	-0.72476	-0.41446
C	-3.67097	-0.29659	-0.48922
H	-3.77936	0.40011	-1.33792
C	-1.10805	-3.01444	-2.61030
H	-0.28045	-2.34351	-2.89914
H	-0.76428	-3.64061	-1.77014
H	-1.32803	-3.68016	-3.46710
C	-1.82522	-3.82130	2.99755
H	-1.77350	-4.44405	3.90081
C	-2.57563	-4.25339	1.89261
H	-3.10799	-5.21182	1.92512
C	-2.35026	-2.19893	-2.22383
H	-3.13313	-2.90499	-1.89055
C	-1.12254	-2.60665	2.93165
H	-0.51774	-2.29756	3.79532
C	-1.13890	-1.80313	1.77338
C	-3.71322	0.50967	0.81489
H	-3.53632	-0.14227	1.68762
H	-2.95075	1.29901	0.83968
H	-4.70638	0.98351	0.93476
C	-2.63918	-3.45557	0.73908
H	-3.23154	-3.80547	-0.11459
C	-1.93007	-2.23760	0.67819
C	-2.89553	-1.40371	-3.42299
H	-3.85635	-0.91085	-3.19475
H	-2.18323	-0.62934	-3.74757
H	-3.06792	-2.08312	-4.28005
N	-0.00820	0.30260	-2.89210
N	-0.01444	0.44850	-4.02763
P	2.06683	-0.80093	-0.81239
C	3.61641	-3.27344	-0.92329
H	4.26906	-2.87492	-1.71808
H	4.09762	-3.06816	0.04924
H	3.57618	-4.37339	-1.04808
C	2.18790	-2.70197	-0.95661
H	1.74042	-2.91230	-1.94535
C	3.55360	1.20037	-2.11638
H	2.59800	1.64385	-2.44578

H	3.81474	1.63237	-1.13626
H	4.33984	1.49215	-2.83967
C	3.89554	-0.37999	3.45128
H	4.28650	-0.27987	4.47262
C	4.78458	-0.46989	2.36906
H	5.86841	-0.44315	2.54036
C	3.42434	-0.32582	-2.04397
H	4.38026	-0.74017	-1.67089
C	2.50998	-0.39389	3.21992
H	1.82933	-0.29855	4.07743
C	1.97802	-0.48346	1.91794
C	1.33647	-3.39176	0.11503
H	1.71728	-3.17223	1.12742
H	0.29193	-3.05694	0.08404
H	1.35342	-4.48918	-0.02978
C	4.28374	-0.59268	1.06367
H	4.99100	-0.66730	0.22897
C	2.89162	-0.60084	0.83822
C	3.15647	-0.91194	-3.44190
H	3.14720	-2.01579	-3.44364
H	2.19126	-0.56358	-3.84068
H	3.94804	-0.58546	-4.14427
P	-0.13544	2.20655	-0.49153
C	1.11677	4.81753	0.02229
H	0.55669	5.30263	-0.79449
H	0.54964	4.96240	0.95870
H	2.07662	5.35927	0.13021
C	1.39762	3.32377	-0.22217
H	1.95624	3.22056	-1.16833
C	-2.45817	2.72490	-2.00192
H	-2.32220	1.74106	-2.48361
H	-3.06558	2.58027	-1.09301
H	-3.02424	3.37837	-2.69438
C	-2.00263	2.82333	3.73866
H	-2.42514	2.93052	4.74636
C	-2.22322	3.82185	2.77720
H	-2.81652	4.71003	3.02858
C	-1.09616	3.34448	-1.66259
H	-1.27676	4.29083	-1.11879
C	-1.26208	1.67926	3.39695
H	-1.12151	0.89355	4.15265
C	-0.73822	1.49649	2.10125
C	2.27111	2.78623	0.91709
H	1.74364	2.85091	1.88521
H	2.54201	1.73405	0.76464
H	3.20575	3.37331	0.99537

C	-1.68380	3.68129	1.48883
H	-1.86420	4.47138	0.75055
C	-0.94628	2.52782	1.14910
C	-0.30251	3.67726	-2.93924
H	0.64882	4.19036	-2.71895
H	-0.07206	2.77118	-3.51927
H	-0.89964	4.34908	-3.58708

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